IRON

Annual Survey Covering the Year 1981*

JOHN J. ALEXANDER

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221, USA

Contents

---

* See also Ruthenium and Osmium Annual Survey Covering the Year 1981, see J.B. Keister, J. Organomet. Chem. 245 (1983) pp. 409-502.

METAL CARBONYLS

Simple Carbonyls and Carbonylate Anions

Laser pyrolysis experiments on $Fe(CO)_5$ have provided a value for the first CO dissociation energy of 200 ± 16 kJ $mole^{-1}$ [1]. An ICR study on $Fe(CO)_5$ gave [2] a proton affinity of 854 ± 16 kJ $mole^{-1}$ and a homolytic bond dissociation energy of 310 ± 21 kJ $mole^{-1}$ for $Fe(CO)_5H^+$. Reduction of $Fe(CO)_5$ with alkali metals or their alloys produces the radicals $Fe_2(CO)_8^{\dot{-}}$, $Fe_3(CO)_{12}^{\dot{-}}$, $Fe_3(CO)_{11}^{\dot{-}}$ and $Fe_4(CO)_{13}^{\dot{-}}$ which were identified by ESR [3]. This suggests the importance of one-electron processes.

A discussion of the use of the band intensity/frequency-factored force field method for the determination of bond angles in metal carbonyl fragments including $Fe(CO)_n$ (n = 3,4) has appeared [4].

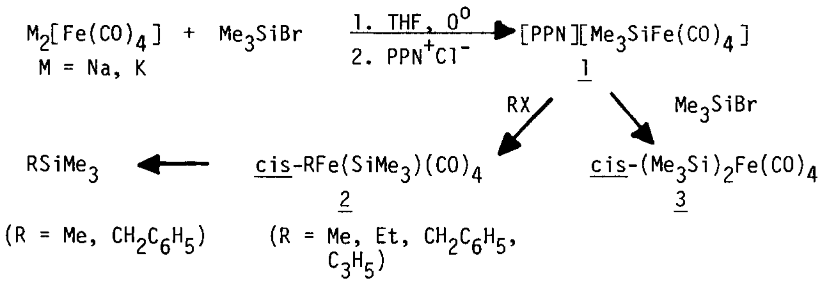
Sonication of $Fe(CO)_5$ in hydrocarbon solvents gives Fe and $Fe_3(CO)_{12}$. The lack of any $Fe_2(CO)_9$ presumably rules out the production of $Fe(CO)_4$ [5]. In the presence of n-decane, $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ all isomerize 1-pentene with $Fe(CO)_5$ being most effective.

Also reported [6] are graphite intercalation compounds of $Fe(CO)_5$, $Na_2Fe(CO)_4$ and $Fe_3(CO)_{12}$ as well as the synthesis of $L_2CdFe(CO)_4$ (L = N,N'-dimethylethylenediamine, 1,3-propylenediamine) [7].

Complexes With Group IV Ligands

Fe-Si complexes can be prepared via the route in Scheme 1 [8,9].

SCHEME 1



2 can be oxidized to trans-$(SiMe_3)_2Fe_2(CO)_8$ by $C_7H_7^+$. 3 is sensitive to ethers, presumably because of the affinity of Si for O [10].

SCHEME 2

$$\underline{\text{cis}}\text{-}(\mathrm{Me_3Si})_2\mathrm{Fe(CO)_4} + \mathrm{ROSiMe_3} \longrightarrow$$

$$(\mathrm{R} = \mathrm{Me},\ \mathrm{CH_2C_6H_5})$$

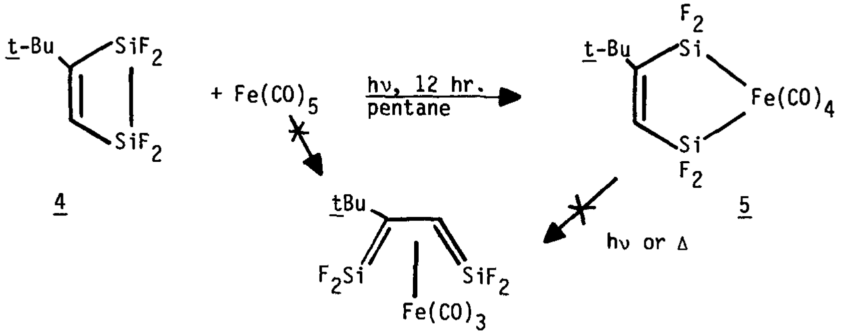
$$(\mathrm{Me_3Si})_2\mathrm{O} + \mathrm{RFe(CO)_4(SiMe_3)} \longrightarrow \mathrm{RSiMe_3}$$

With the unsymmetrical ether $C_6H_5CH_2OMe$, regioselective benzyl-O bond cleavage occurs to afford Me_3SiOMe and $C_6H_5CH_2SiMe_3$.

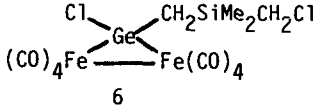
In a similar reaction $Na_2Fe(CO)_4$ and $ClMe_2SiSiMe_2Cl$ gave $Na^+[ClMe_2SiSiMe_2\text{-}Fe(CO)_4]^-$[11].

4 has been shown to react with $Fe(CO)_5$ to produce 5 in 60% yield instead of a siladiene complex [12].

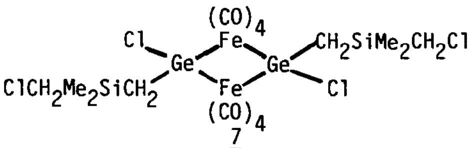
SCHEME 3



$ClCH_2SiMe_2CH_2GeCl_3$ and $Fe_2(CO)_9$ react to give 6 and 7 containing three- and four-membered rings, respectively. With $ClCH_2CH_2CH_2GeCl_3$ and $MeGeCl_3$, only analogues of 7 were obtained. X-ray structures of 6 and 7 were reported [13].



6



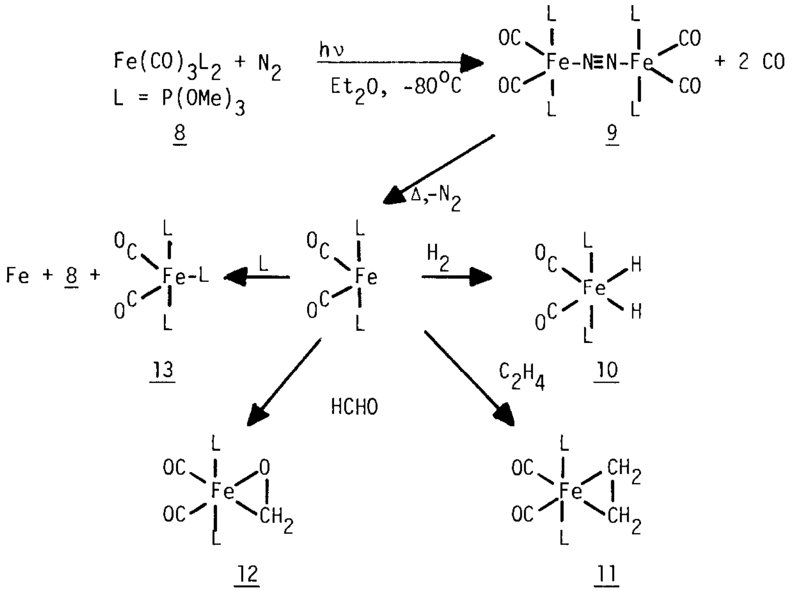
7

$[(R_2Sn)Fe(CO)_4]_2$ in the presence of strong Lewis bases establishes an equilibrium with a monomeric species $Fe(CO)_4(SnR_2\{B\})$ which is known to rapidly exchange bases. When B = THF or $4\text{-}MeC_6H_4NO$, hydridic reagents give H_2 and $[Fe(CO)_4SnR_2]^{2-}$. Presumably this reaction involves displacement of B by H^-. Mossbauer measurements indicate that the dianion is the product of one-electron reduction of both Fe and Sn[14].

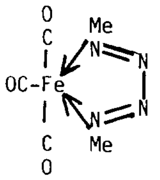
Complexes With Group V Ligands

8 reacts with N_2 at low temperature giving 9 from which 10-13 can be prepared [15]. The X-ray crystal structures of 9 and 13 were determined.

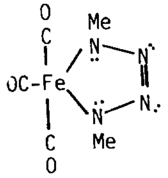
SCHEME 4



CO substitution on 14 was found to proceed via an associative mechanism. The reaction is first order in 14 and in the entering Lewis base. The second-order rate constant varies over some four orders of magnitude depending on the Lewis base. Neither $Fe(CO)_5$ nor $Fe(CO)_4(PPh_3)$ undergoes ligand substitution under comparably mild conditions. The tetraazadiene ligand is apparently a good π-acceptor permitting Fe to delocalize a pair of electrons giving 15 and promoting nucleophilic attack on Fe [16].



14



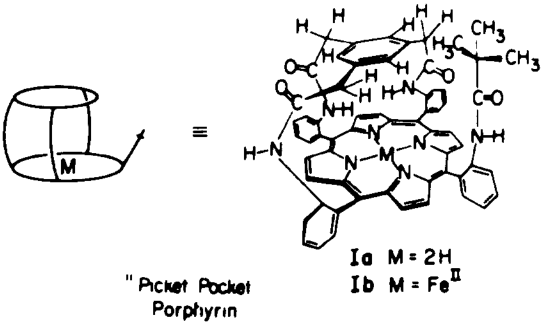
15

Hückel MO and SCC-DV-Xα calculations on complexes such as 14 indicate that the Fe-N_4 ring is to be regarded as a 6π-aromatic ring. The photoelectron spectra have been interpreted in accord with this view [17].

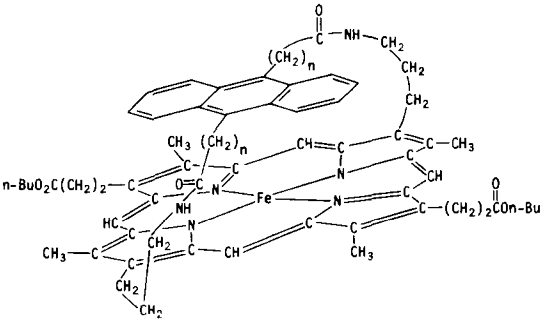
Numerous investigations on heme complexes and complexes with macrocyclic ligands have appeared. An iron complex 16 was prepared and found to exhibit enhanced O_2 affinity and diminished CO affinity compared to that of the "picket fence" porphyrin [18]. The reason could be that the pocket in 16 prevents linear Fe-C-O bonding. However, kinetic studies of O_2 and CO bonding to 17 showed no differentiation due to distal side steric effects between the complexes with n = 1 and n = 2 [19]. Measured rates of CO and O_2 association and dissociation as well as affinity constants for some Fe-Cu cofacial porphyrins and strapped hemes showed steric effects. However, no clear-cut distinction was possible for species with bent vs. linear Fe-C-O bonds [20].

Complexes 18 showed no appreciable variation in kinetics or equilibrium constants for CO binding as a function of R = CH=CH_2, Et, $CH_3C(O)$ [21].

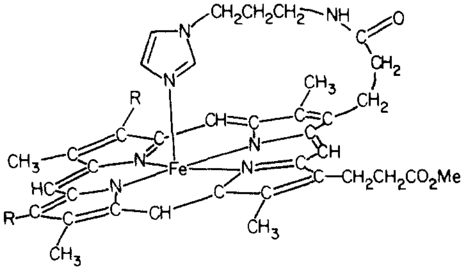
A family of synthetic models of CO adducts of heme proteins, 19, has been synthesized with a sheltered void of controllable dimensions encompassing the CO binding site. The equilibrium constant for CO binding depends on available space. An X-ray structure determination of one complex shows a bent Fe-C-O linkage [22].



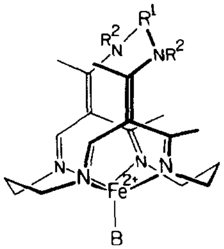
16



17



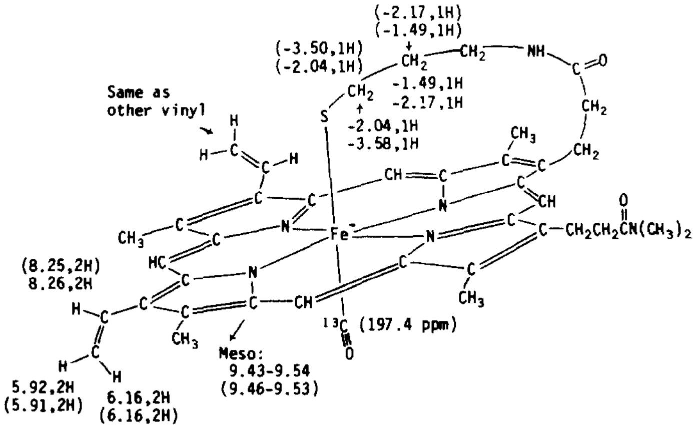
18



19

R^2	R^1
H	(CH$_2$)$_n$ (n = 4-6)
Me	(CH$_2$)$_6$
H	3-(fluorenyl)propyl
H	p-xylyl
H	m-xylyl
Me	m-xylyl

19



20

A mercapto chelated protoheme 20 was prepared as a model compound for cytochrome P-450. This compound has a lower CO affinity than P-450 [23].

The kinetics and thermodynamics of CO binding to phthalocyaninatoiron (II) in dmso were studied [24]. MCD has been used as a fingerprint method for determining spin state and axial coordination environment of synthetic ferroporphyrins including species with bound CO [25]. Evidence has been reported that carboxyhemoglobin may display a variety of magnetic states depending on conditions [26].

Reaction of $Fe(CO)_5$ with o-phthalonitrile in DMF produces Fe(phthalocyaniine)(CO)(DMF). The X-ray structure shows that Fe is six-coordinate with axial positions occupied by CO and the DMF O. Axial DMF can be replaced by tetrahydrothiophene, THF, $PrNH_2$, H_2O, MeOH and Me_2SO [27].

The X-ray crystal structures of $[P(NMe_2)_3]Fe(CO)_4$ at 21°C and $[P(NMe_2)_3]_2$-$Fe(CO)_3$ at -35°C were determined. In the mono complex two NMe_2 form a trigonal arrangement with P while the angles in the other are more nearly tetrahedral [28].

Reaction of $Fe_2(CO)_9$ with L = Me_2NPCl_2, $(Et_2N)_2PCl$, $(\underline{i}\text{-}Pr_2N)_2PCl$, $[(Me_3Si)_2N]_2PCl$, $(\underline{t}\text{-}Bu)(Me_2N)PCl$ in hexane afforded complexes $LFe(CO)_4$. These chlorophosphine complexes give phosphenium ion complexes such as $[(Me_2N)P(Cl)Fe(CO)_4]^+$ on treatment with a stoichiometric quantity of Al_2Cl_6 in CH_2Cl_2. The phosphenium ions behave as π-acceptor ligands [29].

The water soluble 21 is prepared by quaternization or by direct reaction with cationic phosphine [30].

SCHEME 5

$$Fe(CO)_5 + Ph_2PCH_2CH_2NMe_2 \xrightarrow{Me_3NO}$$

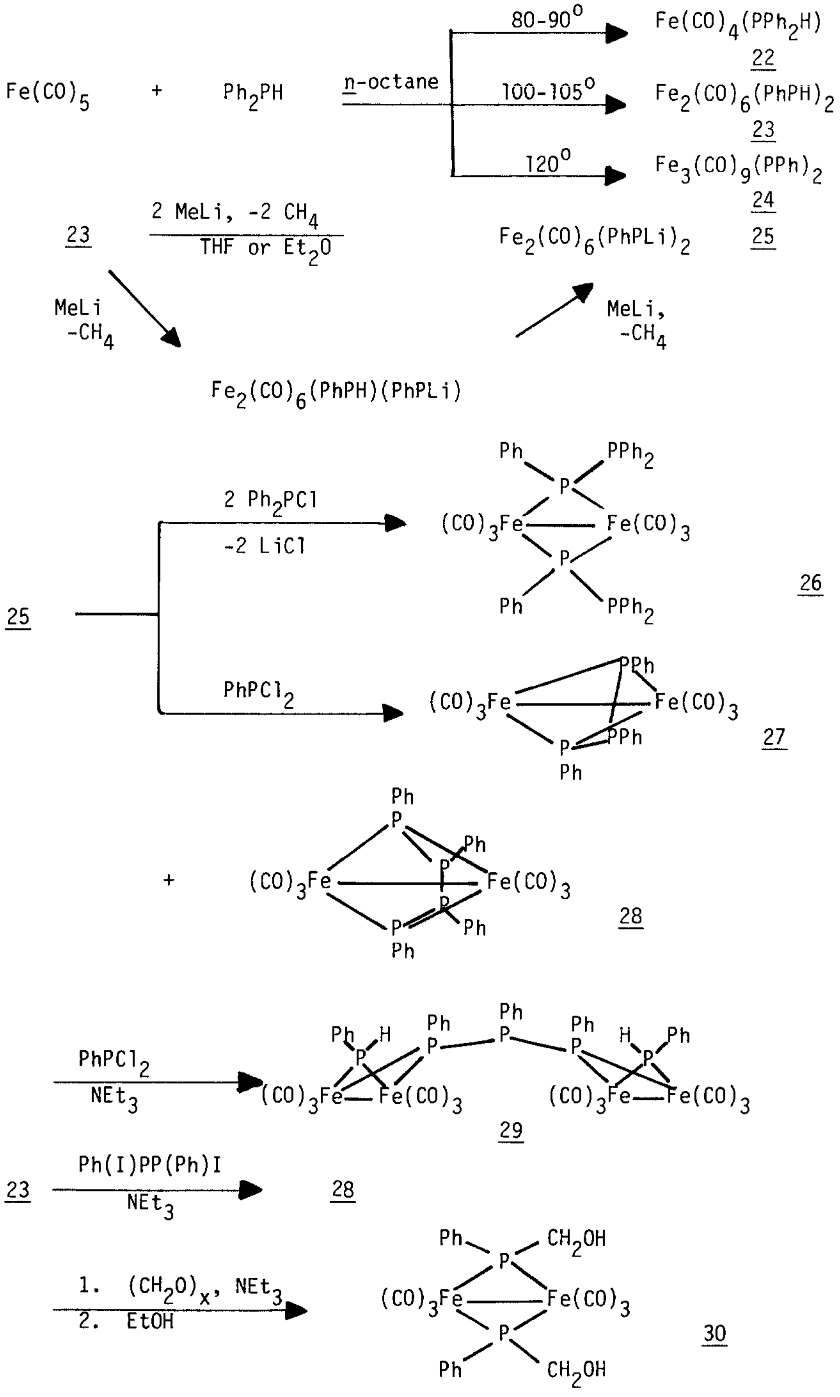
$$(CO)_4FeP(Ph)_2CH_2CH_2NMe_2 \xrightarrow{CH_3I}$$

$$[(CO)_4FeP(Ph)_2CH_2CH_2\overset{+}{N}Me_3]I^-$$

21

Secondary phosphine complexes were prepared and the P-H functionality employed to obtain complexes with bridging phosphido groups [31].

SCHEME 6


Fe(CO)5 + Ph2PH
n-octane
80-90°
Fe(CO)4(PPh2H) 22
100-105°
Fe2(CO)6(PhPH)2 23
120°
Fe3(CO)9(PPh)2 24
23
2 MeLi, -2 CH4
THF or Et2O
Fe2(CO)6(PhPLi)2 25
MeLi -CH4
Fe2(CO)6(PhPH)(PhPLi)
MeLi, -CH4
25
2 Ph2PCl
-2 LiCl
Ph
PPh2
P
(CO)3Fe
Fe(CO)3
P
Ph
PPh2
26
PhPCl2
PPh
(CO)3Fe
Fe(CO)3
P
PPh
Ph
27
+
Ph
P
Ph
P
(CO)3Fe
Fe(CO)3
P
Ph
P
Ph
28
PhPCl2
NEt3
Ph H
P
Ph
P
Ph
P
Ph
P
H Ph
P
(CO)3Fe
Fe(CO)3
(CO)3Fe
Fe(CO)3
29
23
Ph(I)PP(Ph)I
NEt3
28
1. (CH2O)x, NEt3
2. EtOH
Ph
CH2OH
P
(CO)3Fe
Fe(CO)3
P
Ph
CH2OH
30

$CoCl_2 \cdot 2\,H_2O$ and $CoI_2 \cdot 4\,H_2O$ were found to catalyze substitution of $Fe(CO)_5$ by Group V ligands. In refluxing toluene $Fe(CO)_4(PPh_3)$ can be prepared almost quantitatively and free from contamination by the disubstituted product. The order of reactivity for substituting ligands is $PPh_3 \sim AsPh_3 \sim P(OPh)_3 > SbPh_3 > PPh_2Me > PPhMe_2 > P(C_6H_{11})_3 > P(OEt)_3 > P(\underline{n}\text{-}Bu)_3 > P(OMe)_3$ [32].

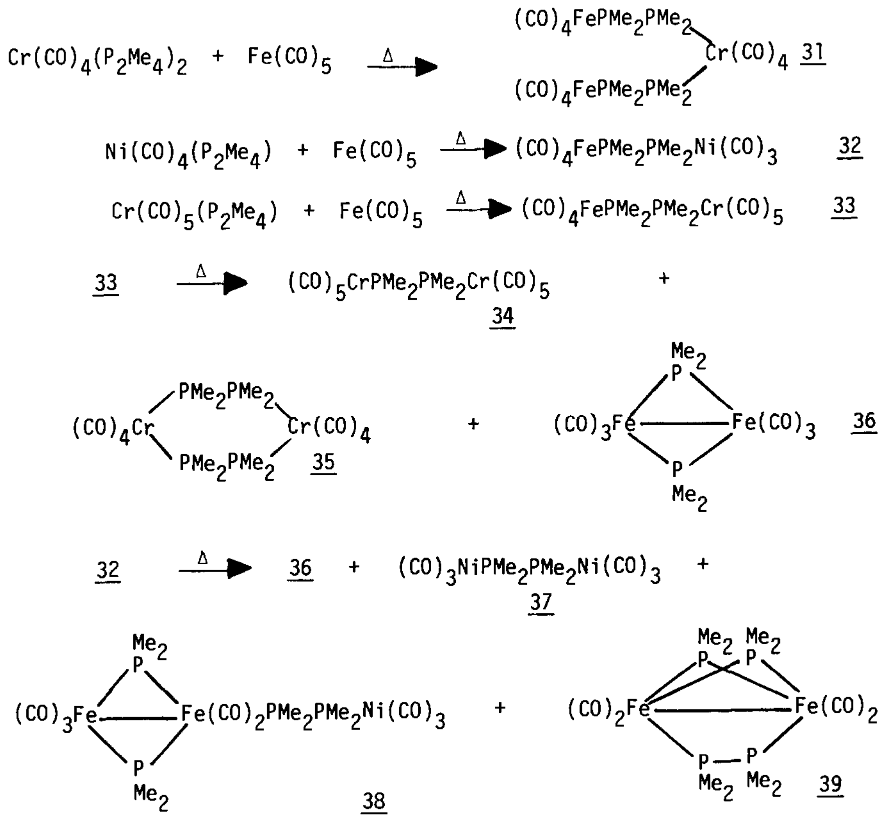
$(PPh_3)Fe(CO)_4$ was also a product (along with $Fe(CO)_5$, $Fe_3(CO)_{12}$ and $CpCo(CO)_2$) of the reaction between excess $Fe_2(CO)_9$ and $CpCo(PPh_3)Me_2$ [33].

A paramagnetic complex having trigonal bipyramidal geometry, $[P(CH_2CH_2PPh_2)_3Fe(SO_2\underline{p}\text{-}C_6H_4Me)]BPh_4$ has been reported [34].

The electrochemistry of $Fe(CO)_4L$ and $Fe(CO)_3L_2$ ($L = PPh_3, AsPh_3, SbPh_3$) in organic solvents was investigated at Hg and Pt electrodes [35]. At Pt electrodes all oxidized species are unstable. With Hg electrodes, reversibility was seen with all complexes except the disubstituted ones of $AsPh_3$ and $SbPh_3$.

The chemistry of diphosphine complexes has been investigated [36]:

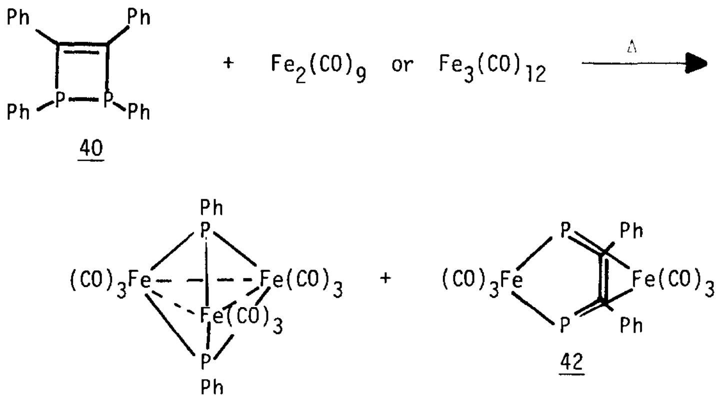
SCHEME 7



The UV gas phase and photoelectron spectra of the diphosphine complexes $Fe_2L(CO)_7$ and $Fe_2L_2(CO)_5$ where L = $PF_2N(Me)PF_2$ were reported [37].

The diphosphine 40 was found to react with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ giving 41, 42 and a third compound of unknown structure [38].

SCHEME 8



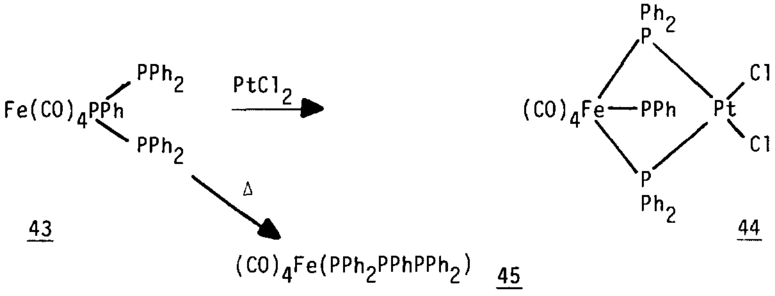
40

41

42

An X-ray structure of the triphosphine complex 43 shows that the molecule is trigonal bipyramidal with an equatorial phosphine. The complex can act as a ligand itself. On heating, the $Fe(CO)_4$ moiety migrates to a terminal P giving 45 [39].

SCHEME 9

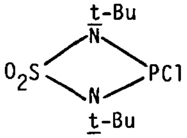


43

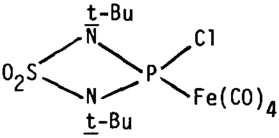
44

45

46 reacts with $Fe_2(CO)_9$ in pentane affording 47 [40]. When SO_2 in 46 is replaced by PCl, the resulting ligand can chelate or bridge metals.



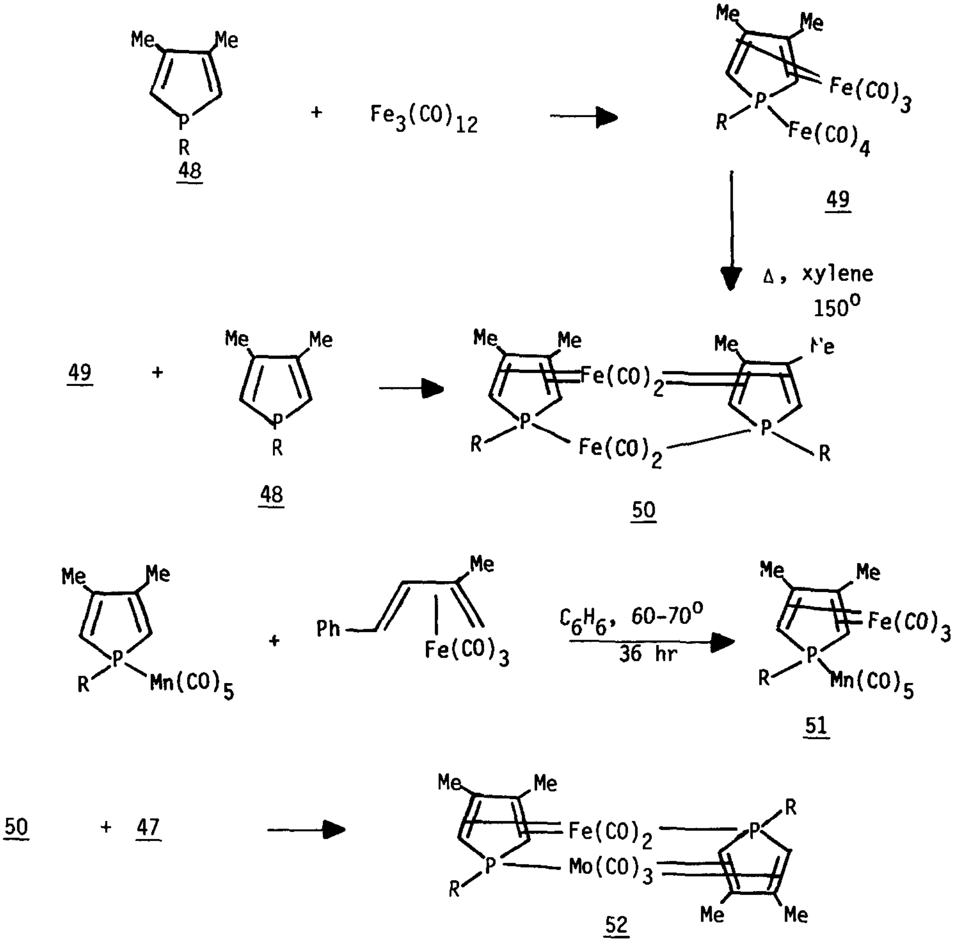
46



47

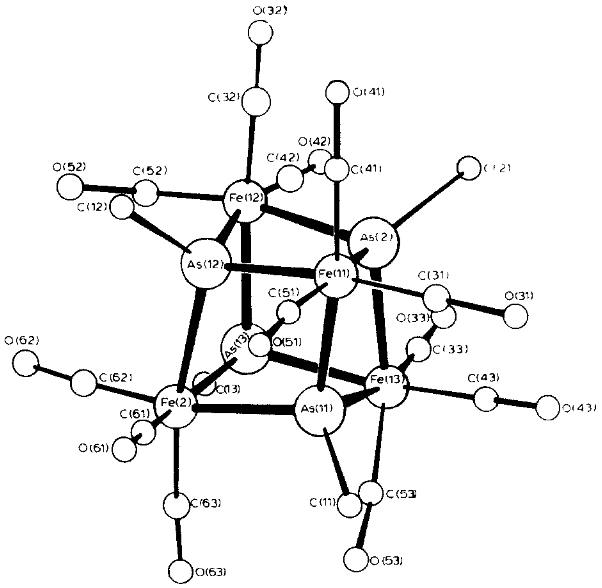
A re-investigation of the reaction of the phosphole 48 (R = t-Bu) with $Fe_3(CO)_{12}$ showed that 49 (R = t-Bu) was produced which, on heating, gave 50. 50 is also accessible from another route. An X-ray structure of 50 (R = Ph) was reported. Complexes such as 51 and 52 containing two different metals are also accessible [41].

SCHEME 10



The primary arsine complex $Fe(CO)_4(AsMeH_2)$ is the product of the reaction of

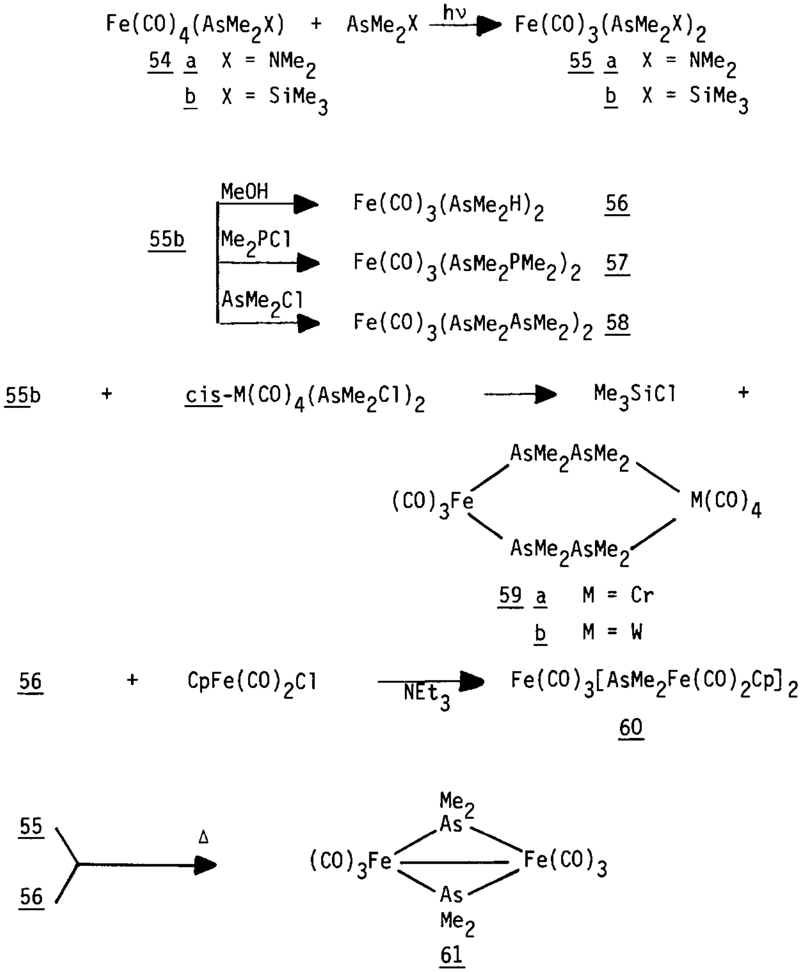
$Fe_2(CO)_9$ with excess arsine [42]. On heating, the arsine complex 53, having a cubane-like structure, results.



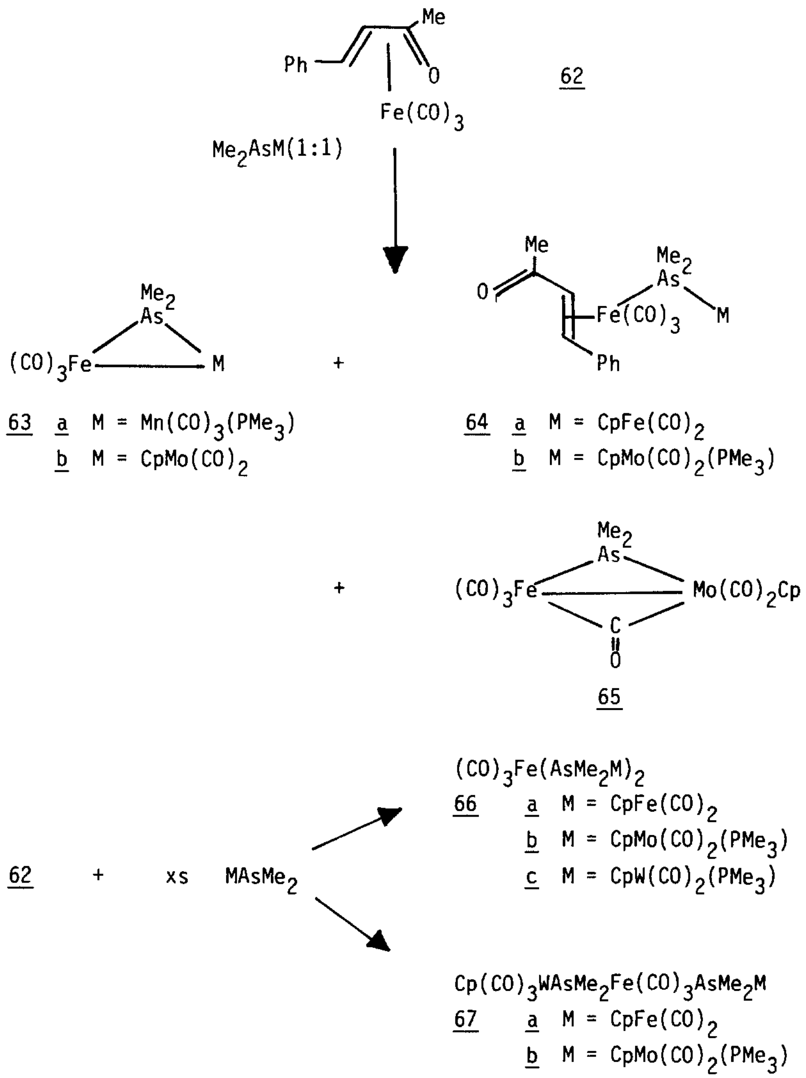
53

The photochemical reaction of 54 with $AsMe_2X$ affords 55. 55b is a precursor to 56-59. The free As-P ligand in 57 is not known. 55 and 56 can be employed in the synthesis of mixed-metal species and both decompose thermally to 61 as shown in Scheme 11 [43]. Other such complexes can be obtained starting with (benzylideneacetone)tricarbonyl iron, 62 [43]. See Scheme 12.

SCHEME 11


Fe(CO)4(AsMe2X) + AsMe2X hν Fe(CO)3(AsMe2X)2
54 a X = NMe2
b X = SiMe3
55 a X = NMe2
b X = SiMe3
55b
MeOH
Fe(CO)3(AsMe2H)2 56
Me2PCl
Fe(CO)3(AsMe2PMe2)2 57
AsMe2Cl
Fe(CO)3(AsMe2AsMe2)2 58
55b + cis-M(CO)4(AsMe2Cl)2 Me3SiCl +
AsMe2AsMe2
(CO)3Fe
M(CO)4
AsMe2AsMe2
59 a M = Cr
b M = W
56 + CpFe(CO)2Cl NEt3 Fe(CO)3[AsMe2Fe(CO)2Cp]2
60
55
56
Δ
Me2
As
(CO)3Fe
Fe(CO)3
As
Me2
61

SCHEME 12



Finally, electrochemical syntheses of Group V substituted iron carbonyls starting with acac complexes were described [44,45].

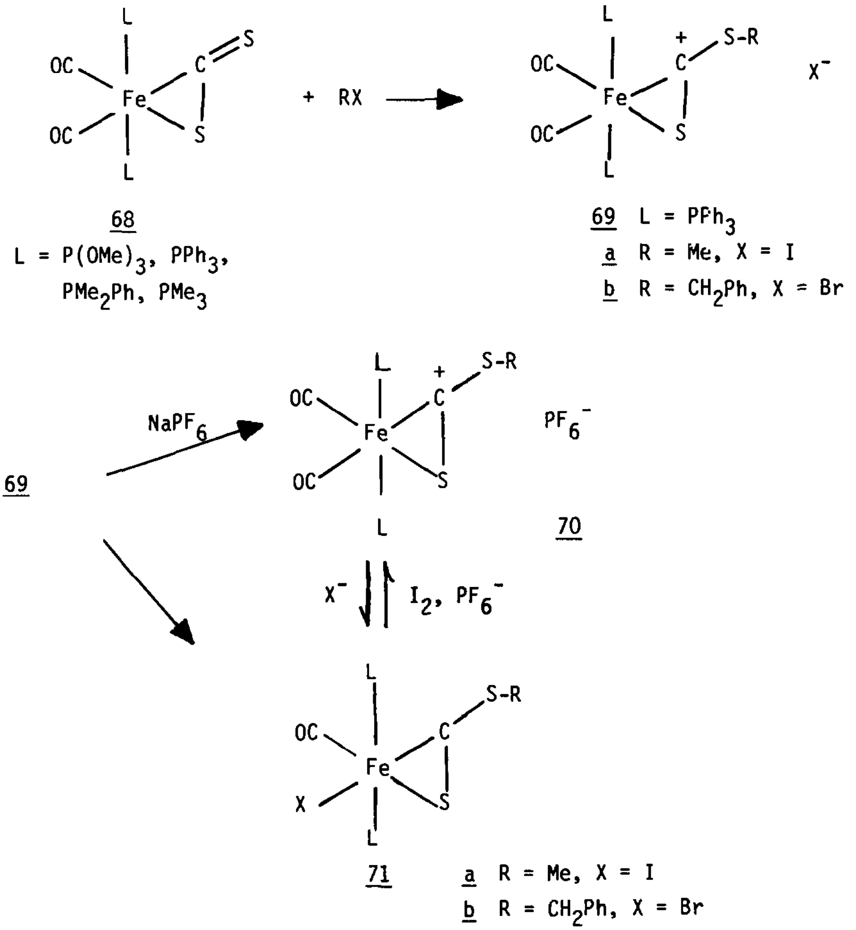
Fe(II) Phosphine Complexes Containing Hydrido, Halo and Other Ligands

A complex of the linear tetraphosphine $P_4 = H_2PCH_2CH_2PHCH_2CH_2PHCH_2CH_2PH_2$, $Fe(P_4)X^+$ (X = Br, I) reacts with $NaBH_4$ in the presence of N_2 affording $[Fe(H)(N_2)(P_4)]X$. An X-ray structure of the bromo salt shows H and linear N_2 in axial positions. In the absence of N_2, $NaBH_4$ produces five-coordinate $[Fe(H)(P_4)]X$. This behavior is in contrast to that of other similar hydrido complexes of bidentate phosphines which are six-coordinate [46].

Complexes With Group VI Ligands

A full paper has appeared concerning the reaction of 68 with alkyl halides. When L = PPh_3, 69a and 69b can be isolated. In the absence of PF_6^- and when L is a good donor ligand such as PMe_2Ph or PMe_3, carbonyl replacement by X giving 71 may occur [47a]. CO and phosphines were found to replace CS_2 in 68 (L = PMe_3, $P(OMe)_3$) on photolysis [47b].

SCHEME 13



68
L = $P(OMe)_3$, PPh_3,
PMe_2Ph, PMe_3

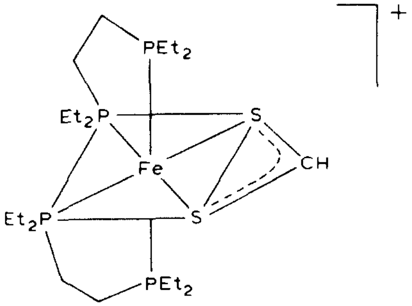
69 L = PPh_3
a R = Me, X = I
b R = CH_2Ph, X = Br

69

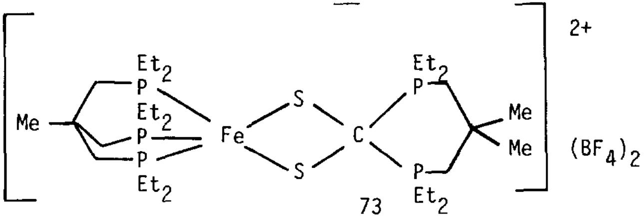
70

71 a R = Me, X = I
b R = CH_2Ph, X = Br

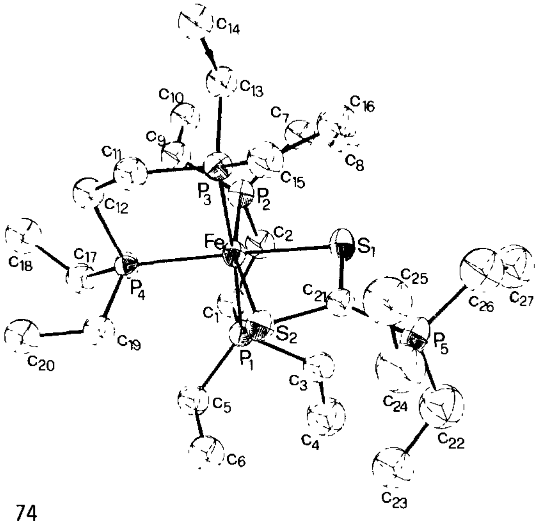
Two S-containing complexes were obtained by reaction of $Fe(BF_4)_2$ with P-containing ligands. Reaction with Et_3PCS_2 and $Et_2PCH_2CH_2PEt_2$ gives 72 [48] while CS_2 and $MeC(CH_2PEt_2)_3$ produces 73, the first diamagnetic Fe(I) five-coordinate complex [49]. Reaction of 72 with $NaBH_4$ affords the thioformate complex 74. X-ray structures were reported for both 72 and 73.



72



73



74

Carbonyl Halide, Hydride and Cyanide Complexes

$CpMo(CO)_3H$ acts as a hydride donor toward $Fe(CO)_5$ giving $[HFe(CO)_4]^-$ [50]. $K[HFe(CO)_4]$ behaves as a hydride donor toward $(PhN_2)BF_4$ giving $(NH_4)(BF_4)$ and $PhNH_2$ [51].

At 0° $H_2Fe(CO)_4$ reacts with L = $P(OPh)_3$, $P(OCH_2)_3CEt$, $AsPh_3$, $SbPh_3$ giving fac-$H_2Fe(CO)_3L$ or $H_2Fe(CO)_2L_2$ with L's trans depending on the reaction stoichiometry [52]. Other workers [53] have found that PPh_3 and $P(OMe)_3$ react with $H_2Fe(CO)_4$ even at -70°C. This lability (which stands in marked contrast to the substitution inertness of $Fe(CO)_5$ and $Fe(CO)_4^{2-}$) has been attributed to the possibility of hydride migration which produces an unsaturated formyl intermediate.

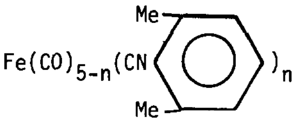
Although they do not contain carbonyl ligands, two other hydrides may be mentioned here. Reaction of $FeCl_3$ with excess Grignard reagaent under H_2 produces $FeH_6Mg_4Br_{3.5}Cl_{0.5}(THF)_8$. The X-ray structure shows that the compound contains an FeH_6^{4-} octahedron capped on alternate faces by Mg^{2+} [54]. Also, FeI_2 was reported to react with $CpMoH_2$ in dioxane yielding $CpMo(\mu\text{-}H)_2FeI_2\cdot diox$ having five-coordinate Fe [55].

Photochemical Reactions

Co-condensation of $Fe(CO)_5$ and Na in an Ar matrix at 20 K with simultaneous photolysis by an Hg lamp gives $Fe(CO)_4^-$ of C_{3v} symmetry [56]. Photolysis of $H_2Fe(CO)_4$ in an Ar matrix leads to elimination of H_2. The elimination can be reversed on irradiation with the Nernst glower of an IR instrument [57]. $Fe(dppe)_2H_2$ eliminates H_2 on photolysis while $Fe(dppe)_2(H)Cl$ eliminates HCl. The $Fe(dppe)_2$ intermediate can be trapped by CO [58]. In contrast to thermal substitution [16], photochemical substitution of 14 involves a dissociative mechanism. Disubstituted products are obtained for PPh_3, PMe_3, $P(OMe)_3$ and $Me_2PCH_2CH_2PMe_2$. A trisubstituted $P(OMe)_3$ product was also produced [59].

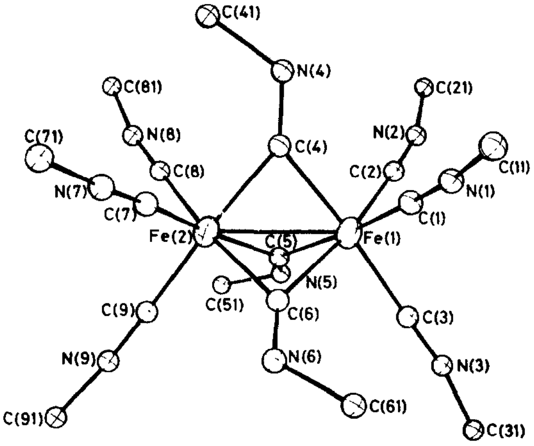
Fe(tpp)(py)(CO) and Fe(deuterioporphyrin dimethyl ester)(py)(CO) were photolyzed in the presence of triplet sensitizers [60]. The results provide evidence that CO photodissociation occurs from a $^3(\pi\text{-}\pi^*)$ excited state.

ISOCYANIDE AND CARBENE COMPLEXES



$Fe(CO)_{5-n}(CN\ \ )_n$ (n = 1-5) can be prepared in high yield by the reaction of $Fe(CO)_5$ and isocyanide catalyzed by $Rh(PPh_3)_3Cl$, $Rh(PPh_3)_2(CO)Cl$ or polymer-supported Rh species [61].

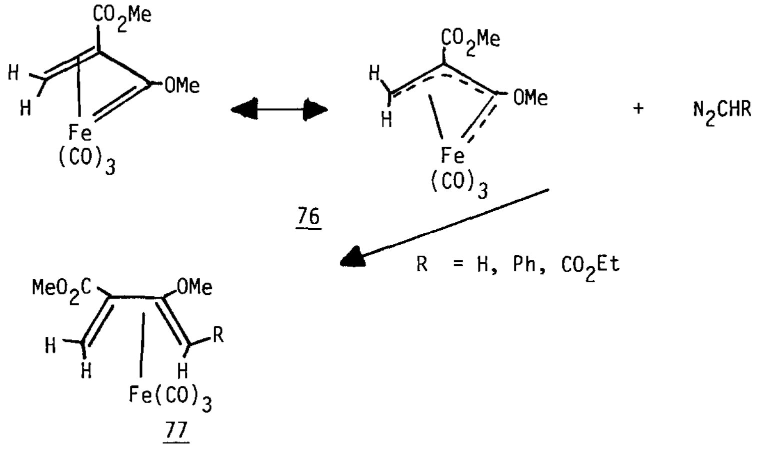
Photolysis of $Fe(CNR)_5$ (R = Et, i-Pr) gives $Fe_2(CNR)_9$. The X-ray structure of $Fe_2(CNEt)_9$, 75, is similar to that of $Fe_2(CO)_9$ with three μ-CNEt. $Fe_2(CNEt)_9$ reacts with RI (R = Me, Et) to produce$[Fe_2(CNEt)_7[CN(Et)(R)]_2]I_2]$ which is formulated as containing μ-carbyne ligands. Photolysis of $Fe(CN\underline{t}\text{-}Bu)_5$ leads to the dealkylation product $Fe(CN)_2(CN\underline{t}\text{-}Bu)_3$. In the presence of cot, irradiation leads to (η^4-cot)$Fe(CN\underline{t}\text{-}Bu)_3$ [62].

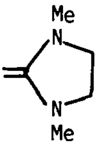


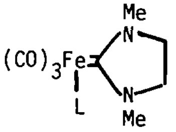
75

The carbene complex 76 inserts a substituted methylene group when allowed to react with substituted azomethanes [63].

SCHEME 14

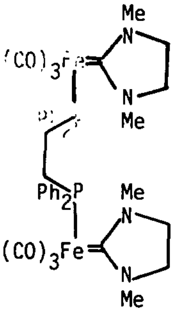


Carbene complexes 78, 79 and $Fe_2(CO)_6$=  (dppe) were prepared from olefins [64].



78

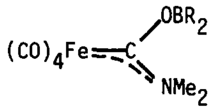
L = $PMePh_2$, PEt_2Ph, PPh_2H, PPh_3, $P(C_6H_{11})_3$, $P(OPh)_3$, $AsPh_3$



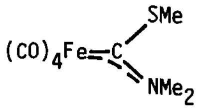
79

These could be oxidized with Ag^+ salts to paramagnetic Fe(I) complexes. 79 gave a diiron cation with two non-interacting Fe(I) ions. ESR measurements indicate that the cations are distorted square pyramids in contrast to the trigonal bipyramidal neutral complexes. The cations undergo CO displacement with phosphines and phosphites, but the substitution products are often unstable to disproportionation.

Treatment of $[Fe(CO)_4C(O)NMe_2]^-$ at low temperature with BR_2Br (R = Me, Ph, NMe_2) produces carbene complexes 80 which are stable only in solution at low temperature and decompose thermally to $Fe(CO)_5$ and $BR_2(NMe_2)$ [65].



80

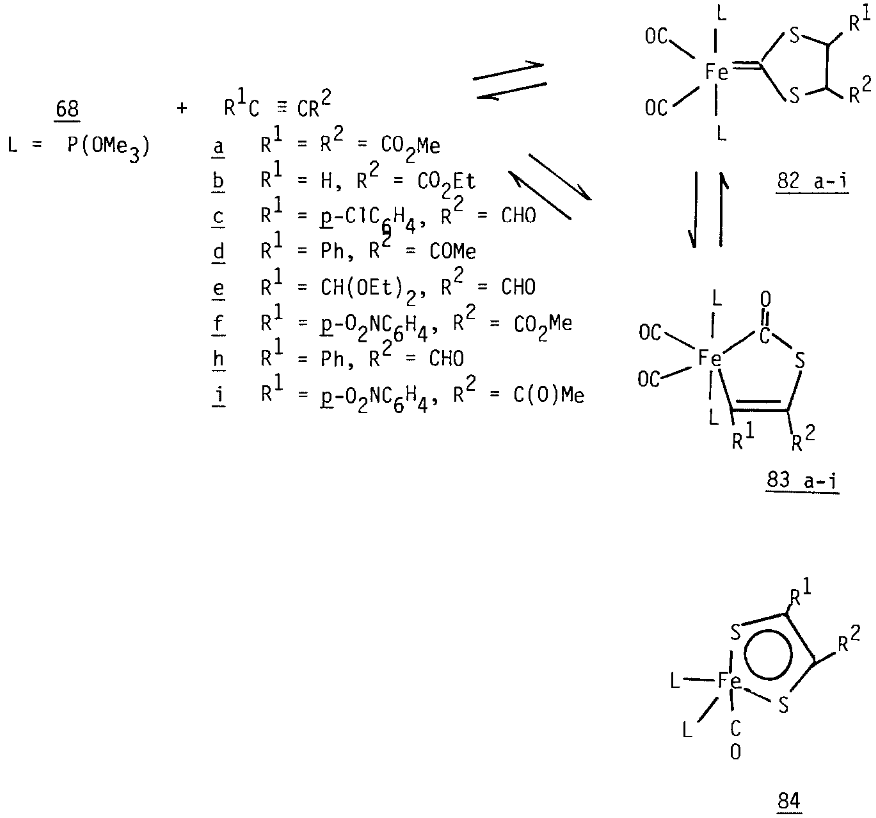


81

$Fe(CO)_4(CS)$ reacts with $C(NMe_2)_4$ and $MeOSO_2F$ yielding 81 [66].

68 (L = $P(OMe)_3$, PPh_3, PMe_2Ph, PMe_3) undergoes electrophilic attack by electron-withdrawing alkynes to afford the carbene complexes 82. The position of the equilibrium between 82 a-e and 83 a-e is controlled by the identity of L favoring 83 (the product of 1,3-dipolar addition) for more basic L [67,68].

SCHEME 15

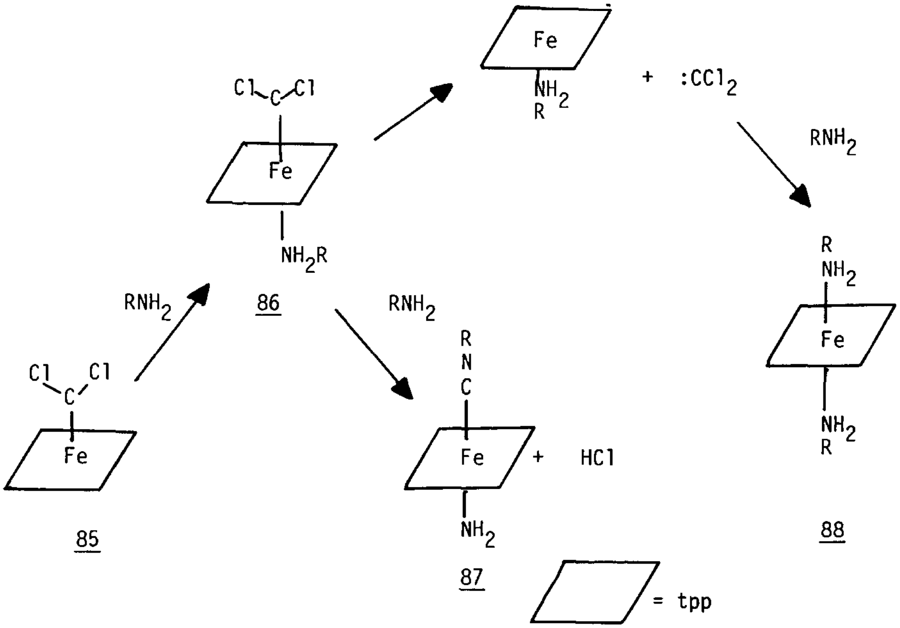


The complexes 82a,c,d,g,h,i are reported [68] to rearrange thermally to dithiolene complexes 84. An X-ray structure of 84i shows distorted trigonal bipyramidal coordination around Fe and a planar dithiolene coordinated at axial and equatorial positions [68].

Stable Fe(II) tetraphenylporphine(tpp) complexes were prepared via the reaction in benzene of RCX_3 with Fe(tpp) followed by treatment with $Na_2S_2O_4$. Prepared in this way were Fe(tpp)[C(X)R] (X = Cl, R = Me, CH_2OH, CH(OH)Me, CH(OH)Ph, $C(OH)Me_2$; X = Br, R = CH_2OH) [69]. An attempt to use Me_3SiCCl_3 to prepare carbene complexes containing an α-Me_3Si group by the above procedure led to unstable products which decomposed to dimers, $[Fe(porphyrin)]_2C$ or to thiocarbonyl complexes [Fe(porphyrin)(CS)] [70].

A kinetic study [71] of the reaction of primary amines with the dichlorocarbene complex 85 showed two alternate pathways. The first reaction product 86 contains an axially coordinated amine. Sterically hindered or weakly basic amines give both 87 and 88. The remaining amines give only 87.

SCHEME 16

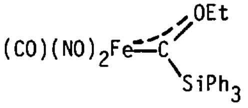


Oxidation of iron porphyrin carbene complexes leads to species in which a vinylidene group has been inserted into an Fe-pyrrole N bond. This has been confirmed by X-ray structure [72] and NMR [73]. In the case of (2,2-bis(*p*-chlorophenyl)vinylidene tetraanisylporphinotoiron(II), oxidation by excess Fe-Cl_3 produces a complex in which a substituted vinylidene grup bridges two of the pyrrole N's. This product presumably arises via an Fe-N insertion product of the type mentioned above [74].

The visible and UV spectra of some porphyrin complexes containing the RS^- ligand along with carbene or CS were also reported [75].

NITROSYL COMPLEXES

A nitrosyl carbene complex 89 results from treatment of $Fe(CO)_2(NO)_2$ first with $LiSiPh_3$ in Et_2O followed by $Et_3O^+BF_4^-$ in CH_2Cl_2 [76].

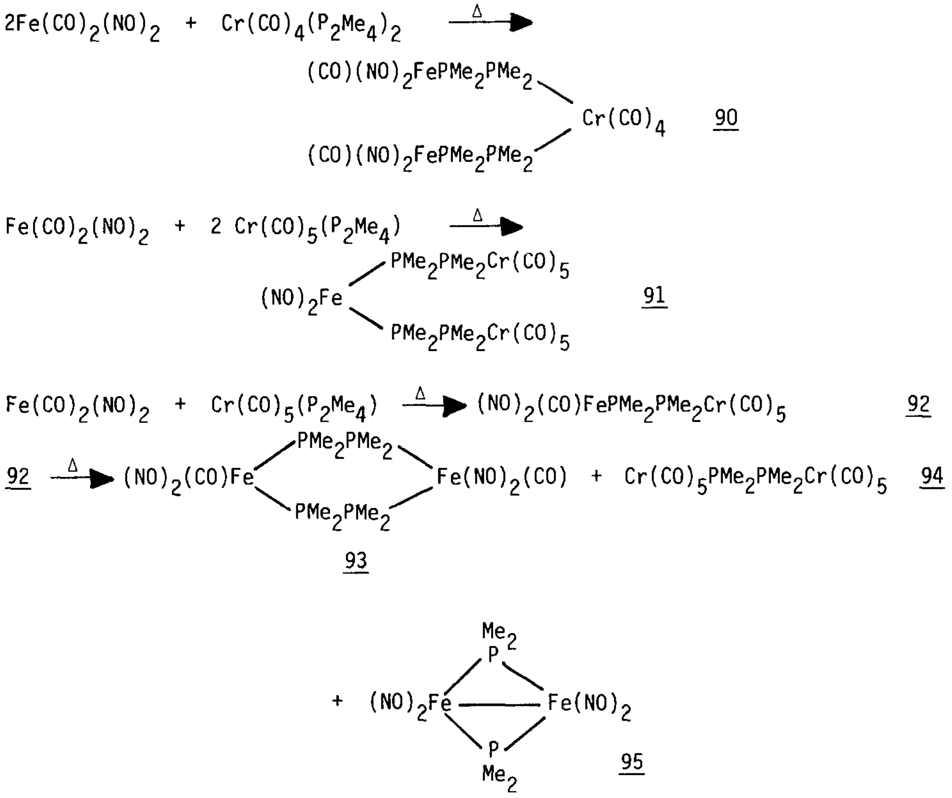


$(CO)(NO)_2Fe{\overset{\cdots}{=}}C(OEt)(SiPh_3)$

89

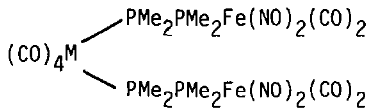
Some nitrosyl complexes containing diphosphine ligands were prepared and their thermolysis investigated [36]:

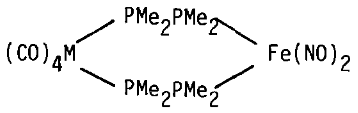
SCHEME 17



The ESR spectrum of the dimer formed by nitrosyl(meso-2,3,7,8,12,13,17,18-octaethyl-5-nitroporphinato)iron(II) was reported [77].

The thermolysis of 96a-c produced 97a-c [78]. Also prepared were oligomers such as $Fe(CO)(NO)_2P_2Me_4Ni(CO)_2P_2Me_4Fe(NO)_2P_2Me_4Ni(CO)_3$.



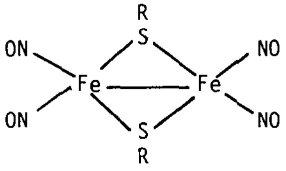


96 a M = Cr
b M = Mo
c M = W

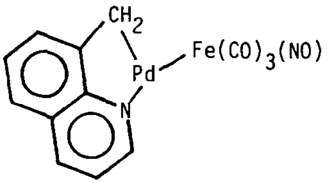
97 a M = Cr
b M = Mo
c M = W

The anion of Roussin's red salt was found to react with electrophiles at the μ-S producing 98 (R = H, Me [79]; Me, Et, $CH_2CH{=}CH_2$, CH_2Ph, $SnMe_3$, $SnPh_3$, $PbPh_3$,

$CpFe(CO)_2$) [80]. cis-$Pt(PPh_3)_2Cl_2$ also gives a 1:1 adduct of unknown structure [80].



98



99

A compound with an Fe-Pd bond 99 was produced when $Na[Fe(CO)_3NO]$ was allowed to react with the corresponding chloro-Pd complex [81].

CLUSTER COMPOUNDS

The usual definition of cluster compounds is that they contain three or more metals and three or more M-M bonds. In order to conform to past practice in reviews of Fe organometallic chemistry, binuclear complexes have been included here as well as some complexes with fewer than three Fe-Fe bonds. However, complexes which do not contain Fe-Fe bonds have been relegated to other sections of this review.

Several complexes containing M-M bonds have already been mentioned as starting materials or products of reactions previously reported in this review. These include 6, 7 [13], $[(R_2Sn)Fe(CO)_4]_2$ [14], 23, 24, 25, 26, 27, 28, 29, 30 [31], 36, 38, 39 [36], $Fe_2[PF_2N(Me)PF_2](CO)_7$ and $Fe_2[PF_2N(Me)PF_2]_2(CO)_5$ [37], 53 [42], 61, 63, 65 [43], 75 and $[Fe_2(CNEt)_7[CN(Et)(R)]_2]I_2$ [62], 95 [36], 99 [81] and $Fe(CO)(NO)_2P_2Me_4Ni(CO)_2P_2Me_4Fe(NO)_2P_2Me_4Ni(CO)_3$[79,80].

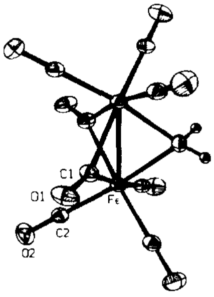
Of general interest is a full paper on the estimation of bond enthalpies in clusters including Fe-Fe bonds [82]. Also, microcrystals of $Fe(CO)_5$ in a supersonic beam were irradiated with a laser beam at 1930 Å. Cluster ions $Fe_x(CO)_y$ (x = 1-30) were detected by mass spectroscopy [83].

Binuclear Species (Excluding (η^5-C_5H_5) Compounds)

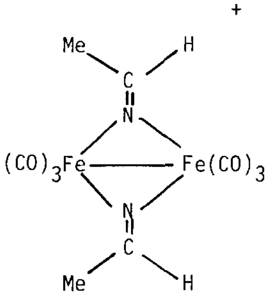
AC polarography of some metal carbonyls including $Fe_2(CO)_9$ was investigated in non-aqueous solvents [84].

Irradiation of $Fe(CO)_5$ in olefin-free pentane produces the radicals $HFe_2(CO)_8\cdot$ and $HFe_3(CO)_{11}\cdot$ which are stable to -40°C and were identified by ESR [85].

The X-ray structure of $Fe_2(CO)_8(\mu\text{-}CH_2)$, 100, at -35°C and +22°C shows a resemblance to that of $Fe_2(CO)_9$[86]. Also reported was the X-ray structure of the syn isomer of 101 [87].

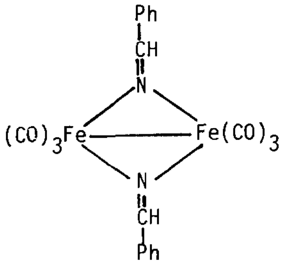


100

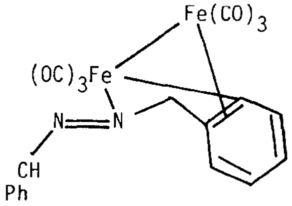


101

A related complex 102 is a product of the reaction of benzalazine with $Fe_3(CO)_{12}$. The other product is 103 having a bridging ligand with a bonded phenyl and a saturated CH_2 group. The X-ray structure of 103 was reported [88].

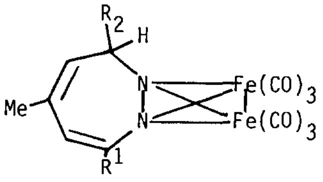


102

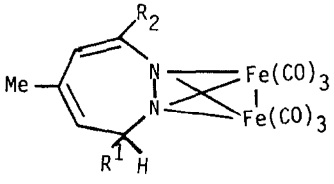


103

Reaction of 3H-1,2-diazepines with $Fe_2(CO)_9$ affords 104 and 105 which are related by a [1,5] sigmatropic H shift [89]. This shift is too rapid in the free ligand to isolate either form pure.



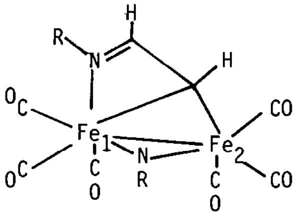
104 a-f



105 a-f

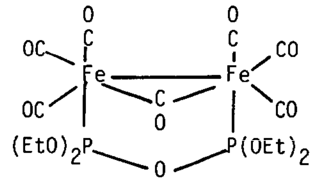
a $R^1=R^2=Me$; b $R^1=Ph,R^2=H$; c $R^1=Me,R^2=H$; d $R^1=Me,R^2=Et$; e $R^1=Me,R^2=i\text{-}Pr$;
f $R^1=Me,R^2=CH_2CH_2Ph$

The ^{13}C NMR of 106 a-c indicates that local scrambling of CO groups occurs with very different activation energies on the two different Fe atoms. The signals for CO's bonded to Fe_1 coalesce ∿ -50°C while those for Fe_2- bonded CO's coalesce above room temperature [90].



106

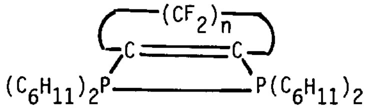
a R = t-Bu
b R = i-Pr
c R = c-C_6H_{11}



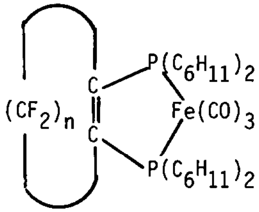
107

$(EtO)_2P$-O-$P(OEt)_2$ can act only as a bridging and not a chelating ligand because of the P-O-P angle. Its reaction with $Fe_2(CO)_9$ gave 107. Also prepared were $Fe_2(CO)_5[(EtO)_2P$-O-$P(OEt)_2]_2$ and $[Fe(CO)_2(SMe)_2][(Et_2O)_2P$-O-$P(OEt)_2]$ [91].

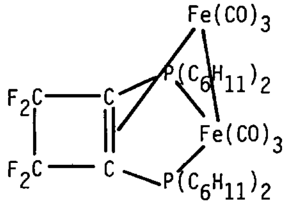
108a reacts with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ giving 109a and 110 while 108b gives only 109b with $Fe(CO)_5$.



108 a n = 2
b n = 3

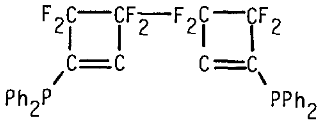


109 a n = 2
b n = 3

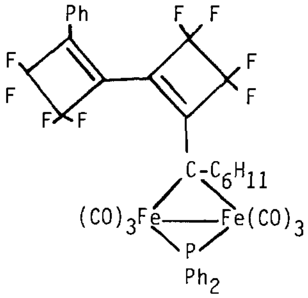


110

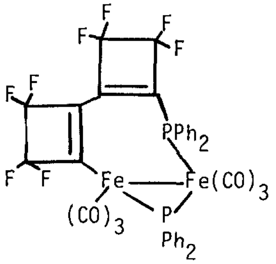
111 produces 112 and 113 (whose X-ray structures are reported) when allowed to react with $Fe(CO)_5$ or $Fe_3(CO)_{12}$ [92].



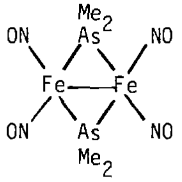
111



112

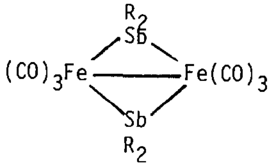


113



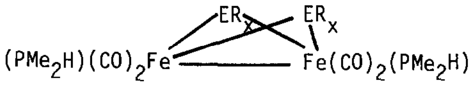
114

114 is the product of thermolysis of $Fe(CO)_4(As_2Me_4)$ [78]. The reaction of $Fe_2(CO)_9$ with Sb_2R_4(R = Et, t-Bu) affords $Fe(CO)_4(SbR_2SbR_2)$, $[Fe(CO)_4]_2(Sb_2R_4)$ and 115 [93].



115 a R = Et
b R = t-Bu

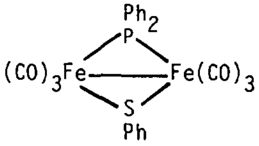
116 is synthesized by reaction of excess phosphine with the corresponding hexacarbonyl complex [94]. A monosubstituted complex results from addition of a stoichiometric quantity of the phosphine.



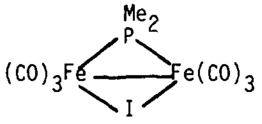
116 a $ER_x = PMe_2$
b $ER_x = SMe$

117 was prepared by a new route involving photolysis of Ph_2PSPh and $Fe(CO)_5$ in a 1:2 ratio in benzene. The interatomic distances found by X-ray diffraction

resemble those in Fe_2S_2 systems [95]. The related complex 118 has a short Fe-Fe bond of length 258.8 pm [96].

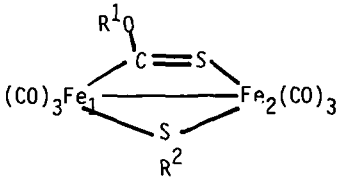


117

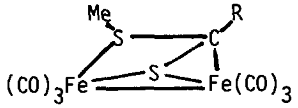


118

$Fe_2(CO)_9$ reacts with a series of xanthates $R^1OC(S)SR^2$ where R^1 are steroids and terpenes. The products 119 feature insertion of an $Fe(CO)_3$ group into a C-S bond [97]. The X-ray structure was reported for 119 R^1 = (adamantyl)methyl, R^2 = Me.



119

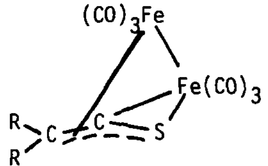


120 a R = i-Pr; b R = C_6H_{11}; c R = Ph; d R = p-$MeOC_6H_4$; e R = p-$NMe_2C_6H_4$; f R = p-MeC_6H_4; g R = p-BrC_6H_4; h R = p-CH_2-CHC_6H_4; i R = CH_2Ph; j R = naphthyl; k R = SPh

^{13}C NMR of 119 and analogous complexes monosubstituted on Fe_2 by $P(OMe)_3$ shows that, over the temperature range - 100 to + 50°C, the CO's bonded to Fe_1 are involved in local exchange while those on Fe_2 are static [98].

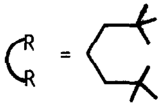
Thioesters RC(S)SMe react with $Fe_2(CO)_9$ yielding 120. The crystal structure of 120 j indicated that Fe is coordinated to C=S [99].

In pentane 121 a,b are the products of the reaction of $Fe_2(CO)_9$ with the

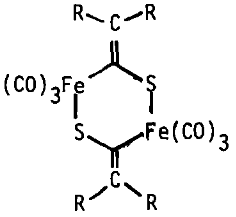


121

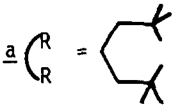
a



b R = t-Bu



122 a

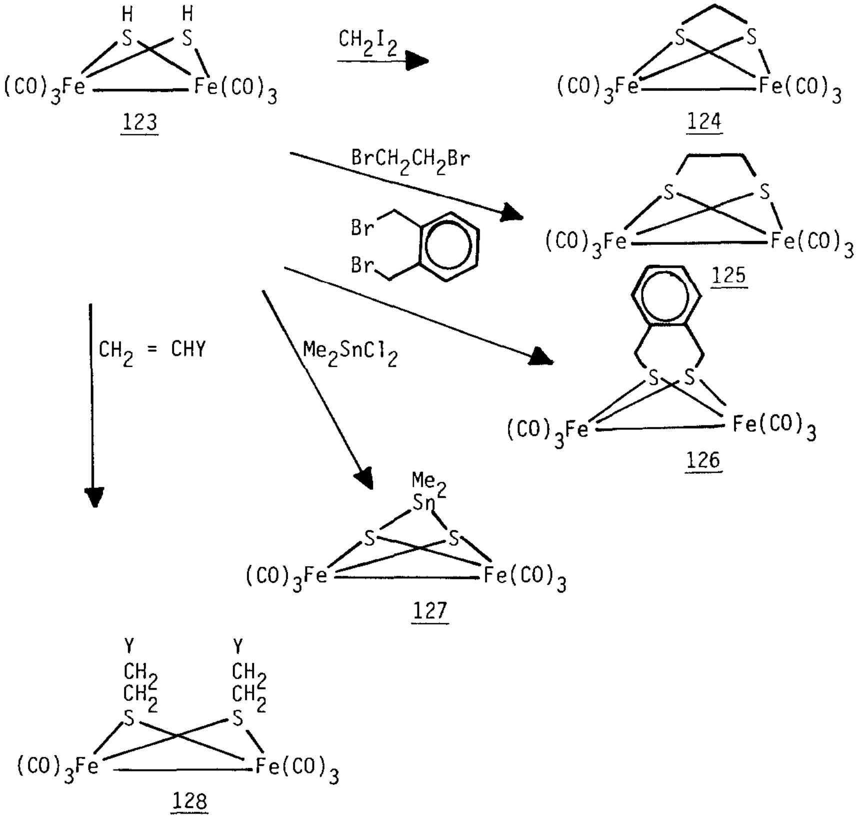


b R = t-Bu

corresponding substituted thioketene. However, in THF 122 a,b are formed. The X-ray structure of 122a was reported [100].

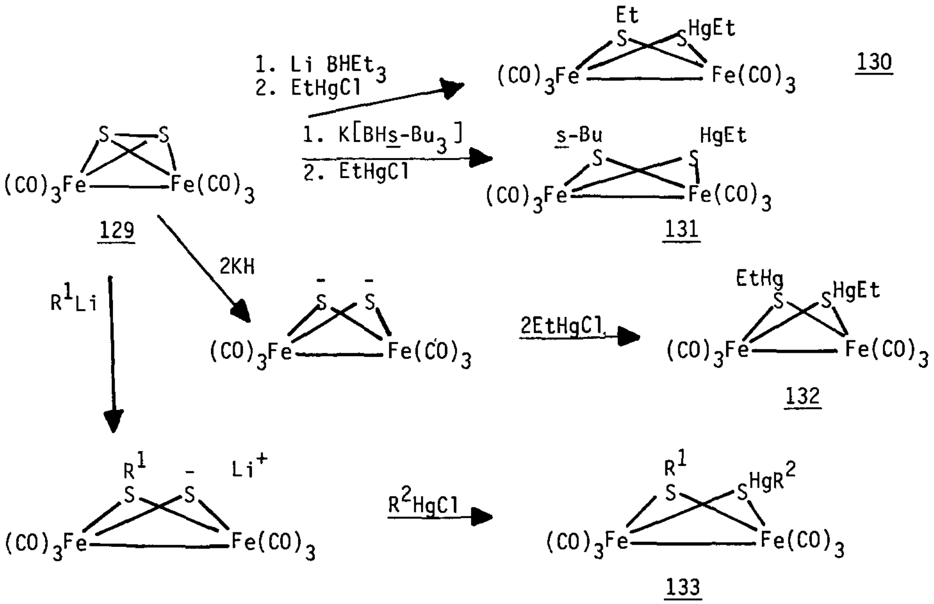
The chemistry of S-bridged species was the subject of several publications. Electrophilic reagents effect substitution of H on 123 confirming its similarity to organic thiols [101].

SCHEME 18



When $Li_2[Fe_2(CO)_6S_2]$ is generated from $LiHBEt_3$ and 129 and subsequently treated with EtHgCl(2 moles), the unexpected product is 130 in which the SEt group originates in the Li reagent [102]. When the anion is generated using K-$[B(s\text{-}Bu)_3H]$, a similar result 131 was observed. 132 could be obtained when KH was employed as the reducing agent. Generation of a monoanion from R^1Li followed by treatment with R^2HgCl produces 132. NMR studies showed that only a single isomer of 132 and of 133 is present in solution [102].

SCHEME 19

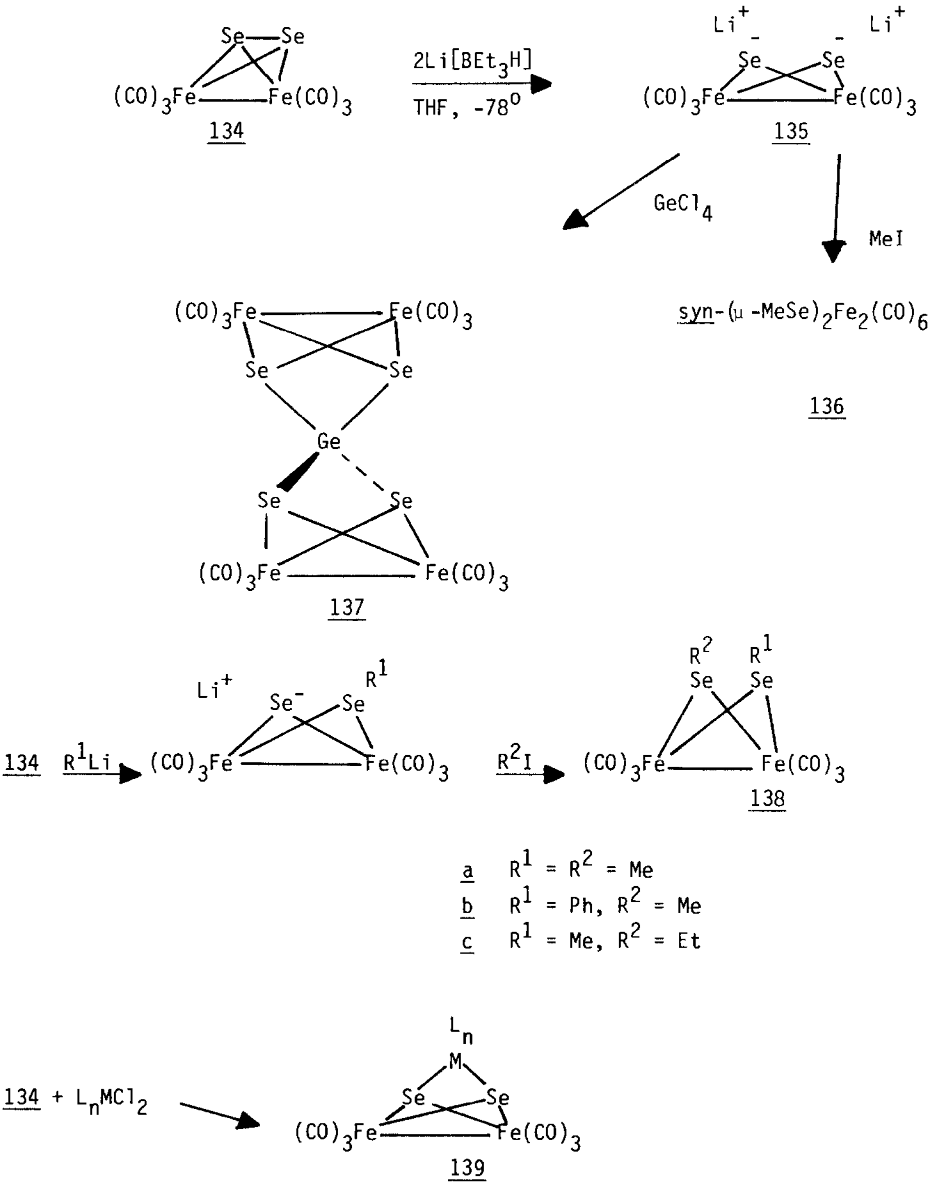


^{13}C NMR spectra of 129 and the *syn*- and *anti*- isomers of $Fe_2(CO)_6(\mu\text{-SMe})_2$ as well as of $Fe_3(CO)_{12}$ were measured and ^{57}Fe satellites observed [103].

Reaction of $Fe_2(CO)_6(\mu\text{-X})_2$ (X = S, Se) with Lewis bases was reported [104] to give replacement of one or two CO's as well as $Fe_3(CO)_9L_n(\mu_3\text{-X})_2$ (X = S, Se; n = 0, 1,2).

134 mimics the reactivity of organic disulfides as shown in Scheme 20 [105].

SCHEME 20



134

135

136

137

138

a R^1 = R^2 = Me
b R^1 = Ph, R^2 = Me
c R^1 = Me, R^2 = Et

139

a ML$_n$ = Pt(PPh$_3$)$_2$
b ML$_n$ = CpCo
c ML$_n$ = Ni(diphos)
d ML$_n$ = Me$_2$Sn

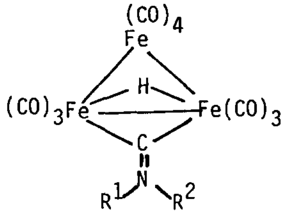
The mass spectra of (μ_2-ECF$_3$)$_2$Fe$_2$(CO)$_6$ (E = S, Se) were reported [106]. A preparation of $(\mu\text{-Te})_2Fe_2(CO)_6$ from $Fe(CO)_5$, OH^- and $KTeO_3$ was developed [107]. Treatment of the dimer with MeNO affords $(\mu_3\text{-Te})_2Fe_3(CO)_9$.

Trinuclear Species (All Same Metal)

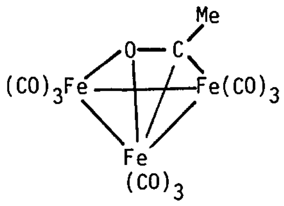
The ^{13}C NMR spectrum of isotopically enriched $Fe_3(CO)_{12}$ shows six signals in 2:2:2:2:2:2 ratio. The spectrum was interpreted as indicating a fluxional process consistent with time averaging of the two disordered molecules observed crystallographically via rotation of the Fe_3 triangle within the plane [108]. The solution photochemistry of $[Fe_3(CO)_{11}]^{2-}$ was studied in several solvents. In MeCN, CO dissociation is the primary photoprocess. In CH_2Cl_2, CO dissociation is followed by photofragmentation. In H_2O, both CO dissociation and photofragmentation occur simultaneously [109].

The ESR of the radical $[HFe_3(CO)_{11}]^{\bullet}$ was reported [85]. This species results from irradiation of $Fe(CO)_5$ or $AgBF_4$ oxidation of $[HFe_3(CO)_{11}]^-$. Two preparations of $[Et_4N][HFe_3(CO)_{11}]$ were developed. One involving $[Et_4N][BH_4]$ reduction of $Fe_3(CO)_{12}$ in a phase-transfer-catalyzed reaction gives a yield of 90% [110,111]. The other involves reduction by Na_2C_2 and gives a 38% yield [112].

The crystal structure of 140a has been determined [113]. Treatment of $[Fe_2(CO)_8]^{2-}$ with MeI produces 141 which probably arises from Me attack on Fe and subsequent migration [114]. In contrast, the harder carbocation of $ClCH_2OMe$ attacks an O of $[Fe_2(CO)_8]^{2-}$ producing 142. X-ray structures of 141 and 142 were determined [114,115].

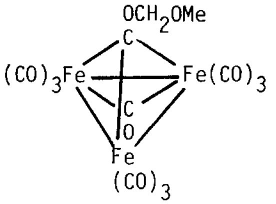


140 a $R^1 = R^2 = Me$
b $R^1 = Me$, $R^2 = Et$
c $R^1 = R^2 = Et$
d $R^1 = i\text{-Pr}$, $R^2 = Et$
e $R^1 = H$, $R^2 = Me$

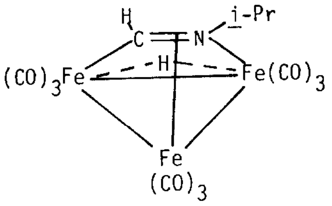


141

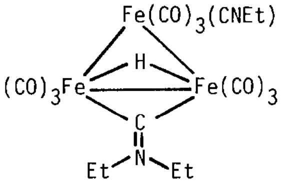
When $[PPN][HFe_3(CO)_{11}]$ is treated with CNR^1 (R^1 = Me, Et, i-Pr), $[HFe_3(CO)_{10}(CNR^1)]^-$ is formed *in situ*. Treatment with H^+ or carbocation source yields 140 b-e. Thermolysis of the intermediate affords 143 [116]. Prolonged reaction with CNEt followed by protonation gives 144.



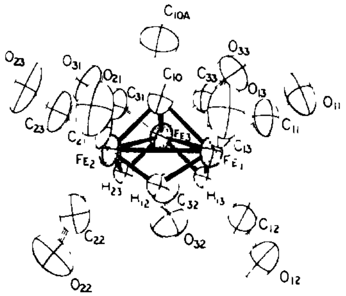
142



143



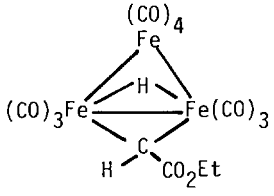
144



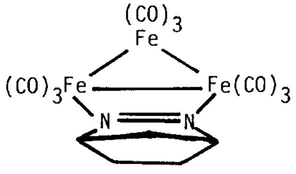
145

$Fe_3(\mu\text{-}H)_3(CO)_9(CMe)$, 145, results when $Fe(CO)_5$ is allowed to react with $NaH_2Al(OEt)_2$ in the presence of B_5H_9. The CMe ligand results from CO reduction. The structure is similar to that of isoelectronic $Co_3(CO)_9CMe$ [117]. The UV photoelectron spectrum of 145 shows an increase of metal I.P.'s as compared to that of the isoelectronic Co compound [118].

When $[HFe_3(CO)_{11}]^-$ reacts with N_2CHCO_2Et, 146 is isolated as the PPh_4^+ salt [119].



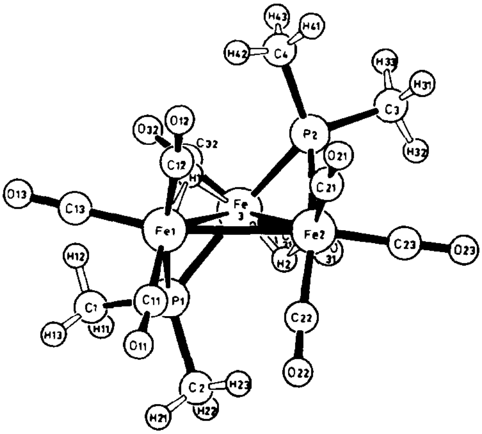
146



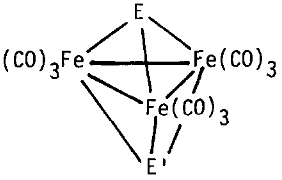
147

Mass spectra of some isomeric compounds $Fe_3(CO)_8(HC_2R)_4$ (R = Me, Et, *i*-Pr) isolated from cyclooligomerization reactions of alkynes were published [120].

Several trinuclear clusters containing Group V ligands were studied. The synthesis and X-ray structure of (2,3-diazanorbornene)$Fe_3(CO)_9$, 147, were reported [121]. The ^{13}C NMR of some $Fe_3(CO)_{11}L$ (L = phosphine or phosphite) were interpreted in terms of an icosahedral $\rightleftarrows$ cubooctahedral exchange of ligands [122]. Reaction of $Fe(CO)_4(PMe_2H)$ with bis(η^3-allyl)nickel or photolysis of a mixture of PMe_2H and $Fe_3(CO)_{12}$ produces $Fe_3(\mu\text{-}H)_2(\mu\text{-}PMe_2)_2(CO)_8$, 148, whose X-ray structure is reported [123].

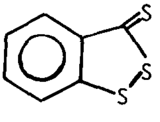


148

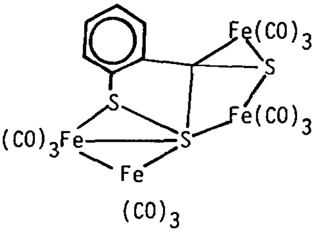


149 a E = S, E' = SO
b E = E' = S
c E = S, E' = CO

IR spectra of 149 a,b allowed assignment of vibrational frequencies associated with μ_3-S in the region ~ 240-350 cm^{-1} [124]. The electrochemistry of 149 a-c was also investigated [125]. 150 was found to react with $Fe_2(CO)_9$ to produce 151 whose X-ray structure was determined [126].

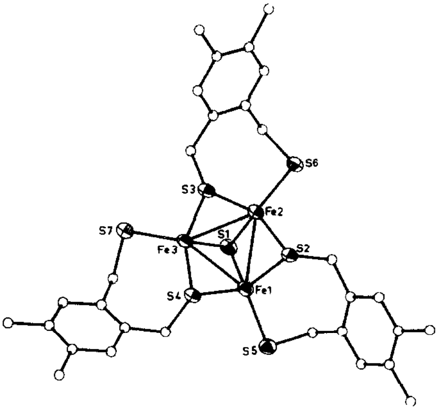


150

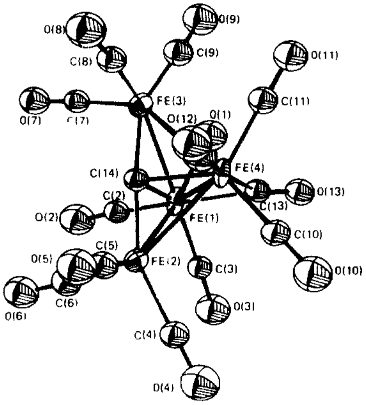


151

When 1,2-bis(mercaptomethyl)-4,5-dimethylbenzene, NaOMe, p-thiocresol and $FeCl_3$ are allowed to react in anhydrous methanol, 152 can be isolated. The structure is derived from the $Fe_4S_4(SR)_4$ cubane structure with one tetrahedral vertex unoccupied [127].



152

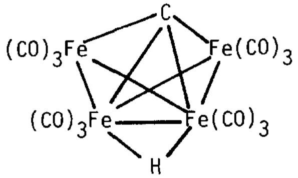


153

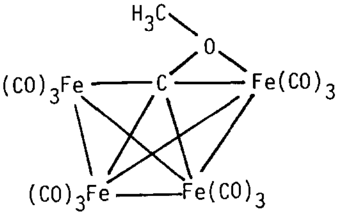
Polynuclear Clusters

Protonation of $[Fe_4(CO)_{13}C(CO_2Me)]^-$ gives $Fe_4(CO)_{13}C$, 153, which features an exposed μ_4-C. The reaction can be reversed by methanol. The X-ray structure shows a butterfly arrangement of the Fe_4 unit [128]. The isoelectronic anions $[HFe_4C(CO)_{12}]^-$ and $[Fe_4C(CO)_{12}]^{2-}$ were synthesized [129]. The X-ray structure of the dianion as its $[Zn(NH_3)_4]^{2+}$ [129] and $[NMe_3CH_2Ph]^+$ [130] salts showed an Fe_4 butterfly arrangement with μ_4-C. The dianion can be reversibly protonated, the second proton adding to the carbide C giving $HFe_4(\mu^2\text{-}CH)(CO)_{12}$, 154. Methylation occurs at the carbide C along with CO insertion. The dianion can be oxidized to $Fe_4C(CO)_{12}$ which, in turn, reacts with H_2 producing 154 [129]. An X-ray and neutron diffraction study was carried out on 154 [131]. This is a 62-electron cluster having a closed three-center two-electron Fe-C-H bond.

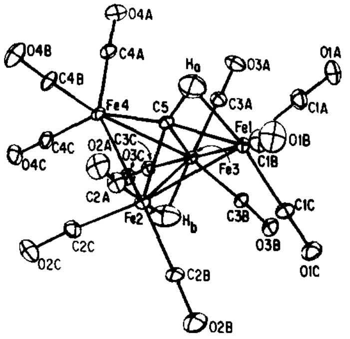
$[Fe_4(CO)_{13}]^{2-}$ can be protonated with HSO_3CF_3 giving $[HFe_4(CO)_{12}C]^-$, 155, isolated as a PPN salt [132]. When the anion is treated with a CH_3^+ source $(\mu\text{-}H)Fe_4(CO)_{12}(\mu^2\text{-}COMe)$, 156, is obtained. The X-ray structures of both these species show an Fe_4 butterfly arrangement with 155 having an exposed carbide C [132]. Similarities in the ^{13}C NMR spectra of 156 and $H_2Fe_4(CO)_{13}$ (obtained from protonation of 155) indicate that the latter compound contains μ^2-COH [133].

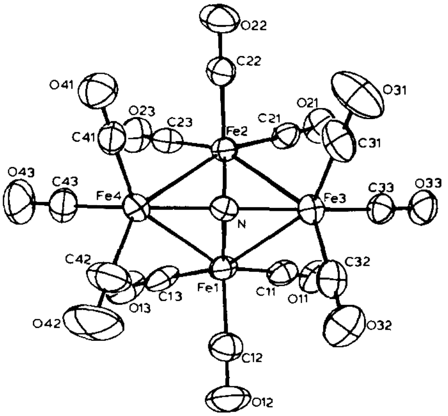


155



156





<u>154</u> <u>157</u>

An improved preparation of $[PPN][Fe_4N(CO)_{12}]$, <u>157</u>, was reported [134,135]. The X-ray structure again showed a butterfly Fe_4 group with μ_4-N in this anion which is isoelectronic with $[Fe_4C(CO)_{12}]^{2-}$. The anion of <u>157</u> can be protonated with HSO_3CF_3 to give $HFe_4N(CO)_{12}$. A mixture of products results from <u>157's</u> reactions with H_3PO_4 [135].

SCHEME 21

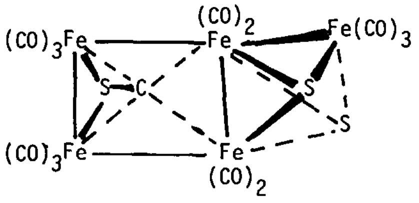
$$PPN\,[Fe(CO)_3(NO)] + Fe_3(CO)_{12} \xrightarrow{THF} PPN[\,Fe_4N(CO)_{12}] \quad 50\% \quad \underline{157}$$

$$\underline{157} + HSO_3CF_3 \xrightarrow{CH_2Cl_2} HFe_4N(CO)_{12} \quad 92\%$$

$$Na[Fe_4N(CO)_{12}] + H_3PO_4 \longrightarrow HFe_4N(CO)_{12}\ (43\%) + Fe_4(CO)_{11}N(NO) + Fe_3(NH)(CO)_{10} + Fe_3(NH)_2(CO)_9$$

Thermolysis of $Fe(CO)_4(AsMeH_2)$ gave <u>53</u>, $[\,Fe(CO)_3AsMe]_4$, having a cubane-like structure [42].

CS_2 was found to react with $Fe_3(CO)_{12}$ under CO pressure affording $Fe_4S_2(CS_2)(CO)_{13}$, <u>158</u>. The X-ray structure shows that CS_2 acts as a six-electron donor [136].



<u>158</u>

The cation $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$ consists of an octahedron of Fe atoms with all faces triply bridged by S. The complex has μ_{eff} = 6.04 B.M. at 291 K. If S is considered to contribute four electrons, this is a 90-electron cluster in contrast to the more usual 86-electron count [137].

Heterometallic Clusters

The compounds mentioned in this section are organized according to the identity of the hetero metals in the clusters. Where more than one kind of hetero metal is present, the entry is under the earliest in the periodic table. An exception of a variety of carbide clusters using polyhedral expansion and contraction reactions set out in Scheme 22 [138]:

SCHEME 22

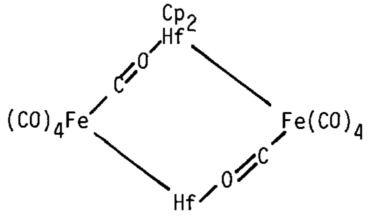
$$[Fe_4C(CO)_{12}]^{2-} + \left[\begin{array}{lcl}
Cr(CO)_3py_3 & \longrightarrow & [Fe_4CrC(CO)_{15}]^{2-} \\
W(CO)_3py_3 & \longrightarrow & [Fe_4WC(CO)_{15}]^{2-} \\
Mo(CO)_3(THF)_3 & \longrightarrow & [Fe_4Mo_2C(CO)_{18}]^{2-} \\
[Rh(CO)_2Cl]_2 & \longrightarrow & [Fe_4RhC(CO)_{14}]^{-} \\
[M(cod)Cl]_2 & \longrightarrow & [FeMC(CO)_{12}(cod)]^{-} \quad M = Rh,\ Ir \\
[Pd(\eta^3\text{-}C_3H_5)Cl]_2 & \longrightarrow & [Fe_4PdC(CO)_{12}(\eta^3\text{-}C_3H_5)]^{-} \\
Ni(cod)_2,\ CO & \longrightarrow & [Fe_4Ni_2C(CO)_{14}]^{2-} \\
Cu(NCMe)_4^{+} & \longrightarrow & [Fe_4CuC(CO)_{12}(NCMe)]^{-}
\end{array}\right.$$

$$[Fe_5C(CO)_{14}]^{2-} + \left[\begin{array}{lcl}
M(CO)_3L_3 & \longrightarrow & [Fe_5MC(CO)_{17}]^{2-} \quad M = Cr,\ Mo,\ W \\
Fe_2(CO)_9 & \longrightarrow & [Fe_6C(CO)_{16}]^{2-} \\
Rh_2(CO)_4Cl_2 & \longrightarrow & [Fe_5RhC(CO)_{16}]^{-} \\
[M(cod)Cl]_2 & \longrightarrow & [Fe_5MC(CO)_{14}(cod)]^{-} \quad M = Rh,\ Ir \\
Ni(cod)_2 & \longrightarrow & [Fe_5NiC(CO)_{15}]^{2-} \\
[Pd(\eta^3\text{-}C_3H_5)Cl]_2 & \longrightarrow & Fe_5PdC(CO)_{16} \\
Cu(NCMe)_4^{+} & \longrightarrow & [Fe_4CuC(CO)_{14}(NCMe)]^{-}
\end{array}\right.$$

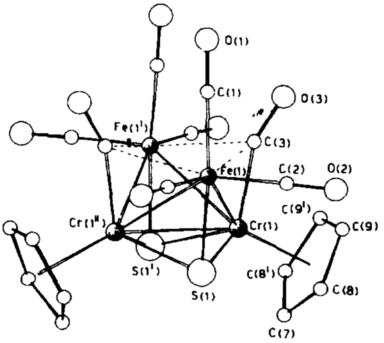
$$\left.\begin{array}{l}
[Fe_5CrC(CO)_{17}]^{2-} \\
[Fe_5Mo(CO)_{17}]^{2-} \\
[Fe_5W(CO)_{17}]^{2-} \\
[Fe_5RhC(CO)_{16}]^{-}
\end{array}\right] \xrightarrow{Fe^{3+}} \begin{array}{l}
Fe_4CrC(CO)_{16} \\
Fe_4MoC(CO)_{16} \\
Fe_4WC(CO)_{16} \\
[Fe_4RhC(CO)_{14}]^{-}
\end{array}$$

The Fe clusters chosen for the polyhedral expansion reactions have open faces and high electron density to promote attack by coordinatively unsaturated fragments. ^{13}C NMR indicates that the cluster products are stereochemically non-rigid at low temperatures

Cp_2HfX_2 (X = Cl, I) reacts with $Na_2Fe(CO)_4$ to afford <u>159</u> containing Fe-Hf bonds [139].



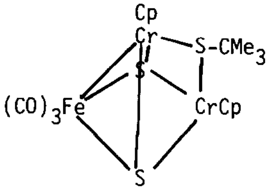
159



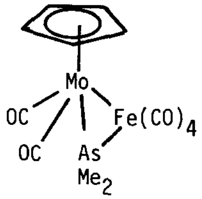
160

$Cp_2Cr_2(CO)_6$ and $Fe_2S_2(CO)_6$, when refluxed in toluene/hexane, afford $Cp_2Fe_2Cr_2(\mu_3\text{-}S)_2(\mu_3\text{-}CO)_{26}$, 160. The X-ray structure shows a butterfly arrangement of metal atoms in which Fe atoms occupy the "wings". This is a 62-electron cluster [140].

161, $(CpCr)_2(\mu_2\text{-}SCMe_3)(\mu_3\text{-}S)_2Fe(CO)_3$, is the product of irradiation of $Fe(CO)_5$ with $(CpCrSMe_3)_2S$ [141]. The temperature-dependent ^1H and ^{13}C NMR spectra

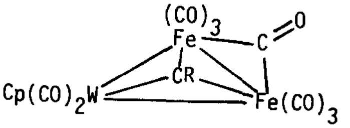


161

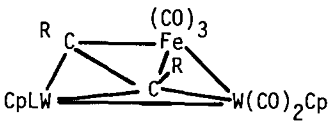


162

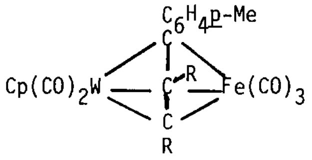
of 162 were interpreted [142] in terms of the occurrence of no fewer than three distinguishable fluxional processes. $Fe_2(CO)_9$ in excess reacts with the $CpW(CO)_2$ C(p-tolyl) giving 163. When the W complex is in excess, 164a is produced and its X-ray structure was reported. When $Fe_3(CO)_{12}$ is a reactant 163, 164a and a small amount of 164b are produced [143]. 163 reacts with alkynes in toluene to afford 165.

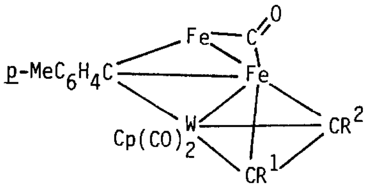


163 R = p-tolyl



164 R = p-tolyl a L = CO
b L = O



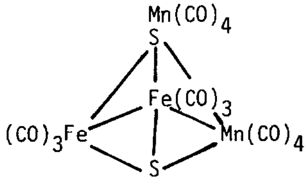


165 a R = Me, b R = Ph,
c R = CF_3, d R = p-tolyl

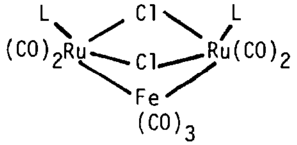
166 a $R^1 = R^2 = SiMe_3$
b $R^1 = SiMe_3$, R^2 = t-Bu
c R^1 = t-Bu, $R^2 = SiMe_3$

When the alkynes are $Me_3SiC{\equiv}CSiMe_3$ or t-BuC≡Ct-Bu, 166a or 166b,c are the products, respectively [144]. The X-ray structures of 165a and 166a were determined.

129 was found to yield 167 on irradiation in THF solution with $Fe(CO)_5$. X-ray structure determination showed the presence of both three- and four-coordinate S [145].



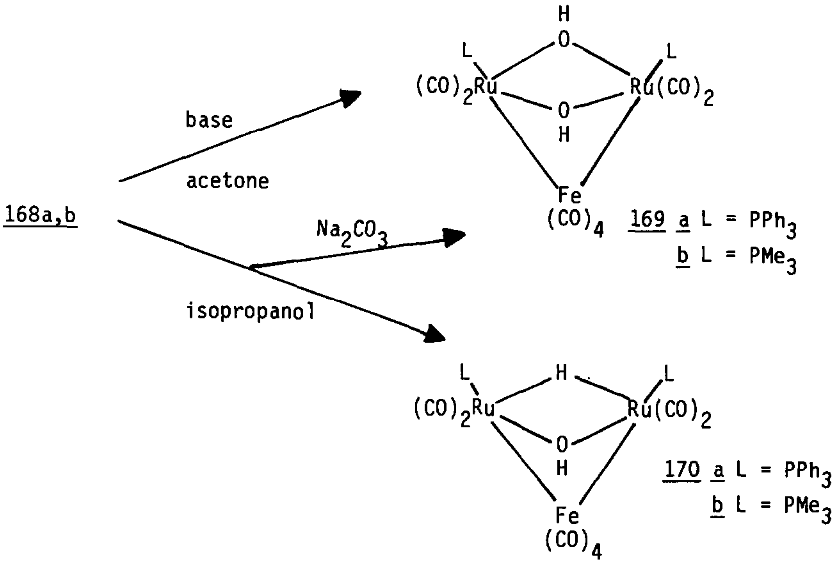
167



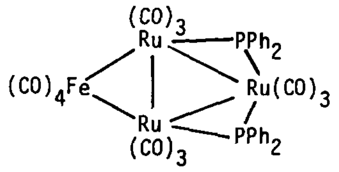
168 a L = $P(OMe_3)$,
b L = PPh_3, c L = PMe_2Ph,
d L = PMe_3,
e L = $P(C{\equiv}Ct\text{-}Bu)Ph_2$

Microcalorimetric measurements on $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ were employed to estimate an Fe-Ru bond energy of 95±20 kJ $mole^{-1}$. This value is greater than the mean of the Fe-Fe and Ru-Ru bond energies [146]. Trinuclear species 168a-e along with $Ru_3(CO)_{10}L_2$ and $FeRu_2(CO)_{10}L_2$ were the products of reactions between $Fe_2(CO)_9$ and $(\eta^6\text{-}C_6H_6)Ru(L)Cl_2$. The X-ray structure of 168e was reported [147, 148]. The μ-Cl's can be replaced in 168b and d [149]:

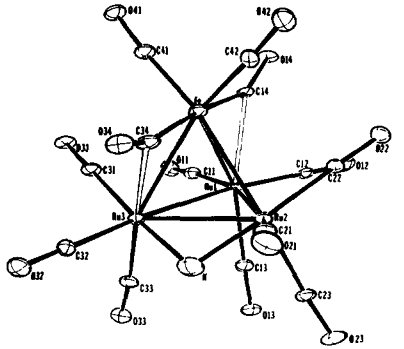
SCHEME 23



$Ru_3(CO)_{12}$ and $Fe(CO)_4(Ph_2PPPh_2)$ give 171, $FeRu_3(CO)_{13}(\mu\text{-}PPh_2)_2$, which has a triangulated rhombic array of metal atoms and a planar geometry similar to that of isoelectronic $[Re_4(CO)_{16}]^{4-}$ [150].



171

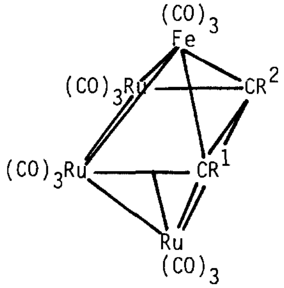


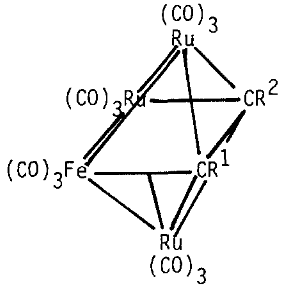
172

$[PPN][HFeRu_3(CO)_{13}]$ (47%), 172, and $[PPN][HFe_2Ru_2(CO)_{13}]$ (4%), 173, are the products when $Ru_3(CO)_{12}$ and $[PPN][HFe(CO)_4]$ are refluxed in THF. The structure of 172 determined both by neutron and by X-ray diffraction is similar to that of $H_2FeRu_3(CO)_{13}$ except for a shortening of the unbridged Ru-Ru bond. Neutron and X-ray diffraction structures were also reported for 173. In this species the H still bridges a Ru-Ru bond. Surprisingly, an analogous preparative route did not give $[HFe_3Ru(CO)_{13}]^-$ [151].

$H_2FeRu_3(CO)_{13}$ was found to react thermally with various phosphines and phosphites. Preferential substitution on Ru was observed. Monosubstituted products of C_s symmetry were obtained for PPh_3, PPh_2Me, PMe_2Ph, $PPhEt_2$, $P(OMe)_3$, $P(OEt)_3$, $P(OEt)_2Ph$ and P(*i*-Pr)$_3$. $H_2FeRu_3(CO)_{12}(PMe_3)$ gave an isomer mixture. Disubstituted species were obtained with PPh_3, PMe_3, and $P(OMe_3)$. Kinetic measurements revealed a first-order dependence on the cluster and zero-order dependence on PPh_3 [152]. NMR studies showed that the substitution products are stereochemically non-rigid in solution and that exchange processes are similar to those previously reported for $H_2FeRu_3(CO)_{13}$ [153]. The photochemistry of $H_2FeRu_3(CO)_{13}$, $H_2FeOs_3(CO)_{13}$ and $H_2Ru_4(CO)_{13}$ also was investigated. In hydrocarbon solution in the presence of PPh_3, clean photosubstitution of CO occurred giving first a mono-, then a disubstituted product. In the presence of H_2, $H_4FeM_3(CO)_{12}$ (M = Ru, Os) could be obtained. The primary photoprocess must be photodissociation of CO since the aforementioned reactions are retarded in the presence of CO [154].

$H_2FeRu_3(CO)_{13}$ was found to react with alkynes to give *closo* clusters 174 and 175. With unsymmetrical $MeC\equiv CPh$ the isomer mixture 174c, 175d is produced.



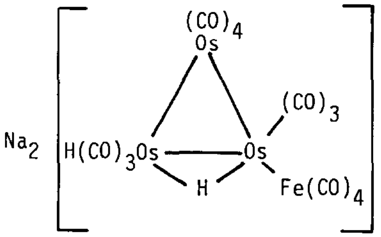


174 a $R^1 = R^2 = Me$
b $R^1 = R^2 = Ph$
c $R^1 = Me$, $R^2 = Ph$

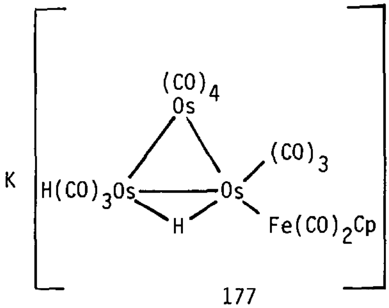
175 a $R^1 = R^2 = Me$
b $R^1 = R^2 = Ph$
c $R^1 = Me$, $R^2 = Ph$
d $R^1 = Ph$, $R^2 = Me$

X-ray structures of 174b and 175b were reported [155].

Treatment of $H_2Os_3(CO)_{10}$ in THF at -78°C with $Na_2[Fe(CO)_4]$ or $K[CpFe(CO)_2]$ gives 176 and 177, respectively. Both compounds are thermally unstable [156].

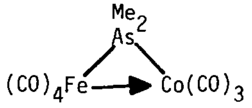


176

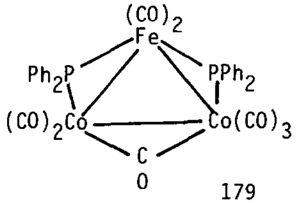


177

The kinetics of the heterolytic fission of the Fe → Co bond in 178 show first-order dependence on entering P-, As-, or Sb- donor entering ligands[157].



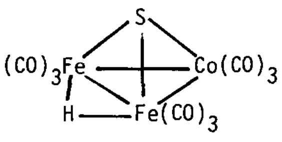
178



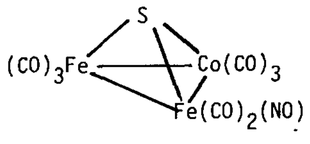
179

Electrolytic or chemical reduction of $SFeCo_2(CO)_9$ produces the radical anion $SFeCo_2(CO)_9^{\dot{-}}$ whose ESR spectrum was reported [158].

A 71% yield of 179 was obtained from the reaction between $Fe(CO)_4(PPh_2PPh_2)$ and $Co_2(CO)_8$ in refluxing hexane. An X-ray structure of 179 shows that the μ-CO is semi-bridging in spite of the equality of both Fe-CO bond lengths. The semi-bridging structure persists in solution at -95°C [159]. The reaction of $[Fe_3(CO)_9S]^{2-}$ and $Co_2(CO)_8$ affords $[Fe_2Co(CO)_9S]^-$ which, on protonation, gives 180. If NO_2^- and H^+ are allowed to react with $[Fe_2Co(CO)_9S]^-$, 181, is the product [160]. 134 and $Co_2(CO)_8$ produce $FeCo_2(CO)_9Se$ isoelectronic with 180 and having a pyramidal structure with capping Se [105].

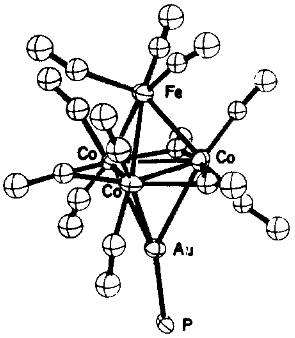


180

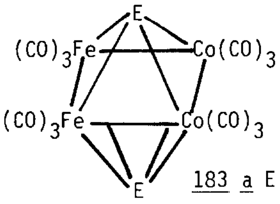


181

The five-vertex closo cluster $FeCo_3(CO)_{12}Au(PPh_3)$, 182, results from treatment of $[FeCo_3(CO)_{12}]^-$ with $[Au(PPh_3)]^+$ in acetone [161].



182

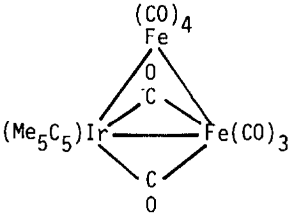


183 a E = S
b E = PPh

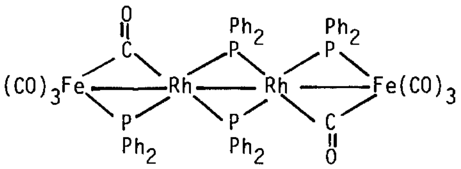
^{17}O NMR of $HFeCo_3(CO)_{12}$ is in agreement with a C_{3v} structure with apical $Fe(CO)_3$ group and three $Co(CO)_2$ groups in the trigonal plane bridged by μ_2-CO. The H triply bridges the Co atoms and lies on the C_3 axis [162]. Reaction of $HFeCo_3(CO)_{12}$ with PMe_2Ph leads to the trisubstituted product $\{HFe(CO)_2(PMe_2Ph)[Co(CO)(PMe_2Ph)]_2Co(CO)_2(\mu_2\text{-}CO)_3\}$ which was found by X-ray diffraction to have the same basic geometry as the parent carbonyl. The position of H was not located [163].

Treatment of 129 or $Fe_2(CO)_6(\mu\text{-PPhH})_2$ with $Co_2(CO)_8$ leads to 183a and 183b, respectively [164].

The X-ray structure of 184, the reaction product of $Fe_3(CO)_{12}$ with $[(\eta^5\text{-}Me_5C_5)Ir(\mu\text{-Cl})Cl]_2$, was reported [165].



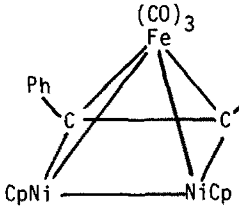
184



185

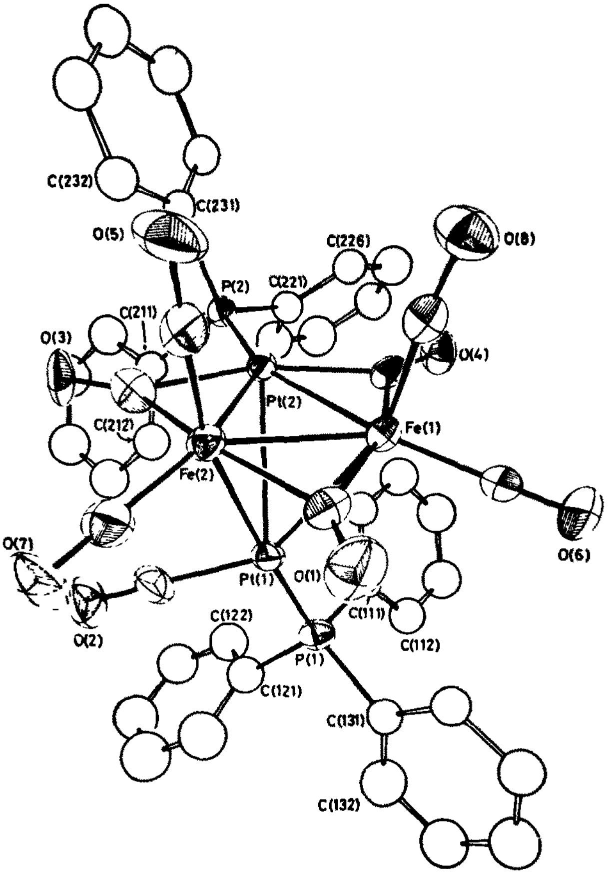
The reaction of $[(\eta^3\text{-}C_3H_5)RhCl]_2$ with 4 moles of $Fe(CO)_4(PPh_2H)$ was found to give 185 which X-ray diffraction showed to have a chain structure [166].

The X-ray structure of 186 was determined [167] as well as that of a related Ni complex $CpNiFe_2(CO)_6(C\underline{t}\text{-}Bu)_2$ [168].



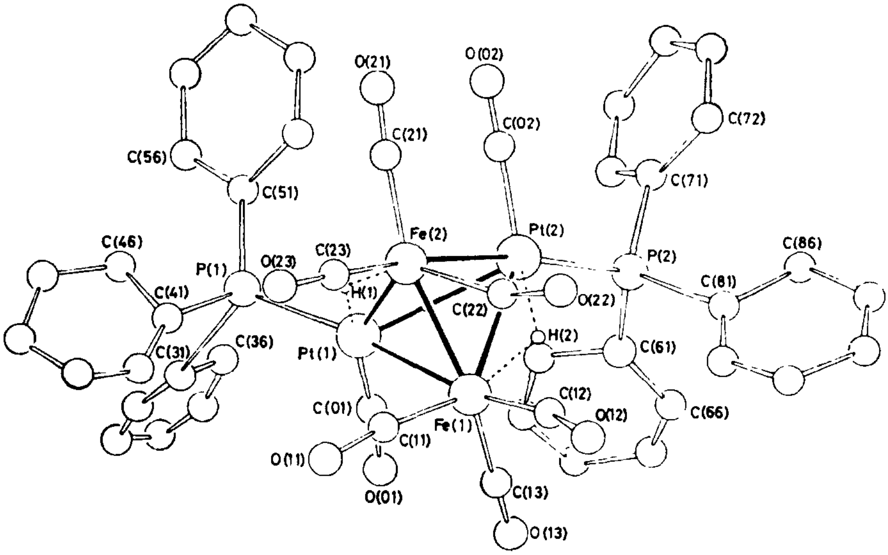
186

Reaction of $\mathrm{Pt(PPh_3)(C_2H_4)}$ with $\mathrm{[Et_4N][Fe_2(\mu\text{-}H)(\mu\text{-}CO)_2(CO)_6]}$ in THF gave the anion 187, $\mathrm{[Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]^-}$. The X-ray diffraction study did not locate the H; its position was inferred as involving the longest Pt-Fe distance.



187

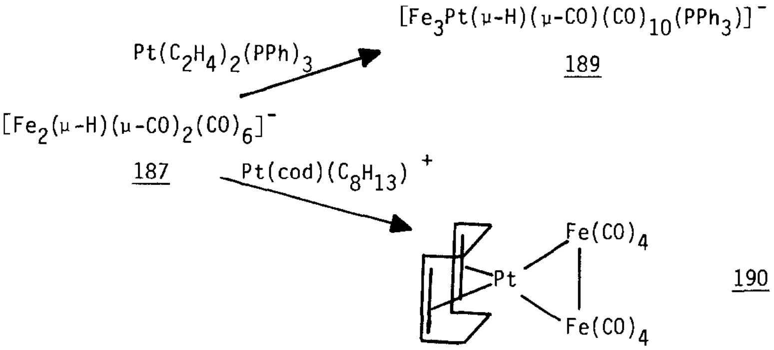
Protonation of 187 with $\mathrm{HBF_4\cdot 2Et_2O}$ affords 188, $\mathrm{Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2}$, in which all the CO's are terminal [169].



188

Other reactions of the anion lead to other cluster products [169]. See Scheme 24. The X-ray structure of 190 was reported.

SCHEME 24

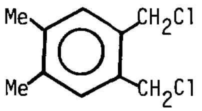


ESR measurements on $[Fe_3Pt_3(CO)_{15}]^-$ showed [170] that the unpaired electron density lies mainly in a non-degenerate Pt_3 MO. The crystal structure of another Fe-Pt cluster $[Fe_4Pt_6(CO)_{22}]^{2-}$ was determined [171].

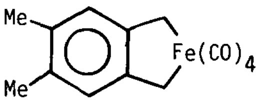
METAL-CARBON σ-BONDED SPECIES

Metal Alkyl Complexes

$[Fe(CO)_4]^{2-}$ was allowed to react with 191 giving 192 which, on treatment with PPh_3, yields $Fe(CO)_4(PPh_3)$ [172].

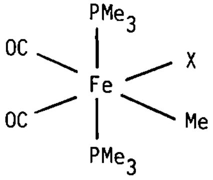


191

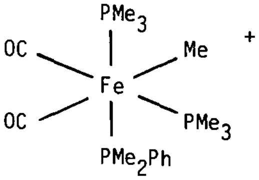


192

Photolysis of $FeCl_2(CO)_2(PEt_3)_2$ or $[FeCl(CO)_3(PMe_3)]^+$ in the presence of Cp_2TiMe_2 afforded $Fe(Me)Cl(CO)_2(PEt_3)_2$ or $[Fe(Me)(CO)_3(PMe_3)]^+$, respectively,[173]via a free-radical process. Similar treatment of $Fe(CO)_3(PMe_3)_2$ produces 193 (X = Cl).



193



194

The first asymmetric Fe complex containing only monodentate ligands, 194, results from treatment of $Fe(CO)_2(PMe_3)_2(Me)I$ with PMe_2Ph and isomerization of the kinetic product [174].

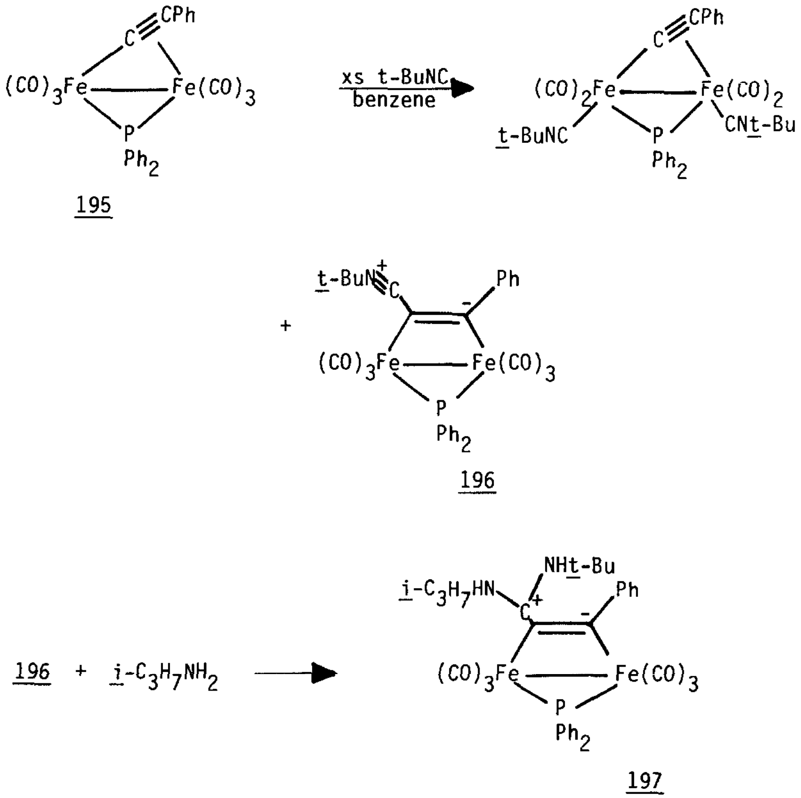
Electrogenerated Fe(I) porphyrins were allowed to react with alkyl halides to produce Fe(II)R complexes [175]. Steady-state radiolysis of MeCl-saturated solutions of ferrous or ferric deuteroporphyrins or chemical reduction of methyl iodide solutions of ferric deuteroporphyrin gives the MeFe(III) deuteroporphyrin complex which is stable under anaerobic conditions [176].

Evidence was presented for the formulation of the oxidation product of Fe vinylidene porphyrins as involving N-alkylation and an intermediate-spin (S = 3/2) Fe [177].

A theoretical study of external nucleophilic attack on η^2-olefin complexes which converts them to alkyl products has demonstrated that slippage to η^1-coordination activates olefins toward nucleophilic attack [178].

External nucleophilic attack on an acetylide ligand of 195 was found to be competitive with CO substitution. When 196 reacts with i-$C_3H_7NH_2$, 197 is the product. The X-ray structure of 197 was reported [179].

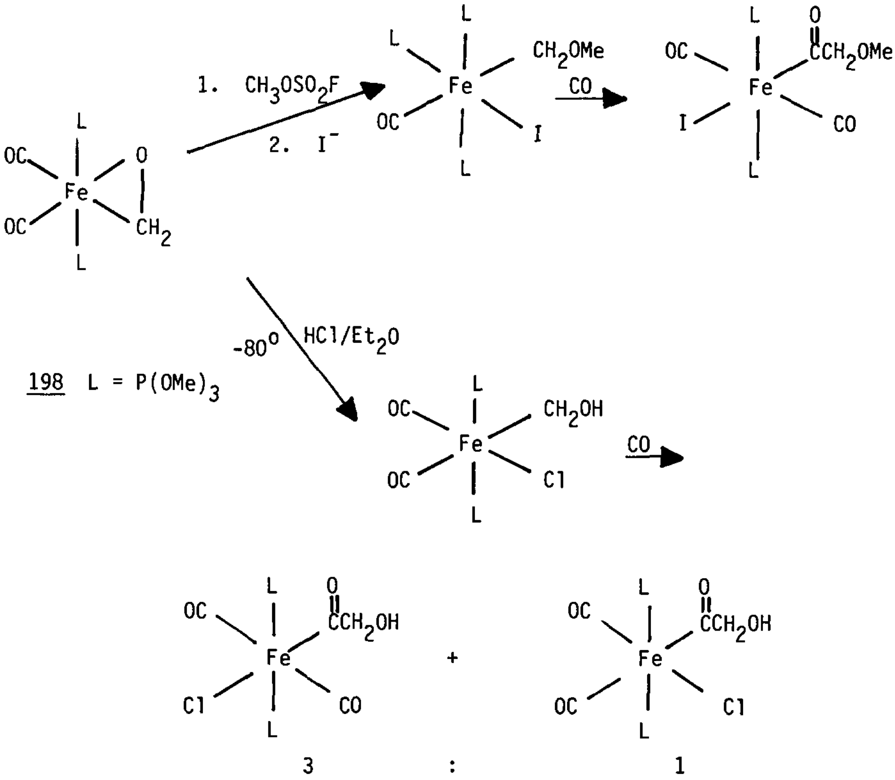
SCHEME 25



Formyl, Acetyl and Related Complexes

Kinetic evidence for the intermediacy of a formyl species in the substitution reactions of $H_2Fe(CO)_4$ has already been mentioned [53]. An X-ray structure of 198 was reported along with some of its chemistry [180].

SCHEME 26

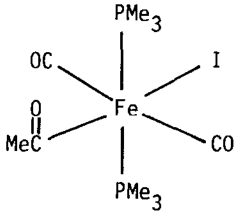


198 $L = P(OMe)_3$

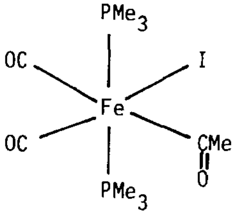
cis-$[RC(O)]_2Fe(CO)_4$ ($R = CF_3$, C_3F_7) were prepared and thermally decarbonylated to produce cis-$R_2Fe(CO)_4$. For $R = C_3F_7$, rotamers were detected by IR and the complex underwent thermal isomerization to trans-$(C_3F_7)_2Fe(CO)_4$. In contrast, cis-$(CF_3)_2Fe(CO)_4$ was stable to isomerization. NMR evidence indicated the presence of cis- and trans-$(R)[RC(O)]Fe(CO)_4$ as decarbonylation intermediates [181].

193 ($X = Cl$, Br, NCS, NCO, CN, OMe, Me) were prepared by CO displacement from $[Fe(CO)_3(PMe_3)_2Me]^+[BF_4]^-$ and found to react with CO to give acetyl complexes [182].

Although 199 is the initial product of carbonylation of 193 ($X = I$) and is consistent with methyl migration, 200 is the one isolated. The mechanism of its formation from 199 is not understood [183].



199

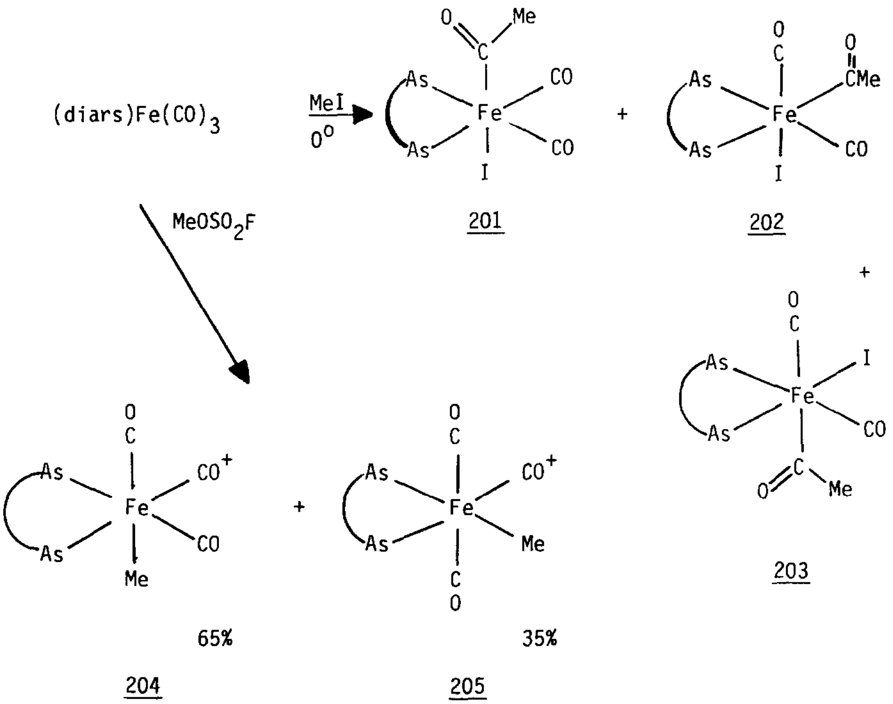


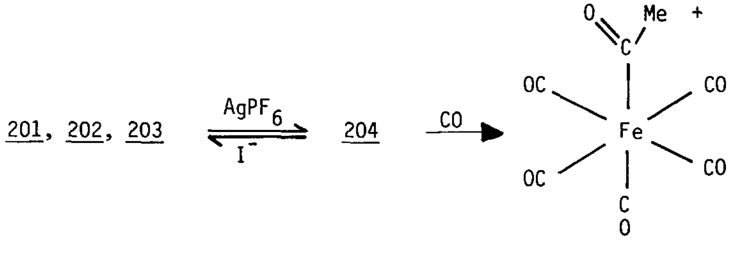
200

The kinetics of the reaction of $Fe(CO)_3(PMe_3)_2$ with MeI to produce $Fe(CO)_2$-$(PMe_3)_2[COMe]I$ were discovered to be second-order and to involve a cationic intermediate which suffers re-attack by I^- leading to insertion [184].

Related chemistry on a diars compound is depicted in Scheme 27. The production of 201, 202 and 203 likely involves a cationic intermediate and I^- re-attack with insertion. CF_3I also leads to an acyl product with (diars) $Fe(CO)_3$. The production of 204 from 203 involves Ag^+- promoted I^- extrusion leading to a five-coordinate intermediate where CO migration may occur. The production of 204 from 201 or 202 can be accounted for by methyl migration in the intermediate [185].

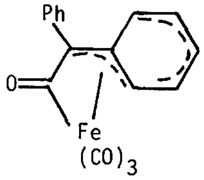
SCHEME 27



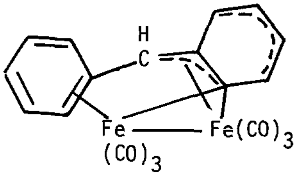


206

The acyl complex 207 results when $Fe(CO)_5$ is irradiated in Et_2O with $Ph_2C{=}C{=}C{=}O$ [186].



207



208

Aryl Complexes and o-Metallation

$Li_2[Fe(C_{10}H_7)_4]\cdot 2Et_2O$ is the product of a reaction between $FeCl_3$ and $C_{10}H_7Li$ in Et_2O. It is said to be the first Fe(II) complex containing only σ-aryl ligands [187].

Unsymmetrical (pentafluorophenyl)(alkyl)iron complexes, $(C_6F_5)RFe(CO)_4$ (R = C_3F_7, C_6F_{13}) were prepared by treatment of $RFe(CO)_4I$ with AgC_6F_5 [188].

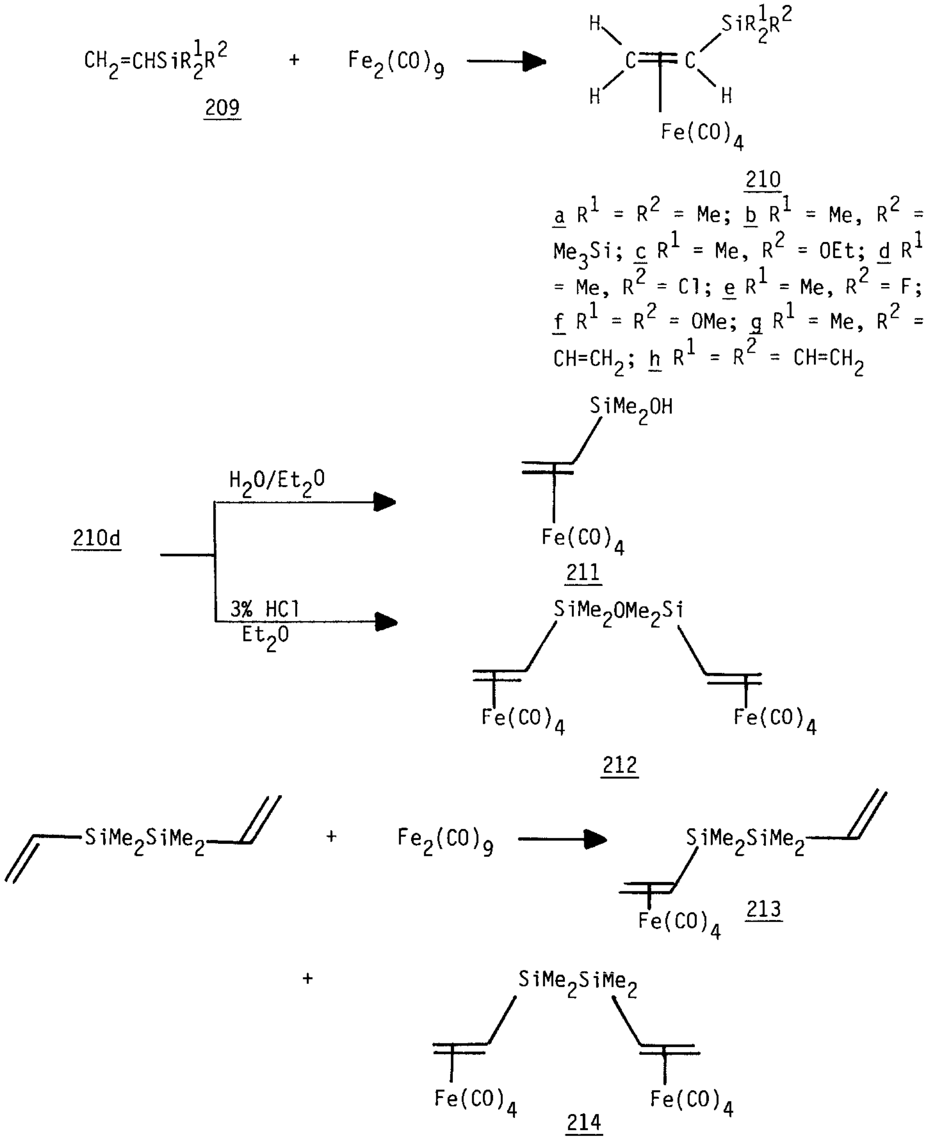
207 was found to afford 208 (whose X-ray structure was determined) on treatment with $Fe_2(CO)_9$ [186].

MONOALKENE COMPLEXES

One-bond ^{13}C-^{13}C spin coupling constants were reported [189] for a variety of η^2-alkene iron carbonyl complexes.

Treatment of $Fe_2(CO)_9$ with RCH=CHC(O)F (R = H, Me, Ph, trans-C(O)F) gives $[\eta^2\text{-RCH=CHC(O)F}]Fe(CO)_4$. The corresponding acid chlorides afford dinuclear products containing μ-Cl [190]. Several complexes of vinyl silanes were prepared from reactions of the ligand with $Fe_2(CO)_9$ [191, 192] (Scheme 28). 213 had been previously reported to involve an allyl silane ligand. Polyvinyl silanes gave products in which practically all vinyl groups were coordinated to Fe [192]. NMR studies on 210a, f, h, 211 and 214 indicated that these complexes are best formulated as metallacyclopropanes [193].

SCHEME 28



209

210

a $R^1 = R^2 = Me$; b $R^1 = Me$, $R^2 = Me_3Si$; c $R^1 = Me$, $R^2 = OEt$; d $R^1 = Me$, $R^2 = Cl$; e $R^1 = Me$, $R^2 = F$; f $R^1 = R^2 = OMe$; g $R^1 = Me$, $R^2 = CH{=}CH_2$; h $R^1 = R^2 = CH{=}CH_2$

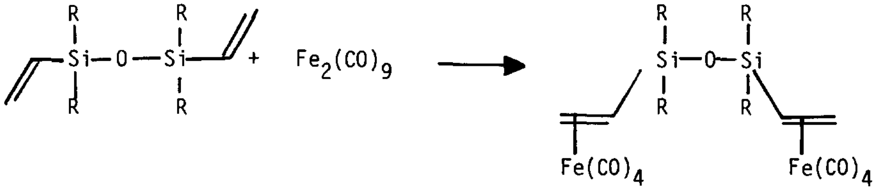
210d

211

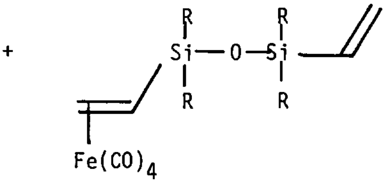
212

213

214

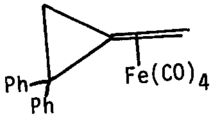


215 a R = Me
b R = Ph

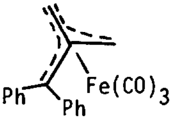


216 a R = Me
b R = Ph

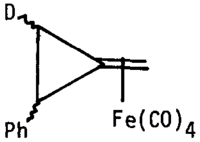
Frontier-orbital control of stereochemistry in the ring opening of 217 to 218 and of 219 to 220 and 221 was demonstrated [194].



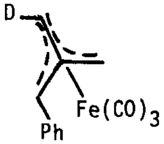
217



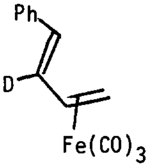
218



219



220



221

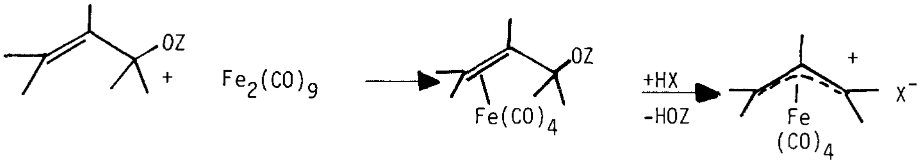
C_8F_8 was found to afford (η^2-C_8F_8)Fe(CO)$_4$ on reaction with $Fe_2(CO)_9$ or $Fe(CO)_5$ [195] at room temperature. The reaction with $Fe(CO)_5$ required irradiation.

ALLYL COMPLEXES

NMR studies of ^{13}C-^{13}C spin coupling constants [189] included allyl complexes.

A new preparative route to cationic allyl complexes has been found to give high yields [196] from allyl alcohols.

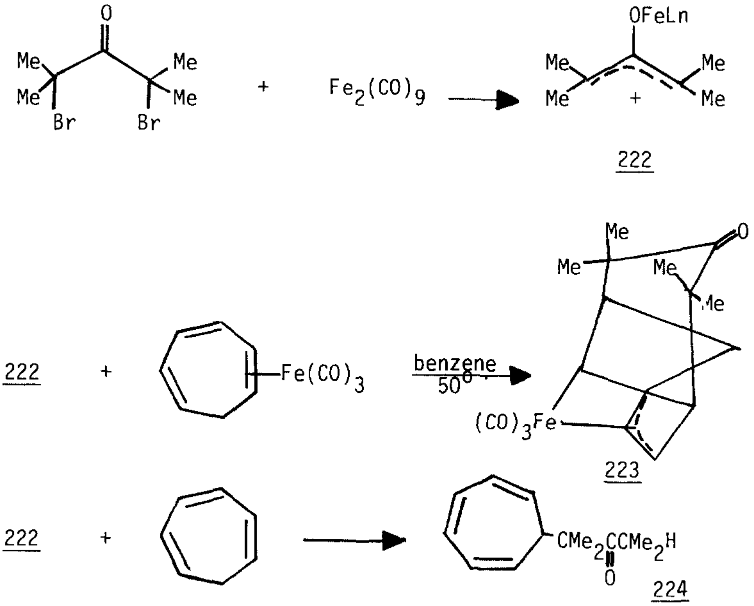
SCHEME 29



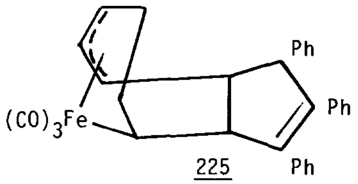
Z = H, R, COR

Reactions of a 2-oxallyl complex 222 prepared *in situ* were studied. 222 reacts with tropones and with 6-(dimethylamino)fulvalene with high periselectivity in second-order reactions whose rates increase with the ionizing power of the medium [197]. Note the difference in products 223 and 224 depending on the presence of an $Fe(CO)_3$ group. The X-ray structure of 223 was determined [198, 199].

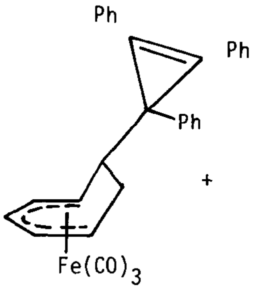
SCHEME 30



Treatment of $(\eta^4\text{-cot})Fe(CO)_3$ with $C_3Ph_3^+$ is a synthetic route to 225, the X-ray structure of which was reported. The precursor analogue to 225, 226, can be isolated from the reaction of $(C_7H_8)Fe(CO)_3$ and $C_3Ph_3^+$ [200].

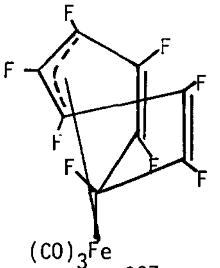


225

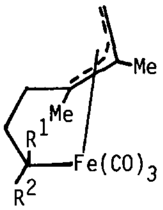


226

In refluxing hexane, C_8F_8 and $Fe_2(CO)_9$ produce 227 containing an η^1,η^3-C_8 ring as in 225 [195]. The photochemistry of 228a,b was studied in inert and reactive matrices at 10-12 K. The only primary photoreaction is CO loss. The product from photodissociation of 228b recaptures CO or takes up a ligand from an N_2 or ^{13}CO matrix while that from 228a does not, presumably due to coordination of the ester group. No 228a $\not\rightleftarrows$ 228b rearrangement was seen in these matrices. Hence, the rearrangement observed on irradiation in solution must result from a thermal process which follows photodissociation [201].



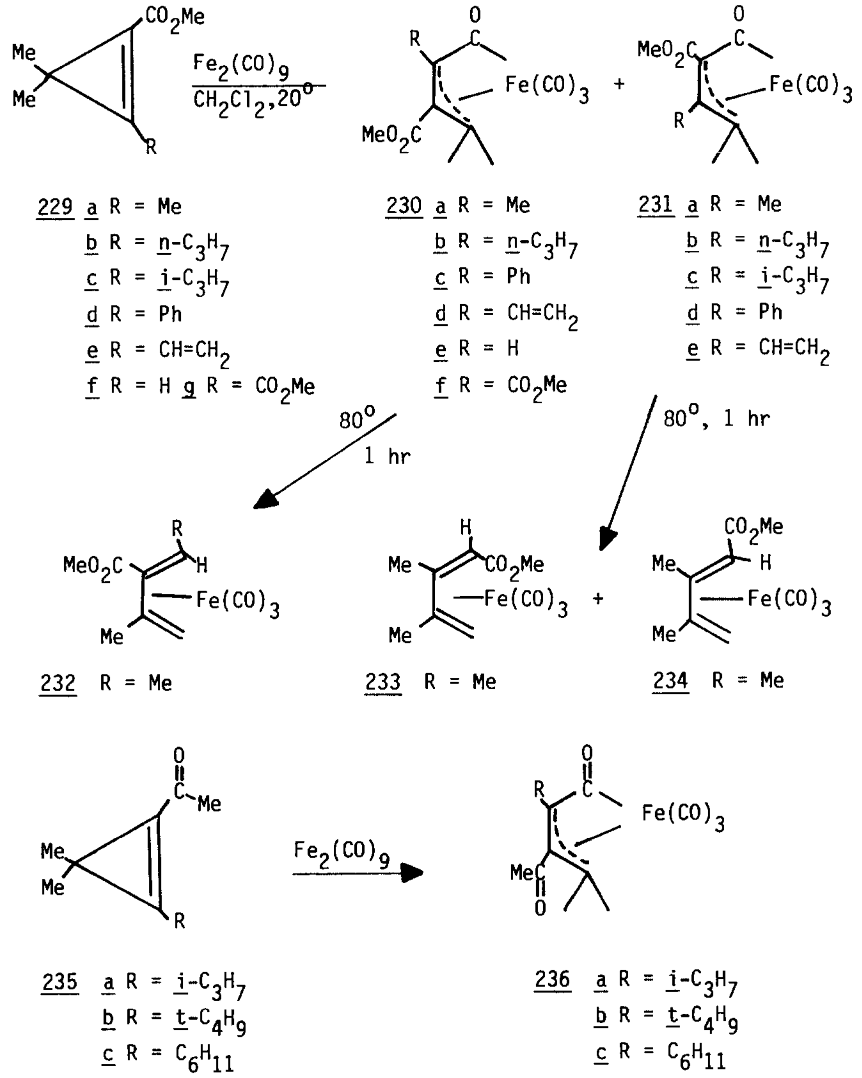
227



228 a $R^1 = H$, $R^2 = CO_2Me$
b $R^1 = CO_2Me$, $R^2 = H$

$Fe_2(CO)_9$ and electrophilic cyclopropenes lead to allyl complexes which thermally rearrange to diene complexes when R = Me. The direction of ring opening to give the allyl complex is adjacent to CO_2Me when R = H, Me and occurs at this site as well as adjacent to R for other R. The regioselectivity seems to be governed by steric factors. However, electronic factors become increasingly important as R becomes more π-donating. For example, 229c gives only 231c where R is anti and no 230 while 229e gives a 12:1 mixture of 230d:231e [202,203].

SCHEME 31



229 a R = Me
b R = n-C_3H_7
c R = i-C_3H_7
d R = Ph
e R = $CH{=}CH_2$
f R = H g R = CO_2Me

230 a R = Me
b R = n-C_3H_7
c R = Ph
d R = $CH{=}CH_2$
e R = H
f R = CO_2Me

231 a R = Me
b R = n-C_3H_7
c R = i-C_3H_7
d R = Ph
e R = $CH{=}CH_2$

232 R = Me

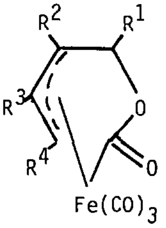
233 R = Me

234 R = Me

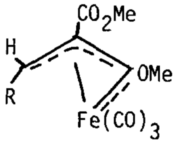
235 a R = i-C_3H_7
b R = t-C_4H_9
c R = C_6H_{11}

236 a R = i-C_3H_7
b R = t-C_4H_9
c R = C_6H_{11}

A large number of vinyloxirans produced complexes of structure 237 when allowed to react with $Fe(CO)_5$. These allyl complexes led to lactones on oxidation by Ce(IV) [204].

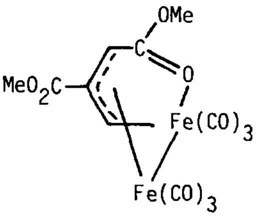


237



238 a R = H

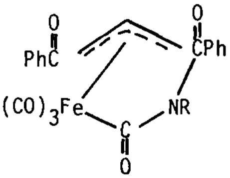
b R = CO_2H



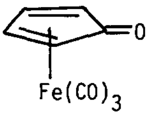
239

The η^3-vinylcarbene complex 238a gives 239 (whose X-ray structure was reported) on reaction with $Fe_2(CO)_9$ [205].

240 results from addition of BF_3 followed by RNH_2 (R = Me, i-C_3H_7, C_6H_{11}) to η^2-trans-PhC(O)CH=CHC(O)Ph $Fe(CO)_4$. The cis-η^2-olefin complex does not react with amines [206].



240 a R = Me; b R = i-C_3H_7; c R = C_6H_{11}

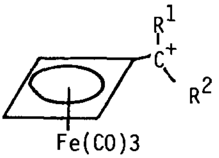


241

CYCLOBUTADIENE AND TRIMETHYLENEMETHANE COMPLEXES

Photolysis of $(\eta^4\text{-}C_4H_4)Fe(CO)_3$ in a CO matrix at 12K affords 241, the product of CO insertion into the ring [207].

A set of pK_{R^+} values was determined for 242a-f by a Hammet-Deno indicator study in CF_3CO_2H/H_2O [208].

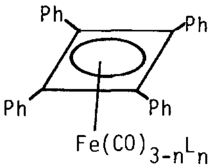


242

	R^1	R^2	pK_{R^+}
a	H	Ph	-3.42
b	H	p-tolyl	-2.79
c	H	Me	---
d	Ph	Ph	-2.89
e	Me	Ph	---
f	H	p-anisyl	-1.72

Oxidation of 243 a-c could be accomplished by $AgBF_4$ in CH_2Cl_2, $[N(p\text{-}BrC_6H_4)]_3[PF_6]$ or electrochemically at a Pt electrode. Salts of 243a and

243c were isolated. The product of $AgNO_3$ oxidation of $(\eta^4\text{-}C_4Ph_4)Fe(CO)_2\text{-}[P(OMe)_3]$ in CH_2Cl_2 is $(\eta^4\text{-}C_4Ph_4)Fe(CO)(NO)[P(OMe)_3]$[209].

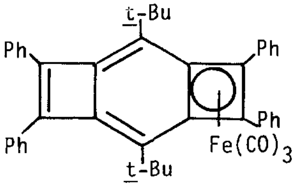


243

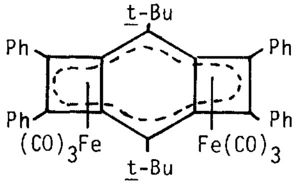
a L = PPh_3, n=1
b L = $P(OMe)_3$, n=1
c L = $P(OMe)_3$, n=2

Photolysis of substituted cyclobutadieneiron tricarbonyls with unsymmetric alkynes was studied. The nature of the cyclobutadiene substituent has a large effect on the isomer distribution of the product benzenes. The results were consistent with electrophilic attack on the ring by alkyne [210].

X-ray structures of 244 and 245 (which are obtained on reaction of $Fe_2(CO)_9$ with the parent organic fused-ring system) were reported [211].

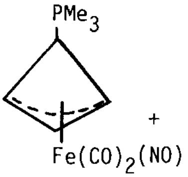


244



245

$[(\eta^4\text{-}C_4H_4)Fe(CO)_2(NO)]^+PF_6^-$ undergoes nucleophilic ring attack yielding 246, the X-ray structure of which has been determined [212].



246

The trimethylenemethane complexes 218 and 220 have been mentioned previously[194].

DIENE AND HIGHER OLEFIN COMPLEXES

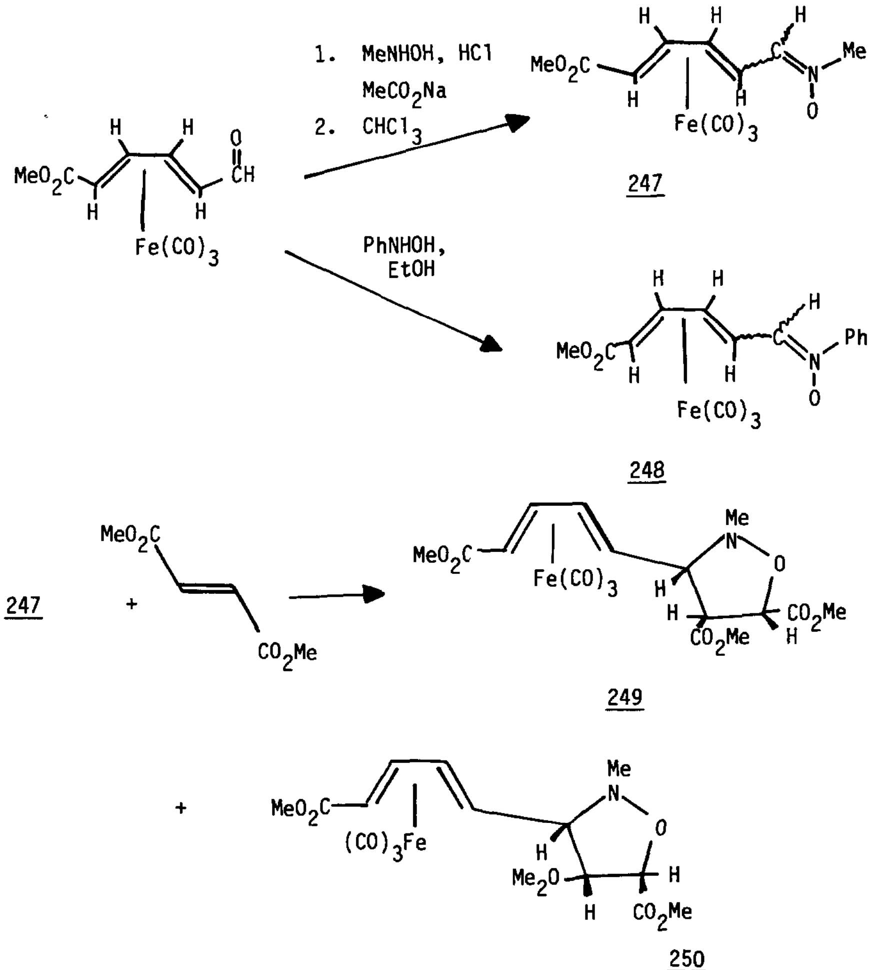
Acylic Diene Species

A complete assignment of the vibrational spectra of $(\eta^4\text{-}C_4H_6)Fe(CO)_3$ and the d_6 analogue has been made [213].

A number of the ^{13}C - ^{13}C spin coupling constants measured for Fe complexes were for diene complexes [189]. The ^{57}Fe NMR spectra of thirty-five organoiron complexes, mostly diene complexes, have been measured. The ^{57}Fe chemical shift range so far observed is 3000 ppm and almost all compounds lie at higher field than $Fe(CO)_5$ which was proposed as a secondary standard [214].

Nitrones having a butadiene iron tricarbonyl moiety in the α-position were synthesized. 247 undergoes 1,3-dipolar addition reactions producing 249, 250 and 251 [215].

SCHEME 32

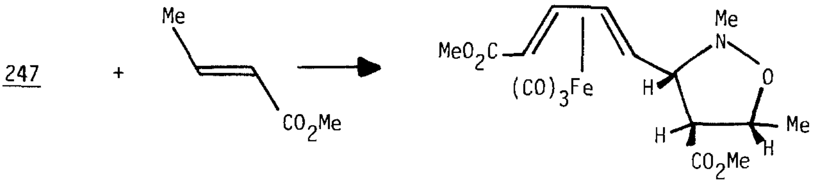


247

248

249

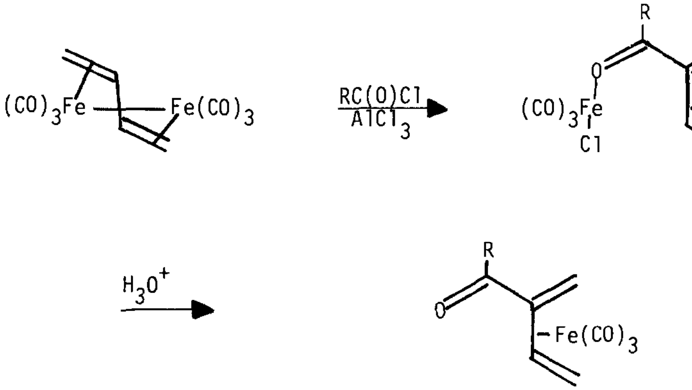
250



251

252 has been prepared even though the free ligands cannot be isolated[216].

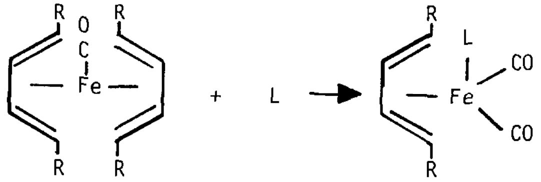
SCHEME 33



252 a R = Me
b R = Ph

254 are the products of treating 253 with L = pyridine, pyrazoline or quinoline [217].

SCHEME 34

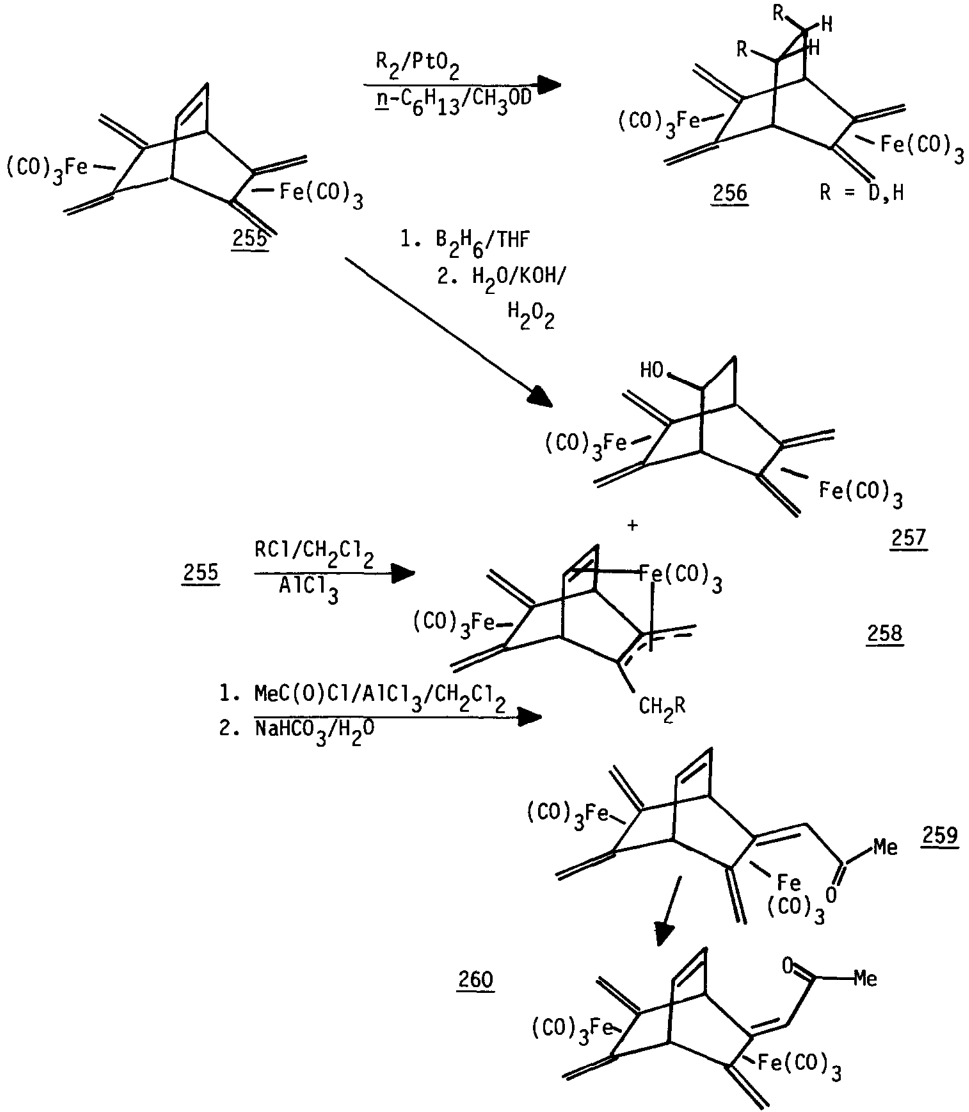


254 a R = CO_2Et
b R = diethylmuconate

253 a R = CO_2Et
b R = diethylmuconate

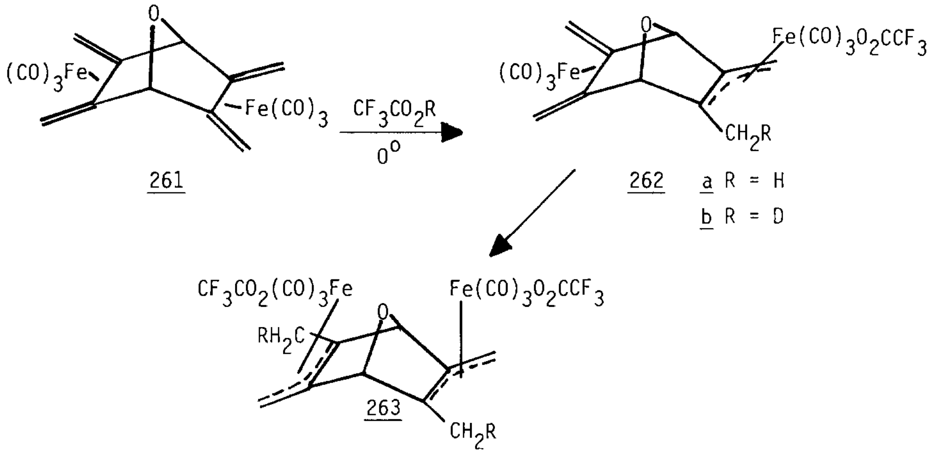
The $Fe(CO)_3$ group may be used as a protective group to induce stereospecificity in reactions of the endocyclic double bond of 255 whose X-ray structure was determined also[218].

SCHEME 35



The X-ray structure of 259 was determined. It isomerizes to the more thermally stable 260 [219]. Similar chemistry was observed with the O - bridged analogue. 261, the endo, endo isomer is the main product treatment of the diene with $Fe_2(CO)_9$. 261 may add one or two protons regiospecifically affording 262 or 263 which are stable as solids. The crystal structure of 261 was reported [220].

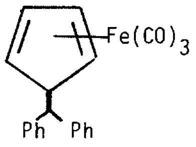
SCHEME 36



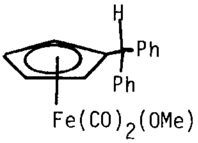
Homoconjugative stabilization of carbocations resulting from acidolysis of Fe complexes of exocylic dienes was found to compete with destabilizing inductive effects [221, 222] .

Cyclic Diene and Higher Olefin Species

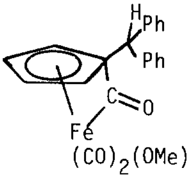
A reinvestigation of the reaction of 264 with OMe$^-$ showed that the product is 265 and not 266 as previously thought [223].



264



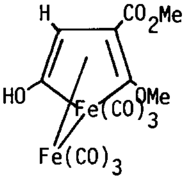
265



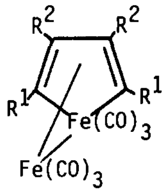
266

A redetermination of the X-ray structure of $[(\eta^4\text{-}C_5H_4O)Fe(CO)_4]_2\cdot$(hydroquinone) shows H bonds between the ketone O and OH of hydroquinone[224].

In the reaction of 238b with $Fe_2(CO)_9$ 267 was found to be the product[205]. Compare the production of 239 from 238a.



267

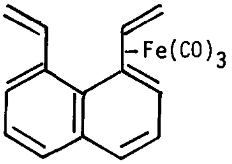


268 a $R^1 = R^2 = Et$

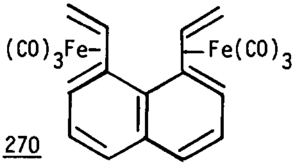
b $R^1 = H$, R^2 = t-Bu

The ^{13}C NMR spectra of enriched 268a,b and (η^4-1,3-hexadiene)$Fe(CO)_3$ permitted the first observation of $^2J_{C-C}$ cis values which are an order of magnitude smaller than $^2J_{C-C}$ trans [225]. ^{13}C studies on complexes of substituted 1,3-hexadienes indicated that the LUMO of the diene ligand is depopulated as CO's on Fe are substituted by progressively stronger donors. The X-ray structure of (η^4-2-MeO,1,4-hexadiene)$Fe(CO)_2(PPh_3)$ seems to confirm this view [226].

Photolysis of $Fe(CO)_5$ with the free ligand leads to 269 (major product) and 270 in which Fe is complexed to both cyclic and exocyclic double bonds [227].

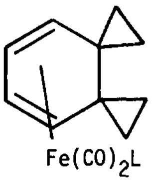


269



270

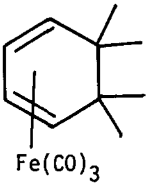
A series of 1,3- and 1,4-hexadienes was found to produce only (η^4-1,3-hexadiene)$Fe(CO)_3$ complexes when treated with $Fe(CO)_5$ in $(n\text{-}Bu)_2O$. Classical steric hindrance of alkyl substituents on the hexadienes seems to control the steric direction. However, the CO_2Me group exerts a directive effect apparently resulting from complexation to Fe [228]. Compounds 271a-c and 272 can be made by allowing the 1,3-hexadiene ligand to react with (benzylideneacetone)$Fe(CO)_2L$ (L=CO,PPh_3 $P(OPh)_3$) [229]. The X-ray structure of 271b was reported.



271 a L = CO

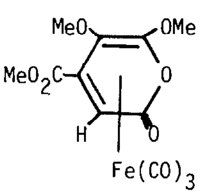
b L = PPh_3

c L = $P(OPh)_3$

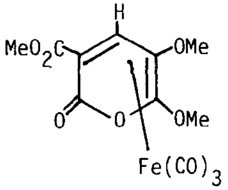


272

At 58^0 under a CO atmosphere, 273 isomerizes to 274. The X-ray structures of both isomers were determined [230].



273

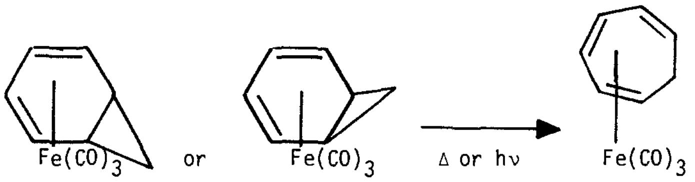


274

(Diene)$Fe(CO)_3$ complexes were employed for totally stereospecific syntheses of insect pheremones having (E)- and (E,E)-skeletons. $Fe(CO)_3$ functions as a protecting group [231].

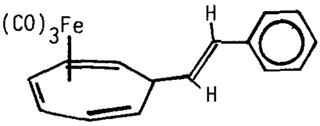
Both syn- and anti- norcarnadiene iron tricarbonyl, 275a,b were prepared and shown to rearrange to 276 under both thermal and photolytic conditions. This demonstrates the thermodynamic favorability of the C_7 ring over bicyclic species [232].

SCHEME 37

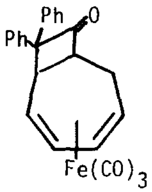


275a 275b 276

The tropylium ion was found to react with (η^4-cot)$Fe(CO)_3$ producing 277 whose X-ray structure showed rearrangement of the cyclooctatetraene ring[233]. The fused four-and seven-membered ring complex 278 undergoes ring opening to give 279 on treatment with acid or base. Thermolysis, however, yields 280 [234].

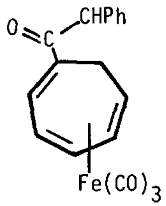


277

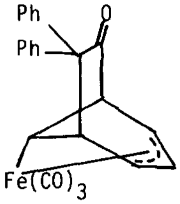


278

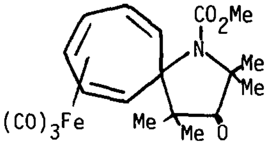
281 is isolated when the oxallyl cation 222 reacts with [η^2-(N(CO_2Me))C_7H_6]-$Fe(CO)_3$ [199].



279



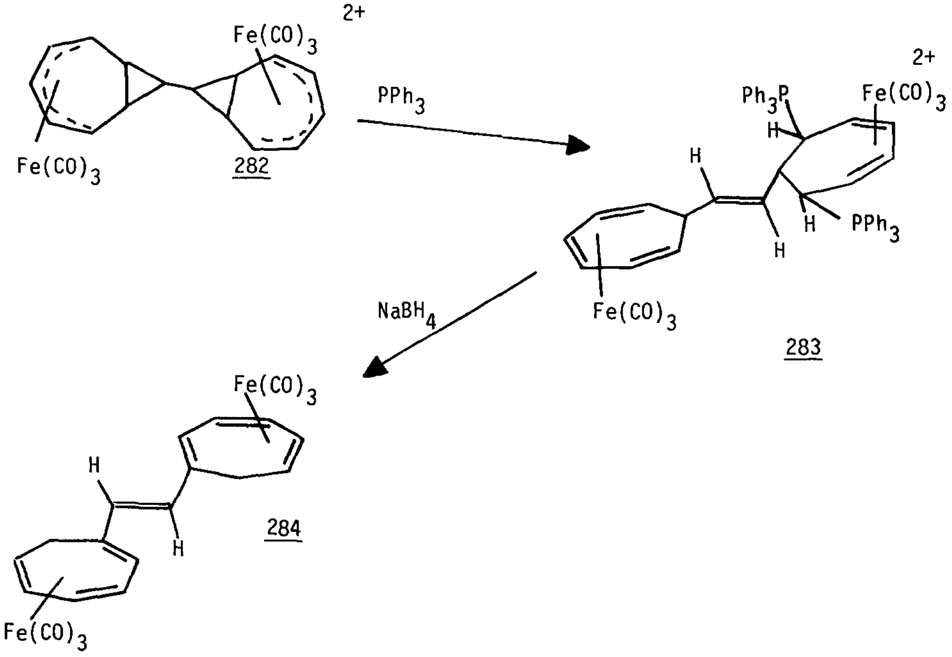
280



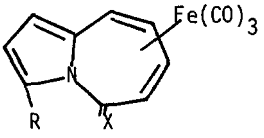
281

On reaction with PPh_3 the cation 282 undergoes a ring opening affording 283 (X-ray structure described) which is reduced to 284 by $NaBH_4$ [235].

SCHEME 38



3a-azoniaazulenes produced 285a-e on treatment with $Fe_2(CO)_9$ [236] .

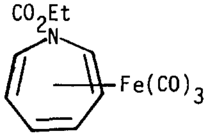


285

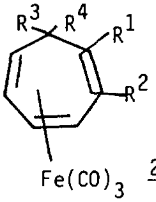
285	R =	X =
a	H	O
b	CHO	O
c	CH=CHCOMe	O
d	$CH=C(COMe)_2$	O
e	H	CHCN

The addition reactions of tcne to 286 [237] and 287a-e were studied.

Frontier orbital calculations indicated that 1,3-addition yielding 288 is preferred. 288 was found to be the initial product from 286; it isomerizes to the 1,6-adduct, 289. In 287a-e 1,3-addition was also seen in second-order reactions. However, for 287e a parallel non-reversible 4,6-addition competes with reversible 1,3-addition [238].

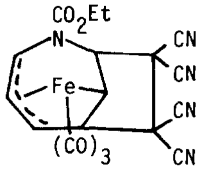


286

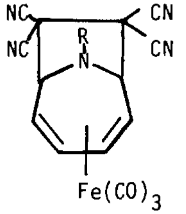


287

	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	C_7H_7	H	H
c	H	H	COMe	H
d	H	H	H	COMe
e	CHO	H	H	H



288

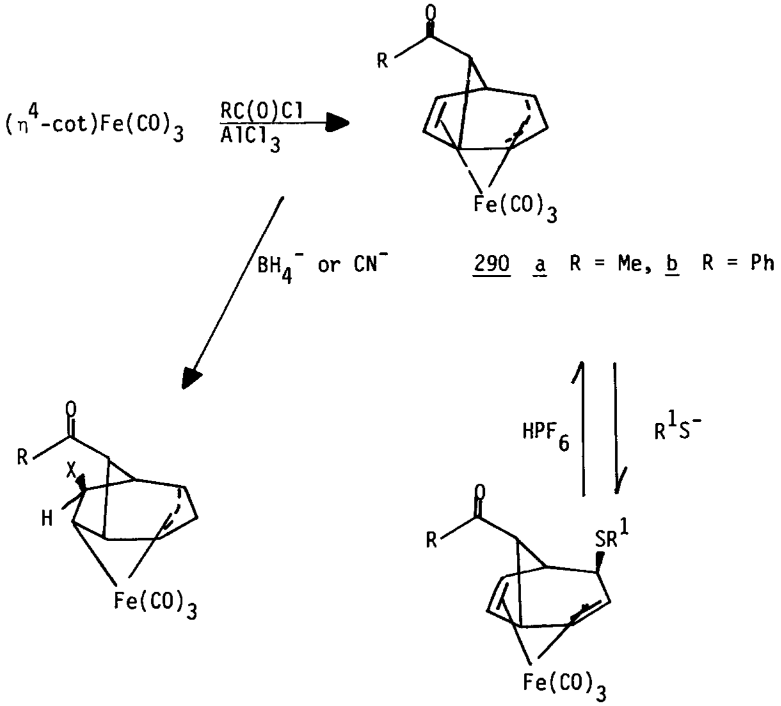


289

R = CO_2Et

Several Fe complexes containing eight-membered rings were studied. (η^4-cot)$Fe(CO)_3$, on Friedel-Crafts acylation, produces 290 in which the acyl is endo. The double bond of 290 can be reduced to give 291 while SR^- attacks the ring [239]. Electrochemical reduction of (η^4-1,3-cot)$Fe(CO)_3$ and (η^4-cot)$Fe(CO)_2(PPh_3)$ produces $[(cot)Fe(CO)_3]^-$ and $[(cot)Fe(CO)_2PPh_3]^-$, respectively. The ESR spectra indicate that the unpaired electron is in a ring orbital [240].

SCHEME 39

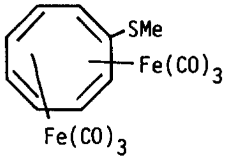


290 a R = Me, b R = Ph

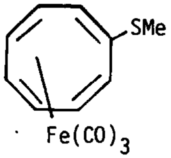
291 a R = Me, X = H
b R = Me, X = CN
c R = Ph, X = H
d R = Ph, X = CN

292 a R = Me, R^1 = i-C_3H_7
b R = Me, R^1 = t-Bu
c R = Me, R^1 = Ph
d R = Ph, R^1 = i-C_3H_7
e R = Ph, R^1 = t-Bu
f R = R^1 = Ph

The substituted ligand (C_7H_8SMe) reacts with $Fe_2(CO)_9$ yielding 293 (major) and 294 (minor) as products. S is not coordinated to Fe. Longer reaction times give $Fe_2(CO)_6(\mu\text{-SMe})_2$ [241].

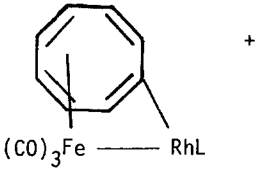


293



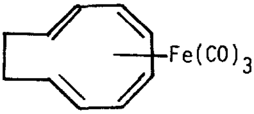
294

$(diglyme)_3Mo(CO)_3$ and $(cot)Fe(CO)_3$ afford $(CO)_3Fe(C_8H_8)Mo(CO)_3$ having a fluxional μ-cyclooctatetraene [242]. The cations $[(cod)_2Rh]^+$, [Rh(norbornadiene)$_2$]$^+$ and [Rh(CO)$_2$]$^+$ also react with (cot)Fe(CO)$_3$ to produce 295a-c, respectively, having fluxional μ-cot and olefin ligands [243].



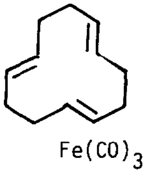
295

a L = cod
b L = norbornadine
c L = $(CO)_2$

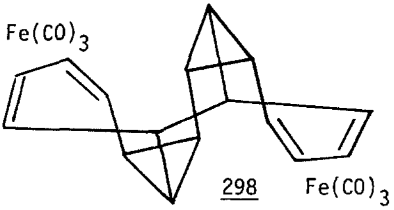


296

The X-ray structure of 296 was reported. The ring defines four distinct planes [244]. 1,5,9-cyclododecatriene forms 297 on reaction with $Fe_2(CO)_9$ [245].

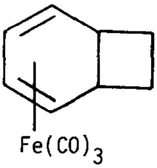


297

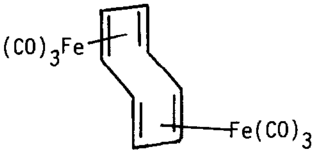


298

Under olefin metathesis conditions (cot)Fe(CO)$_3$ and (η^4-cycloheptatriene)-Fe(CO)$_3$ produce 298, 299 and 300, which cannot be rationalized from accepted mechanisms for metathesis [246]. (η^4-cycloheptatriene)Fe(CO)$_3$ alone affords cis- and trans-isomers of a new dimer [(η^4-C_7H_8)Fe(CO)$_2$]$_2$ as well as (η^4-C_7H_8)Fe(CO)$_2$Cl [246].



299

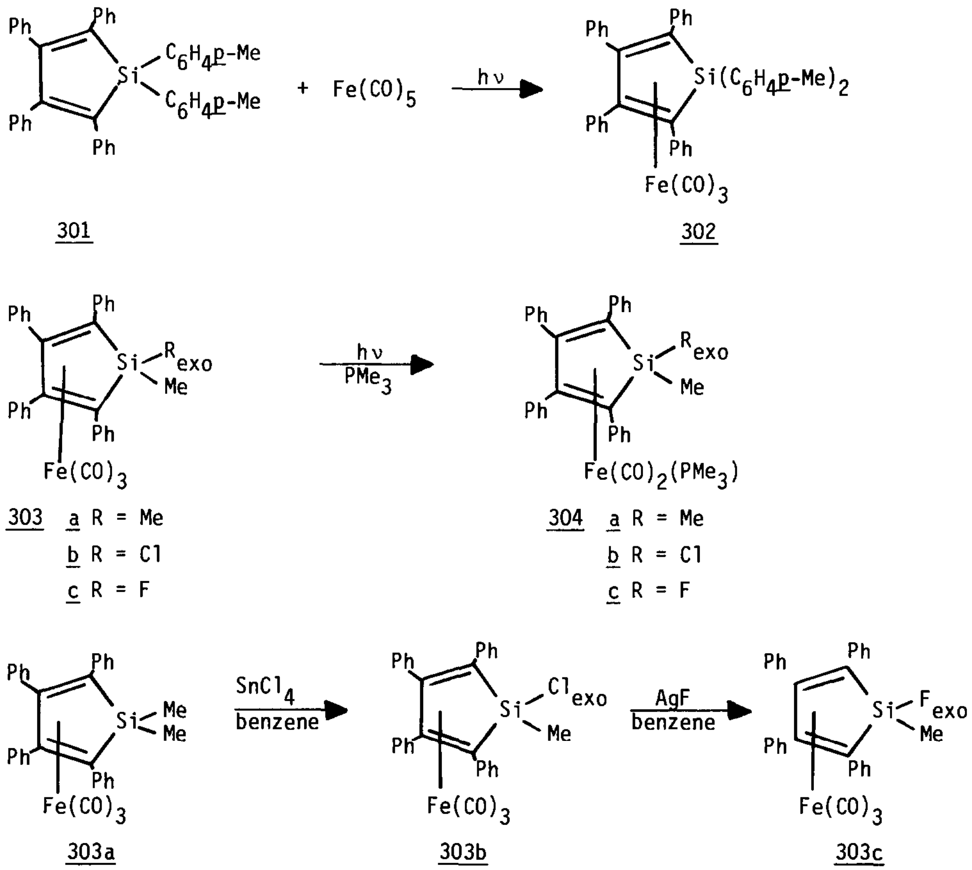


300

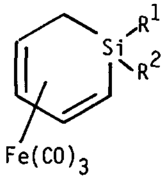
Heterodiene Species

Several silacyclopentadiene complexes have been prepared. Two isomers of 304a-c are detectable by IR implying square pyramidal coordination around Fe. Abstraction of exo anions did not yield the hoped-for silicium cation [247].

SCHEME 40

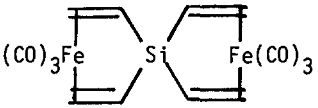


The mass spectra of 305a-g have been obtained. Successive elimination of CO's is followed by decomposition of the remaining fragment to $(C_5H_6R^1R^2)^+$ and Fe^+ or to R^1H and $(C_5H_5SiR^2Fe)^+$ [248].



305

	R^1	R^2
a	H	H
b	Cl	Cl
c	Me	Me
d	Ph	Ph
e	OH	OH
f	OEt	OEt
g	Cl	Me

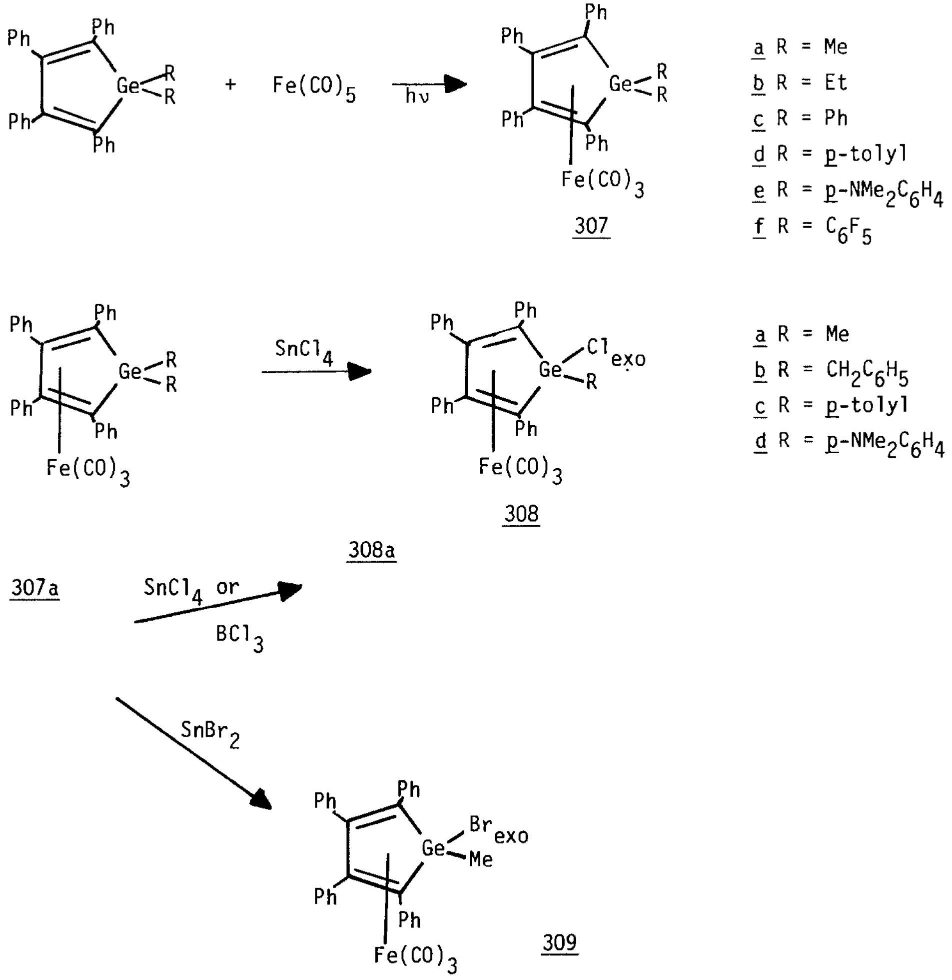


306

Synthesis of 306 was reported by two groups [192, 249]. The X-ray structure was reported as well [249].

A series of diene complexes of germanacycles has been made. The exo-substituent is reactive as in the corresponding Si complexes.

SCHEME 41



307

a R = Me
b R = Et
c R = Ph
d R = p-tolyl
e R = p-$NMe_2C_6H_4$
f R = C_6F_5

308

a R = Me
b R = $CH_2C_6H_5$
c R = p-tolyl
d R = p-$NMe_2C_6H_4$

307a

308a

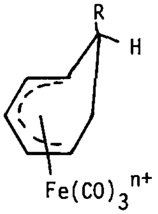
309

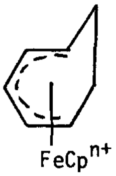
The exo-Cl in 308a-d can be replaced using NaOMe, AgF, NaI or $LiAlH_4$. The X-ray structure of $[\eta^4\text{-}Ph_4C_4Ge(F)Me]Fe(CO)_3$ shows square-planar coordination about Fe [250].

The heterodiene complexes $(\eta^4\text{-}PhCH{=}CHCH{=}NPh)Fe(CO)_2L$ (L=CO,PPh_3, $AsPh_3$ $SbPh_3$) react with diphos to produce trisubstituted $Fe(CO)_2$(diphos)diphos where one diphos ligand is monodentate. The kinetics of the reaction were investigated for L=CO [251].

DIENYL COMPLEXES

^{57}Fe NMR of enriched 310a and 311a enabled determination of $J_{^{13}C-^{57}Fe}$ [252]. 310b is oxidized by Ce(IV) yielding 311a [253]. The X-ray structure of 310c, Fitton's salt, was established [254].



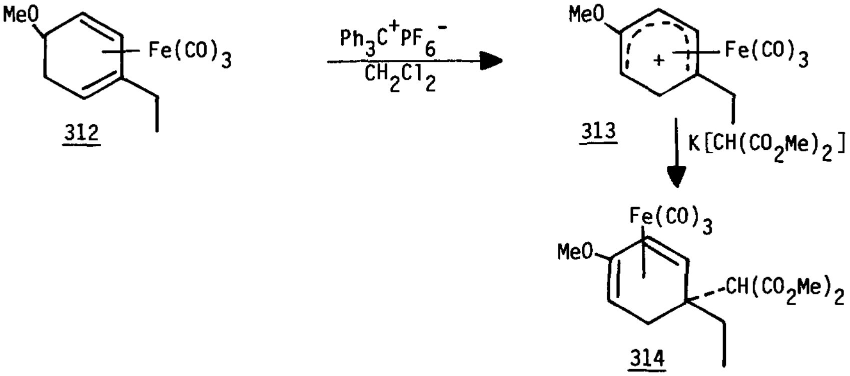


310 a R = H, n = 1
b R = Me_2CCN, n = 0
c R = i-C_3H_7, n = 1

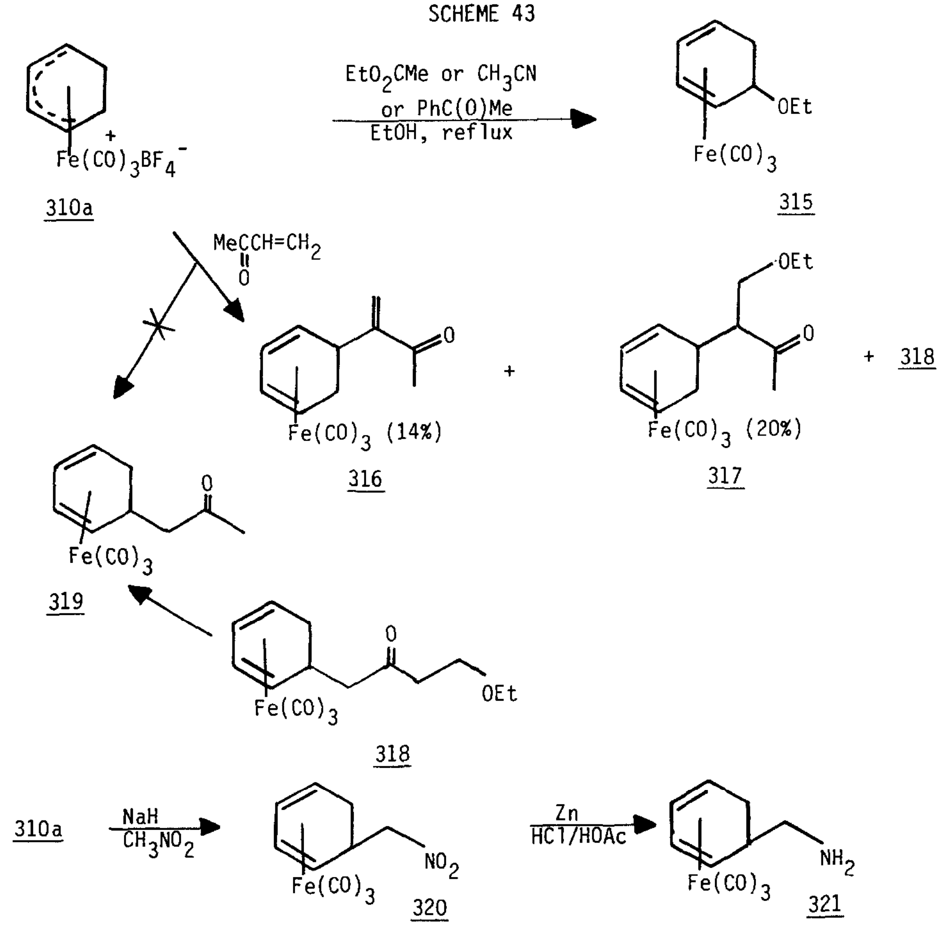
311 a n = 0
b n = 1

Tricarbonyl(η^5-cyclohexadienylium)iron cations can be regarded as synthetic equivalents of aryl cations and have attracted a good deal of attention in this regard. A useful preparative method for these cations involves hydride abstraction from neutral η^4-cyclohexadiene complexes. The cation can then react with nucleophiles [255]. (Schemes 42,43)

SCHEME 42



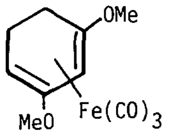
SCHEME 43



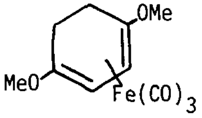
This method has been employed using a variety of alkyl Li reagents. Oxidation of the product complexes leads to alkyl-substituted cyclohexenones [256]. Not all potential nucleophiles are active. In refluxing EtOH, solvolysis products, 315, are sometimes isolated. All additions are exo and multiple attack sites are possible for $MeC(O)CH=CH_2$ [257]. 317 and 318 result from subsequent solvent attack.

A similar route can be employed to synthesize steroidial rings from $[(\eta^5\text{-1-Me-4-MeOC}_6H_5)Fe(CO)_3]^+$ [258].

An alternative route to cyclohexadienylium cations involves protonation and MeOH elimination from complexes 322 or 323. The resulting cationic complexes 324

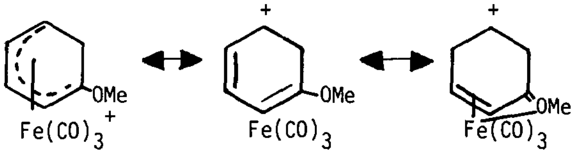


322

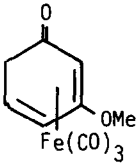


323

from 322, can be regarded as cations derived from substituted cyclohexenones. In fact, the complexes of 1,4-cyclohexadienes 323 afford mainly cyclohexadienone complexes of type 325 [259].

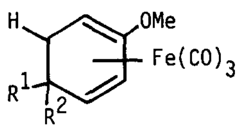


324

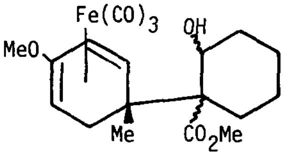


325

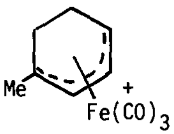
Cations derived from 6,6-disubstituted cyclohexadienyl iron tricarbonyl complexes such as 326 cannot be prepared via the hydride abstraction route for steric reasons. They were synthesized by oxidative cyclization of complexes such as 327 having an OH group in the β-position of a 5-exo substituent using $Tl(CF_3CO_2)_3$ or $FeCl_3$ on silica gel. Cations derived from 327 and related species can be converted to 4,4-disubstituted cyclohexa-2,5-dienones [260].



326



327

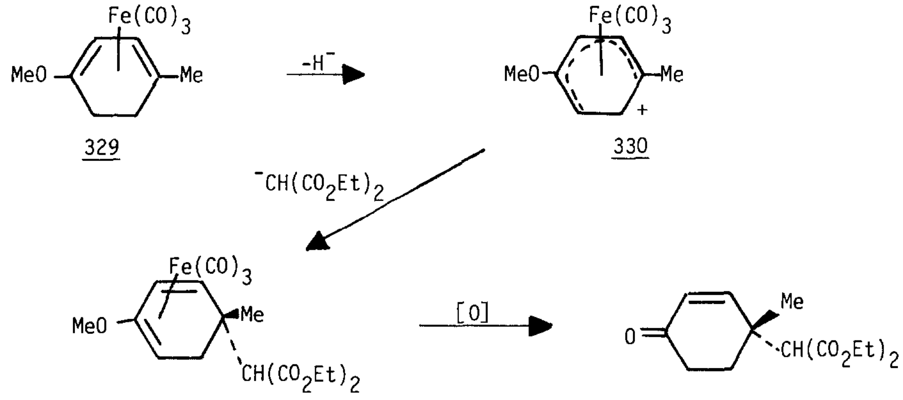


328

The regioselectivity of hydride addition to 328 by $NaBH_4$, $LiBH_4$, $LiBEt_3H$ and $KB(\underline{sec}\text{-}Bu)_3H$ was investigated. Addition occurred at the 1- or 5-positions (Me is at the 2-position). Surprisingly, the regioselectivity decreased at low temperatures. At higher temperatures the bulky hydride reagents add preferentially to C_5. Addition of C nucleophiles such as $CH(CO_2Me)_2^-$ or CN^- occurs almost exclusively at C_5 [261].

Aspects of optical activity of cyclohexadienylium cations have received attention. Stereospecific reactions of cations derived from unsymmetrically substituted cyclohexadiene complexes were used to establish absolute configurations of several complexes by chemical correlation [262]. Olefin complexes having asymmetry because of Fe coordination were employed in asymmetric synthesis such as that in Scheme 44 [263].

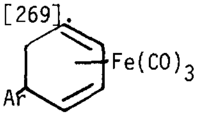
SCHEME 44



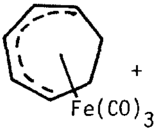
Several studies of the kinetics of reactions of nucleophiles with (η^5-cyclohexadienylium)tricarbonyliron cations showed behavior consistent with attack on the ring as well as correlation with the basicity of the attacking nucleophile [264-267].

310a attacks di- and trimethoxybenzenes (Ar) giving 333. Kinetic results are consistent with a pre-equilibrium formation of a π-complex followed by rate-determining rearrangement to a Wheland-type intermediate and subsequent rapid proton loss [268].

226, a dienyl complex involving a seven-membered ring, has previously been mentioned [200]. When 334 is allowed to react with phosphines in CH_2Cl_2, the 5-exo isomer is formed with PEt_3, PPr_3, P(n-Bu)$_3$ and PMe_2Ph. In MeCN, the 5-endo isomer is formed [269].

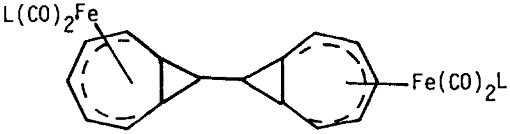


333



334

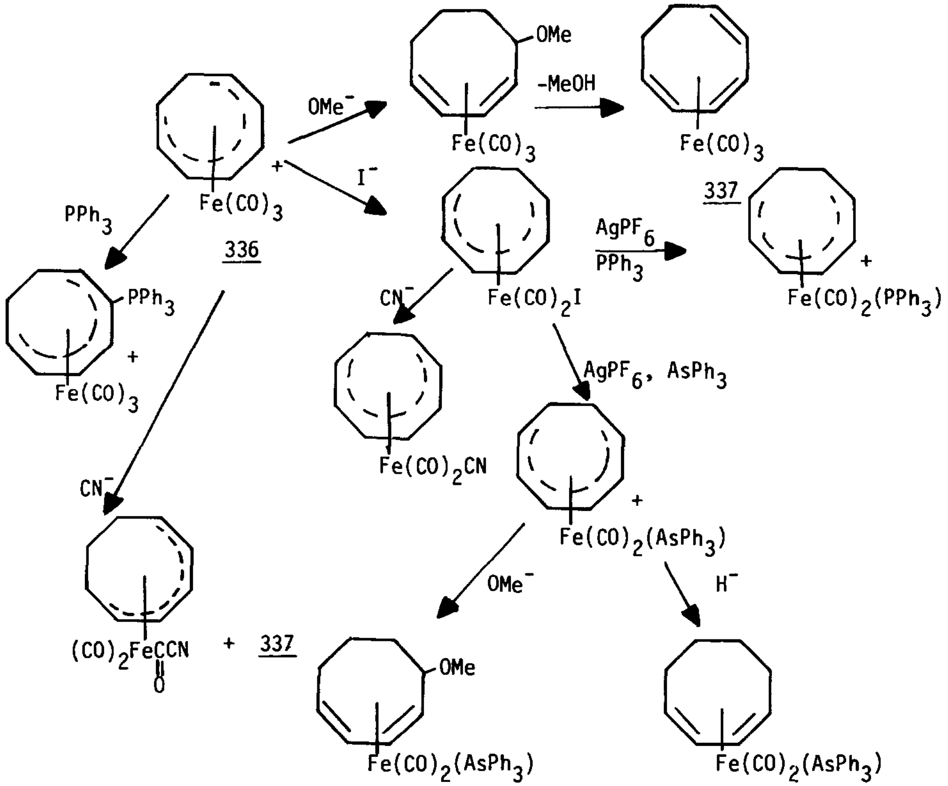
The cations 282, 335 can be generated by oxidation of (η^4-cot)Fe(CO)$_2$L (L=CO,P(OMe)$_3$) with Ag(I) salts or with [N(p-BrC$_6$H$_4$)$_3$]PF$_6$. Dimerization and isomerization occur. Electrochemical oxidation at a Pt electrode was found to be a one-electron irreversible process for (η^4-cot)Fe(CO)$_{3-n}$L$_n$(n=0-3,L=P(OEt$_3$); n=1, L=P(NMe$_2$)$_3$,PPh$_3$,P(OCH$_2$)$_3$CMe,P(OPh)$_3$). The structure of 335 was determined by X-ray diffraction [270].



335 $L = P(OMe)_3$

$[(\eta^5\text{-cyclooctadienyl})Fe(CO)_3]^+$, 336, can undergo attack by a variety of nucleophiles, some of which displace CO [271].

SCHEME 45



CYCLOPENTADIENYL COMPLEXES

Binuclear Species

AC polarography in non-aqueous solvents of several metal carbonyls, including $[CpFe(CO)_2]_2$, 338a, was studied [84]. An electrochemical synthesis of this dimer was also developed [272].

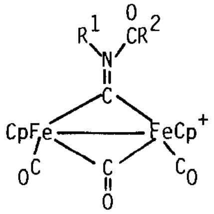
The dimers $[Cp_2Fe_2(CO)_2(CNMe)]$ (L=CO,CNMe), on treatment with HgX_2(X= Cl,Br,I) produce almost quantitative yields of $CpFe(CO)_2HgX$ and $CpFe(CO)_2X$. A plausible mechanism involves attack of the electrophile on a bridging ligand [273].

338b-d afford cationic complexes 339a-f on treatment with acid chlorides.

338 $Cp_2Fe_2(CO)_{4-n}L_n$

a n = 0
b n = 1, L = CNMe
c n = 1, L = CNEt
d n = 1, L = $CNCH_2C_6H_5$
e n = 1, L = $CN\underline{i}\text{-}C_3H_7$
f n = 2, L = CNPh
g n = 2, L = $CN(\underline{p}\text{-}ClCH_2C_6H_4)$
h n = 2, L = $CNCH_2Ph$
i n = 2, L = $CN(\underline{p}\text{-}MeCH_2C_6H_4)$
j n = 2, L = $CN(\underline{p}\text{-}MeOCH_2C_6H_4)$
k n = 2, L = CN(D(+)-PhCMeH)
l n = 2, L = CNMe
m n = 2, L = CNEt
n n = 2, L = CNC_3H_7
o n = 2, L = CN(n-Bu)
p n = 2, L = $CN(\underline{i}\text{-}C_3H_7)$
q n = 2, L = CNC_6H_{11}
r n = 2, L = CNt-Bu

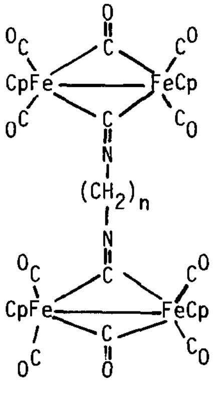
The cations 339 are unstable to hydrolysis to species such as $[Cp_2Fe_2(CO)_3\{CN(Me)H\}]^+$, $[Cp_2Fe_2(CO)_2(CNMe)\{CN(Me)H\}]^+$ or $[Cp_2Fe_2(CO)_2\{CN(Me)H\}]_2^{2+}$ and with respect to Fe-Fe bond cleavage leading to $[CpFe(CO)_2(CNMe)]^+$ [274].



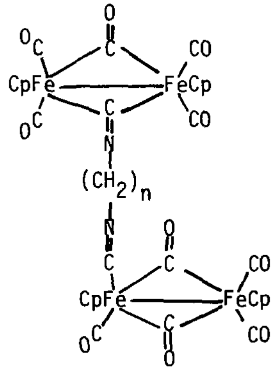
339
a $R^1 = R^2 = Me$
b $R^1 = Et$, $R^2 = Me$
c $R^1 = CH_2Ph$, $R^2 = Me$
d $R^1 = Me$, $R^2 = Ph$
e $R^1 = Et$, $R^2 = Ph$
f $R^1 = R^2 = CH_2Ph$

Preparation of 338a,b,d,f-r was described. In solution these complexes exist as isomer mixtures. For n = 1 (338a,b,d) one isomer tends to predominate- that with terminal CNR. For n = 2 (338f-r) isomer distribution is determined by the tendency of bulky isocyanides to be terminal and those with electron-withdrawing R to be bridging. The amount of μ-CNR isomer decreases in the order 338 f > g > i ···· > r. The X-ray structure of crystalline 338p shows that it contains two μ-CO's [275].

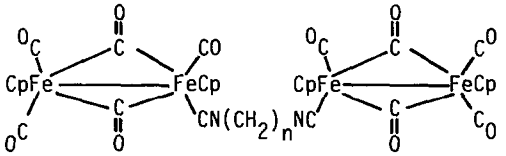
When 338a is allowed to react with diisocyanides $CN(CH_2)_nNC$ (n=2,3,4,6) the complexes $[Cp_2Fe_2(CO)_3]_2[\mu\text{-}CN(CH_2)_nNC]$ (n=2,3,4,6) result. In solution a mixture of isomers exists in which the diisocyanide may function as a bridging ligand toward each Fe-Fe pair (340a), μ toward one and terminal toward the other



340a



340b

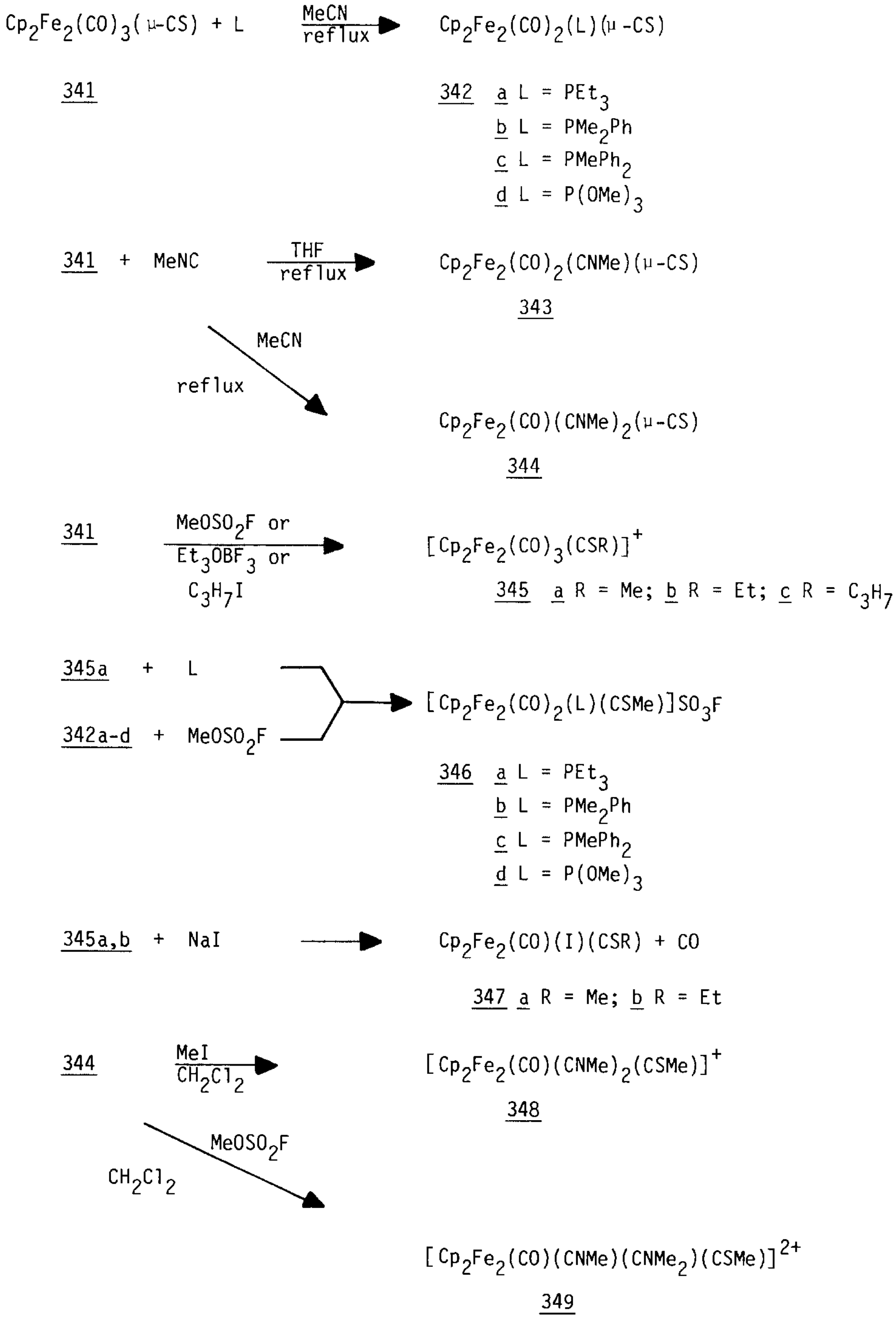


340c

(340b) or terminal toward both (340c). The proportion of 340c increases with n. The complexes can be diprotonated giving $\{[Cp_2Fe_2(CO)_3]_2[\mu\text{-}CN(H)(CH_2)_nN(H)C]\}(PF_6)_2$ (n=2,3,4,6). For n = 2,6 treatment with I_2 produces equimolar quantities of $[CpFe(CO)I]_2[\mu\text{-}CN(CH_2)_nNC]$ (n = 2,6) and $CpFe(CO)_2I$. $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ gave $[Fe(CO)_4]_2[\mu\text{-}NC(CH_2)_2NC]$ (n = 2,3,4,6) on reaction with the diisocyanides [276].

The reactions of the thiocarbonyl complex 341 (See Scheme 46) show that in products of CO displacement, 342a-d, 343 and 344, μ-CS is retained. In MeCN, reaction rates are in the order $PEt_3 \sim PMe_2Ph > P(OMe)_3 > PMePh_2$. Amines, PPh_3 and $P(OPh)_3$ are unreactive. Substitution by MeNC proceeds only as far as 344 in contrast to $Cp_2Fe_2(CO)_4$ which affords the trisubstitution product. Both 343 and 344 exist in solution in two isomeric forms differing in the identity of the second bridging ligand as CNMe or CO. The S atom can be alkylated; this occurs in preference to N alkylation in 344 giving 348. The I ligand in 347a,b is terminal [277].

SCHEME 46



$$\underset{341}{Cp_2Fe_2(CO)_3(\mu\text{-}CS)} + L \xrightarrow[\text{reflux}]{\text{MeCN}} Cp_2Fe_2(CO)_2(L)(\mu\text{-}CS)$$

342 a L = PEt_3
b L = PMe_2Ph
c L = $PMePh_2$
d L = $P(OMe)_3$

$$341 + MeNC \xrightarrow[\text{reflux}]{\text{THF}} \underset{343}{Cp_2Fe_2(CO)_2(CNMe)(\mu\text{-}CS)}$$

$$341 + MeNC \xrightarrow[\text{reflux}]{\text{MeCN}} \underset{344}{Cp_2Fe_2(CO)(CNMe)_2(\mu\text{-}CS)}$$

$$341 \xrightarrow[\substack{Et_3OBF_3 \text{ or} \\ C_3H_7I}]{MeOSO_2F \text{ or}} [Cp_2Fe_2(CO)_3(CSR)]^+$$

345 a R = Me; b R = Et; c R = C_3H_7

$$\left.\begin{array}{l} 345a + L \\ 342a\text{-}d + MeOSO_2F \end{array}\right\} \longrightarrow [Cp_2Fe_2(CO)_2(L)(CSMe)]SO_3F$$

346 a L = PEt_3
b L = PMe_2Ph
c L = $PMePh_2$
d L = $P(OMe)_3$

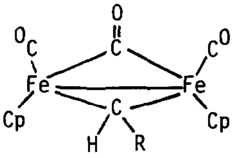
$$345a,b + NaI \longrightarrow Cp_2Fe_2(CO)(I)(CSR) + CO$$

347 a R = Me; b R = Et

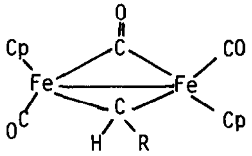
$$344 \xrightarrow[CH_2Cl_2]{MeI} \underset{348}{[Cp_2Fe_2(CO)(CNMe)_2(CSMe)]^+}$$

$$344 \xrightarrow[CH_2Cl_2]{MeOSO_2F} \underset{349}{[Cp_2Fe_2(CO)(CNMe)(CNMe_2)(CSMe)]^{2+}}$$

The X-ray structure of the μ-alkylidene dimer $[Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CHMe)]$, 350, was determined. Ignoring the Fe-Fe bond, coordination around Fe is approximately tetrahedral [86].

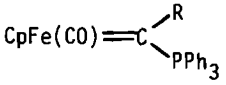


351 cis a R = H;
b R = Me; c R =
n-C_3H_7



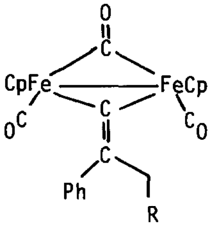
352 trans a R = H;
b R = Me; c R =
n-C_3H_7

A new preparative method for μ-alkylidene species is reaction of $[Cp_2Fe_2(CO)_4]$ with phosphorus ylids, $Ph_3P{=}CH(R)$. The products are 351, 352, and 353. The X-ray structure of 352a was determined [278]. The μ-vinylidine dimer, 354, was



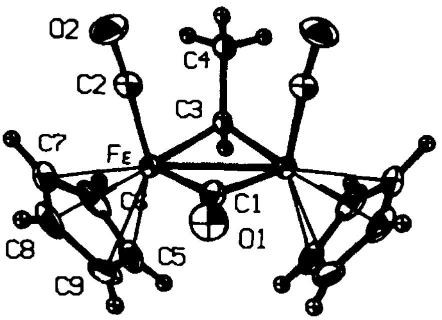
$$CpFe(CO){=}C\overset{R}{\underset{PPh_3}{}}$$

353 a R = H; b R = Me
c R = n-C_3H_7



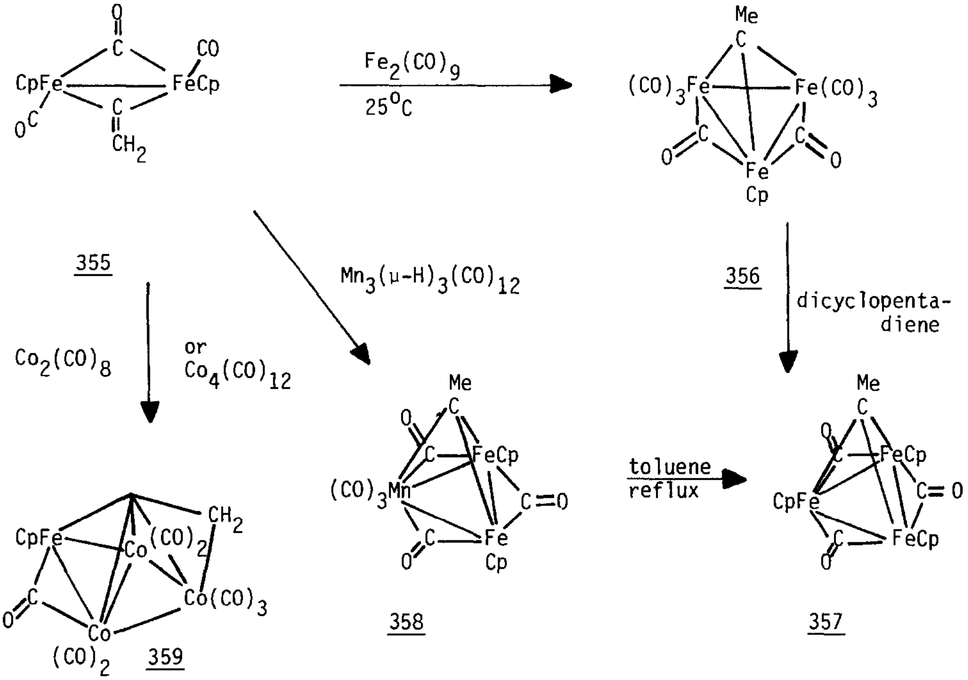
354 a R = Ph,
b R = H

obtained as cis and trans isomers on reaction of substituted gem-dichlorocylopropanes with $[Cp_2Fe_2(CO)_4]$. The X-ray structure of cis-354a was determined [279]. The μ-vinylidene dimer 355 produces several metal-cluster on treatment with metal carbonyls [280]. X-ray structures of 356 and 359 were determined [280].

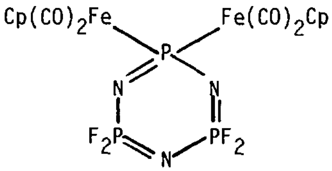


350

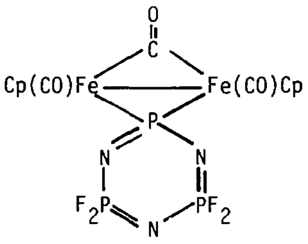
SCHEME 47



360 is the product of a reaction between [$Cp_2Fe_2(CO)_4$] and the cyclic trimer $(NPF_2)_3$. Photochemical decarbonylation of 360 yields 361 containing a spirocyclic ring. Crystal structures of both compounds were reported [281].

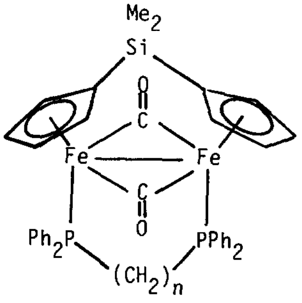


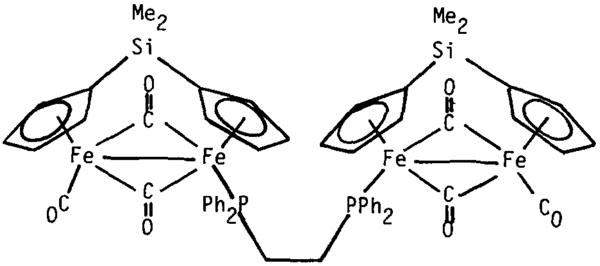
360



361

Photolysis of $Me_2Si[(C_5H_4)Fe(CO)_2]_2$ with $Ph_2P(CH_2)_nPPh_2$ (n = 1,2) affords 362 and 363 [282].

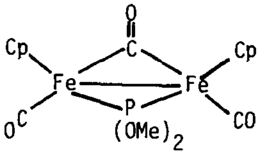




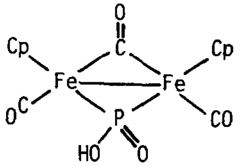
363

362 a n = 1
b n = 2

Other P complexes 364 and 365 are obtainable from photolysis of $\{[CpFe(CO)_2]_2$-$P(OX)_2\}^+$ (X=Me, H, respectively) [283].



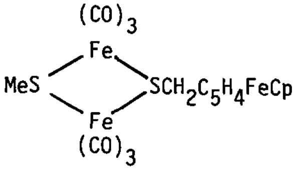
+



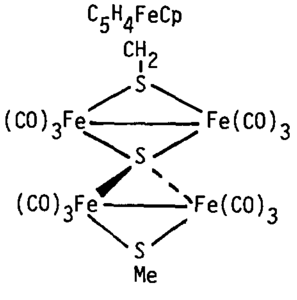
364

365

Group VI ligand chemistry includes the preparation of the unsymmetrically bridged 366 in a mixture of syn- and anti-isomers from the reaction of $[CpFe(\eta^5$-$C_5H_4CH_2S)]C(O)SMe$ and $Fe_2(CO)_9$. The other product, whose X-ray structure is reported, is 367 [284].



366



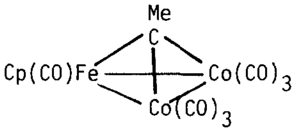
367

The electron impact mass spectrum of $CpFe(CO)_2SeCF_3$ was reported [106]. Two geometric isomers (cis- and trans-) of $Cp_2Fe_2(CO)_2(\mu_2$-TeC_6H_4p-$OEt)_2$ were separated and their crystal structures determined. In both cases some folding of the

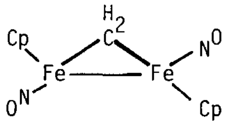
Fe_2Te_2 ring occurs along the Fe-Fe axis [285].

An improved preparation of $[CpFe(CO)]_4$ gives an 80% yield [286].

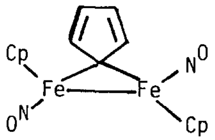
The cluster compound 368 was prepared by direct metal exchange in $MeCCo_3(CO)_9$ using $[Cp_2Fe_2(CO)_4]$ [287].



368



369



370

The nitrosyl dimers 369 and 370 were both prepared from $[Cp_2Fe_2(NO)_2]$ [288, 289].

Anionic and Cationic Species

Potassium benzophenone ketyl reduces $[Cp_2Fe_2(CO)_4]$ in THF. $K[CpFe(CO)_2]$ is obtained in 75-80% yield and can be stored under an inert atmosphere [290].

Catonic P-containing species can be prepared as shown in Scheme 48. 372 and 373 are precursors to 364 and 365 [283].

SCHEME 48

$$2CpFe(CO)_2X + Me_3SiPH_2 \xrightarrow[\text{20}^{\circ}\ -Me_3SiX]{\text{toluene}} [(CpFe(CO)_2)_2PH_2]^+X^-$$

371 a X = Cl
b X = Br
c X = BPh_4

$$\text{371a,b} + 2CX_4 \xrightarrow{\text{MeOH}} [(CpFe(CO)_2)_2P(OMe)_2]^+X^-$$

372 a X = Cl; b X = Br

$$\xrightarrow{H_2O} [(CpFe(CO)_2)_2P(OH)_2]^+X^-$$

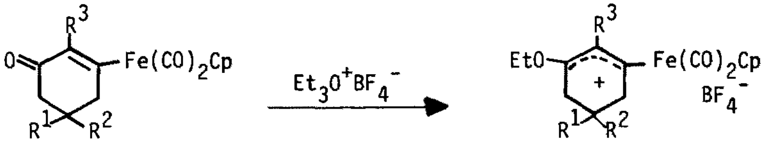
373 a X = Cl; b X = Br

Oxidation of $[Cp_2Fe_2(CO)_4]$ with quinone in CH_2Cl_2 in the presence of L = acetic acid, nitriles, dmso, olefins, ketones, aldehydes, lactones, nitro compounds, THF and A^- = PF_6^- or BF_4^- offers an improved synthesis for $[CpFe((CO)_2L]A$. Some thirty-six complexes were thus prepared [291].

Carbene, Alkylidene and Vinylidene Complexes

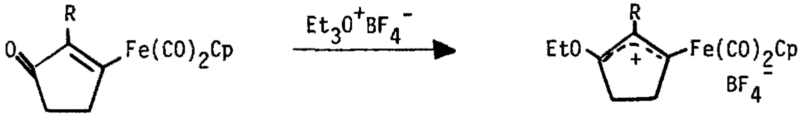
Ethylation of enone complexes using $Et_3O^+BF_4^-$ is a preparative route to a series of cationic vinyl carbene complexes. The EtO group can be replaced by NMe_2 on treatment with Me_3SiNMe_2 [292].

SCHEME 49



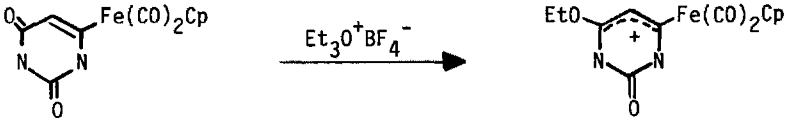
374		R^1	R^2	R^3
	a	H	H	H
	b	Me	Me	H
	c	Me	Me	Me
	d	Ph	H	H
	e	i-Pr	H	H

375		R^1	R^2	R^3
	a	H	H	H
	b	Me	Me	H
	c	Me	Me	Me
	d	Ph	H	H
	e	i-Pr	H	H



376 a R = H; b R = Me

377 a R = H; b R = Me

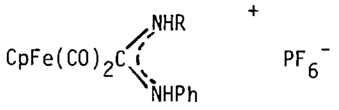


378

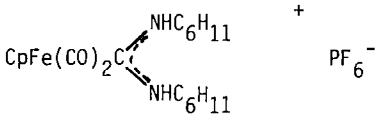
379

Unsymmetric amino carbene complexes 380a-e can be made by treatment of $[CpFe(CO)_2]^-$ with RN=C=NPh or by addition of RNH_2 to $[CpFe(CO)_2(CNPh)]^+$. Amine elimination from 380 induced by $COCl_2$ and NEt_3 gives either the CNPh or CNR complex or a mixture. The direction of amine elimination from 380 depends greatly on R and may be related to the rotamer population. Amine elimination from the symmetrical complexes 380g and 381 gives $[CpFe(CO)_2(CNPh)]^+$ and [CpFe

$(CO)_2(CNC_6H_{11})]^+$, respectively [293].



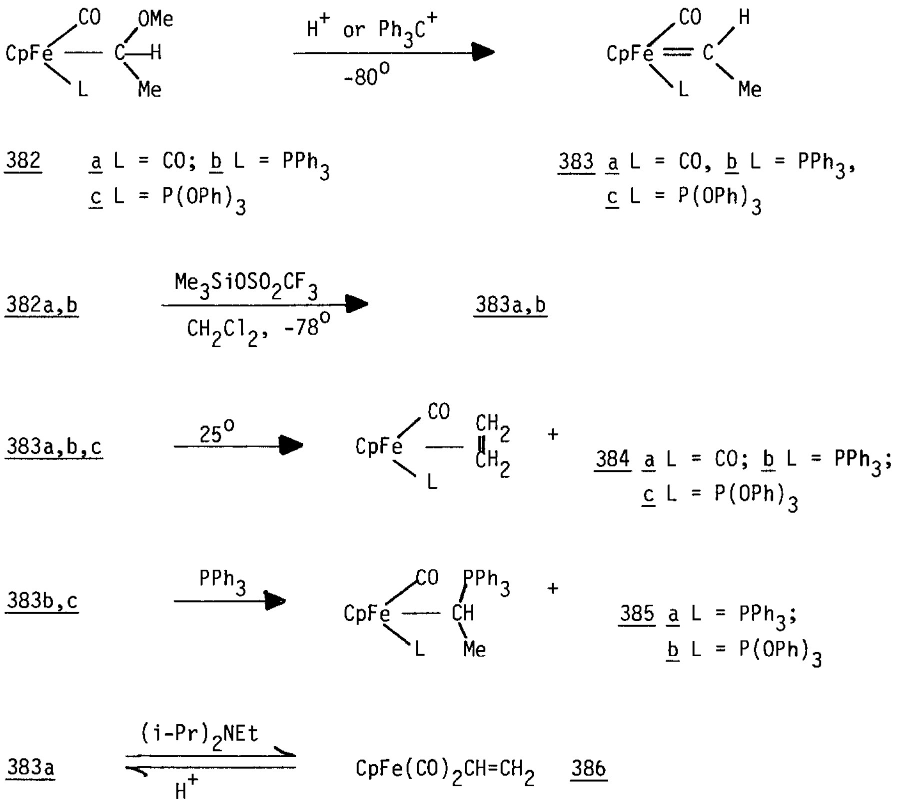
380 a R = i-Pr; b R = C_6H_{11};
c R = t-Bu; d R = Me;
e R = C_3H_5; f R = Ph



381

The alkylidene complex 383 has been generated *in situ* by two groups [294, 295]. In neither case was it isolated. However, 383b,c can be trapped by reaction with PPh_3 while 383a undergoes deprotonation or reaction with excess 382a or 386 producing 387 [294]. Alternatively, treatment of 383a,b with propenes affords cyclopropanes as products [295].

SCHEME 50



382 a L = CO; b L = PPh_3
c L = $P(OPh)_3$

383 a L = CO, b L = PPh_3,
c L = $P(OPh)_3$

382a,b $\xrightarrow[CH_2Cl_2,\ -78^o]{Me_3SiOSO_2CF_3}$ 383a,b

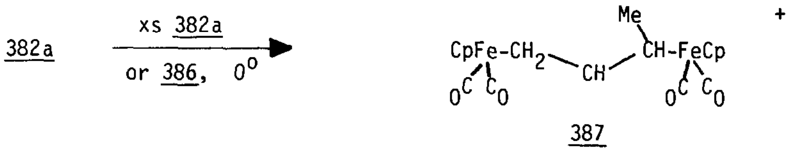
383a,b,c $\xrightarrow{25^o}$

384 a L = CO; b L = PPh_3;
c L = $P(OPh)_3$

383b,c $\xrightarrow{PPh_3}$

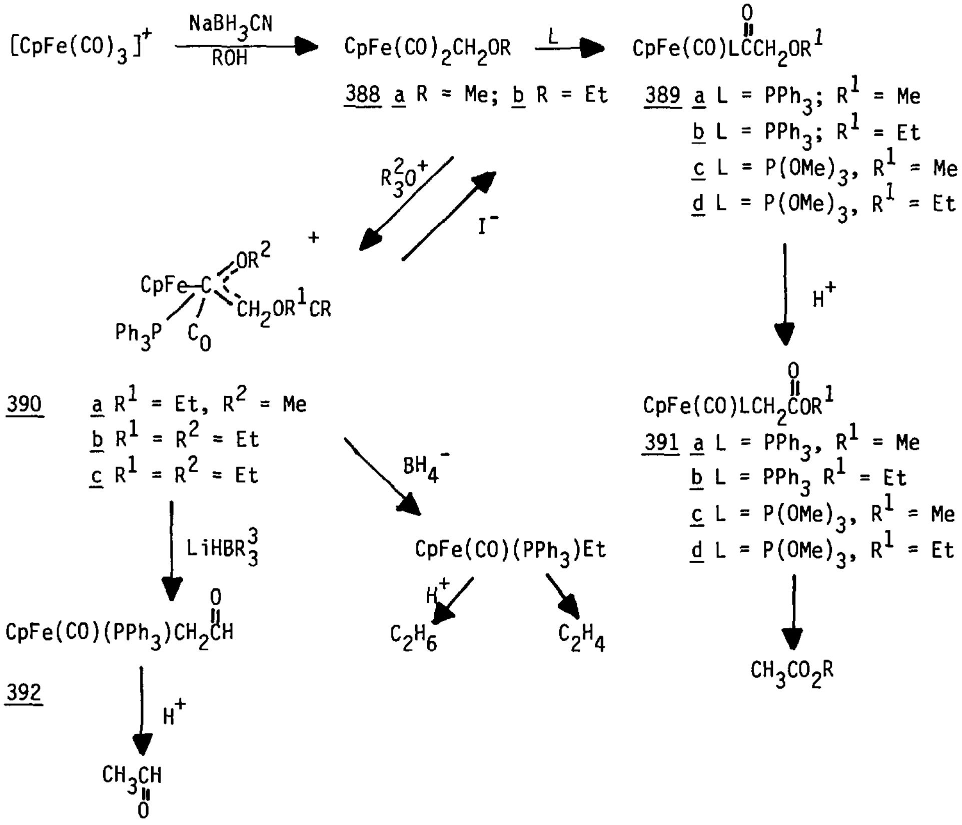
385 a L = PPh_3;
b L = $P(OPh)_3$

383a $\underset{H^+}{\overset{(i\text{-}Pr)_2NEt}{\rightleftharpoons}}$ $CpFe(CO)_2CH{=}CH_2$ 386



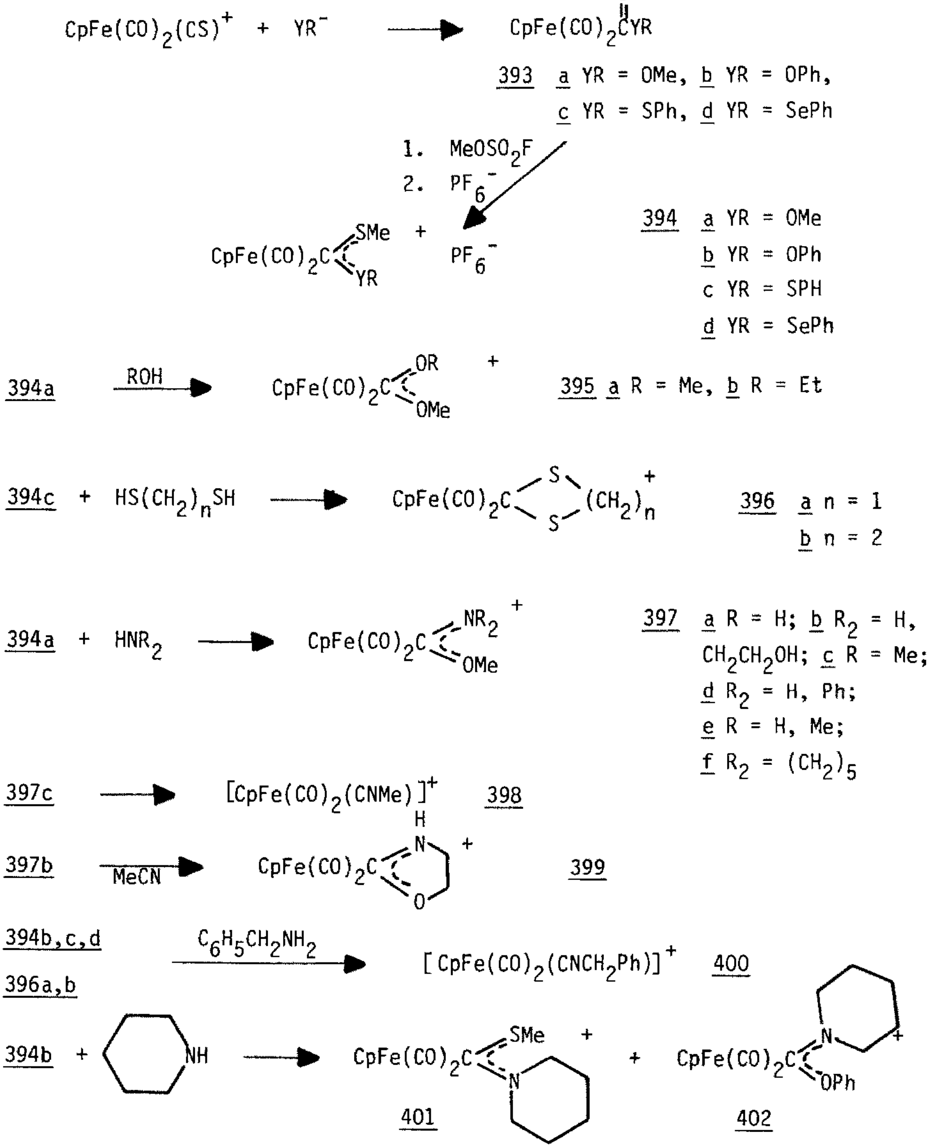
Other recent chemistry involving carbene complexes such as 390 converts two CO ligands into C_2 organic compounds [296].

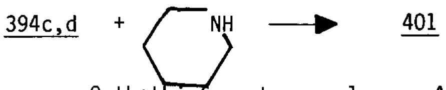
SCHEME 51



The cation $[CpFe(CO)_2(CS)]^+$ is the starting point for preparation of several thiocarbene complexes 394. 394a is thermally unstable, but its triflate salt reacts with alcohols affording 395a,b. 394c reacts with dithiols giving cyclic carbene complexes 396a,b. No correlation was found between k_{CO} and δ_{CO} for these thiocarbene complexes [297]. Aminocarbene complexes 397 can be prepared from 394a. 395a also gives aminocarbene comlexes, but other products are formed as well. Thermolysis of 397c leads to the isocyanide complex 398 via MeOH extrusion. Similarly, 397b produces the cyclic carbene complex 399. When $C_6H_5CH_2NH_2$ is added to 394b,c or d or to 396a or b the isocyanide complex 400 is obtained presumably via aminocarbene intermediates involving successive elimination of MeSH and RYH or *vice versa*. The behavior of piperidine with 394b,c,d is somewhat more complicated depending on the identity of Y. $C_6H_{11}NH_2$ does not react. The aminocarbene complexes display a correlation between k_{CO} and δ_{CO} as well as between δ_{CO} and gas-phase amine basicity [298].

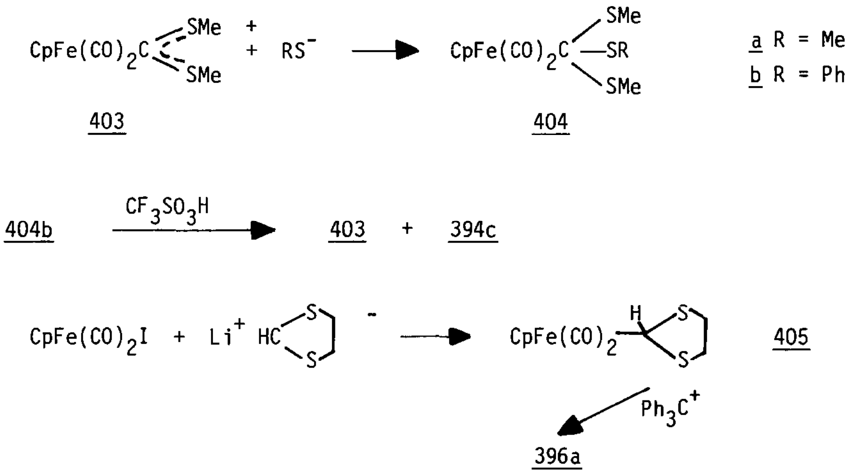
SCHEME 52



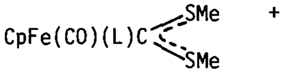


Orthothioformate complexes, 404, are the products of reactions between $[CpFe(CO)_2\ C(SMe)_2]^+$ and thiolates. These are stable at low temperature. Carbene complexes can be prepared, including the unsymmetric 394c, by treatment of 404b with CF_3SO_3H. A route to cyclic thiocarbenes 405 was also discovered and the X-ray structure of 404a reported [299].

SCHEME 53



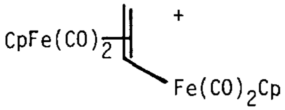
When 403 is irradiated with MeCN, 406a is the product. MeCN can be replaced by a variety of ligands leading to 406b-h. A correlation between the chemical shift of the carbene C and π-acceptor ability of L was noted. Complexes 406 react with primary and secondary amines yielding isocyanide complexes $[CpFe(CO)(L)CNR]^+$ and aminocarbene complexes $[CpFe(CO)(L)=C(SMe)NR_2]^+$, respectively [300].



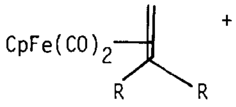
406 a L = MeCN, b L = $P(OPh)_3$, c L = $P(OMe)_3$,
d L = PPh_3, e L = $AsPh_3$, f L = $SbPh_3$,
g L = CNMe, h L = py

Alkene and Alkyne Derivatives

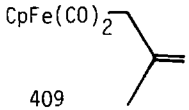
A convenient route to a number of alkene derivatives is replacement of O-bonded ligands L in the conveniently generated $[CpFe(CO)_2L]^+$ cations [291] and from $[CpFe(CO)_2(THF)]^+$ [301]. Improved syntheses for 407 and its analogues involves reaction of 408a $[CpFe(CO)_2(CH_2{=}CMe_2)]^+$ with complexes such as 409 and 410 containing uncoordinated double bonds [302]. 408b was employed in the synthesis of α-methylene γ-lactones [303].



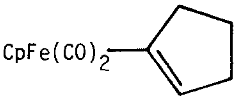
407



408 a R = H
b R = CO_2Et
c R = Me



409



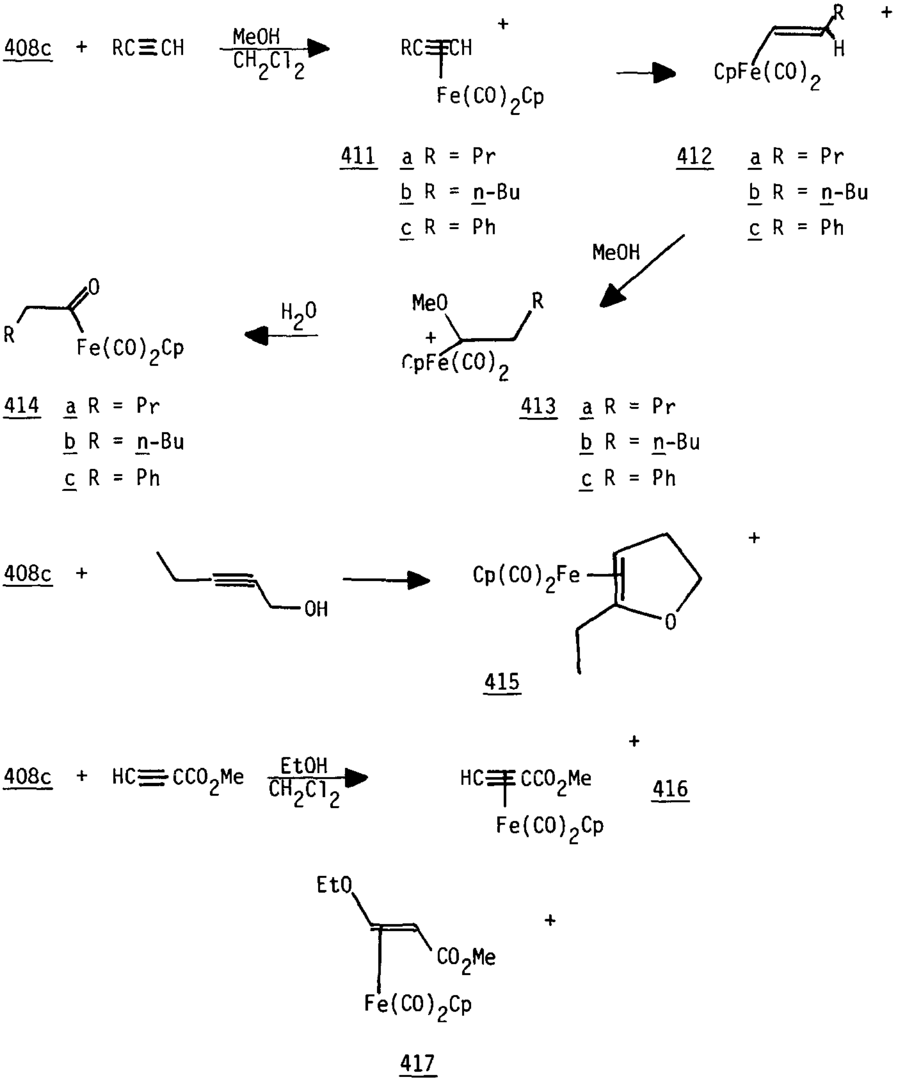
410

Recently, the suggestion was made on theoretical grounds that coordinated olefins were activated to nucleophilic attack by displacement toward an η^1-geometry [178]. Hence, one might expect olefin complexes with ground state geometries distorted toward η^1-coordination to display enhanced reactivity toward nucleophiles. X-ray structure determination of some complexes $[CpFe(CO)_2(\eta^2\text{-}CH_2{=}CHR)]^+$ showed that the distortions lie in the order $R{=}H < OMe < NMe_2$. With the soft nucleophile $[CpFe(CO)_2CH_2CH{=}CH_2]$ the NMe_2 cation is unreactive because the heteroatom lone pair interacts with the ligand LUMO. However, the OMe complex reacts faster than the unsubstituted one in accord with expectation [304].

408c was found to react with hydroxyallenes with displacement of isobutylene. The coordinated allene cyclizes to give dihydrofuran complexes [305].

Alkyne complexes 411a-c rearrange in alcohol/CH_2Cl_2 to vinylidene complexes 412a-c which then add alcohols to produce carboxonium - Fe complexes 413a-c [306].

SCHEME 54



The hydroxyalkyne gives a cyclized product. With HC ≡ CCO_2Me, the rearrangement to a vinylidene apparently does not occur and the alcohol attacks 416 [306].

Complexes Containing M-C σ-Bonds

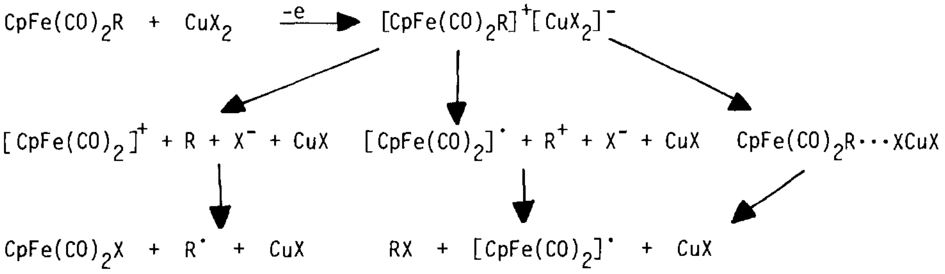
An ICR study of $CpFe(CO)_2Me$ (418c) has determined the proton affinity of this complex as 194 ± 2 kcal/mol and the bond dissociation energy of $[CpFe(CO)_2(Me)H]^+$ to $[CpFe(CO)_2Me]^+$ + H as 53 ± 3 kcal/mol [2]. Photolysis of $CpFe(CO)_2Me$ (418c) at high dilution in CO matrix produces $(\eta^3\text{-}C_5H_5)Fe(CO)_2Me$. Wavelength-selective photolysis of $CpFe(CO)_2[(CO)Me]$ (418e) in Ar, CH_4 and CO produces CpFe

$(CO)_2Me$ via a $CpFe(CO)[C(O)Me]$ intermediate [307]. Radicals resulting from the photolysis of 418a-e were trapped by nitrosodurene and their ESR spectra obtained [308].

$CpFe(CO)_2R$ 418 a R = CH_2Ph, b R = CH_2SiMe_3, c R = Me, d R = $C(O)CH_2Ph$, e R = $C(O)Me$, f R = Et, g R = CH_2CH_2Ph, h R = $CH_2CH_2CMe_3$, i R = CH_2CHMe_2, j R = CHDPh, k R = n-Bu, l R = Ph, m R = p-$MeOC_6H_4$

Cleavage reactions of 418 (R = alkyl) are initiated by $CuCl_2$ and by electrochemical means (as well as by several electrophilic reagents). Electrochemical oxidations of several such complexes were irreversible up to a scan rate of 200 Vs^{-1}. At low temperature and with increased scan rates a short-lived electrochemically active oxidation product is detectable. In CH_2Cl_2 medium with n-Bu_4NCl as supporting electrolyte, exhastive electrolysis yields $CpFe(CO)_2Cl$ and RCl. Coulometric experiments suggest one-electron oxidation. In CH_2Cl_2, oxidations by CuX_2 (X = Cl, Br) afford $CpFe(CO)_2X$, RX and 2CuX. Both electrochemical and CuX_2 oxidations seem to proceed via similar mechanisms, possiblities being indicated in Scheme 55.

SCHEME 55



The actual pathway followed depends on the identity of R. For (-)-418j the oxidation gave C_6H_5CHDX with > 90% inversion suggesting attack of X^- or CuX_2^- on $CpFe(CO)_2R$ and ruling out the presence of $R^\cdot$ or R^+. When no good nucleophile is present, or when R is not very susceptible to nucleophilic attack, the homolytic path involving $R^\cdot$ becomes competitive. For 418i and 418k, the presence of free radicals is detected by halogen abstraction from CH_2I_2. For 418a and 418c the normal nucleophilic attack process is apparently operative also.

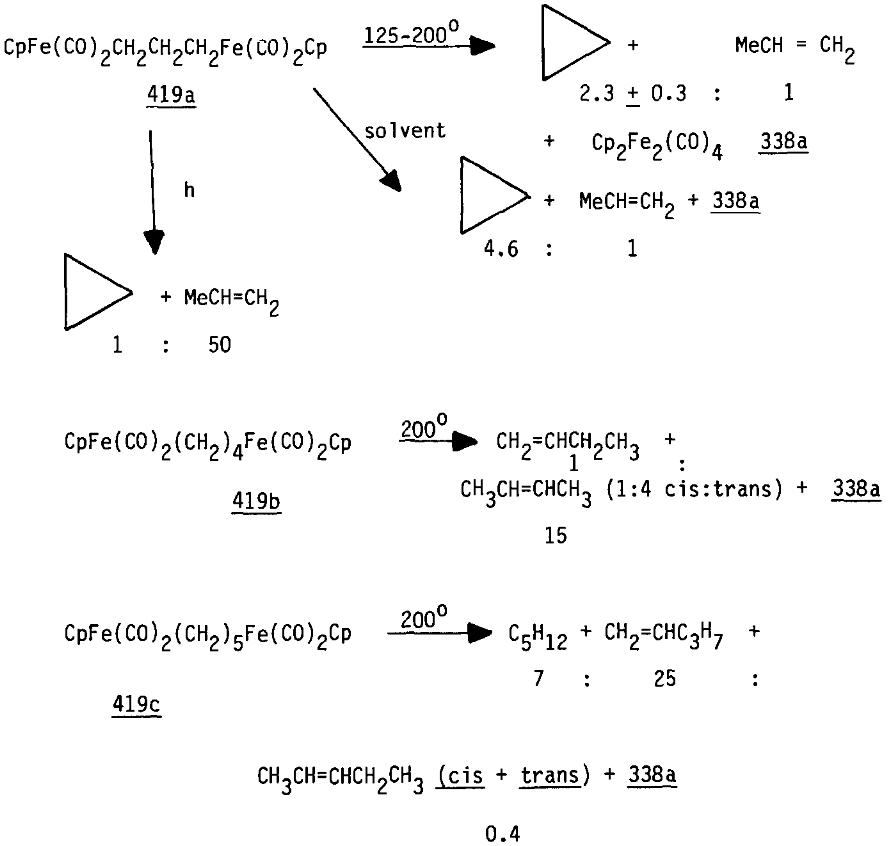
Kinetic studies show that the cleavage rate is virtually independent of R ruling out the S_{E_2} mechanism encountered for HgX_2 [309].

H-D exchange on the benzene ring of 418a in the presence of CF_3CO_2D and CH_3CO_2D was studied and suggested to involve electrophilic attack via a carbenium ion intermediate [310].

418c was found to act as a methyl transfer agent toward complexes of the type $[(HC\equiv CR^1R^2)Co_2(CO)_6]^+$ giving low yields of $[(HC\equiv CR^1R^2)(Me)Co_2(CO)_6]$ [311].

The dimeric alkyl-bridged complexes 419a-c eliminate hydrocarbons and quantitative yields of $[Cp_2Fe_2(CO)_4]$ on thermolysis or photolysis. Results with 419c suggest free-radical processes. A mechanism involving dimetallacycle formation can account for the observations for 419a,b [312].

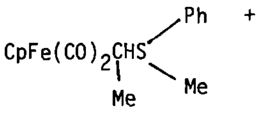
SCHEME 56



420 behaves as an alkylidene transfer agent toward ethylene in the presence of $MeOSO_2F$ via 421 [313]. The product is the cyclopropane C_3H_5Me.

$CpFe(CO)_2CH(Me)(SPh)$

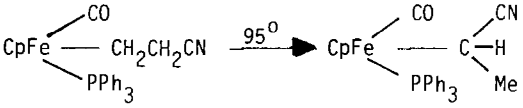
420



421

PPh_3 displaces Cl^- from $CpFe(CO)_2CH_2Cl$ producing $[CpFe(CO)_2CH_2PPh_3]^+$ [314]. Among alkyl complexes containing phosphine ligands, the one shown in Scheme 57 is one of the most interesting since the usual direction of isomerization is opposite. The 2^0 alkyl is apparently stabilized by the electron-withdrawing CN [315].

SCHEME 57

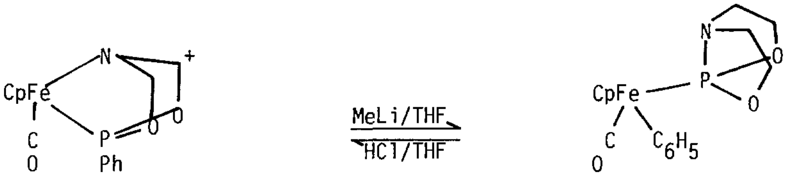


422 423

Another fascinating result involves carbonylation of $(-)_{546}$-Cp$\overset{*}{\mathrm{F}}$e(CO)[PPh_2N(Me)-$\underline{\mathrm{S}}$-$\overset{*}{\mathrm{C}}$H(Me)(Ph)]Me in benzene under CO pressure. The stereochemistry of the acetyl product reflects > 90% configuration retention at Fe corresponding to a "CO insertion" rather than a "methyl migration" mechanism [316].

Proton abstraction from 424 with MeLi affords 425 in which Ph has migrated from P to Fe. The reaction can be reversed by HCl [317].

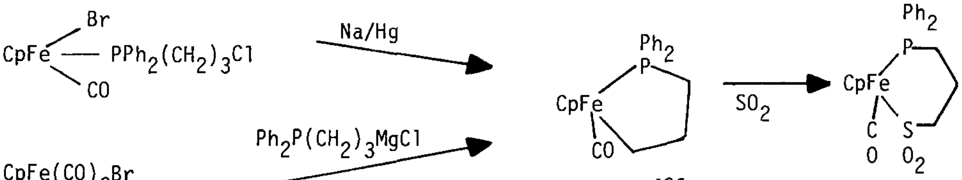
SCHEME 58



424 425

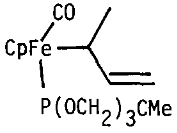
426 can be synthesized by two different routes. It inserts SO_2 to give 427 [318].

SCHEME 59

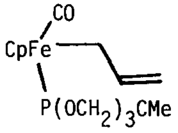


426 427

Allyl complexes can be synthesized via reaction of $CpFe(CO)_2X$ (X = Cl, Br, I) and $CH_2{=}CHCH_2Br$ in the presence of OH^- and a phase-transfer catalyst. The products are $CpFe(CO)_2CH_2CH{=}CH_2$ and $CpFe(CO)(\eta^3\text{-}C_3H_5)$ [319]. The substituted allyl complex 428 undergoes a [1,3] sigmatropic shift (= allylic rearrangement) to 429 considerably slower than does the corresponding dicarbonyl complex. Crossover experiments indicate that the process is intermolecular. A radical chain mechanism is proposed [320].



428

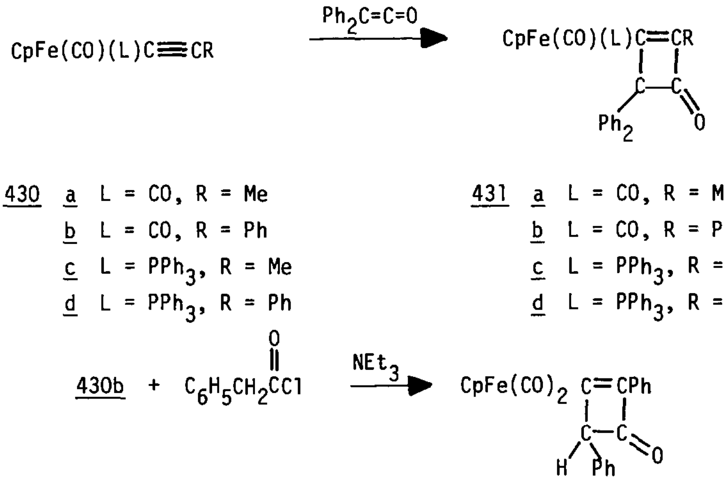


429

Cycloaddition reactions of p-tolylsulfonylisocyanate, with iron η^1-allyl and propargyl complexes were investigated kinetically. The data were compatible with electrophilic attack and the importance of both steric and electronic factors in determining the rate [321].

The propargyl complexes 430 undergo cycloaddition reactions with ketenes or benzyl chloride in the presence of NEt_3 giving 431 and 432, respectively [322].

SCHEME 60



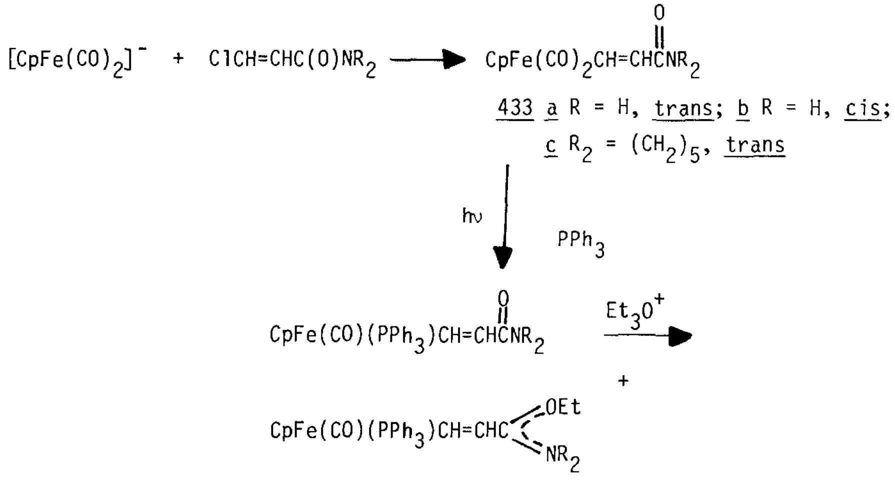
430 a L = CO, R = Me
b L = CO, R = Ph
c L = PPh_3, R = Me
d L = PPh_3, R = Ph

431 a L = CO, R = Me
b L = CO, R = Ph
c L = PPh_3, R = Me
d L = PPh_3, R = Ph

432

Several complexes containing σ-bonded vinyl ligands which also have an acyl functionality were synthesized. Ethylation leads to carbene complexes. The X-ray structure of 433b was determined [323].

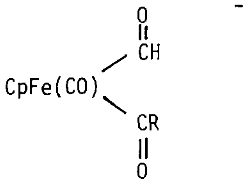
SCHEME 61



433 a R = H, trans; b R = H, cis;
c R_2 = $(CH_2)_5$, trans

434 a R = H, b R_2 = $(CH_2)_5$

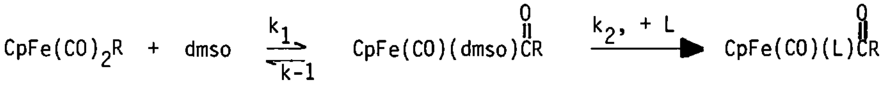
Reduction of 418c,f with $LiAlD_4$ was found to yield hydrocarbons with D incorporation. When the alkyl complexes 418c,f were reduced in the presence of ^{13}CO, C_{n+1} hydrocarbons with no ^{13}C were produced suggesting that CO insertion occurs. The acetyl complex 418e incorporates D. The dimer $[Cp_2Fe_2(CO)_4]$ incorporates ^{13}C when reduced under a ^{13}CO atmosphere again suggesting insertion [324]. When 418c,l,m are reduced with $Li[Et_3BH]$ 435a,b,c are produced in situ. A previous report of H_2 generation via protonation of 435b could not be reproduced [325].



435 a R = Me
b R = Ph
c R = p-$MeOC_6H_4$

The kinetics of CO insertion induced by PPh_3 with several complexes of type 418 were studied in dmso. The results were interpreted in terms of the mechanism depicted in Scheme 62 and values of k_1, k_{-1} and k_2 were extracted from the data. There is some question as to whether the intermediate 436 is really the one on the insertion pathway since other workers observed the formation of such species spectroscopically but failed to observe any specific increase in the carbonylation rate in dmso. The values of k_1 indicate that bulky R groups migrate fastest [326].

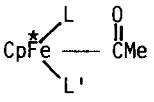
SCHEME 62



$$\mathrm{CpFe(CO)_2R} + \mathrm{dmso} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CpFe(CO)(dmso)\overset{\overset{O}{\|}}{C}R} \xrightarrow{k_2,\ +\ L} \mathrm{CpFe(CO)(L)\overset{\overset{O}{\|}}{C}R}$$

418 436

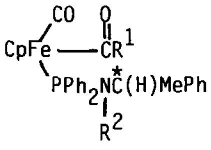
A series of acyl complexes CpFe(L)(L')[C(O)Me], 437 and 438d was prepared and each resolved into enantiomers. Absolute configurations at Fe were assigned based on ORD curves [327].



437

	L	L'
a	$PPh_2N(H)\overset{*}{C}(H)MePh$	PMe_3
b	$PPh_2N(H)\overset{*}{C}(H)MePh$	$CN\overset{*}{C}(H)MePh$
c	PMe_3	$CN\overset{*}{C}(H)MePh$
d	PMe_3	CNC_6H_{11}
e	PPh_3	$CN\overset{*}{C}(H)MePh$
f	CO	$PPh_2(N(H)\overset{*}{C}(H)MePh$
g	CO	$PPh_2N(Me)\overset{*}{C}(H)MePh$
h	CO	$PPh_2N(CH_2C_6H_5)\overset{*}{C}(H)MePh$

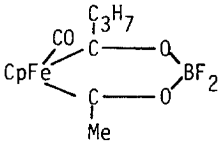
The X-ray structure of $(-)_{436}$-437f shows strong H-bonding between the N-H and acetyl O [328]. When the optically active complexes 438 are heated, rearrangement to $CpFe(CO)_2R$ occurs faster than epimeriztion at Fe. Heating in the presence of phosphine ligands gives phosphine exchange with predominant retention at Fe. These results require the presence of a chiral intermediate $Cp\overset{*}{F}e(CO)[C(O)R]$. With high L' concentration bimolecular inversion occurs at Fe [329].



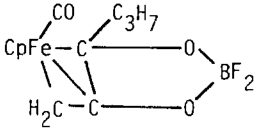
438

	R^1	R^2
a	Me	H
b	Me	Me
c	Me	Et
d	Me	$CH_2C_6H_5$
e	Et	H
f	i-Pr	H

The diacyl complex 439 on reduction with KH affords 440, a π-allyl complex derived from transannular C-C coupling in 439 [330].



<u>439</u>

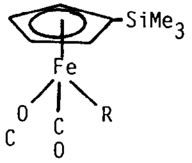


<u>440</u>

The acetyl complex <u>418e</u> transfers the C(O)Me group to phosphorus ylids giving species of the type $R^1_3P = C(R)^2C(O)Me$ [331].

<u>Compounds Containing Group IV Ligands Other Than C</u>

$CpFe(CO)_2SiMe_3$, on treatment with <u>n</u>-BuLi or $LiNEt_2$ followed by alkyl halide gives <u>441</u> in which the $SiMe_3$ group has migrated to the ring. <u>441b</u> can be carbonylated by reaction with PPh_3 or converted to an η^2-CH_2=CH_2 complex by H^- abstraction [332]. When $CpFe((CO)_2SiR_3$ (R_3 = $MePh_2$; MePh 1-$C_{10}H_7$; Me_3) was irradiated with $P(OPh)_3$, R_3SiH was formed. In the case of phosphine-substituted complexes, CpFe(CO)L (SiR_3) an iron-containing product resulting from <u>o</u>-metallation by the naphthyl ring could be isolated when L = P(Me)(Ph)(1-$C_{10}H_7$) [333]. CpFe(diphos)$GePh_3$ was prepared by treatment of CpFe(diphos)MgBr with Ph_3GeBr.



<u>441</u> <u>a</u> R = Me
<u>b</u> R = Et
<u>c</u> R = <u>n</u>-Br

Cl $Os(CO)_4$ $_3SnCl_2Fe(CO)_2Cp$

<u>442</u>

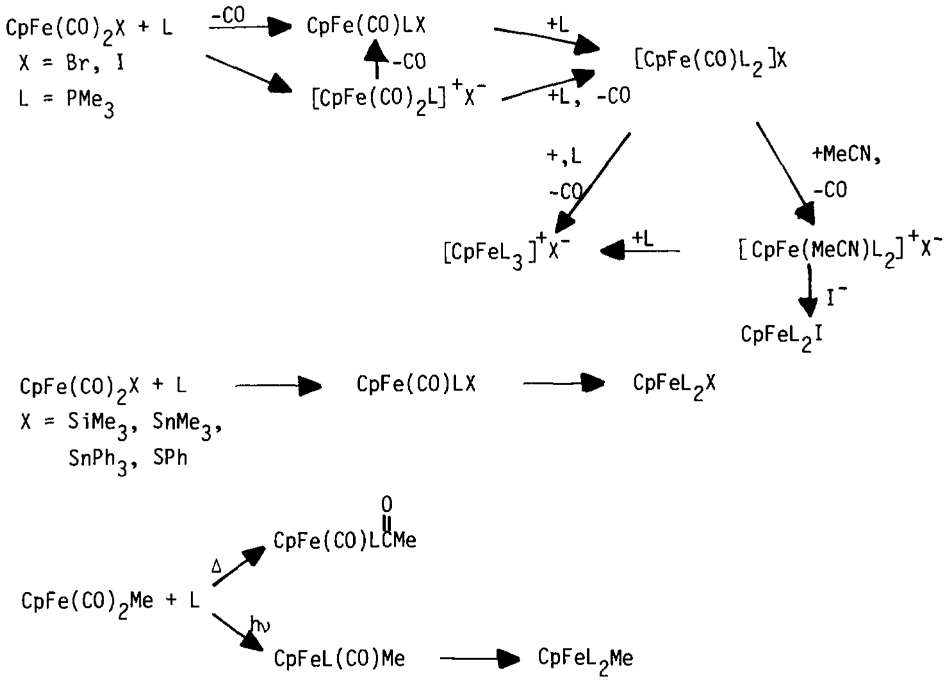
If $Ph_2MeGeBr$ is used, CpFe(diphos)Br is obtained [334]. Synthesis of polynuclear <u>442</u> containing an Fe-Sn bond was accomplished by reaction of $Cl[Os(CO)_4]_3SnCl_3$ with $Na[CpFe(CO)_2]$ [335].

<u>Compounds Containing Group V Ligands</u>

A 1:1 adduct between $[CpFe(CO)_2(NH_3)]^+$ and 18-crown-6 and dibenzo-18-crown-6 was detected by IR. H-bonding between N protons and ether O is involved [336].

Several complexes of L = PMe_3 were prepared as shown in Scheme 63 [337].

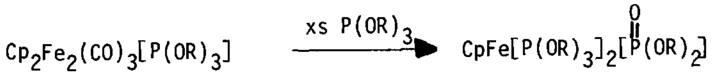
SCHEME 63



The ^{19}F NMR spectrum of $CpFe(CO)[PF_2(NMe_2)](\eta^1\text{-}C_5H_4Me)$ shows two diastereotopic F at all temperatures. Even at the fast-exchange limit the 'H NMR spectrum shows the non-equivalence of the four C_5H_4Me protons. This is consistent with a fluxional process for the η^1-ligand involving [1,5]-migration of the Fe with configuration retention in accord with the Woodward-Hoffmann rules [338].

Excess phosphite produces mononuclear products from phosphite-substituted dimers 443. 446 is produced only when R = Me. 447 results from H abstraction from free PPr_3 [339].

SCHEME 64



$$Cp_2Fe_2(CO)_3[P(OR)_3] \xrightarrow{\text{xs } P(OR)_3} CpFe[P(OR)_3]_2[\overset{O}{\overset{\|}{P}}(OR)_2]$$

443 a R = Me
b R = Et

444 a R = Me, b R = Et

$+ \ CpFe(CO)(COR)[P(OR)_3] \ + \ CpFe(CO)[P(OMe)_3]Me$

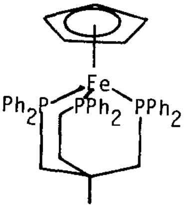
445 a R = Me, b R = Et 446

$$Cp_2Fe_2(CO)_3(PPr_3) \xrightarrow{\text{xs } PPr_3} Cp_2Fe + CpFe(CO)(PPr_3)H$$

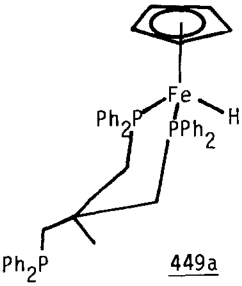
447

The acidity of coordinated phosphinous acid ligands in $\{CpFe(CO)_2[PPhR(OH)]\}Br$ (R = Ph, t-Bu) was increased compared to the free acids. The crystal structure of dimeric $\{[CpFe(CO)_2(PPh\text{t-}BuO)]_2H\}BF_4$ shows a very short O-H-O distance of 240.3 pm [340].

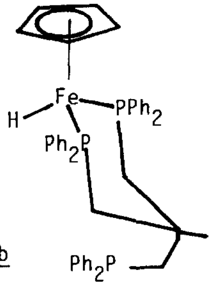
$LiAlH_4$ gives nucleophilic attack on Fe in 448 to produce 449a,b. In the analogous Ru compound, the Cp ring is the site of hydride attack [341].



448

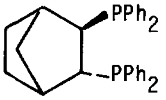


449a

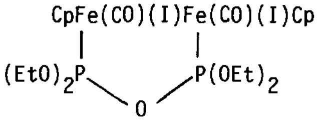


449b

(-)-norphos, 450, forms the complex $[CpFe(CO)(norphos)]^+$. The two diastereomers of the PF_6^- salt have almost the same ORD and CD spectra because the chelate ring adopts the λ configuration for both diastereomers [342]. The preparation of 451 was reported [91].



450



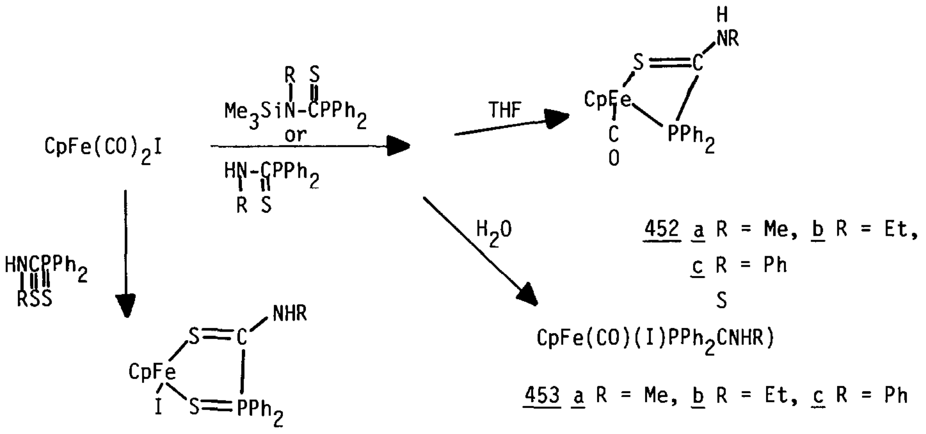
$$\begin{array}{ccc} CpFe(CO)(I) & - & Fe(CO)(I)Cp \\ | & & | \\ (EtO)_2P & -O- & P(OEt)_2 \end{array}$$

451

Ligands having P, N and S capable of coordination were allowed to react with $CpFe(CO)_2I$. P and S were preferentially attached in the products [343]. The corresponding oxides gave 1:1 adducts. (Scheme 65)

The first cationic complex containing CS and an organoarsenic ligand, 455, was synthesized [344].

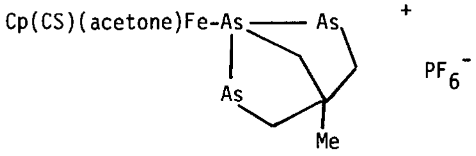
SCHEME 65



452 a R = Me, b R = Et, c R = Ph

453 a R = Me, b R = Et, c R = Ph

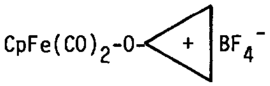
454 a R = Me, b R = Ph



455

Compounds Containing Group VI Ligands

The formate complex $CpFe(CO)_2OC(O)H$ was prepared and its crystal structure determined [345, 346]. The complex undergoes CO exchange faster than decarboxylation and decarboxylates much more slowly than $CpFe(CO)_2COOH$. The crystal structures of O-bonded sulfato and nitrato complexes were also reported [347]. The first cyclopropenone complex isolated without ring opening, 456, was prepared by olefin displacement from $[CpFe(CO)_2(\underline{i}\text{-}C_4H_8)]^+$ [348]. Photolysis of $CpFe(CO)_2I$ in 2-MeTHF at 77K produces CpFe(CO)(2-MeTHF)I [349].



456

$[CpFe(CO)_2(PhSH)]^+BF_4^-$

457

The thiol ligand in 457 behaves as a strong acid in CH_2Cl_2, the acidity being enhanced orders of magnitude over that of free PhSH [350]. $Li[W(CO)_5SH]$ and $CpFe(CO)_2Cl$ afford $CpFe(CO)_2S(H)W(CO)_5$ [351].

Halide Complexes

Electrochemical and spectroscopic studies on $CpFe(CO)_2X$ (X = Cl, Br, I, H, $SnCl_3$, $SnPh_3$, $GePh_3$, $SiPh_3$) at Hg electrodes showed that the LUMO is primarily localized on Fe-X. The mechanism of electrode processes depends on the stability of the one-electron reduction products $CpFe(CO)_2X^-$ [352].

Halide abstraction from $CpFe(CO)_2I$ by $AgBF_4$ was investigated in CH_2Cl_2. The initial product is the adduct <u>458</u> which, in excess $CpFe(CO)_2I$ gives <u>459</u> and AgI. <u>459</u> reacts with 0.5 equivalent of $AgBF_4$ producing AgI and <u>460</u> in which BF_4^- is coordinated to Fe. For $[CpFe(CO)_2]^+$ the coordinating ability decreases in the order acetone $> BF_4^- > CH_2Cl_2 > PF_6^-$ [353].

SCHEME 66

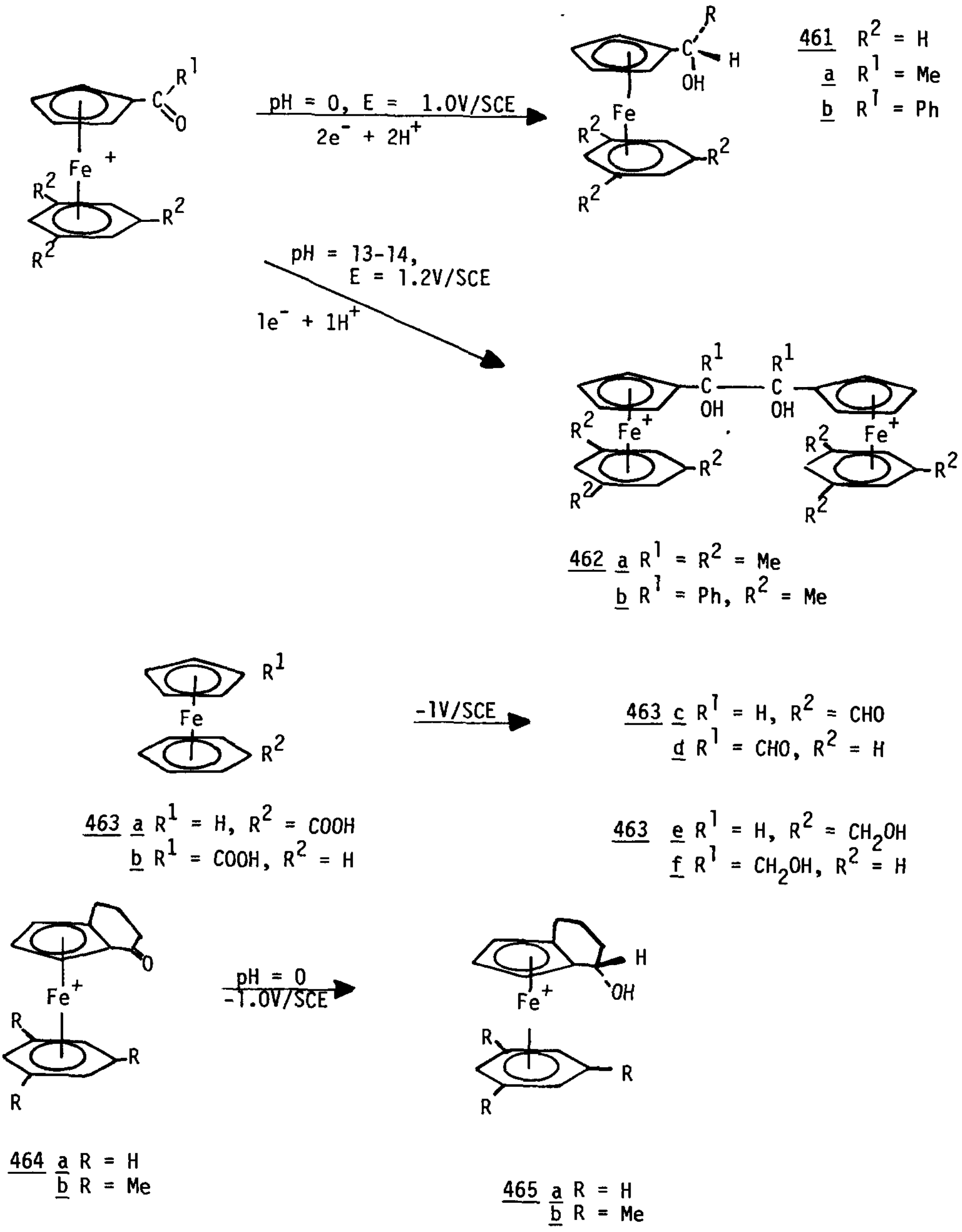
$$CpFe(CO)_2I \; + \; AgBF_4 \longrightarrow \underset{\underline{458}}{[CpFe(CO)_2IAg]^+} \xrightarrow{CpFe(CO)_2I}$$

$$AgI \; + \; \underset{\underline{459}}{[CpFe(CO)_2]_2I^+ \; BF_4^-} \xrightarrow{0.5\ AgBF_4} AgI \; + \; 2\,\underset{\underline{460}}{CpFe(CO)_2BF_4}$$

ARENE AND RELATED COMPLEXES

A good deal of effort has recently focused on complexes of the type $[(\eta^5\text{-}C_5H_5)Fe(\eta^6\text{-}C_6H_6)]^+$ with various ring substituents. Cathodic reduction of some of these complexes, as shown in Scheme 67, is regiospecific on the functional group instead of on the ring in contrast to the behavior of chemical reducing agents. The reduction of <u>464</u> to <u>465</u> is also stereospecific yielding only the <u>endo</u> alcohol. All the product cations can be reduced to cyclohexadienyl species by hydridic reagents [354]. A series of 19-e neutral complexes (η^5-Cp)Fe-(η^6-arene) is stabilized by peralkylation of the arene and destabilized by peralkylation of the Cp.

SCHEME 67



461 $R^2 = H$
a $R^1 = Me$
b $R^1 = Ph$

462 a $R^1 = R^2 = Me$
b $R^1 = Ph$, $R^2 = Me$

463 a $R^1 = H$, $R^2 = COOH$
b $R^1 = COOH$, $R^2 = H$

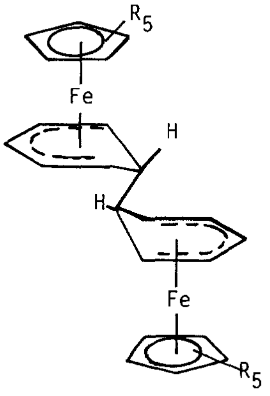
463 c $R^1 = H$, $R^2 = CHO$
d $R^1 = CHO$, $R^2 = H$

463 e $R^1 = H$, $R^2 = CH_2OH$
f $R^1 = CH_2OH$, $R^2 = H$

464 a R = H
b R = Me

465 a R = H
b R = Me

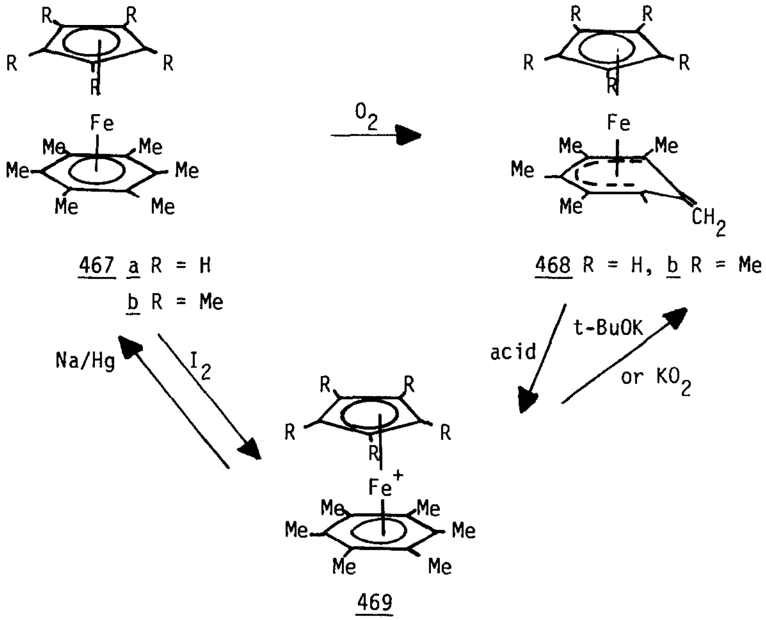
These can be synthesized by Na/Hg reduction of the cationic precursors. The complexes dimerize through the arene ring at rates depending on ring substituents giving species such as 466 [355]. 466a is produced slowly at 0° while 466b is produced rapidly at -80°. As seen in Scheme 67, O_2 can abstract a proton from 467 producing 468 containing a cyclohexadienyl ligand with a double-bonded exocyclic methylene group. Low temperature studies indicate that C-H activation occurs by electron abstraction to give $O_2^{\cdot -}$ (which was identified by its ESR spectrum) and subsequent H atom abstraction. 468 can also be made by deprotonation of 469, the cation precursor to 467a. 468a is an excellent nucleophile reacting with a variety of organic and organometallic reagents. It is oxidized by I_2 to 477 [356].



466 a R = H
b R = Me

AC polarography of the cations $[(\eta^5\text{-}Cp)Fe(\eta^6\text{-naphthalene})]^+$ showed waves corresponding to neutral and to anionic species. In protic media the latter was irreversible on account of reaction with protons to give an η^5-cyclohexadienyl complex [357]. Electrochemical reduction gave analogous results and addition of electrophilic reagents to the arene ring of the anion was used to synthesize [CpFe(cyclohexadienyl)] complexes [358].

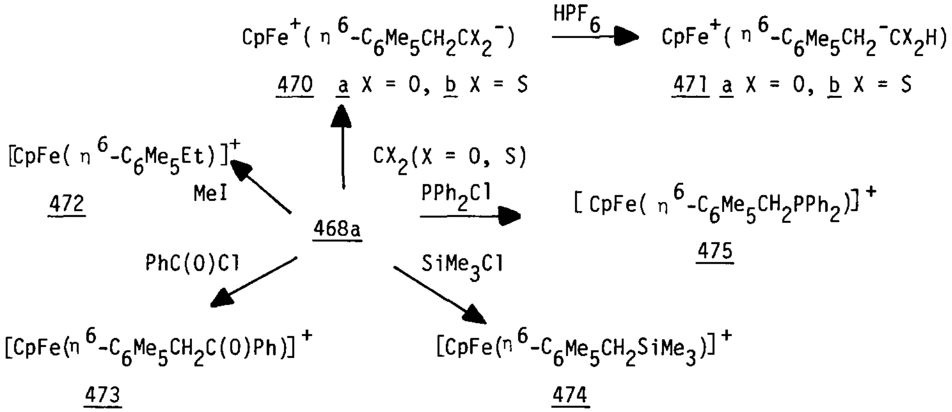
SCHEME 68

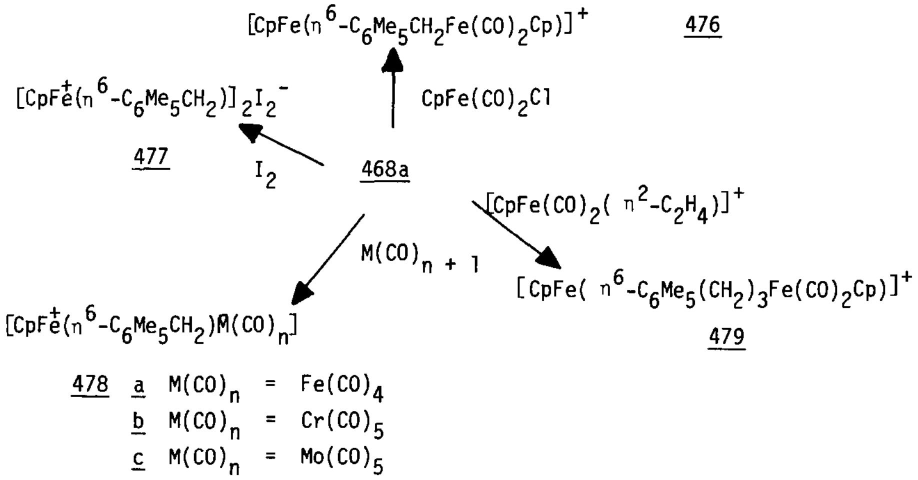


467 a R = H
b R = Me

468 R = H, b R = Me

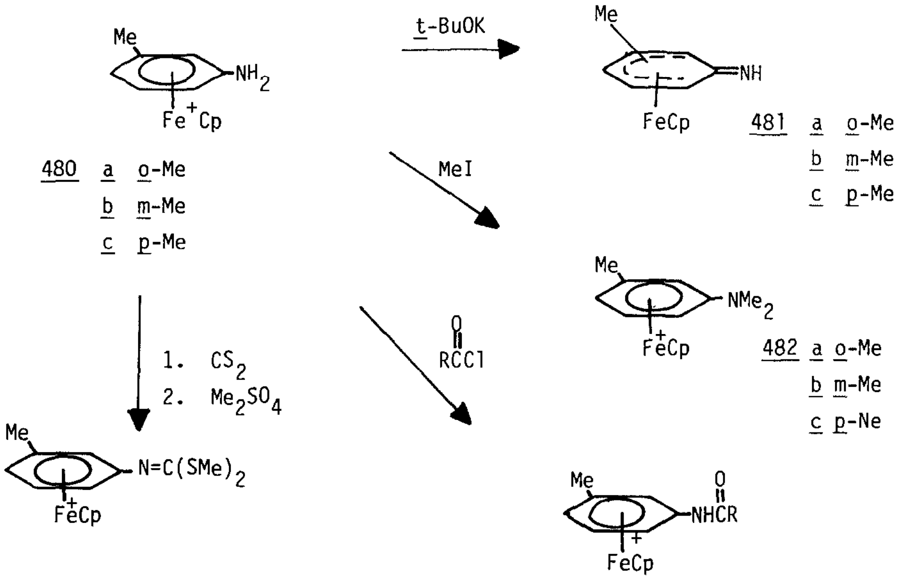
469





Ring substituents on cationic species are also reactive to nucleophilic attack as shown in Scheme 69 [359].

SCHEME 69



480 a o-Me
b m-Me
c p-Me

481 a o-Me
b m-Me
c p-Me

482 a o-Me
b m-Me
c p-Ne

484 a o-Me
b m-Me
c p-Me

483 a o-Me, R = Me
b o-Me, R = Et
c o-Me, R = Ph
d m-Me, R = Me
e m-Me, R = Et
f m-Me, R = Ph
g p-Me, R = Me
h p-Me, R = Et
i p-Me, R = Ph

The kinetics of nucleophilic replacement of Cl in $[CpFe(\eta^6\text{-}(Cl)(R)C_6H_4)]^+$ by OPh^- in EtOH were second-order and increase in the sequence R = m-Cl < m-CO_2Me < p-Me < H < m-Me < p-Me [360].

The production of $[CpFe(\eta^6\text{-}C_6H_5NMe)]^+$ and $[CpFe(\eta^5\text{-}C_5H_4CN)]$ on photolysis of $[CpFe(\eta^6\text{-}C_6H_5N_3)]^+$ was taken as evidence for production of a nitrene intermediate which abstracts protons from solvent or undergoes ring contraction [361].

Low-temperature condensation of Fe atoms with arenes followed by reaction with cyclopentadiene affords significant quantities of cyclohexadienyl complexes $CpFe(\eta^5\text{-}C_6H_6R)$ (R = H, Me, t-Bu) [362].

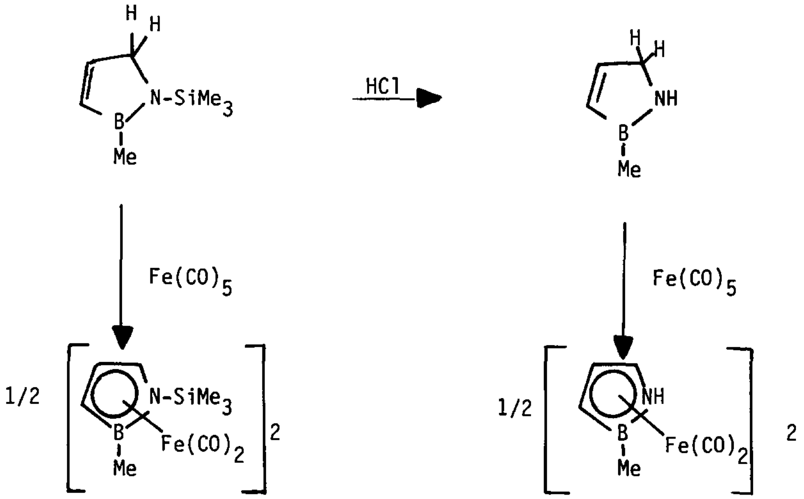
An extensive study of ^{13}C NMR spectra of thirty four complexes of the type $[(\eta^5\text{-}C_5R^1{}_5)Fe(\eta^6\text{-}C_6R^2{}_6)]^+PF_6^-$ was also published [363].

BORANE AND CARBORANE COMPOUNDS

Photoelectron spectra and MO calculations were reported for $Fe_2(CO)_6B_2H_6$ and $Fe_2(CO)_6B_3H_7$. In the latter complex more negative charge was calculated to reside on apical than equatorial Fe [364]. The X-ray structure of $Fe_2(CO)_6B_3H_7$ which is isoelectronicwith B_5H_9 was reported [365]. The compound contains one apical and one planar $Fe(CO)_3$. SCC calculations on the isoelectronic species B_6H_{10}, $Fe(CO)_3B_5H_9$ and $1\text{-}C_2B_3H_7Fe(CO)_3$ were carried out in order to rationalize the apical or planar location of $Fe(CO)_3$ groups [366]. The preparation of $CpFe(CO)_2B_{10}H_{15}$ was reported [367].

Two B-N rings form dimers 485 and 486 which are isoelectronic with $[Cp_2\text{-}Fe_2(CO)_4]$ [368].

SCHEME 70



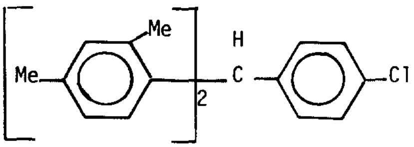
485

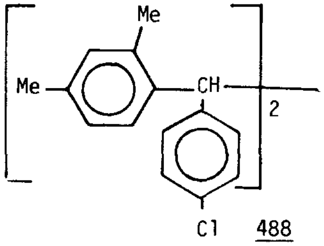
486

ORGANOMETALLIC SPECIES IN SYNTHESIS AND CATALYSIS

Already mentioned is the synthetic utility of (cyclohexadienylium)iron tricarbonyl cations 255-267 as well as the 19-electron reservoirs $(Cp)(Fe)(\eta^6\text{-arene})$ and related species 354-358.

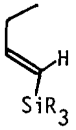
Several other studies of interest in synthesis were made. Aromatic acid chlorides were found to react in aromatic hydrocarbon solvents in the presence of $Fe(CO)_5$ producing triarylmethanes with two of the aryl groups coming from the solvent or tetraarylethanes with two aryl groups derived from solvent. For example, $p\text{-}ClC_6H_4C(O)Cl$ in mesitylene produces a mixture of 487 and 488. Presumably, a free-radical process is involved [369].

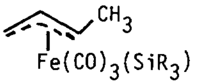

487


488

$[Fe(CO)_4]^{2-}$ was shown to be present in the reaction mixture NaH/t-$C_5H_{10}ONa$/-$FeCl_3$/CO which is known to carbonylate alkyl halides at atmospheric pressure [370]. $Fe_3(CO)_{12}$ in the presence of CO, H_2 and NaOMe was found to carbonylate reductively nitroarenes to a mixture of carbamates ArNHC(O)OMe and ureas ArNHC-(O)NHAr [371].

Hydrosilylation of 1-butane occurs on photolysis in the presence of $Fe(CO)_5$ and $HSiR_3$ (R = Me, n-Bu, Ph). The product mixture contains 489, 490, 491. At low temperatures, 492a can be detected in the reaction mixture. It was prepared separately and found to decompose thermally to 489a + 490a + 491a and an uncharacterized Fe product 492c decomposes to 491c. Isoprene and 2,3-dimethylbutadiene also undergo hydrosilylation under these conditions [372].





489 a R = Me
b R = n-Bu
c R = Ph

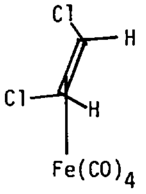
490 a R = Me
b R = n-Bu
c R = Ph

491 a R = Me
b R = n-Bu
c R = Ph

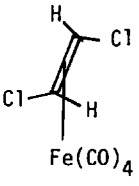
492 a R = Me
b R = n-Bu
c R = Ph

$Et_3NH \cdot HFe(CO)_4$ reduces n-butyraldehyde in EtOH to the alcohol. The reaction can be made catalytic in the presence of $Fe(CO)_5$ and Et_3N at 100° [373].

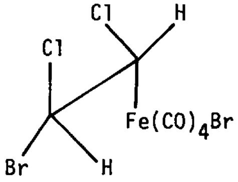
Vicinal dibromides are known to be dehalogenated by $Fe_2(CO)_9$ to olefins while 1,4-dihalobut-2-enes give dienes. An interesting study has shed light on mechanistic possibilities for this process. 493 and 494 react with Br_2 at -120° to -96° giving adducts which decompose to olefin and cis-$Fe(CO)_4Br_2$. The behavior of these adducts is similar to that of 495 and 496 which have hindered rotation around the C-C bond. 495 decomposes thermally with >95% stereospecificity to cis-ClHC=CHCl while 496 gives >99% trans-CHCl=CHCl. These decompositions are just the reverse of exo-addition of halide to a metal olefin complex and suggest the formation of analogues of 495 and 496 by exo-Br^- attack on (olefin)$Fe(CO)_4$ to be produced from $Fe_2(CO)_9$, the decomposition occurs too fast for the alkyl complexes to be observed. Nevertheless, the dehalogenation of vicinal dibromides displays great stereoselectivity [374].



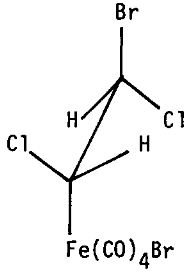
493 cis



494 trans

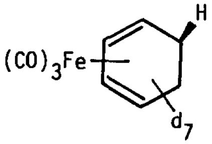


495 threo

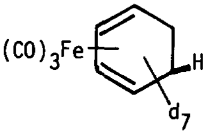


496 erythro

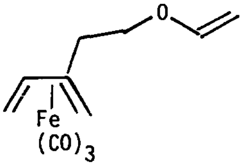
Photolysis of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ produces a thermally active catalyst which isomerizes pentane. In the presence of Et_3SiH hydrosilylation products also result [375]. Formal [1,5]-H shifts are known to be catalyzed by Fe complexes in cyclic dienes. These might be two consecutive [1,3]-shifts via Fe allyl complexes. Isomerizations of enantiomeric 497 and 498 were followed by NMR to determine initial ratios of H incorporation into various sites. The data were only consistent with consecutive [1,3]-shifts [376]. Fourier transform measurement of catalyst lifetime in the $Fe(CO)_5$ photocatalyzed isomerization of olefins showed lifetimes ranging from 7 to 28 sec and may reflect time required for dissociation of (olefin) $Fe(CO)_3$ [377].



497



498

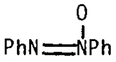


499

Methylene-bridge compounds such as 100 were postulated to be intermediates in Fischer-Tropsch chemistry since 100 reacts thermally with MeOH or EtOH producing MeC(O)OR (R = Me, Et). Labeling studies showed that μ-CH_2 was the source of the acetyl C [378]. An IR study of Fischer-Tropsch catalysts supported on silica or alumina revealed the presence of iron carbonyl species [379].

Polymerization of organometallic compounds containing vinyl groups is often hampered by catalyst attack on the metal. Several types of polymers were prepared from 499, however [380].

[$Cp_2Fe_2(CO)_4$] was found to act as a catalyst for substitution reactions by isocyanides on transition metal compounds [381]. $Fe(CO)_3(PPh_3)_2$ catalyzes the transformation of C_6H_5NO to 500. However, the corresponding Ru complex is more effective [382]. Mass spectral data on transition metal complexes including $CpFe(CO)_2H$ and [$Cp_2Fe_2(CO)_4$] supported on functionalized polymers showed no fragments associated with Fe [383].



$\mathrm{PhN{=}\overset{\overset{O}{|}}{N}Ph}$

500

REVIEWS AND DISSERTATIONS

Reviews

A second volume of *The Organic Chemistry of Iron* has appeared containing many useful and authoritative articles [384].

"Nucleophilic Addition to Diene and Arene-Metal Complexes" by M.F. Semmelhack [385] treats Fe-diene species.

"Diene and Dienyl Complexes of Iron: Reactivity and Synthetic Utility" by A.J. Pearson [386].

"The Strategy of Lateral Control of Reactivity: Tricarbonylcyclohexadienyl iron Complexes and Their Organic Synthetic Equivalents" by A.J. Birch, *et al.* [387].

"Structural Aspects and Coordination Chemistry of Metal Porphyrin Complexes with Emphasis on Axial Ligand Binding to Carbon Donors and Mono- and Diatomic Nitrogen and Oxygen Donors" by P.D. Smith, B.R. James and D.H. Dolphin [388] includes Fe porphyrins.

"Immobilized Transition-Metal Carbonyls and Related Catalysts" by D.C. Bailey and S.H. Langer [389] includes Fe carbonyls.

Dissertations

"Studies in Transition Metal Chemistry: I. Novel Metal Carbonyl Clusters Containing Iron and Molybdenum. I. Synthesis and Reactivity of Some Arene - Iridium Complexes" by A.C. Sievert [390].

"New Applications of Organometallic Reagents in the Synthesis of Natural Products" by K. Maruoka [391].

"Applications and Scope of Tetracarbonyliron Mediated Michael Reactions of Acrylate Esters" by M. Ross [392].

"Part III. Synthesis and Reactions of Bicyclo 4.2.1 Nonadiene Iron Tricarbonyl Complexes" by W.G.L. Aalbersberg [393].

"Part A. Nucleophilic Addition-Substitution Reactions of Benzocyclobutadienedicarbonylnitrosyliron(I). Part B. Mass Spectral Studies of Certain organometallic Derivatives" by D.A. Liebman [394].

"The Rational Synthesis of Mixed-Metal Clusters by Photogenerated Metal-Fragment Addition to the Coordinatively Unsaturated $[Co_2(\eta^5\text{-}C_5Me_5)_2(\mu_2\text{-}CO)_2]$ Neutral Dimer" by L.M. Cirjak [395].

"A Study of Reactions of N-sulfinylsulfonamides and Disulfonylsulfur Diimides with Some Organometallic Complexes" by T.W. Leung [396].

"Synthesis and Characterization of Iron(II) and Copper(I) Derivatives of Potassium Decahydropentaborate (-I)" by T.A. Schmitkons [397].

"Some Aspects of Organometallic Chemistry" by T.E. Cole is concerned with the chemistry of $[HFe(CO)_4]^-$ [398].

"Reactivity Studies of Mixed-Metal Carbonyl Clusters" by J.R. Fox [399].

"Synthesis and Reactivity of Transition Metal Carbonyl Complexes with Carbon Monoxide Coordinated through Carbon and Oxygen" by A. Wong [400].

"The Chemistry of 2-Pyrone Tricarbonyliron Complexes" by T. Jones [401].

"Reactions of Transition Metal π-Complexed Cations with Selected Nucleophiles" by B.R. Reddy includes Fe cations [402].

"Properties of Bimetallic Catalysts Prepared from Alumina Supported Mixed Metal Catalysts" by S.J. Hardwick [403].

"Some Organometallic Chemistry of Iminium Salts" by D.J. Sepelak includes Fe salts [404].

"Studies in Organotransition Metal Chemistry. Stereochemical Reactions, Structure and Mechanism" by J.E. Jensen includes Fe complexes [405].

"A Synthetic and Structural Study of the Reactivity of the σ, π-Acetylides $Fe_2(CO)_6[C_2R][P(C_6H_5)_2]$ and Some of Their Derivatives by G.N. Mott [406].

"Thermal and Photochemical Transformations of Cationic Iron and Ruthenium Isocyanide Complexes" by A.L. Steinmetz [407].

"Reactions of Trialkylsilyl Metal Carbonyl Complexes with Aldehydes and Ketones" by D.L. Johnson includes $Fe\text{-}SiR_3$ complexes [408].

"Michael Reactions of Highly Stabilized Enolate Anions to Iron(0) Tetracarbonyl Complexes of Acrylate Esters" by J. Wong [409].

"Photochemical and Thermal Reactions of Tricarbonyl(1,4-dimethyltetraazadiene)iron(0) and Related Compounds" by C.E. Johnson [410].

"The Total Synthesis of Aphidicolin and Cyclocarbonylation with Disodium Iron Tetracarbonyl" by W.A. Andrus [411].

"Part I. Synthesis and Characterization of Bis(iron dicarbonyl cyclopentadienyl) Sulfanes" by M.A.-L. El-Hinnawi [412].

"Nucleophilic Addition to (Methyl α-chloroacrylate)tetracarbonyliron. Preparation and Synthetic Applications of α-Acylacrylate and Methylene Malonate Esters" by M.R. Baar [413].

REFERENCES

1. G. P. Smith and R. M. Laine, J. Phys. Chem 85 (1981) 1620.
2. A. E. Stevens and J. L. Beauchamp, J. Am. Chem. Soc. 103 (1981) 190.
3. P. J. Krusic, J. San Filippo, Jr., B. Hutchinson, R. L. Hance and L. M. Daniels, J. Am. Chem. Soc. 103 (1981) 2129.
4. J. K. Burdett, Inorg. Chem. 20 (1981) 2607.
5. K. S. Suslick, P. F. Schubert and J. W. Goodale, J. Am. Chem. Soc. 103 (1981) 7342.
6. P. Bowen, W. Jones, J. M. Thomas, R. Schlögl and H. P. Bohm, Chem Commun. (1981) 679.
7. A. E. Mauro and E. G. Roveri, Ecletica Quim. 4 (1979) 61; CA 95, 161198x.
8. A. J. Blakeney and J. A. Gladysz, Inorg. Chim. Acta 53 (1981) L25.
9. A. J. Blakeney, D. L. Johnson, P. W. Donovan and J. A. Gladysz, Inorg. Chem. 20 (1981) 4415.
10. A. J. Blakeney and J. A. Gladysz, J. Organomet. Chem. 210 (1981) 303.
11. T. Pakkanen and R. C. Kerber, Inorg. Chim. Acta 49 (1981) 47.
12. Y. Chi and C. S. Liu, Inorg. Chem. 20 (1981) 3456.
13. A. L. Bykovets, O. K. Kuz'min, V. M. Vdovin, A. Ya. Sideridu, G. G. Aleksandrov and Yu. T. Struchkov, Izv. Akad. Nauk. SSSR (1981) 341.
14. B. A. Sosinsky, J. Shelly and R. Shong, Inorg. Chem 20 (1981) 1370.
15. H. Berke, W. Bankhardt, G. Huttner, J. v. Seryl and L. Zsolnai, Chem. Ber. 114 (1981) 2754.
16. C.-Y. Chang, C. E. Johnson, T. G. Richmond, Y.-T. Chen, W. C. Trogler and F. Basolo, Inorg. Chem. 20 (1981) 3167.
17. W. C. Trogler, C. E. Johnson and D. E. Ellis, Inorg. Chem. 20 (1981) 980.
18. J. P. Collman, J. I. Brauman, T. J. Collins, B. Iverson and J. L. Sessler, J. Am. Chem. Soc. 103 (1981) 2450.
19. T. G. Traylor, M. J. Mitchell, S. Tsuchiya, D. H. Campbell, D. V. Stynes and N. Koga, J. Am. Chem. Soc. 103 (1981) 5234.

20. B. Ward, C.-B. Wang and C. K. Chang, J. Am. Chem. Soc. 103 (1981) 5236.

21. T. G. Traylor, D. K. White, D. H. Campbell and A. P. Berzinis, J. Am. Chem. Soc. 103 (1981) 4932.

22. D. H. Busch, L. L. Zimmer, J. J. Grzybowski, D. J. Olzanski, S. C. Jackels, R. C. Callahan and G. C. Christoph, Proc. Nat. Acad. Sci. 78 (1981) 5919.

23. T. G. Traylor, T. C. Mincey and A. P. Berzinis, J. Am. Chem. Soc. 103 (1981) 7084.

24. C. Ercolani, F. Monacelli, G. Pennesi, G. Rossi, E. Antonini, P. Ascenzi and M. Brunori, J. Chem. Soc. Dalton Trans. (1981) 1120.

25. J. P. Collman, F. Basolo, E. Bunnenberg, T. J Collins, J. H. Dawson, P. E. Ellis, Jr., M. L. Marrocco, A. Moskowitz, J. L. Sessler and T. Syzmanski, J. Am. Chem. Soc. 103 (1981) 5636.

26. M. Cerdonio, S. Morante and S. Vitale, Isr. J. Chem. 21 (1981) 76.

27. F. Calderazzo, D. Vitali, G. Pampaloni, I. Collamati, G. Pelizzi, S. Frediani and A. Serra, Congr. Naz. Chim. Inorg. 12th (1979) 34; CA 95, 17265z.

28. A. H. Cowley, R. E. Davis and K. Ramadna, Inorg. Chem. 20 (1981) 2146.

29. A. H. Cowley, R. A. Kemp and J. C. Wilburn, Inorg. Chem. 20 (1981) 4289.

30. R. T. Smith and M. C. Baird, Transition Met. Chem. 6 (1981) 197.

31. R. Bartsch, S. Heitkamp, S. Morton and O. Stelzer, J. Organomet. Chem. 222 (1981) 263.

32. M. O. Albers, N. J. Coville, T. V. Ashworth and E. Singleton, J. Organomet. Chem. 217 (1981) 385.

33. H. E. Bryndza and R.G. Bergman, Inorg. Chem. 20 (1981) 1988.

34. C. A. Ghilardi, S. Midollini and S. Moneti, J. Organomet. Chem. 217 (1981) 391.

35. S. W. Blanch, A. M. Bond and A. R. Colton, Inorg. Chem. 20 (1981) 755.

36. A. Trenkle and H. Vahrenkamp, Chem. Ber. 114 (1981) 1366.

37. M. V. Andreocci, C. Cauletti, C. Furlani and G. Mattogno, Proc. Conf. Coord. Chem. 1980, 8th, 5.

38. C. Charrier, J. Guilhem and F. Mathey, J. Org. Chem. 46 (1981) 3.

39. W. S. Sheldrick, S. Morton and O. Stelzer, Z. anorg. allgem. Chem. 475 (1981) 232.

40. A. H. Cowley. S. L. Mehrotra and H. K. Roesky, Inorg. Chem. 20 (1981) 712.

41. C. C. Santini, J. Fischer, F. Mathey and A. Mitschler, Inorg. Chem. 20 (1981) 2848.

42. E. Röttinger and H. Vahrenkamp, J. Organomet. Chem. 213 (1981) 1.

43. M. Börner and H. Vahrenkamp, Chem. Ber. 114 (1981) 1382.

44. J. Grobe and B. H. Schneider, Z. Naturforsch. 36b (1981) 1.

45. J. Grobe and B. H. Schneider, Z. Naturforsch. 36b (1981) 8.

46. C. A. Ghilardi, S. Midollini, L. Sacconi and P. Stoppioni, J. Organomet. Chem. 205 (1981) 193.

47a. D. Touchard, H. Le Bozec, P. H. Dixneuf, A. J. Carty and N. J. Taylor, Inorg. Chem. 20 (1981) 1811.

47b. C. C. Frazier, R .F. Kline and D. D. Barck, Inorg. Chem. 20 (1981) 4009.

48. C. Bianchini, A. Meli, A. Orlandini and G. Scapacci, J. Organomet. Chem. 215 (1981) C59.

49. C. Bianchini, A. Meli, A. Orlandini and L. Sacconi, J. Organomet. Chem. 218 (1981) 81.

50. W. D. Jones, J. M. Huggins and R. G. Bergman, J. Am. Chem. Soc. 103 (1981) 4415.

51. W.-T. Pei, S.-H. Wang and H.-F. Ko, K'o Hsueh. Pao 26 (1981) 869; CA 96, 14547c.

52. H. Berke, G. Huttner and L. Zsolnai, Chem. Ber. 114 (1981) 3549.

53. R. G. Pearson, H. W. Walker, H. Mauermann and P. C. Ford, Inorg. Chem. 20 (1981) 2741.

54. R. Bau, D. M. Ho and S. S. Gibbons, J. Am. Chem. Soc. 103 (1981) 4960.

55. V. K. Vel'skii, E. B. Formicheva, A. V. Aripovskskii and B. M. Bulychev, Koord. Khim. 7 (1981) 1722; CA 96, 85698p.

56. P. A. Breeze, J. K. Burdett and J. J. Turner, Inorg. Chem. 20 (1981) 3369.

57. R. L. Sweany, J. Am. Chem. Soc. 103 (1981) 2410.

58. A. Maldotti, S. Sostero and O. Traverso, Inorg. Nucl. Chem. Lett. 54 (1981) L271.

59. C. E. Johnson and W. E. Trogler, J. Am. Chem. Soc. 103 (1981) 6352.

60. M. A. Stanford and B. H. Hoffman, J. Am. Chem. Soc. 103 (1981) 4104.

61. M. O. Abers, N. J. Coville, C. P. Nicolaides, R. A. Weber, T. V. Ashworth and E. Singleton, J. Organomet. Chem. 217 (1981) 247.

62. J.-M. Bassett, G. K. Barker, M. Green, J. A. K. Howard, F. G. A. Stone and W. C. Wolsey, J. Chem. Soc. Dalton Trans. (1981) 219.

63. T.-A. Mitsudo, H. Watanabe, K. Watanabe, Y. Watanabe and Y. Takegami, J. Organomet. Chem. 214 (1981) 87.

64. M. F. Lappert, J. J. MacQuitty and P. L. Pye, J. Chem. Soc. Dalton Trans. (1981) 1583.

65. W. Petz, Z. Naturforsch. 36b (1981) 335.

66. W. Petz, J. Organomet. Chem. 205 (1981) 203.

67. H. Le Bozec, A. Gorgues and P. Dixneuf, Inorg. Chem. 20 (1981) 2486.

68. A. J. Carty, P. H. Dixneuf, A. Gorgues, F. Hartstock, H. Le Bozec and N. J. Taylor, Inorg. Chem. 20 (1981) 3929.

69. P. Guerin, J.-P. Battioni, J.-C. Chottard and D. Mansuy, J. Organomet. Chem. 218 (1981) 201.

70. J.-P. Battioni, D. Dupre and D. Mansuy, J. Organomet. Chem. 214 (1981) 303.

71. T. C. Bruice, P. G. Furter and S. S. Ball, J. Am. Chem. Soc. 103 (1981) 4578.

72. B. Chevrier, R. Weiss, M. Lange, J.-C. Chottard and D. Mansuy, J. Am. Chem. Soc. 103 (1981) 2899.

73. L. Latos - Grazynski, R.-J. Cheng, G. N. LaMar and A. L. Balch, J. Am. Chem. Soc. 103 (1981) 4270.

74. T. S. Wisnieff, A. Gold and S. A. Evans, Jr., J. Am. Chem. Soc. 103 (1981) 5616.

75. M. Lange, J. P. Battioni and D. Mansuy, Chem. Commun. (1981) 888.

76. E. O. Fischer and P. Stadler, Z. Naturforsch. 36b (1981) 781.

77. H. Kon, M. Chikira and K. M. Smith, J. Chem. Soc. Dalton Trans. (1981) 1726.

78. A. Trenkle and H. Vahrenkamp, Chem. Ber. 114 (1981) 1343.

79. W. Beck, R. Grenz, F. Götzfried and E. Vilsmaier, Chem. Ber. 114 (1981) 3184.

80. D. Seyferth and M. K. Gallagher, J. Organomet. Chem. 218 (1981) C5.

81. M. Pfeffer, D. Grandjean and G. Le Borgne, Inorg. Chem. 20 (1981) 4426.

82. C. E. Housecroft, M. E. O'Neill, K. Wade and B. Smith, J. Organomet. Chem. 213 (1981) 35.

83. M. A. Duncan, T. G. Dietz and R. E. Smalley, J. Am. Chem. Soc. 103 (1981) 5245.

84. P. M. Weissman, D. B. Nuzzio and J. S. Wintermute, Jr., Microchem. Acta 26 (1981) 126.

85. P. J. Krusic, J. Am. Chem. Soc. 103 (1981) 2131.

86. B. B. Meyer, P. E. Riley and R. E. Davis, Inorg. Chem. 20 (1981) 3024.

87. G. Gervasio, P. L. Stanghellini and R. Rossetti, Acta Cryst. B 37 (1981) 1198.

88. N. S. Nametkin, V. D. Tyurin, V. V. Trusov, A. S. Batsanov and Yu. T. Struchkov, J. Organomet. Chem. 219 (1981) C26.

89. C. B. Argo and J. T. Sharp, Tet. Lett. 22 (1981) 353.

90. L. H. Staal, J. Keijsper, L. H. Polm and K. Vrieze, J. Organomet. Chem. 204

(1981) 101.

91. A. L. du Prez, I. L. Marais, R. J. Haines, A. Pidcock and M. Safari, J. Chem. Soc. Dalton Trans. (1981) 1918.

92. R. E. Cobbledick, W. R. Cullen, F. W. B. Einstein and M. Williams, Inorg. Chem. 20 (1981) 186.

93. H. J. Breuning, W. Fichtner and T. P. Knoblaugh, Z. anorg. allgem. Chem. 477 (1981) 126.

94. E. Keller and H. Vahrenkamp, Chem. Ber. 114 (1981) 1111.

95. G. Le Borgne and R. Mathieu, J. Organomet. Chem. 208 (1981) 201.

96. K. Fischer and H. Vahrenkamp, Z. anorg. allgem. Chem. 475 (1981) 109.

97. H. Patin, G. Mignani, A. Benoit, J.-Y. Marouille and D. Grandjean, Inorg. Chem. 20 (1981) 4351.

98. H. Patin, G. Mignani, A. Benoit and M. J. McGlinchey, J. Chem. Soc. Dalton Trans. (1981) 1278.

99. A. Benoit, J.-Y. Le Marouille, C. Mahe and H. Patin, J. Organomet Chem. 218 (1981) C67.

100. D. Wormsbächer, F. Edelmann and U. Behrens, Chem. Ber. 114 (1981) 153.

101. D. Seyferth and R. S. Henderson, J. Organomet. Chem. 218 (1981) C34.

102. D. Seyferth, L.-C. Song and R. S. Henderson, J. Am. Chem. Soc. 103 (1981) 5103.

103. S. Aime and D. Osella, J. Organomet Chem. 214 (1981) C27.

104. G. Gervasio, R. Rossetti and P. L. Stanghellini, Congr. Naz. Chim. Inorg., 12th (1979) 337; CA 94, 181502z.

105. D. Seyferth and R. S. Henderson, J. Organomet. Chem. 204 (1981) 333.

106. M. K. Chaudhuri, H. S. Dasgupta, N. Roy and D. T. Khathing, Org. Mass. Spec. 16 (1981) 534.

107. D. A. Lesch and T. B. Rauchfuss, Inorg. Chem. 20 (1981) 3583.

108. H. Dorn, B. E. Hanson and E. Motell, Inorg. Chim. Acta Lett. 54 (1981) L71.

109. D. R. Tyler and H. B. Gray, J. Am. Chem. Soc. 103 (1981) 1683.

110. D. H. Gibson, F. U. Ahmed and K. R. Phillips, J. Organomet. Chem. 206 (1981) C17.

111. D. H. Gibson, F. U. Ahmed and K. R. Phillips, J. Organomet. Chem. 218 (1981) 325.

112. M. C. Manning and W. R. Trogler, Inorg. Chim. Acta 50 (1981) 247.

113. F. H. Herbstein, Acta Cryst. B 37 (1981) 339.

114. W.-K. Wong, G. Wilkinson, A. M. R. Gales, M. B. Hursthouse and M. Thornton-

Pett, Chem. Commun. (1981) 189.

115. W. K. Wong, G. Wilkinson, A. M. Galas, M. B. Hursthouse and M. Thornton-Pett, J. Chem. Soc. Dalton Trans. (1981) 2496.

116. J.A.S. Howell and P. Mathur, Chem. Commun. (1981) 263.

117. K. S. Wong and T. P. Fehlner, J. Am. Chem. Soc. 103 (1981) 966.

118. K. S. Wong, T. K. Dutta and T. P. Fehlner, J. Organomet. Chem. 215 (1981) C48.

119. R. Mathieu, J. Organomet. Chem. 215 (1981) C57.

120. A. Marinetti, M. Nanni Marchino and E. Sappa, Atti Acad. Sci. Torino, Cl. Sci. Fiz., Mat. Nat. 113 (1979) 399; CA 95, 81172u.

121. H. Kisch, C. Krüger and A. Trautwein, Z. Naturforsch. 36b (1981) 205.

122. R. E. Benfield, P. D. Gavens, B. F. G. Johnson, M. J. Mays, S. Aime, L. Milone and D. Osella, J. Chem. Soc. Dalton Trans. (1981) 1535.

123. E. Keller and H. Vahrenkamp, Chem. Ber. 114 (1981) 1124.

124. I. A. Oxton, D. P. Powell, P. Skinner, L. Marko' and H. Werner, Inorg. Chim. Acta 47 (1981) 177.

125. T. Madach and H. Vahrenkamp, Chem. Ber. 114 (1981) 505.

126. P. H. Bird, U. Siriwardane, A. Shaver, O. Lopez and D. N. Harpp, Chem. Commun. (1981) 513.

127. G. Henkel, W. Tremel and B. G. Krebs, Angew. Chem. Int'l. Ed. 20 (1981) 1033.

128. J. S. Bradley, G. B. Ansell, M. E Leonowicz and E. W. Hill, J. Am. Chem. Soc. 103 (1981) 4968.

129. J. H. Davis, M. A. Beno, J. M. Williams, J. Zimmie, M. Tachikawa and E. L. Muetterties, Proc. Nat. Acad. Sci. 78 (1981) 668.

130. R. F. Boehme and P. Coppens, Acta Cryst. B 37 (1981) 1914.

131. M. A. Beno, J. M. Williams, M. Tachikawa and E. L. Muetterties, J. Am. Chem. Soc. 103 (1981) 1485.

132. E. M. Holt, K. H. Whitmire and D. F. Shriver, J. Organomet. Chem. 213 (1981) 125.

133. K. H. Whitmire and D. H. Shriver, J. Am. Chem. Soc. 103 (1981) 6754.

134. D. E. Fjare and W. L. Gladfelter, J. Am. Chem. Soc. 103 (1981) 1572.

135. D. E. Fjare and W. L. Gladfelter, Inorg. Chem. 20 (1981) 3533.

136. P. V. Broadhurst, B. F. G. Johnson, J. Lewis and P. R. Raithby, J. Am. Chem. Soc. 103 (1981) 3198.

137. F. Cecconi, C. A. Ghilardi and S. Midollini, Chem. Commun. (1981) 640.

138. M. Tachikawa, R. L. Geerts and E. L. Muetterties, J. Organomet. Chem. 213 (1981) 11.

139. J. Abys and W. M. Risen, J. Organomet. Chem. 204 (1981) C5.

140. P. Braunstein, A. Tiripicchio, M. T. Camellini and E. Sappa, Inorg. Chem. 20 (1981) 3586.

141. A. A. Pasynskii, I. L. Eremenko, B. Orazsakhatov, Yu. V. Rakitin, V. M. Novotarsev, O. G. Ellert, V. T. Kalinnikov, G. G. Aleksandrov and Yu. T. Struchkov, J. Organomet. Chem. 210 (1981) 385.

142. C. P. Casey and R. M. Bullock, J. Organomet. Chem. 218 (1981) C47.

143. L. Busetto, M. Green, J. A. K. Howard, B. Hessner, J. C. Jeffery, R. M. Mills, F. G. A. Stone and P. Woodward, Chem. Commun., (1981) 1101.

144. J. C. Jeffery, K. A. Mead, H. Razay, F. G. A. Stone, M. J. Went and P. Woodward, Chem. Commun. (1981) 867.

145. D. Seyferth and A. M. Mazany, J. Organomet. Chem. 213 (1981) C21.

146. A. K. Baev, J. A. Connor, N. I. El-Saied and H. A. Skinner, J. Organomet. Chem. 213 (1981) 151.

147. D. F. Jones, U. Oehmichen, P. Dixneuf, T. G. Southern, J.-Y. Le Marouille and D. Grandjean, J. Organomet. Chem. 204 (1981) C1.

148. D. F. Jones, P. H. Dixneuf, T. G. Southern, J.-Y. Le Marouille, D. Grandjean and P. Guenot, Inorg. Chem. 20 (1981) 3247.

149. D. F. Jones and P. H. Dixneuf, J. Organomet. Chem. 210 (1981) C41.

150. M. R. Churchill, C. Bueno and D. A. Young, J. Organomet. Chem. 213 (1981) 139.

151. F. Takusagawa, A. Fumagelli, T. F. Koetzle, G. R. Steinmetz, R. P. Rosen, W. L. Gladfelter, G. L. Geoffroy, M. A. Bruck and R. Bau, Inorg. Chem. 20 (1981) 3823.

152. J. R. Fox, W. L. Gladfelter, T. G. Wood, J. A. Smegal, T. K. Foreman, G. L. Geoffroy, I. Tavanaiepour, V. W. Day and C. S. Day, Inorg. Chem. 20 (1981) 3214.

153. W. L. Gladfelter, J. R. Fox, J. A. Smegal, T. G. Wood and G. L. Geoffroy, Inorg. Chem. 20 (1981) 3223.

154. H. C. Foley and G. L. Geoffroy, J. Am. Chem. Soc. 103 (1981) 7176.

155. J. R. Fox, W. L. Gladfelter, G. L. Geoffroy, I. Tavanaiepour, S. Abdel-Mequid and V. W. Day, Inorg. Chem. 20 (1981) 3230.

156. S. Kennedy, J. J. Alexander and S. G. Shore, J. Organomet. Chem. 219 (1981) 385.

157. R. A. Jackson, R. Kanluen and A. J. Poe, Inorg. Chem. 20 (1981) 1130.

158. B. M. Peake, P. H Rieger, B. H. Robinson and J. Simpson, Inorg. Chem. 20 (1981) 2540.

159. D. A. Young, Inorg. Chem. 20 (1981) 2049.

160. L. Marko', J. Organomet. Chem. 213 (1981) 271.

161. J. W. Lauher and K. Wald, J. Am. Chem. Soc. 103 (1981) 7648.

162. S. Aime, D. Osella, L. Milone, G. E. Hawkes and E. W. Randall, J. Am. Chem. Soc. 103 (1981) 5920.

163. K. Barth, R. Boese and G. Schmid, J. Organomet. Chem. 206 (1981) 331.

164. H. Vahrenkamp and E. J. Wucherer, Angew. Chem. Int'l. Ed. 20 (1981) 680.

165. E. Guggolz and M. L. Ziegler, Z. Naturforsch. 36b (1981) 1053.

166. R. J. Haines, N.D.C.T. Steen and R. B. English, Chem. Commun. (1981) 587.

167. E. Sappa, A. M. Manotti Lanfredi and A. Tiripicchio, J. Organomet. Chem. 221 (1981) 93.

168. A. M. Lanfredi, A. Tiripicchio, M. Camellini and M. Tiripicchio, Congr. Naz. Chim. Inorg. 12th (1979) 33; CA 94, 201162u.

169. L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A Stone and P. Woodward, J. Chem. Soc. Dalton Trans. (1981) 1134.

170. G. Longoni and F. Morazzoni, J. Chem. Soc. Dalton Trans. (1981) 1735.

171. G. Longoni, M. Manassero and M. Sansoni, Congr. Naz. Chim. Inorg. 12th (1979) 25; CA 95, 143253g.

172. S. S. Ullah, S. E. Kabir, M. K. Begum and A. F. K. Rahman, J. Bangladesh Acad. Sci. 5 (1981) 97; CA 95, 150840z.

173. M. Pankowski and E. Samuel, J. Organomet Chem. 221 (1981) C 21.

174. M. Pankowski, W. Chodkiewicz, M.-P. Simmonnin and M.-J. Pouet, Chem. Commun. (1981) 1071.

175. D. Lexa, J. Mispelter and J.-M. Saveant, J. Am. Chem. Soc. 103 (1981) 6806.

176. D. Brault and P. Neta, J. Am. Chem. Soc. 103 (1981) 2705.

177. H. M. Goff and M. A. Phillipi, Chem. Lett. 17 (1981) 239.

178. O. Eisenstein and R. Hoffmann, J. Am. Chem. Soc. 103 (1981) 4308.

179. A. J. Carty, G. N. Mott and N. J. Taylor, J. Organomet. Chem. 212 (1981) C54.

180. H. Berke, G. Huttner, G. Weiler and L. Zsolnai, J. Organomet. Chem. 219 (1981) 353.

181. D. W. Hensley, W. L. Wurster and R. P. Stewart, Inorg. Chem. 20 (1981) 645.

182. G. Cardaci, G. Bellachioma and G. Reichenbach, Congr. Naz. Chim. Inorg. 13th (1980) 79; CA 95, 97971q.

183. G. Cardaci and G. Bellachioma, Congr. Naz. Chim. Inorg. 12th (1979) 344; CA 95 , 198453g.

184. G. Bellachioma, G. Cardaci and G. Reichenbach, J. Organomet. Chem. 221

(1981) 291.

185. C. R. Jablonski, Inorg. Chem. 20 (1981) 3940.

186. W. A Herrmann, J. Gimeno, J. Weichmann, M. L. Ziegler and B. Balbach, J. Organomet. Chem. 213 (1981) C26.

187. T. A. Bagenova, A. K. Shilova, E. Deschamps, M. Gruselle, G. Leny and B. Tchoubar, J. Organomet. Chem. 222 (1981) C1.

188. Yu. L. Yagupol'skii, I. I. Gerus and L. M. Yagupol'skii, J. Org. Chem. USSR 17 (1981) 2243.

189. S. Zobl-Ruh and W. von Philipsborn, Helv. Chim. Acta 64 (1981) 2378.

190. M. I. Rybinskaya, A. A. Pogrebnyak and L. V. Rybin, Izv. Akad. Nauk SSSR (1981) 1772.

191. P. Radina and J. S. McKennis, Inorg. Chem. 20 (1981) 2054.

192. M. I. Rybinskaya, L. V. Rybin, A. A. Pogrebnyak, G. V. Nurtdinova and Y. P. Yur'ev, J. Organomet. Chem. 217 (1981) 373.

193. A. A. Panasenko, L. M. Khalilov, Ya. B. Yasman, G. V. Nurtdinova and Y. P. Yur'ev, Izv. Akad. Nauk SSSR (1981) 1581.

194. A. R. Pinhas, A. G. Samuelson, R. Risenberg, E. V. Arnold, J. Clardy and B. K. Carpenter, J. Am. Chem. Soc. 103 (1981) 1668.

195. A. C. Barefoot, III, E. W. Corcoran, Jr., R. P. Hughes, D. M. Lemal, W. D. Sanders, B. B. Laird and R. E. Davis, J. Am. Chem. Soc. 103 (1981) 970.

196. J. Dieter and K. M. Nicholas, J. Organomet. Chem. 212 (1981) 107.

197. T. Ishizu, M. Mori and K. Kanematsu, J. Org. Chem. 46 (1981) 526.

198. T. Ishizu, K. Harano, M. Yasuda and K. Kanematsu, Tet. Lett. 22 (1981) 1601.

199. T. Ishizu. K. Harano, M. Yasuda and K. Kanematsu, J. Org. Chem. 46 (1981) 3130.

200. K. Broadley, N. G. Connelly, J. A. K. Howard and W. Risse, J. Organomet. Chem. 221 (1981) C29.

201. F.-W. Grevels and W. E. Klotzbücher, Inorg. Chem. 20 (1981) 3002.

202. M. Franck-Neumann, C. Dietrich-Buchecker and A. Khemiss, Tet. Lett. 22 (1981) 2307.

203. M. Franck-Neumann, C. Dietrich-Buchecker and A. Khemiss, J. Organomet. Chem. 220 (1981) 187.

204. G. D. Annis, S. V. Ley, C. R. Self and R. Sivaramakrishnan, J. Chem. Soc. Perkin Trans. I (1981) 270.

205. T. Mitsudo, H. Watanabe, K. Watanabe, Y. Watanabe, K. Kafuku and K. Nakatsu, Chem. Lett. (1981) 1687.

206. A. N. Nesmeyanov, L. V. Rybin, N.A. Shtel'tser and M. I. Rybinskaya, Izv.

Akad. Nauk. SSSR (1981) 1299.

207. A. J. Rest and D. J. Taylor, Chem. Commun. (1981) 489.

208. P. C. Reeves, J. Organomet. Chem. 215 (1981) 215.

209. N. G. Connelly, R. L. Kelly and M. W. Whitely, J. Chem. Soc. Dalton Trans. (1981) 34.

210. A. V. Gist and P. C. Reeves, J. Organomet. Chem. 215 (1981) 221.

211. T. Butters, W. Winter and F. Todd, Acta Cryst. B 37 (1981) 1532.

212. J. A. Potenza, R. Johnson, D. Williams, B. H. Toby, R. A. La Lancette and A. Efraty, Acta Cryst. B 37 (1981) 442.

213. B. V. Lokshin, Z. S. Klemenkova, L. V. Rybin and V. T. Aleksanyan, Izv. Akad. Nauk SSSR (1981) 757.

214. T. Jenny, W. von Philipsborn, J. Kronenbitter and A. Schwenk, J. Organomet. Chem. 205 (1981) 211.

215. A. Monpert, J. Martelli and R. Gree, J. Organomet. Chem. 210 (1981) C45.

216. M. Franck-Neumann, D. Martina and F. Brion, Angew. Chem. Int'l. Ed. 20 (1981) 864.

217. M. A. De Paoli and N. Makita, J. Organomet. Chem. 216 (1981) 79.

218. Ph. Narbel, A. A. Pinkerton, E. Tagliaferri, J. Wenger, R. Roulet, R. Gabioud, P. Vogel and D. Schwarzenbach, J. Organomet. Chem. 208 (1981) 335.

219. R. Roulet, E. Tagliaferri, P. Vogel and G. Chapius, J. Organomet. Chem. 208 (1981) 353.

220. E. Meier, A. A. Pinkerton, R. Roulet, P. Vogel and D. Schwarzenbach, J. Organomet. Chem. 220 (1981) 341.

221. C. Barras, L. G. Bell, R. Roulet and P. Vogel, Tet. Lett. 22 (1981) 233.

222. C. Barras, L. G. Bell and R. Roulet, Helv. Chim. Acta 64 (1981) 2841.

223. P. Eilbracht and E. Henkes, Chem. Ber. 114 (1981) 1559.

224. K.-J. Jens and E. Weiss, J. Organomet. Chem. 210 (1981) C27.

225. S. Aimee and D. Osella, Chem. Commun. (1981) 300.

226. A. J. Pearson and P. R. Raithby, J. Chem. Soc. Dalton Trans. (1981) 884.

227. R. D. Wilcox, R. M. Pagni, H. M. Hassaneen and G. W. Kabalka, J. Org. Chem. 46 (1981) 1931.

228. B. M. Ratnayake Bandara, A. J. Birch, B. Chauncey and L. F. Kelly, J. Organomet. Chem. 208 (1981) C31.

229. D. Wormsbächer, F. Edelmann, D. Kaufmann, U. Behrens and A. de Meijere, Angew. Chem. Int'l. Ed. 20 (1981) 696.

230. T. Mitsudo, H. Watanabe, T. Sasaki, Y. Watanabe, Y. Takegami, K. Kafuku, K. Kinoshita and K. Nakatsu, Chem. Commun. (1981) 22.

231. G. R. Knox and I. G. Thom, Chem. Commun. (1981) 373.

232. W. Grimme and H. G. Köser, J. Am. Chem. Soc. 103 (1981) 5919.

233. K. Broadley, N. G. Connelly, R. M. Miller, M. W. Whitely and P. Woodward, Chem. Commun. (1981) 19.

234. Z. Goldschmidt and S. Antebi, J. Organomet. Chem. 206 (1981) C1.

235. N. G. Connelly, R. M. Mills, M. W. Whitely and P. Woodward, Chem. Commun. (1981) 17.

236. W. Flitsch and E. R. F. Gesing, J. Organomet. Chem. 218 (1981) 377.

237. S. K. Chopra, G. Moran and P. McArdle, J. Organomet. Chem. 214 (1981) C36.

238. S. K. Chopra, M. J. Hynes and P. McArdle, J. Chem. Soc. Dalton Trans. (1981) 586.

239. A. D. Charles, P. Diversi, B. F. G. Johnson and J. Lewis, J. Chem. Soc. Dalton Trans. (1981) 1906.

240. T. A. Albright, W. E. Geiger, Jr., J. Moraczewski and B. Tulyathan, J. Am. Chem. Soc. 103 (1981) 4787.

241. S. C. Carlton and S. A. R. Knox, J. Chem. Soc. Dalton Trans. (1981) 2230.

242. A. Salzer, T. Egolf, L. Linowsky and W. Petter, J. Organomet. Chem. 221 (1981) 339.

243. A. Salzer, T. Egolf and W. von Philipsborn, J. Organomet. Chem. 221 (1981) 351.

244. F. A. Cotton and J. M. Troup, J. Organomet. Chem. 212 (1981) 411.

245. S. S. Ullah and S. E. Kabir, J. Bangladesh. Acad. Sci. 4 (1980) 47; CA 95, 97966s.

246. H. A. Backmuelen and A. W. Parkins, J. Chem. Soc. Dalton Trans. (1981) 262.

247. P. Jutzi and A. Karl, J. Organomet. Chem. 214 (1981) 289.

248. Yu. S. Nekrasov, O. B. Afanasova, Yu. N. Sukharev, G. A. Nurgalieva, N. G. Komalenkova and E A. Chernyshev, Izv. Akad. Nauk. SSSR (1981) 1841.

249. A. S. Batsanov, Yu. T. Struchov, G. V. Nurtdinova, A. A. Pogrenbnyak, L. V. Rybin, V. P. Yur'ev and M. I. Rybinskaya, J. Organomet. Chem. 212 (1981) 211.

250. P. Jutzi, A. Karl and C. Burschka, J. Organomet. Chem. 215 (1981) 27.

251. G. Bellachioma and G. Cardaci, J. Organomet. Chem. 205 (1981) 91.

252. A. A. Kordize, P. V. Petrovskii, N. M. Astakhova, N. A. Vol'kenau, V. A. Petrakova and A. N. Nesemeyanov, Dokl. Akad. Nauk SSSR 254 (1981) 500.

253. A. Zimniak, Bull. Acad. Pol. Sci., Ser. Sci. Chem. 27 (1979) 743.

254. B. Etemadi, D. S. Moss and R. A. Palmer, J. Inorg. Nucl. Chem. 43 (1981) 1997.

255. A. J. Pearson, Tet. Lett. 22 (1981) 4033.

256. L. F. Kelly, P. Dahler, A. S. Narula and A. J. Birch, Tet. Lett. 22 (1981) 1433.

257. B. F. G. Johnson, J. Lewis, D. G. Parker and G. R. Stephenson, J. Organomet. Chem. 204 (1981) 221.

258. A. J. Pearson and G. C. Heywood, Tet. Lett. 22 (1981) 1645.

259. A. J. Birch, L. F. Kelly and D. J. Thompson, J. Chem. Soc. Perkin Trans. I (1981) 1006.

260. A. J. Pearson and C. W. Ong, J. Chem. Soc. Perkin Trans I (1981) 1614.

261. A. J. Birch and R. Stephenson, J. Organomet. Chem. 218 (1981) 91.

262. A. J. Birch, W. D. Raverty and G. R. Stephenson, J. Org. Chem. 46 (1981) 5166.

263. A. J. Birch and G. R. Stephenson, Tet. Lett. 22 (1981) 779.

264. L. A. P. Kane-Maguire, T. I. Odiaka, S. Turgoose and P. A. Williams, J. Chem. Soc. Dalton Trans. (1981) 2489.

265. L. A. P. Kane-Maguire, T. I. Odiaka and P. A. Williams, J. Chem. Soc. Dalton Trans. (1981) 200.

266. T. I. Odiaka and L. A. P. Kane-Maguire, J. Chem. Soc. Dalton Trans. (1981) 1162.

267. A. J. Birch, D. Bogsanyi and L. F. Kelly, J. Organomet. Chem. 214 (1981) C39.

268. G. R. John and L. A. P. Kane-Maguire, Inorg. Chim. Acta 48 (1981) 179.

269. D. A. Brown, W. K. Glass and F. M. Hussein, J. Organomet. Chem. 218 (1981) C15.

270. N. G. Connelly, R. L. Kelly, M. D. Kitchen, R. M. Mills, R. F. D. Stansfield, M. W. Whitely, S. M. Whiting and P. Woodward, J. Chem. Soc. Dalton Trans. (1981) 1317.

271. F. Schiavon and C. Paradisi, J. Organomet. Chem. 210 (1981) 247.

272. J. Grobe, B. H. Schneider and H. Zimmermann, Z. anorg. allgem. Chem. 481 (1981) 107.

273. R. Kumar and A. R. Manning, J. Organomet. Chem. 216 (1981) C61.

274. S. Willis and A. R. Manning, J. Chem. Soc. Dalton Trans. (1981) 322.

275. M. Ennis, R. Kumar, A. R. Manning, J. A. S. Howell, P. Mathur, A. J. Rowan and F. S. Stephens, J. Chem. Soc. Dalton Trans. (1981) 1251.

276. J. A. S. Howell and A. J. Rowan, J. Chem. Soc. Dalton Trans. (1981) 297.

277. M. H. Quick and R. J. Angelici, Inorg. Chem. 20 (1981) 1123.

278. R. Korswagen, R. Alt, D. Speth and L. M. Ziegler, Angew. Chem. Int'l. Ed. 20 (1981) 1049.

279. D. F. Marten, E. V. Dehmlow, D. J. Hanlon, M. B. Hossain and D. van der Helm, J. Am. Chem. Soc. 103 (1981) 4940.

280. P. Brun, G. M. Dawkins, M. Green, R. M. Mills, J.-Y. Salaün, F. G. A. Stone and P. Woodward, Chem. Commun. (1981) 966.

281. H. R. Allcock, P. P. Greigger, L. J. Wagner and M. Y. Bernheim, Inorg. Chem. 20 (1981) 716.

282. G. O. Nelson and M. E. Wright, J. Organomet. Chem. 206 (1981) C21.

283. H. Schäfer, Angew. Chem. Int'l. Ed. 20 (1981) 608.

284. H. Patin, G. Mignani, C. Mahe, J.-Y. LeMarouille, A. Benoit and D. Grandjean, J. Organomet. Chem. 210 (1981) C1.

285. R. E. Cobbledick, N. S. Dance, W. B. Einstein, C. H. W. Jones and T. Jones, Inorg. Chem. 20 (1981) 4356.

286. S. J. Landon and A. L. Rheingold, Inorg. Chim. Acta 47 (1981) 187.

287. H. Beurick and H. Vahrenkamp, Angew. Chem. Int'l. Ed. 20 (1981) 98.

288. W. A. Herrmann and C. Bauer, J. Organomet. Chem. 204 (1981) C21.

289. W. A. Herrmann, G. Kriechbaum, C. Bauer, E. Guggolz and M. Ziegler, Angew. Chem. Int'l. Ed. 20 (1981) 815.

290. J. S. Plotkin and S. G. Shore, Inorg. Chem. 20 (1981) 284.

291. E. K. G. Schmidt and C. H. Thiel, J. Organomet. Chem. 209 (1981) 373.

292. R. Gompper and E. Kottmaier, Tet. Lett. 22 (1981) 2865.

293. W. P. Fehlhammer, A. Mayr and G. Christian, J. Organomet. Chem. 209 (1981) 57.

294. T. Bodnar and A. Cutler, J. Organomet. Chem. 213 (1981) C31.

295. M. Brookhart, J. R. Tucker and G. R. Husk, J. Am. Chem. Soc. 103 (1981) 979.

296. T. Bodnar, G. Coman, S. La Croce, C. Lambert, K. Menard and A. Cutler, J. Am. Chem. Soc. 103 (1981) 2471.

297. F. B. McCormick and R. J. Angelici, Inorg. Chem. 20 (1981) 1111.

298. F. B. McCormick and R. J. Angelici, Inorg. Chem. 20 (1981) 1118.

299. F. B. McCormick, R. J. Angelici, R. A. Pickering, R. E. Wagner and R. A. Jacobson, Inorg. Chem. 20 (1981) 4108.

300. F. B. McCormick and R. J. Angelici, J. Organomet. Chem. 205 (1981) 79.

301. E. K. G. Schmidt and C. H. Thiel, J. Organomet. Chem. 220 (1981) 87.

302. W. Priester, M. Rosenblum and S. B. Samuels, Syn. React. Inorg. Met.-Org. Chem. 11 (1981) 525.

303. T. C. T. Chang and M. Rosenblum, J. Org. Chem. 46 (1981) 4626.

304. T. C. T. Chang, B. M. Foxman, M. Rosenblum and C. Stockman, J. Am. Chem. Soc. 103 (1981) 7361.

305. D. F. Marten, J. Org. Chem. 46 (1981) 5422.

306. D. J. Bates, M. Rosenblum and S. B. Samuels, J. Organomet. Chem. 209 (1981) C55.

307. D. J. Fettes, R. Naraganaswamy and A. J. Rest, J. Chem. Soc. Dalton Trans. (1981) 2311.

308. A. Hudson, M. F. Lappert, P. W. Lednor, J. J. MacQuitty and R. K. Nicolson, J. Chem. Soc. Dalton Trans. (1981) 2159.

309. W. N. Rogers, J. A. Page and M. C. Baird, Inorg. Chem. 20 (1981) 3521.

310. T. Yu. Orlova, V. N. Setkina and D. N. Kursanov, Inorg. Chim. Acta 51 (1981) 131.

311. S. Padmanabhan and K. M. Nicholas, J. Organomet. Chem. 212 (1981) 115.

312. M. Cooke, N. J. Forrow and S. A. R. Knox, J. Organomet. Chem. 222 (1981) C21.

313. K. A. M. Kremer, P. Helquist and R. C. Kerber, J. Am. Chem. Soc. 103 (1981) 1862.

314. C. Botha, J. R. Mass and S. Pelling, J. Organomet. Chem. 220 (1981) C21.

315. D. L. Reger and P. J. McElligott, J. Organomet. Chem. 216 (1981) C12.

316. H. Brunner and H. Vogt, Angew. Chem. Int'l. Ed. 20 (1981) 405.

317. P. Vierling, J. G. Riess and A. Grand, J. Am. Chem. Soc. 103 (1981) 2466.

318. E. Lindner, G. Funk and T. Bouachir, Chem. Ber. 114, 2563

319. D. H. Gibson, W.-L. Hsu and F. U. Ahmed, J. Organomet. Chem. 215 (1981) 379.

320. M. Rosenblum and P. Waterman, J. Organomet. Chem. 206 (1981) 197.

321. P. Bell and A. Wojcicki, Inorg. Chem. 20 (1981) 1585.

322. P. Hong, K. Sonogashira and N. Hagihara, J. Organomet. Chem. 219 (1981) 363.

323. L. V. Rybin, E. A. Petrovskaya, A. S. Batsanov, Yu. T. Struchkov and M. I. Rybinskaya, J. Organomet. Chem. 212 (1981) 95.

324. A. Wong and J. D. Atwood, J. Organomet. Chem. 210 (1981) 395.

325. J. C. Selover, M. Marsi, D. W. Parker and J. A. Gladysz, J. Organomet. Chem. 206 (1981) 317.

326. J. D. Cotton, G. T. Crisp and L. Latif, Inorg. Chim. Acta 47 (1981) 171.

327. H. Brunner and H. Vogt, J. Organomet. Chem. 210 (1981) 223.

328. J. D. Korp and I. Bernal, J. Organomet. Chem. 220 (1981) 355.

329. H. Brunner and H. Vogt, Chem. Ber. 114 (1981) 2186.

330. C. M. Lukehart and K. Srinivasan, J. Am. Chem. Soc. 103 (1981) 4166.

331. W. Malisch, H. Blau and F. J. Haaf, Chem. Ber. 114 (1981) 2956.

332. S. R. Berryhill and B. Sharenow, J. Organomet. Chem. 221 (1981) 143.

333. G. Cerveau, G. Chauviere, E. Colomer and R. J. P. Corriu, J. Organomet. Chem. 210 (1981) 343.

334. N. Aktogu, S. G. Davies, J. Dubac and P. Mazerolles, J. Organomet. Chem. 212 (1981) C13.

335. S. B. Gubin, O. M. Chentsova, G. M. Burmakina and A. A. Ioganson, Izv. Akad. Nauk SSSR (1981) 2324.

336. H. M. Colquhoun and J. F. Stoddart, Chem. Commun. (1981) 612.

337. P. M. Treichel and D. A. Komar, J. Organomet. Chem. 206 (1981) 77.

338. B. D. Fabian and J. A. Labinger, J. Organomet. Chem. 204 (1981) 387.

339. J. A. S. Howell, A. J. Rowan and M. S. Snell, J. Chem. Soc. Dalton Trans. (1981) 325.

340. P. M. Treichel and L. D. Rosenhein, Inorg. Chem. 20 (1981) 1539.

341. S. G. Davies, H. Felkin, T. Fillebeen-Khan, F. Tadj and O. Watts, Chem. Commun. (1981) 341.

342. H. Brunner and A. F. M. Mohklesur Rahman, J. Organomet. Chem. 214 (1981) 373.

343. U. Kunze and A. Antoniadas, Z. Naturforsch. 13b (1981) 1588.

344. J. Ellermann and M. Lietz, J. Organomet. Chem. 213 (1981) C4.

345. D. J. Darensbourg, C. S. Day and M. B. Fischer, Inorg. Chem. 20 (1981) 3577.

346. D. J. Darensbourg, M. B. Fischer, R. E. Schmidt, Jr. and B. J. Baldwin, J. Am. Chem. Soc. 103 (1981) 1297.

347. Yu. T. Struchkov, G. G. Aleksandrov, V. S. Kaganovich and M. I. Rybinskaya, Koord. Khim. 7 (1981) 949; CA 95, 133109a.

348. J. B. Woell and P. Boudjouk, Angew. Chem. Int'l. Ed. 20 (1981) 387.

349. D. J. Black, M. J. Boylan and P. S. Braterman, J. Chem. Soc. Dalton Trans. (1981) 673.

350. P. M. Treichel and L. D. Rosenhein, Inorg. Chem. 20 (1981) 942.

351. M. Höfler, H. Hausmann and H. A. Heidelberg, J. Organomet. Chem. 213 (1981) C1.

352. D. Miholva and A. A. Vleck, Proc. Conf. Coord. Chem. (1980), 8th 287.

353. B. M. Matteson and W. A. G. Graham, Inorg. Chem. 20 (1981) 3186.

354. E. Roman, D. Astruc and A. Darchan, J. Organomet. Chem. 219 (1981) 221.

355. J.-R. Hamon, D. Astruc and P. Michaud, J. Am. Chem. Soc. 103 (1981) 758.

356. D. Astruc, J.-R. Hamon, E. Román and P. Michaud, J. Am. Chem. Soc. 103 (1981) 7502.

357. A. N. Nesmeyanov, N. A. Vol'kenau, P. V. Petrovskii, L. S. Kotova, V. A. Petrakova and L. T. Denisovich, J. Organomet. Chem. 210 (1981) 103.

358. N. El Murr, Chem. Commun. (1981) 251.

359. C. C. Lee, U. S. Gill and R. G. Sutherland, J. Organomet. Chem. 206 (1981) 89.

360. V. V. Litvak, L. S. Filatova and V. D. Shteingarts, J. Org. Chem. USSR 17 (1981) 1138.

361. C. C. Lee, C. I. Azogu, P. C. Chang and R. G. Sutherland, J. Organomet. Chem. 220 (1981) 181.

362. L. K. Beard, Jr., M. P. Silvon and P. S. Skell, J. Organomet. Chem. 209 (1981) 245.

363. B. R. Steele, R. G. Sutherland and C. C. Lee, J. Chem. Soc. Dalton Trans. (1981) 529.

364. E. L. Anderson, R. L. De Kock and T. P. Fehlner, Inorg. Chem. 20 (1981) 3291.

365. K. J. Haller, E. L. Anderson and T. P. Fehlner, Inorg. Chem. 20 (1981) 309.

366. P. Brint, W. K. Pelin and T. R. Spalding, J. Chem. Soc. Dalton Trans. (1981) 546.

367. A. M. Barriola, Acta Cient. Venez. 32 (1981) 72; CA 96, 96552m.

368. J. Schulze, R. Boese and G. Schmid, Chem. Ber. 114 (1981) 1297.

369. T.-Y. Luh, K. S. Lee and S. W. Tam, J. Organomet. Chem. 219 (1981) 345.

370. J.-J. Brunet, C. Sidot and P. Caubere, J. Org. Chem. 46 (1981) 3147.

371. H. Alper and K. E. Hashem, J. Am. Chem. Soc. 103 (1981) 6514.

372. I. Fischler and F.-W. Grevels, J. Organomet. Chem. 204 (1981) 181.

373. L. Marko', M. A. Rahdi and I. Ötvös, J. Organomet. Chem. 218 (1981) 369.

374. E. K. G. Schmidt, J. Organomet. Chem. 204 (1981) 393.

375. J. C. Mitchener and M. S. Wrighton, J. Am. Chem. Soc. 103 (1981) 975.

376. K. J. Karel, M. Brookhart and R. Aumann, J. Am. Chem. Soc. 103 (1981) 2695.

377. D. B. Chase and F. J. Weigert, J. Am. Chem. Soc. 103 (1981) 977.

378. M. Röper, H. Strutz and W. Keim, J. Organomet. Chem. 219 (1981) C5.

379. D. Bianchi, H. Batis-Landoulsi, C. O. Bennett, G. M. Panjonk, P. Vergnon and S. J. Teichner, Bull. Soc. Chim. Fr. Pt. I (1981) 345.

380. H. Yasuda, Y. Morita, I. Noda, K. Sugi and A. Nakamura, J. Organomet. Chem. 205 (1981) C9.

381. N. J. Coville, M. O. Albers, T. V. Ashworth and E. Singleton, Chem. Commun. (1981) 408.

382. F. Porta, M. Pizzoti and S. Cenini, J. Organomet. Chem. 222 (1981) 279.

383. N. J. Coville and C. P. Nicolaides, J. Organomet. Chem. 218 (1981) 371.

384. *The Organic Chemistry of Iron*, Vol. 2, E. A. Koerner Von Gustorf, F.-W. Grevels and I. Fischler, Academic Press, New York 1981.

385. M. F. Semmelhack, Pure Appl. Chem. 53 (1981) 2379.

386. A. J. Pearson, Trans. Met. Chem. 6 (1981) 67.

387. A. J. Birch, B. M. R. Bandara, K. Chamberlain, B. Chauncey, P. Dahler, A. I. Day, I. D. Jenkins, L. F. Kelly, T.-C. Khor, G. Kretschmer, A. J. Liepa, A. S. Narula, W. D. Raverty, E. Rizzardo, C. Sell, C. R. Stephenson, D. J. Thompson and D. H. Williamson, Tetrahedron, Suppl. 1 37 (1981) 289.

388. P. D. Smith, B. R. James and D. H. Dolphin, Coord. Chem. Rev. 39 (1981) 31.

389. D. C. Bailey and S. H. Langer, Chem. Rev. 81 (1981) 109.

390. A. C. Sievert, Diss. Abstr. Int. B 41 (1981) 2606.

391. K. Maruoka, Diss. Abstr. Int. B 41 (1981) 2614.

392. M. Ross, Diss. Abstr. Int. B 41 (1981) 2618.

393. W. G. L. Aalbersberg, Diss. Abstr. Int. B 41 (1981) 3029.

394. D. A. Liebman, Diss. Abstr. Int. B 41 (1981) 3440.

395. L. M. Cirjak, Diss. Abstr. Int. B 41 (1981) 3777.

396. T. W. Leung, Diss. Abstr. Int. B 41 (1981) 3778.

397. T. A. Schmitkons, Diss. Abstr. Int. B 41 (1981) 3781.

398. T. E. Cole, Diss. Abstr. Int. B 41 (1981) 4118.

399. J. R. Fox, Diss. Abstr. Int. B 42 (1981) 199.

400. A. Wong, Diss. Abstr. Int. B 42 (1981) 205.

401. T. Jones, Diss.Abstr. Int. B 42 (1981) 215.

402. B. R. Reddy, Diss. Abstr. Int. B 42 (1981) 221.

403. S. J. Hardwick, Diss. Abstr. Int. B 42 (1981) 624.

404. D. J. Sepelak, Diss. Abstr. Int. B 42 (1981) 626.

405. J. E. Jensen, Diss. Abstr. Int. B 42 (1981) 1019.

406. G. N. Mott, Diss. Abstr. Int. B 41 (1981) 1448.

407. A. L. Steinmetz, Diss. Abstr. Int. B 41 (1981) 1450.

408. D. L. Johnson, Diss. Abstr. Int. B 41 (1981) 1456.

409. J. Wong, Diss. Abstr. Int. B 41 (1981) 1464.

410. C. E. Johnson, Diss. Abstr. Int. B 42 (1981) 1880.

411. W. A. Andrus, Diss. Abstr. Int. B 42 (1981) 1886.

412. M. A. L. El-Hinnaur, Diss. Abstr. Int. B 42 (1981) 2361.

413. M. R. Baar, Diss. Abstr. Int. B 42 (1981) 2370.