ELSEVIER

Coordination Chemistry Reviews 143 (1995)
383–406

COORDINATION
CHEMISTRY
REVIEWS

Bisalkylidyne cluster compounds of iron

Dieter Lentz

Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabeckstraße 34–36, D-14195 Berlin, Germany

Received 9 September 1994

Contents

Abstract

The syntheses, structures and reactivity of bisalkylidyne clusters of iron are described. Although there is a lack of general synthetic methods the chemistry of the bisalkylidyne clusters of iron has made great progress during the last 10 years. By reaction with alkynes, various diferraallyl cluster and ferrole cluster compounds can be synthesized and structurally characterized. Analogous reactions with phosphaalkynes yield phosphaferrole cluster compounds which themselves can act as ligands. In a cluster expansion reaction with $Cp^*Co(CO)_2$ the first difluoroethyne complex was obtained.

---

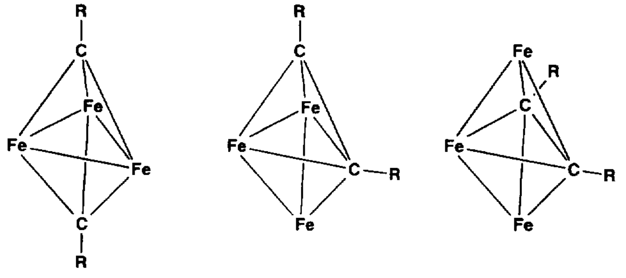
1. Introduction

In contrast to the well-established (extensively studied) chemistry of alkylidyne nonacarbonyl tricobalt cluster complexes [1] the chemistry of bisalkylidyne clusters is less explored. The first bisalkylidyne clusters were isolated using cobalt and rhodium with cyclopentadienyl and pentamethylcyclopentadienyl ligands completing

SSDI 0010-8545(94)07010-5

the coordination sphere [2]. Bisalkylidyne clusters of molybdenum were obtained among the products of the reaction of hexacarbonyl molybdenum, acetic acid and acetic anhydrid [3]. A heterometallic bisalkylidyne cluster $[(CO)_3Fe][CpCo]_2(\mu_3\text{-}C-Ph)_2$ was isolated as a byproduct and structurally characterized by X-ray diffraction [4]. In this review we describe the chemistry of bisalkylidyne cluster compounds of iron of which the first member $Fe_3(CO)_9(\mu_3\text{-}CH_3)(\mu_3\text{-}C-OCH_3)$ (**1**) has been obtained with a low yield by reaction of (μ_3-acetyl)-nonacarbonyl triferrate ($[Fe_3(CO)_9(\mu_3\text{-}CH_3CO)]$) and methyl fluorosulfate by Wilkinson and co-workers [5]. As we are interested in the rare fluoromethylidyne complexes, we realized that nonacarbonylbis(fluoromethylidyne)triiron (**2a**) could be easily synthesized, albeit with a low yield, by reaction of $Fe(CO)_5$ and $CFBr_3$ [6].

Bisalkylidyne cluster compounds belong to the series of *closo*-cluster compounds that derive from $B_5H_5^{2-}$. Of the neutral carborane $B_3C_2H_5$ there exist three possible isomers of which the one with the carbon atoms in an apical position is the most stable [7]. Isolobal replacement of BH units by a metal fragment (CpCo, CpRh, $(CO)_3Fe$, $(CO)_3Os$ etc.) according to Wade's [8] rules results in formation of bisalkylidyne or alkyne cluster compounds. Of the three possible isomers, only isomers **I** and **II** have been observed so far:

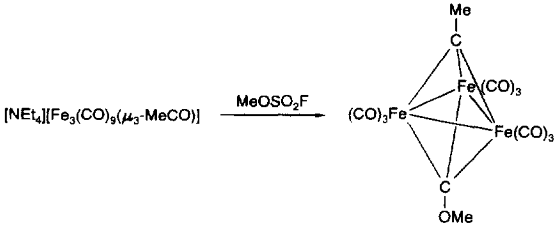


I **II** **III**

I represents a bisalkylidyne cluster whereas **II** belongs to a series of alkyne clusters of which $Fe_3(CO)_9(\mu_3\text{-}\perp\text{-}Ph-C\equiv C\text{-}Ph)$ was obtained in 1959 by Hübel et al. [9] and was structurally characterized by Dahl and co-workers [10].

2. Syntheses of nonacarbonylbis(μ_3-alkylidyne)triiron cluster compounds

Although several nonacarbonylbis(μ_3-alkylidyne)triiron cluster compounds have been synthesized since the first synthesis of $Fe_3(CO)_9(\mu_3\text{-}CH_3)(\mu_3\text{-}C-OCH_3)$ (**1**) [5], there exists no general preparative method. Clusters with the methoxy [5] or ethoxy [11] methylidyne group were prepared by alkylation or protonation [12] of suitable anionic species:



1

$$[PPh_4][Fe_3(CO)_9(\mu_3\text{-}CCH_2R)(\mu_3\text{-}CO)] \xrightarrow{[Et_3O]BF_4} [Fe_3(CO)_9(\mu_3\text{-}CCH_2R)(\mu_3\text{-}COEt)]$$

3

R = H, n-Pr, Bz, $CH_2C(O)CH_3$, $CH_2C(O)OCH_3$

Reaction of dodecacarbonyltriiron with butyllithium followed by alkylation with trimethyloxoniumtetrafluoroborate gives a moderate yield of $Fe_3(CO)_9(\mu_3\text{-}COMe)_2$ (**4**) [13]:

$$[Fe_3(CO)_{12}] \xrightarrow[2.\ [Me_3O]BF_4]{1.\ BuLi} [Fe_3(CO)_9(\mu_3\text{-}COMe)_2]$$

4

Protonation of $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CCOEt)]^-$ results in the μ_3-η^2-$\perp$-alkyne cluster **5** [12] which, however, was found to be unstable at ambient temperature:

$$[PNP]_2[Fe_3(CO)_9(\mu_3\text{-}CCO)] \xrightarrow[2.\ HSO_3F]{1.\ EtOSO_2CF_3} [Fe_3(CO)_9(\mu_3\text{-}HCCOEt)]$$

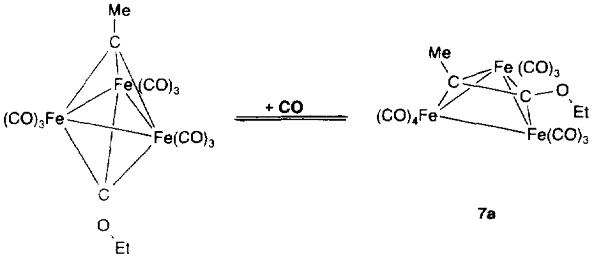
5

Under very mild conditions an alkyne scission reaction occurs, yielding the bisalkylidyne cluster $Fe_3(CO)_9(\mu_3\text{-}CH)(\mu_3\text{-}COEt)$ (**6**):

$$5 \longrightarrow [Fe_3(CO)_9(\mu_3\text{-}CH)(\mu_3\text{-}COEt)]$$

6

As found earlier by Mathieu and co-workers [11], the very similar bisalkylidyne cluster $Fe_3(CO)_9(\mu_3\text{-}COEt)(\mu_3\text{-}CMe)$ (**3a**) reacts with carbon monoxide, at ambient temperature and 20 atm, leading quantitatively to $Fe_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}H_3C{-}C{\equiv}C{-}OEt)$ (**7a**) [14]:



7a

3a

This nido-alkyne cluster reacts back to the bis(alkylidyne) starting material **3a** in solution at room temperature, or more slowly, even in the solid state. By replacing one carbonyl ligand by a triphenylphosphine ligand, crystals of **7b** suitable for an X-ray structure determination could be obtained (Fig. 1).

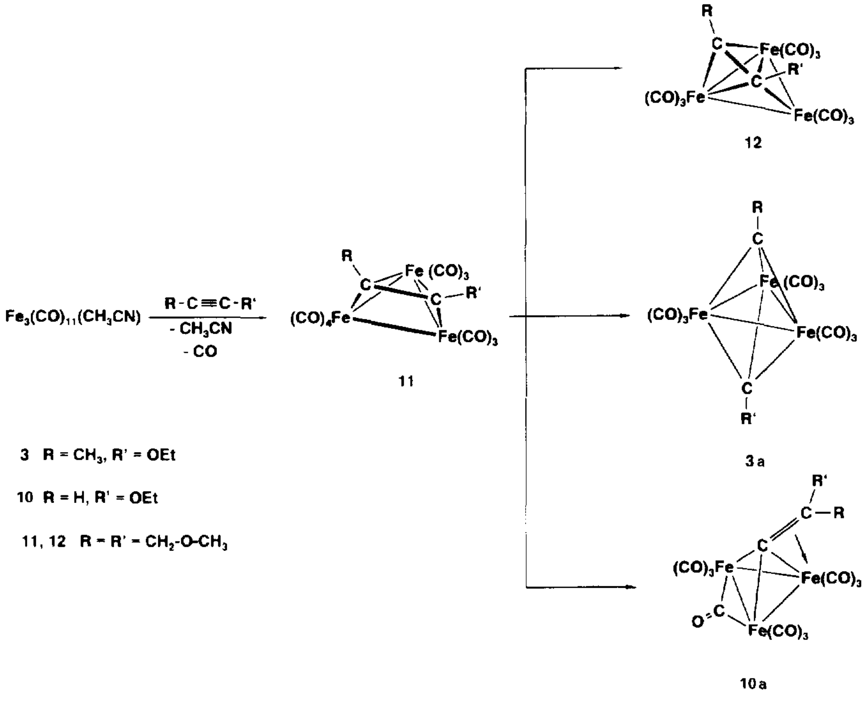
Interestingly the alkyne moiety is oriented not exactly parallel to one Fe—Fe edge and the tenth carbonyl ligand occupies a semibridging position. Although the formation of $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}C{-}NEt_2)$ (**8**) from $Fe_2(CO)_9$ and $H_3C{-}C{\equiv}C\text{-}NEt_2$ is not straightforward and the yield is low [15], it obviously requires an alkyne scission:

$$Fe_2(CO)_9 \xrightarrow{Me\text{-}C\equiv C\text{-}NEt_2} [Fe_3(CO)_9(\mu\text{-}CMe)(\mu\text{-}CNEt_2)]$$

8

Reaction of $HFe_3(CO)_{10}(\mu_3\text{-}CMe)$ with 3,3-dimethyl-1-butyne gives two cluster compounds: the alkyne cluster $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}Me{-}C{\equiv}C{-}CH_2{-}{}^tBu)$ (**9a**) and the bisalkylidyne cluster $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}C{-}CH_2{-}{}^tBu)$ (**9b**) [16]. It has been shown that the cluster compounds **9a** and **9b** cannot be interconverted under the reaction conditions used for their synthesis.

In order to understand the substitution effects on alkyne scission reaction on triangular iron clusters we have studied the reaction of the recently described $Fe_3(CO)_{11}(MeCN)$ [17] with various alkynes [18]:



As expected, $H_3C{-}C{\equiv}C{-}OEt$ yields the bisalkylidyne cluster $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}C{-}OEt)$ (**3**) [18] already obtained by other methods [11]. However,

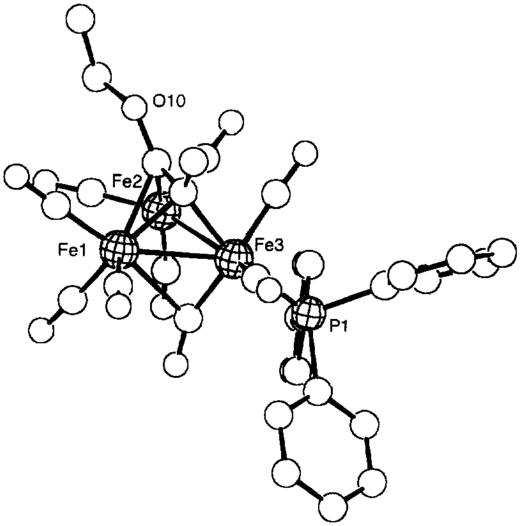


Fig. 1. Molecular structure of $Fe_3(CO)_9(PPh_3)(\mu_3\text{-}\eta^2\text{-}\|\text{-}H_3C{-}C{\equiv}C{-}OEt)$ (**7b**).

replacing the methyl group by a hydrogen substituent results in completely different products. At ambient temperature and with a short reaction time the vinylidene cluster $Fe_3(CO)_{10}[\mu_3\text{-}\eta^2\text{-}C{=}C(H)OEt]$ (**10a**) is obtained by a 1,2 proton shift, whereas keeping the reaction mixture at −30°C for 5 days results in the dinuclear fly-over complex $Fe_2(CO)_6[\mu\text{-}EtO{-}C{=}CH{-}CO{-}CH{=}C{-}OEt]$ (**10b**).

If the ether functions are separated from the alkyne carbon atom by methylene groups or substituted methylene groups, alkyne clusters and dinuclear butatriene compounds are obtained depending on the substituents and the reaction conditions. The products from 1,4-dimethoxybutyne are $Fe_3(CO)_9(\mu_2\text{-}CO)(\mu_3\text{-}\eta^2\text{-}\|\text{-}MeO{-}CH_2{-}C{\equiv}C{-}CH_2{-}OMe)$ (**11**) and $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}MeO{-}CH_2{-}C{\equiv}C{-}CH_2{-}OMe)$ (**12**) respectively. Interestingly, $Fe_3(CO)_9(\mu_2\text{-}CO)(\mu_3\text{-}\eta^2\text{-}\|\text{-}MeO{-}CH_2{-}C{\equiv}C{-}CH_2{-}OMe)$ (**11**) is the only example of an alkyne cluster of iron with ten carbonyl ligands and a parallel orientation of the alkyne ligand which has enough stability to be structurally fully characterized (Fig. 2).

According to the crystal structure determination the molecule has a crystallographic mirror plane and an exact parallel orientation of the alkyne triple bond to one iron iron edge which in addition is bridged by the tenth carbonyl ligand. Thus its structure differs from that of $Fe_3(CO)_9(PPh_3)(\mu_3\text{-}\eta^2\text{-}H_3C{-}C{\equiv}C{-}OEt)$ (**7b**) [14] which has only a semibridging carbonyl ligand and exhibits a strong deviation of the alkyne moiety from the parallel orientation. $Ru_3(CO)_{10}(Me{-}C{\equiv}C{-}Me)$ [19] and $Os_3(CO)_{10}(Et{-}C{\equiv}C{-}Et)$ [20] have structures almost identical with that of **11** with the carbonyl bridge being only slightly asymmetric whereas $Os_3(CO)_9(PPh_3)(Et{-}C{\equiv}C{-}Et)$ [20], $Os_3(CO)_9[P(OMe)_3](Et{-}C{\equiv}C{-}Et)$ [21] and $Os_3(CO)_{10}(Ph{-}C{\equiv}C{-}Ph)$ [22] have similar structures to **7b**.

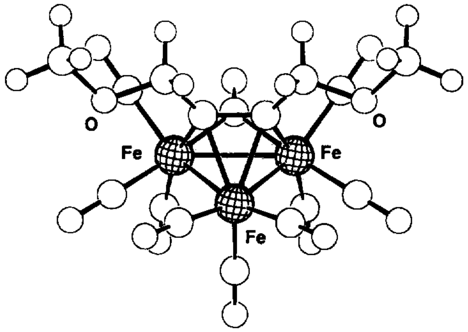


Fig. 2. Molecular structure of $Fe_3(CO)_9(\mu_2\text{-}CO)(\mu_3\text{-}\eta^2\text{-}\|\text{-}MeO{-}CH_2{-}C{\equiv}C{-}CH_2{-}OMe)$ (**11**).

$Fe_3(CO)_9(\mu_2\text{-}CO)(\mu_3\text{-}\eta^2\text{-}\|\text{-}MeO{-}CH_2{-}C{\equiv}C{-}CH_2{-}OMe)$ (**11**) is non-rigid on the nuclear magnetic resonance (NMR) time scale, exhibiting a simple line for the diastereotropic methylene protons at ambient temperature. An activation barrier $\Delta G^{\#}(253\ K) = 54.2 \pm 2\ kJ\ mol^{-1}$ has been determined by line shape analysis comparable with the value of $60.4 \pm 2\ kJ\ mol^{-1}$ for $Os_3(CO)_{10}(Et{-}C{\equiv}C{-}Et)$ [20].

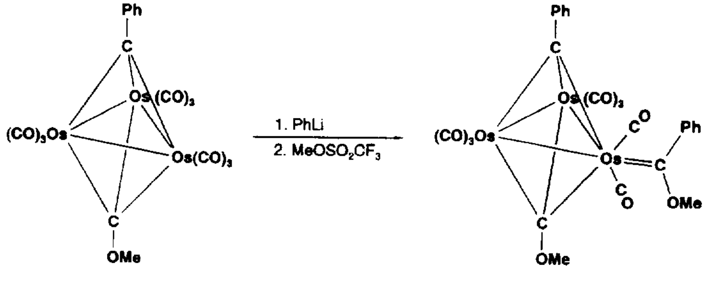
$Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\|\text{-}MeO{-}CH_2{-}C{\equiv}C{-}CH_2{-}OMe)$ (**11**) slowly decomposes in solution at ambient temperature forming $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}MeO{-}CH_2{-}C{\equiv}C{-}CH_2{-}OMe)$ (**12**), which is decomposed further to $Fe_2(CO)_6(CH_2{=}C{=}C{=}CH_2)$ (**13a**) in refluxing hexane. No bisalkylidyne cluster could be observed from an alkyne cleavage reaction.

From our results [18] and other results [14–16], one can conclude that the alkyne scission reaction on trinuclear iron carbonyl clusters requires alkynes with at least one ether or amine substituent directly bonded to the alkyne carbon atom. In addition a terminal hydrogen atom may result in a 1,2-proton shift if a $Fe_3(CO)_{10}$(alkyne) intermediate is formed whereas $Fe_3(CO)_9(H{-}C{\equiv}C{-}OEt)$ (**5**) rearranges to the bisalkylidyne cluster $Fe_3(CO)_9(\mu_3\text{-}CH)(\mu_3\text{-}C{-}OEt)$ (**6**) [12].

No bisalkylidyne cluster compound of ruthenium is known so far and only a few examples, $Os_3(CO)_9(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ (**14**) [23], $Os_3(CO)_8(PPh_3)(\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ (**15**) [23] and $Os_3(CO)_8[\eta^1\text{-}C(OMe)Ph](\mu_3\text{-}CPh)(\mu_3\text{-}COMe)$ (**16**) [24] have been characterized for osmium:

$$(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}COMe) \xrightarrow[2.\ MeOSO_2CF_3]{1.\ PhLi} \underset{\mathbf{14}}{Os_3(CO)_9(\mu\text{-}CPh)(\mu\text{-}COMe)} + (\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}CPh)$$

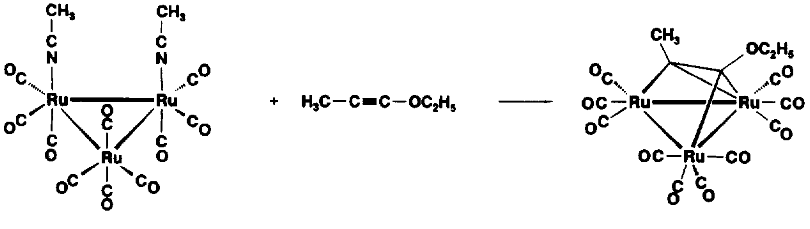
$$\mathbf{14} \xrightarrow{PPh_3} \underset{\mathbf{15}}{Os_3(CO)_8(PPh_3)(\mu\text{-}CPh)(\mu\text{-}COMe)}$$



16

Hydrogenation of **14** at 1 atm results in alkylidyne–alkylidyne coupling, forming the alkyne cluster complex (μ-H)$_2$Os$_3$(CO)$_9$(μ_3-η^2-Ph—C≡C—OMe) (**17**) [25]. Reduction of **14** followed by protonation yields the phenylacetylide complex (μ-H)Os$_3$(CO)$_9$(μ_3-η^2-C≡CPh) (**18**) [25].

The obvious reaction of Ru(CO)$_{11}$(MeCN) or Ru$_3$(CO)$_{10}$(MeCN)$_2$ with Me—C≡C—OEt gives a complicated mixture of products of which Ru$_3$(CO)$_{10}$(Me—C≡C—OEt) (**20**) could be isolated by thin layer chromatography [26]:



20

Its thermolysis in boiling heptane yields the cluster compound **21** by proton shift which had been characterized by an X-ray crystal structure determination (Fig. 3):

21

No bisalkylidyne clusters could be obtained in the reaction Ru$_3$(CO)$_{10}$(MeCN)$_2$ with various alkynes HC≡CR (R≡H, COOH or CHO) and R—C≡C—R (R≡Et, CH$_2$OH or Ph) [27].

A very successful approach to bisalkylidyne clusters of iron follows a completely

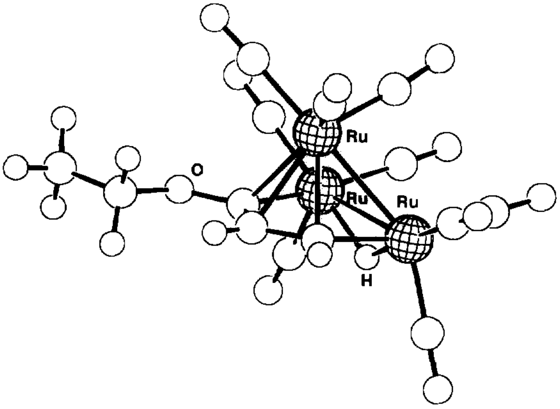
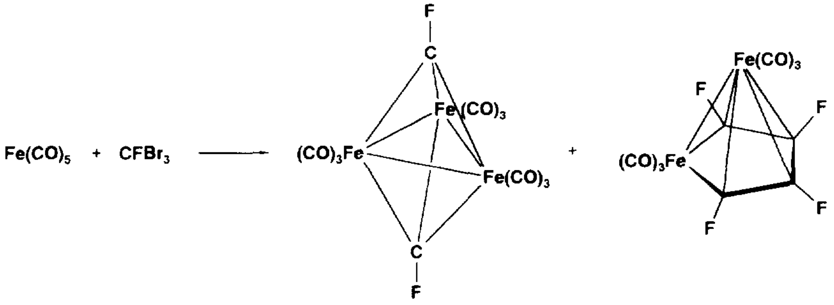


Fig. 3. Molecular structure of **21**.

different strategy. Reaction of pentacarbonyliron or eneacarbonyldiiron with tribromofluoromethane yields $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ (**2a**) and traces of the interesting dinuclear perfluorinated ferrole cluster $Fe(CO)_6(Fe{-}CF{=}CF{-}CF{=}CF)$ (**22**) [28]:



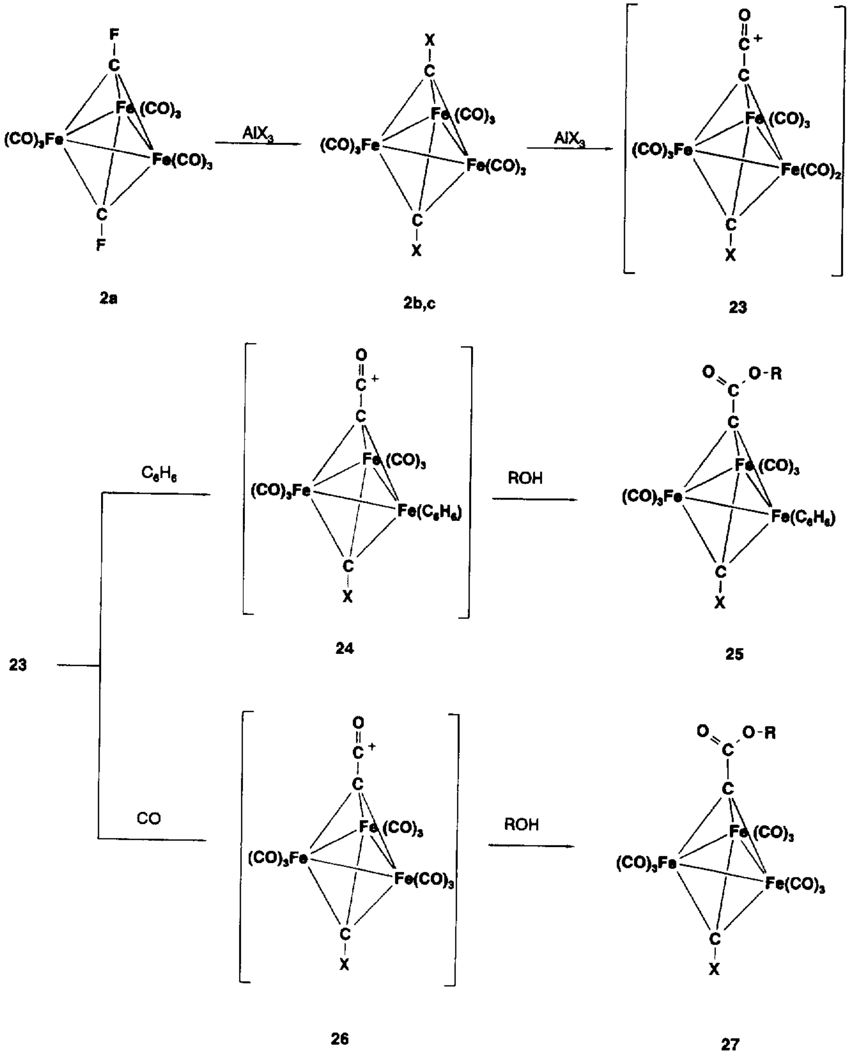
2a **22**

Although the yield of this reaction could not be increased above about 1 g of the cluster compound from 0.5 mol of $Fe(CO)_5$, $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ is a versatile starting material as the CF moieties can act as a functional group.

As demonstrated in the early work of Reger and Dukes [29] and Richmond and Shriver [30], metal-coordinated trifluoromethyl (perfluoroalkyl) groups can be attacked by electrophiles (Lewis acids) at the α position. Fluorinated Lewis acids, such as SbF_5, yield cationic difluorocarbene complexes [31]. If boron halides are used, a halogene–fluorine exchange reaction takes place at the fluorine substituents in α position whereas the β fluorine atoms of a pentafluoroethyl group are not attacked at all.

The reaction products of $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ (**2a**) strongly depend on the Lewis acid used. Aluminium trichloride or boron tribromide results in a simple halogen exchange reaction in dichloromethane at ambient temperature giving good yields of the cluster compounds $Fe_3(CO)_9(\mu_3\text{-}CCl)_2$ (**2b**) [32] and $Fe_3(CO)_9(\mu_3\text{-}CBr)_2$ (**2c**) [33] which can be used for further reactions.

However, if the reaction temperature is raised to refluxing benzene or if aluminium bromide is used as a Lewis acid, different reactions occur, resulting in brown precipitates which are insoluble in non-polar solvents. These precipitates react readily with alcohols, yielding the bisalkylidyne cluster compounds $Fe_3(CO)_6(\eta^6\text{-}C_6H_6)(\mu_3\text{-}CX)(\mu_3\text{-}C{-}COOR)$ (**25**) ($X \equiv Cl$ or Br; $R \equiv CH_3$ or C_2H_5), whose formation can easily be explained by the following mechanism:



Obviously the reaction does not stop after the halogen exchange, but the halogen substituent is attacked again by the electrophile. This results at least in a strong polarization of the C—X bond or even in the formation of a cationic species. Migration of a carbonyl ligand to the electrophilic apical carbon atom results in an intermediate cationic ketenylidyne cluster compound **23** with a vacant site in the coordination sphere of one of the iron atoms. This vacant site can be occupied by the solvent molecule benzene, resulting in an elimination of 2 mol of carbon monoxide, forming the cationic ketenylidyne cluster **24**. However, the electrophilicity of **24** is too low for an electrophilic attack of the benzene ring but the esters **25** are formed via reaction with alcohols.

The proposed mechanism is supported by reaction of **2a** with $AlBr_3$ in dichloromethane under an atmosphere of carbon monoxide which results in the cluster **27** after reaction with alcohols. Apart from a shift of the absorptions to higher wavenumbers, which is due to the positive charge the IR spectrum of the intermediate compound **26** (2160 (w), 2139 (s), 2094 (vs), 2053 (s) cm^{-1}) closely resembles that of $[Os_3(CO)_9(\mu_3\text{-}CCO)]^{2-}$ [34]. Compound **26** can be trapped with a variety of nucleophiles such as alcohols, secondary amines or reactive aromatic compounds such as pyrrole.

Further evidence for the above mechanism comes from the fact that $[Co_3(CO)_9(\mu_3\text{-}CCO)]^+$ isolated by Seyferth et al. [35] yields similar alkylidyne cluster compounds upon reaction with nucleophiles [36]. In addition reactions of μ_3-bromomethylidyne clusters of ruthenium [37] and osmium [38] with aluminium trichloride have been reported.

The bisalkylidyne clusters **2a**, **2b**, **2c**, **25** and **27** possess functional groups, which allow further modifications. Thus the reaction of **2c** (X≡Br) with tributyl stannane yields the parent compound $Fe_3(CO)_9(\mu_3\text{-}CH)_2$ (**2d**) and **27a** (X≡Br) is converted into $Fe_3(CO)_9(\mu_3\text{-}C{-}COOMe)(\mu_3\text{-}CH)$ (**28**) which has been characterized by a crystal structure determination [33]. In principle it should be possible by the correct choice of the nucleophile to prepare a whole range of bisalkylidyne cluster compounds.

Occasionally, an unexpected byproduct $Fe_3(CO)_{10}(\mu_3\text{-}\eta^1\text{-}C)(\eta^1\text{-}O){-}HC{-}CHO)$ (**29**) is formed in the reaction of $Fe_3(CO)_9(\mu_3\text{-}CBr)_2$ with Br_3SnH [39] (Fig. 4). The crystal structure determination revealed the presence of the unusual bridging HC—C(H)O ligand which is coordinated to two iron atoms by the carbon atom and to the remaining iron atom by the oxygen atom.

3. Ligand substitution reactions at bisalkylidyne triiron cluster compounds

Ligand substitution reactions have been studied only with the $Fe_3(CO)_9(\mu_3\text{-}CF)$ system. A selective exchange of a single carbonyl ligand can be achieved by photolysis in the presence of acetonitrile or benzonitrile. The crystalline isolable compounds $Fe_3(CO)_8(RCN)(\mu_3\text{-}CF)_2$ R≡CH_3 (**30a**) or C_6H_5 (**30b**) are reactive enough for a facile substitution of the labile nitrile ligand by a phosphine ligand to yield

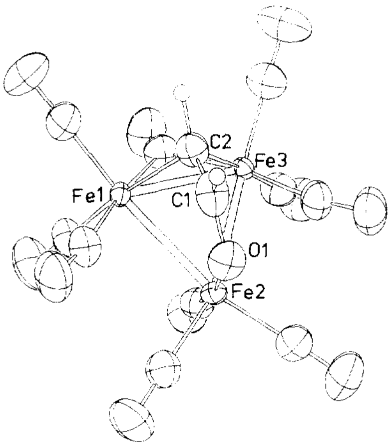


Fig. 4. Molecular structure of $Fe_3(CO)_{10}(\mu_3\text{-}\eta^1\text{-}C)[\eta^1\text{-}O)-HC-CHO]$ (**29**).

$Fe_3(CO)_8(PR_3)(\mu_3\text{-}CF)_2$ ($R \equiv CH_3$ (**31a**) or C_6H_5 (**31b**)) together with small amounts of the disubstitution products [40]:

$$\underset{\mathbf{2a}}{Fe_3(CO)_9(\mu_3\text{-}CF)_2} \xrightarrow[RCN]{h\nu} \underset{\mathbf{30}}{Fe_3(CO)_8(RCN)(\mu_3\text{-}CF)_2}$$

$$\mathbf{30a} + PR_3 \longrightarrow \underset{\mathbf{31}}{Fe_3(CO)_8[PR_3](\mu_3\text{-}CF)_2}$$

$$R = CH_3,\ C_6H_5 \qquad + \ Fe_3(CO)_7(PR_3)_2(\mu_3\text{-}CF)_2$$

The thermal or photochemical ligand exchange with triphenylphosphine and trimethylphosphite results in a mixture of monosubstituted, disubstituted and trisubstituted products.

For monosubstituted products there exist two principal isomers which differ in the position of the phosphine ligand. According to the crystal structure determination the phosphine ligand in **31a** is outside the plane of the iron triangle (Fig. 5).

The ^{19}F NMR spectra of **31** exhibit a single resonance which is split into a doublet because of coupling with one ^{31}P nuclei. The ^{13}C NMR spectra consists of two signals for the carbonyl carbon atoms in an intensity ratio of 6:2, indicating a rapid positional exchange of the ligands on the iron atoms but no exchange between different iron atoms. The assumption of a fixed position of the phosphine ligands in the plane of the iron atoms seems unlikely because of the solid state structure of $Fe_3(CO)_8[P(CH_3)_3](\mu_3\text{-}CF)_2$ (**31a**); furthermore this model requires a rigid $Fe(CO)_2L$ and a non-rigid $Fe(CO)_3$ moiety.

According to spectroscopic data the disubstituted clusters have different structures depending on the phosphine ligands. The trimethylphosphine derivative $Fe_3(CO)_7[PMe_3]_2(\mu_3\text{-}CF)_2$ (**32a**) is observed as the 1,1 isomer, whereas the more

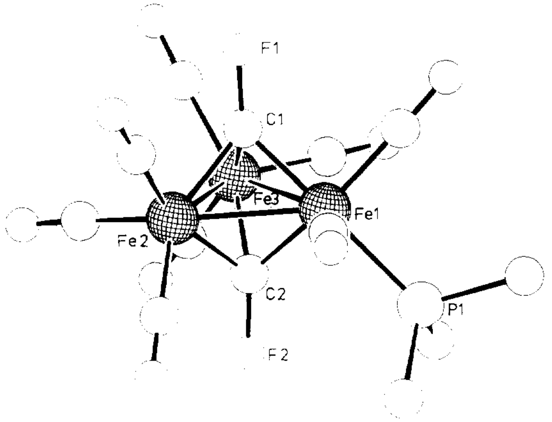


Fig. 5. Molecular structure of $Fe_3(CO)_8[P(CH_3)_3](\mu_3\text{-}CF)_2$ (**31a**).

bulky triphenylphosphine ligand in $Fe_3(CO)_7[PPh_3]_2(\mu_3\text{-}CF)_2$ (**32b**) stabilizes the 1,2 isomer.

4. The structure of bisalkylidyne triiron cluster compounds

The structure of several bisalkylidyne iron clusters with very different substituents at the methylidyne carbon atoms and various ligands was determined by X-ray crystallography. The molecular structures of some typical examples are depicted in Fig. 6.

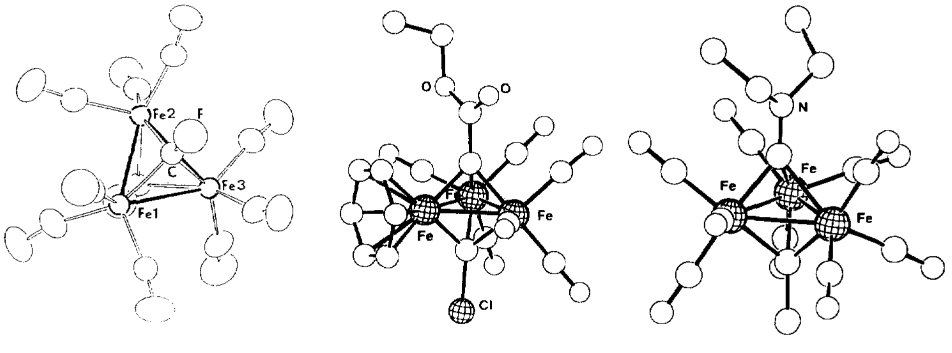


Fig. 6. Molecular structures of $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ [6], $Fe_3(CO)_9(\mu_3\text{-}CMe)[\mu_3\text{-}CNEt_2]$ [15] and $Fe_3(CO)_6(\eta_6\text{-}C_6H_6)(\mu_3\text{-}C-Cl)(\mu_3\text{-}C-COOEt)$ [32].

The iron–carbon distances range from 184.3 to 221.5 pm depending on the substituent (Table 1). In general, two similar and one different Fe—C distance are observed for each alkylidyne group; thus the alkylidyne ligands are bonded more or less asymmetrically to the iron triangles. This asymmetry is most distinct for $Fe_3(CO)_9(\mu_3\text{-CMe})[\mu_3\text{-C—NEt}_2]$ [15].

5. The electronic structure of $Fe_3(CO)_9(\mu_3\text{-CF})_2$ and electrochemical results

The electronic structures of the four symmetrical bisalkylidyne clusters $Fe_3(CO)_9(\mu_3\text{-CX})_2$ (X ≡ F (**2a**), Cl (**2b**) Br (**2c**) or H (**2d**)) have been investigated by means of He I–He II gas-phase UV photoelectron spectroscopy [41]. A detailed assignment of these spectra has been achieved by making use of DV-Xα calculations of $Fe_3(CO)_9(\mu_3\text{-CF})_2$ [42]. The highest occupied molecular orbital (HOMO) e'' is antibonding with respect to the metal–metal bonds.

The cluster compounds $Fe_3(CO)_9(\mu_3\text{-CR})_2$ (R ≡ F (**2a**), Cl (**2b**), Br (**2c**) or H (**2d**)) are electrochemically active and can be reduced and oxidized in single electron processes [43]. The data are summarized in Table 2. Only $Fe_3(CO)_9(\mu\text{-CF})_2$ shows a second irreversible reduction ($E_{1/2} = -2.0$ V) in addition to the oxidation ($E_{1/2} = 1.58$ V (SCE) with respect to a saturated calomel electrode and the reversible reduction ($E_{1/2} = -0.88$ V) within the range of solvent stability.

The closo-alkyne clusters $Fe_3(CO)_9(\mu_3\text{-R—C≡C—R})$ (R ≡ Me, Et, or Ph) showing reversible single electron reduction processes at −0.36 to −0.49 V and −0.60 to −0.67 V (SCE) are much easier to reduce [44]. Thus both the monoanion and the dianion are rather stable compounds, it was possible to synthesize the dianion by electrolysis and to characterize it by NMR spectroscopy.

Table 1
Selected metal carbon distances for bisalkylidyne iron cluster compounds

$Fe(CO)_9(\mu_3\text{-CR}^1)(\mu_3\text{-CR}^2)$	Fe–CR^1 (pm)	Fe–CR^2 (pm)
$R^1 \equiv R^2 \equiv F$ [6]	189.4(4), 190.5(4), 194.9(3)	189.4(4), 190.5(4), 194.9(3)
$R^1 \equiv H$; $R^2 \equiv COOMe$ [33]	192.6(5), 190.7(5), 192.5(5)	195.3(5), 194.5(5), 194.3(5)
$R^1 \equiv CH_3$; $R^2 \equiv COMe$ [5]	197.9(7), 196.2(7), 193.6(7)	192.0(8), 193.7(7), 191.9(7)
$R^1 \equiv R^2 \equiv OMe$ [13]	193.3(2), 189.8(2), 205.7(2)	189.8(2), 203.4(3), 189.2(3)
$R^1 \equiv Me$; $R^2 \equiv C\text{-NEt}_2$ [15]	185.3(4), 199.9(3), 199.3(3)	221.5(4), 193.1(3), 193.1(3)
$Fe_3(CO)_8(PMe_3)(\text{-CR}^1)(\mu_3\text{-CR}^2)$; $R^1 \equiv R^2 \equiv F$ [40]	189.5(8), 189.4(7), 190.2(8)	189.4(7), 193.3(7), 192.5(7)
$Fe_3(CO)_6(\eta^6\text{-C}_6H_6)(\mu_3\text{-CR}^1)(\mu_3\text{-CR}^2)$; $R^1 \equiv Cl$; $R^2 \equiv COOEt$ [32]	195.4(5), 193.6(5), 184.3(6)	195.6(5), 194.6(5), 187.9(5)

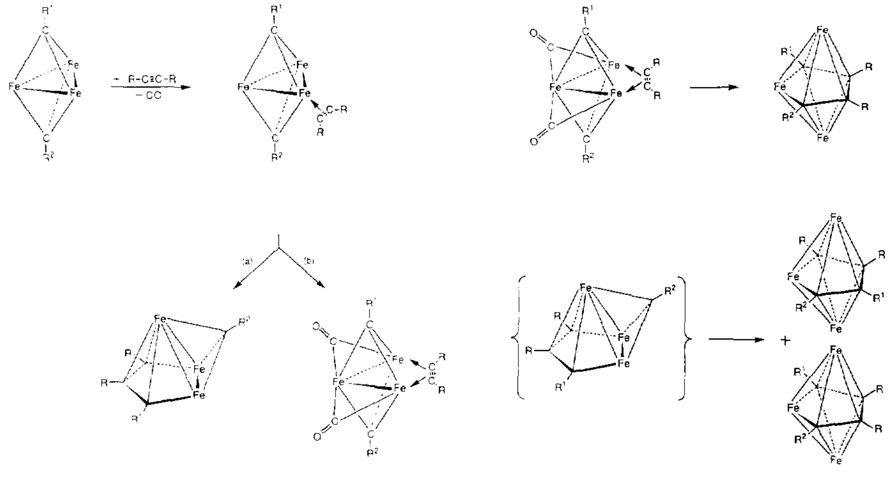
Table 2
Electrochemical data for bisalkylidyne iron cluster compounds

$Fe(CO)_9(\mu_3\text{-}CR)_2$	$E_{1/2}$ (0/+1) (eV (SCE))	$E_{1/2}$ (0/−1) (eV (SCE))	$E_{1/2}$ (−1/−2) (eV (SCE))
R≡H (**2d**)	1.59	−0.86	
R≡F (**2a**)	1.58	−0.88	−2.0
R≡Cl (**2b**)	1.68	−0.72	
R≡Br (**2c**)	1.72	−0.72	

6. Reactions of bisalkylidyne iron clusters

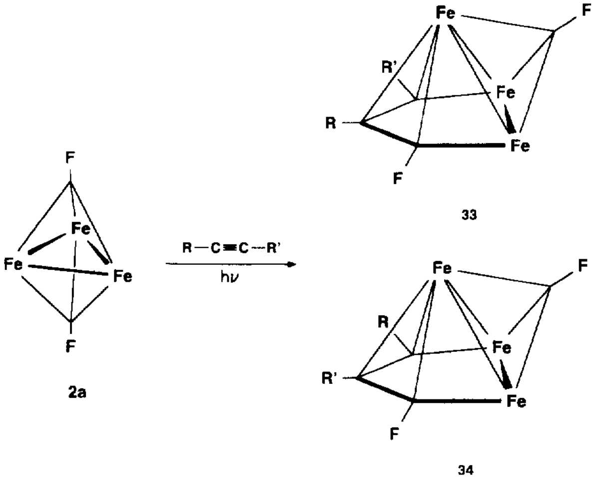
6.1. Reactions with alkynes

The formation of alkylidyne ligands and their carbon–carbon bond formation reactions are important steps in catalytic processes such as the Fischer–Tropsch process [45]. Thus the study of reactions of bisalkylidyne clusters with unsaturated organic molecules are important. Mathieu and co-workers reported the formation of trinuclear ferrol clusters in the thermal reaction of $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COEt)$ (**3**) with alkynes [11]. In addition, dinuclear ferroles were described as yellow products. The presence of several isomers has been explained by a complicated mechanism outlined as follows, which postulated the formation of intermediate diferraallyl clusters:



However, in the photolytic reaction of $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ (**2a**) with various alkynes we obtained diferraallyl clusters in a very regioselective reaction [46,47].

No ferrole-type clusters were observed among the products. Within the limits of the NMR sensitivity the hydrogen-substituted alkynes yield only one of the two possible isomers, whereas the methyl-substituted alkynes yield both isomers in a ratio depending on the size and electronic effects of the substituent R:



2a **33** **34**

	a	b	c	d	e	f
R	CH_3	C_6H_5	OC_2H_5	$Si(CH_3)_3$	CF_3	SF_5
R'	H	H	H	H	H	H

	g	h	i	k	l
R	C_2H_5	$i\text{-}C_3H_7$	OC_2H_5	C_6H_5	$COOCH_3$
R'	CH_3	CH_3	CH_3	CH_3	CH_3

	m	n	o	p	q
R	H	CH_3	CH_2Cl	C_6H_5	$COOC_2H_5$
R'	H	CH_3	CH_2Cl	C_6H_5	$COOC_2H_5$

According to the NMR spectroscopy data and a crystal structure determination for $Fe_3(CO)_8(\mu_3\text{-}CF{-}CH{-}COEt)$ (**34c**) (Fig. 7), carbon–carbon bond formation has occurred at the sterically less hindered site at the CH carbon atom.

The diferraallyl clusters **33** and **34** are capped *nido* clusters according to Wade's [8] rules, whereas the trinuclear ferroles are *closo* clusters. Thus it seems possible that the *nido* clusters might rearrange, forming the corresponding *closo* cluster compounds. On the assumption of no further bond cleavage of a once formed C(3) fragment, exactly two structural isomeric ferroles are expected.

Thermolysis of the diferraalkyl clusters **34a**, **34i**, **34m** and **34n** in hexane yields the

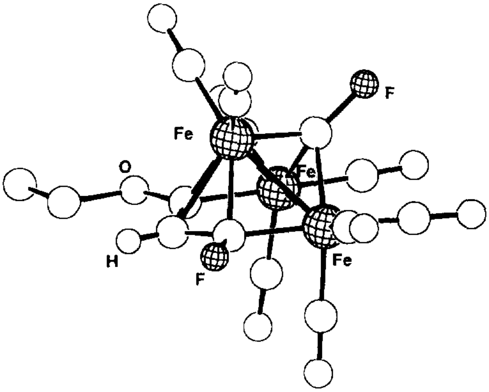
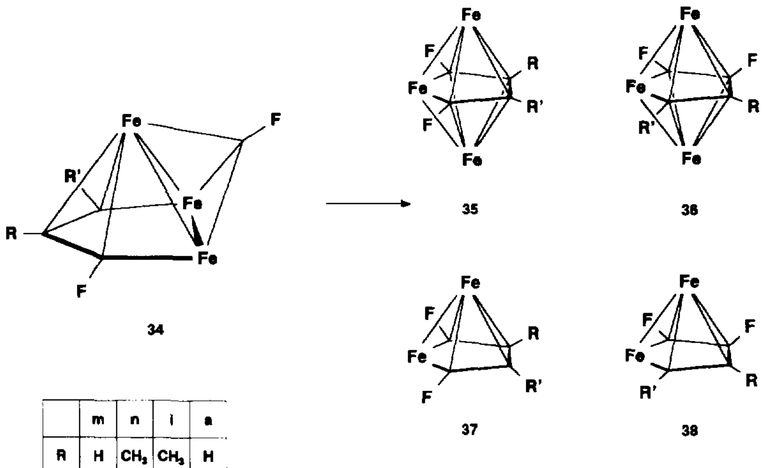


Fig. 7. Molecular structure of $Fe_3(CO)_8(\mu_3\text{-}CF)(\mu_3\text{-}CF)(\mu_3\text{-}CF{-}CH{-}COEt)$ (**34c**).

isomeric trinuclear ferroles **35** and **36** [48] and, in addition, the corresponding dinuclear species **37** and **38** are obtained:



34

35

36

37

38

	m	n	l	a
R	H	CH_3	CH_3	H
R'	H	CH_3	C_6H_5	CH_3

The structures of the two isomeric clusters **35m** and **36m** were elucidated by X-ray crystallography (Fig. 8). In all these compounds the isomer formed by carbon–carbon bond formation at the non-fluorinated carbon atom prevails; this is in agreement with the fact that the iron–carbon bond to the fluorinated carbon atom is shorter (stronger) than that to the non-fluorinated carbon atom. On thermolysis of compound **33a** ($R \equiv H$; $R' \equiv Me$) a single isomer **35a** is formed.

Thermolysis of pure **35** or **36** does not result in any isomerization only to some decomposition due to cluster fragmentation, yielding the corresponding dinuclear species **37** and **38** respectively. Because of the high regioselectivity of the reaction of $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ (**2a**) with alkynes and the thermal rearrangement of the

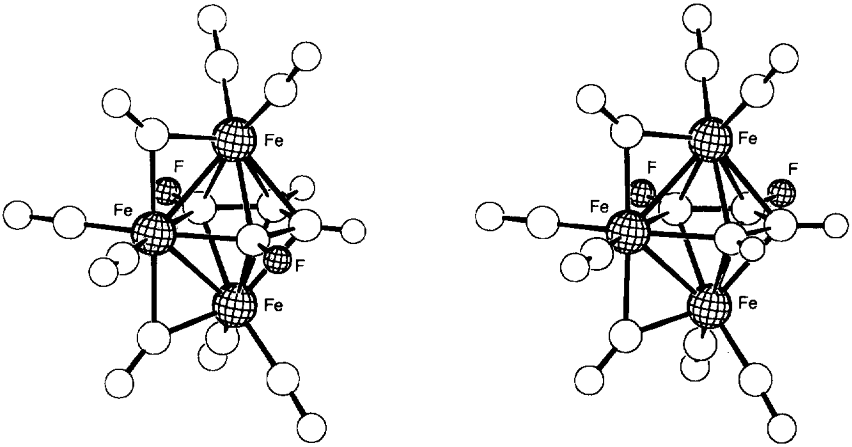


Fig. 8. Molecular structures of **35m** and **36m**.

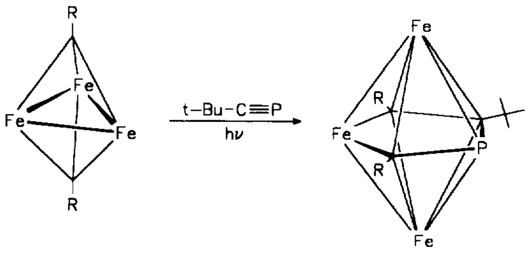
resulting diferraallyl clusters into ferrole clusters, this reaction sequence is an excellent method for the systematic building of fluorinated ferrole cluster frameworks with substituents in well-defined positions. Interestingly, this is the only rational synthesis of fluorinated ferroles as the perfluorinated ferrole $Fe(CO)_6(Fe-CF=CF-CF=CF)$ is only a minor by product [28] and the only further example proved to be erroneous [49].

Diferraallyl clusters **39a** and **39b** are the sole products of the reaction of $Fe_3(CO)_9(\mu_3\text{-}CCl)_2$ with ethyne or phenylethyne whereas $Fe_3(CO)_9(\mu_3\text{-}CH)_2$ reacts with phenylethyne, directly yielding a trinuclear ferrole cluster **40** [50]. Reaction of the phosphine-substituted bisfluoromethylidyne cluster **31a** with ethyne results in several products of which the major product, a diferraallyl cluster $Fe_3(CO)_7(PMe_3)(\mu_3\text{-}CF-CH-CH)(\mu_3\text{-}CF)$ (**41**) could be isolated by chromatography [40] and the structure of one isomer was elucidated crystallographically.

6.2. Reactions with phosphaalkynes

According to photoelectron spectroscopy data for phosphaalkynes ($R-C\equiv P$) the HOMO is a π orbital and the energy difference between the π orbital and the n orbital is larger than in nitriles [51]. Thus the similarities between the phosphaalkynes and alkynes are greater than between the phosphaalkynes and nitriles in both reactivity and ligand properties [52]. The form of coordination for the phosphaalkynes is side-on with end-on coordination being the exception [52]. In addition, many dimerization, codimerization, cotrimerization and coupling reactions were studied [52].

The bisalkylidyne clusters $Fe_3(CO)_9(\mu_3\text{-}CR)_2$ ($R\equiv F$, Cl, Br or H) react with the phosphaalkyne $^tBu-C\equiv P$ yielding a single coupling product, namely the phosphaferrole cluster compounds **42**:

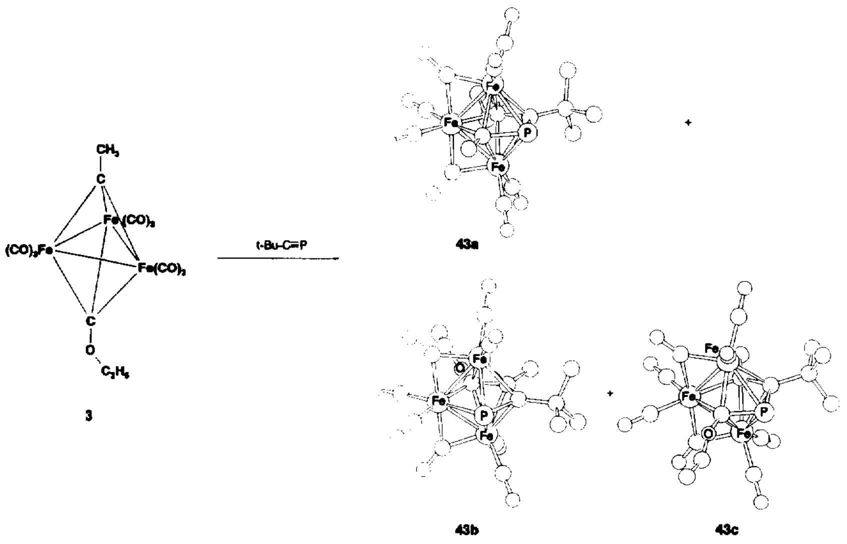


2a-d **42**

R = F, Cl, Br, H

Surprisingly only one isomer is formed and there is no hint of any isolable diferraphosphaallyl intermediate [53,54]. The structures of all compounds **42** (Fig. 9) were determined by X-ray crystallography showing no significant substitution effects [53,54].

The reaction of the asymmetrical substituted bisalkylidyne cluster $Fe_3(CO)_9(\mu_3\text{-}COEt)(\mu_3\text{-}CMe)$ **3** with ^{t}-Bu—C≡P yields three isomeric phosphaferrole clusters **43a**–**43c** which were unambiguously characterized by X-ray crystallography:



The isomers differ in the position of the phosphorus atom in the phosphaferrole ring and the positions of the substituents [54].

According to Wade's rules, all these phosphaferrole clusters are *closo* clusters as long as the phosphorus atom has a non-bonding electron pair and therefore contributes three skeletal electrons. Thus the clusters **42** and **43** should be able to act as ligands as the phosphorus atom occupies the apex of a distorted tetragonal pyramide formed by the iron, the phosphorus and one carbon atom. The coordination to a metal center

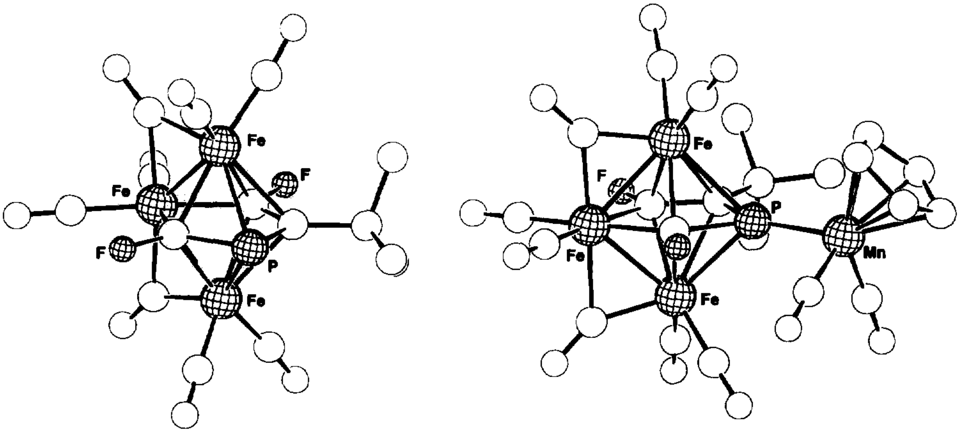
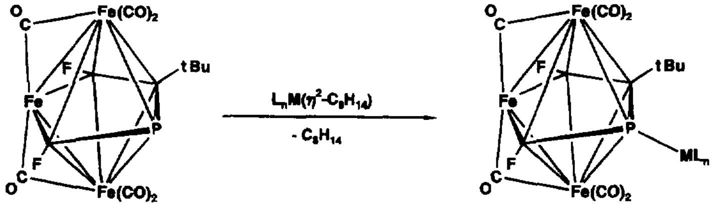


Fig. 9. Molecular structures of **42a** (left) and **44b** (right).

should not result in significant changes within the cluster framework. To test this hypothesis the reaction of **42a** with complexes which after elimination of a labile ligand produce 16-electron fragments was studied [53,54]. The stable compounds **44** with the $Cr(CO)_5$ and $CpMn(CO)_2$ ($Cp \equiv C_5H_5$ or C_5Me_5) fragment were isolated:



42a

44

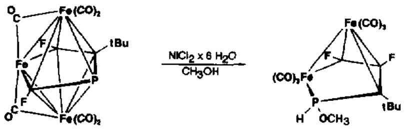
44a, $ML_n = Cr(CO)_5$

44b, $ML_n = CpMn(CO)_2$

44c, $ML_n = Cp^*Mn(CO)_2$

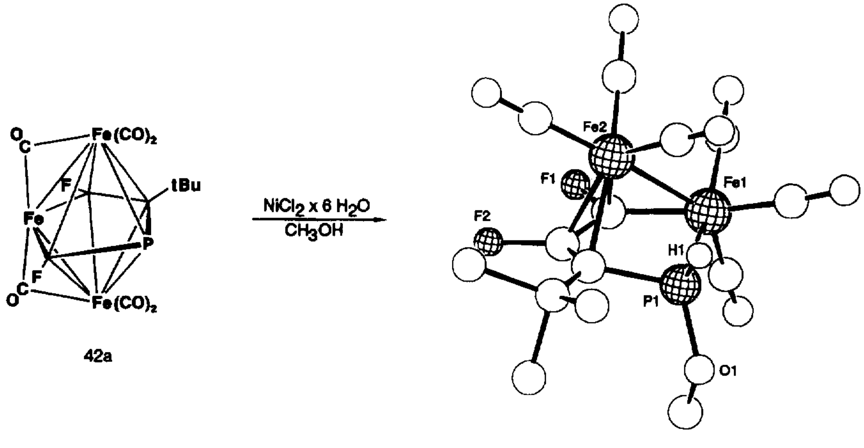
A crystal structure determination of **44b** verifies that the influence of coordination on the cluster framework is negligible (Fig. 9) [53].

Attempts to obtain complexes which contain more than one of these cluster ligands has so far failed. In the reaction of nickel chloride with **42a** in methanol an interesting cluster degradation product **45** was isolated [54]:



42a

45



42a

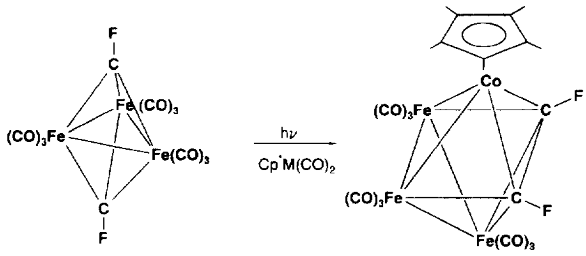
45

This dinuclear iron complex **45** contains the unusual μ_2-η^1-(P)-η^3-(C)$-$CF$-$CF$-$C(^{t}Bu)$-$P(H)(OCH$_3$) ligand in addition to six terminal carbonyl ligands. The mechanism of the reaction which results in a complete change in the connectivity of the ring atoms and an oxidative addition of methanol to the phosphorus atom is still a mystery.

6.3. Cluster expansion reactions and difluoroethyne complexes

Halogenated alkynes are rather unstable compounds [55]. In particular the existence of difluoroethyne has not been proved unambiguously [56]. Only recently, Bürger and Sommer [57] succeeded in synthesizing and characterizing FC≡CF, which slowly decomposes even at liquid-nitrogen temperature. This instability has prevented the synthesis of difluoroethyne complexes.

However, two different types of difluoroethyne complex can be prepared by indirect methods. On reacting $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ (**2a**) with Cp*Co(CO)$_2$ or Cp*Rh(CO)$_2$ a cluster expansion reaction takes places with simultaneous coupling of the fluoromethylidyne groups forming a difluoroethyne ligand [58]:



2a

46

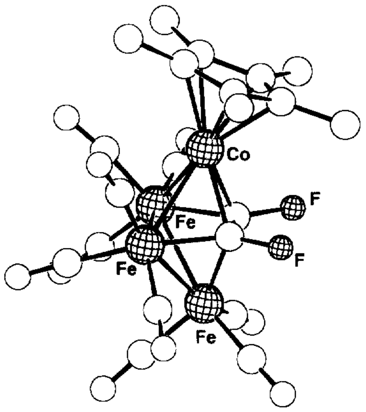
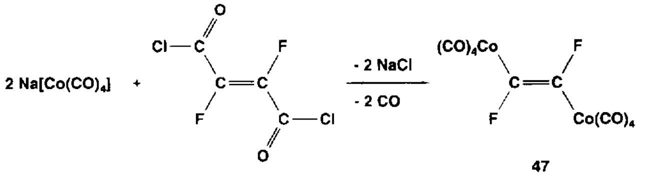


Fig. 10. Molecular structure of $Cp^*Co(CO)_9Fe_3(\mu_4\text{-}\eta^2\text{-}FC{\equiv}CF)$ (**46**).

According to the crystal structure determination of **46a** ($M{\equiv}Co$) (Fig. 10), the difluoroethyne ligand is coordinated to the butterfly arrangement of four metal atoms with distances ranging from 192(1) to 208(2) pm. Obviously the C—C bond of the difluoroethyne ligand is greatly lengthened by coordination, and the C—C—F structural unit is bent. Thus the coordinated difluoroethyne has lost its identity and should be viewed as a component of the *closo* cluster. Similar cluster expansion reactions of $Fe_3(CO)_9(R{-}C{\equiv}C{-}R)$ with $CpRh(CO)_2$ and $Fe_2(CO)_9$ which require no alkylidyne coupling reactions have been observed [59]. Attempts to prepare dichloroethyne and dibromoethyne complexes by analogous cluster expansion reactions starting with **2b** or **2c** failed thus far.

However, a second type of difluoroethyne complex **47** could be obtained by reaction of difluorofumaric dichloride with tetracarbonylcobaltate [60]:



47

According to the X-ray crystal structure determination of **47** the difluoroethyne ligand is coordinated in the unusual $\mu_2\text{-}\eta^1\text{-}\eta^1$ coordination which has been observed only in few other alkyne complexes [61].

6.4. Miscellaneous reactions

A carbon–carbon and nitrogen–carbon bond formation reaction induced by the reaction of $Fe_3(CO)_9(\mu_3\text{-}CMe)(\mu_3\text{-}COMe)$ (**3**) and diphenyldiazomethane yielding $Fe_2(CO)_6[Ph_2C{=}N{-}N{-}C(O)\text{-}C(Me){-}COEt]$ (**48**) has been reported by Mathieu and co-workers [62]. $[Fe_3(CO)_9(\mu_3\text{-}C{=}CCH_2R)]^-$ (**49**) was isolated as the product of the two electron reduction of $Fe_3(CO)_9(\mu_3\text{-}CCH_2R)(\mu_3\text{-}COEt)$ (**3**) by pentacarbonylmanganate(I) [11,63] but, when $R \equiv C(O)CH_3$ or $C(O)OCH_3$, the major products of the reaction are $[Fe_3(CO)_9(\mu_3\text{-}C(OEt){=}C{=}C(H)R]^-$ complexes (**50**) [11] containing an allenyl ligand.

References and notes

[1] D. Seyferth, Adv. Organomet. Chem., 14 (1976) 97; B.R. Penfold and B.H. Robinson, Acc. Chem. Res., 6 (1973) 73.

[2] J.R. Fritch, K.P.C. Vollhardt, M.R. Thompson and V.W. Day, J. Am Chem. Soc., 101 (1979) 2768; H. Yamazaki, Y. Wakatsuki and K. Aoki, Chem. Lett., (1979) 1041; A.D. Clauss, J.R. Shapley, C.N. Wilker and R. Hoffmann, Organometallics, 3 (1984) 619; R.D.W. Kemmitt and D.R. Russel, in G. Wilkinson (ed.), Comprehensive Organometallic Chemistry, Vol. 5, Pergamon, Oxford, 1982, p. 162; R.B. King and C.A. Harmon, Inorg. Chem., 15 (1976) 879; D.E. van Horn and K.P.C. Vollhardt, J. Chem. Soc., Chem. Commun. (1982) 203; A.V. de Miguel, K. Isobe, P.M. Bailey, N.J. Meanwell and P. Maitlis, Organometallics, 1 (1982) 1604; R.B.A. Pardy, G.W. Smith and M.E. Vickers, J. Organomet. Chem., 252 (1983) 341; B. Eaton, J.M. O'Connor and K.P.C. Vollhardt, Organometallics, 5 (1986) 394; H. Wadepohl and H. Pritzkow, Polyhedron, 8 (1989) 1939; S.M. Elder, B.H. Robinson and J. Simpson, J. Organomet. Chem., 398 (1990) 165.

[3] A. Bino, F.A. Cotton and Z. Dori, J. Am. Chem. Soc., 103 (1981) 243; M. Ardon, A. Bino, F.A. Cotton, Z. Dori, M. Kaftoy, B.W.S. Kolthammer, M. Kapon and G. Reisner, Inorg. Chem., 20 (1981) 4083.

[4] B.H. Freeland, N.C. Payne, M.A. Stalteri and H. Van Leeuwen, Acta Crystallogr., Sect. C, 39 (1983) 1533.

[5] W.-K. Wong, K.W. Chiu, G. Wilkinson, A.M.R. Galas, M. Thornton-Pett and M.B. Hursthouse, J. Chem. Soc., Dalton Trans. (1983) 1557.

[6] D. Lentz, I. Brüdgam and H. Hartl, Angew. Chem., 97 (1985) 115; Angew. Chem., Int. Edn. Engl., 24 (1985) 119.

[7] W. Stumpf, I. v. Wilucki and V. Amerl, Gmelin Handbuch der Anorganischen Chemie, Borverbindungen, Teil 2, Carborane 1, Band 15, Springer Verlag, Berlin/Heidelberg/New York, 1974, pp. 176–180.

[8] K. Wade, Adv. Inorg. Chem. Radiochem., 18 (1976) 1.

[9] W. Hübel, E.H. Braye, A. Clauss, E. Weiss, W. Krüerke, D.A. Brown, G.S.D. King and C. Hoogzand, J. Inorg. Nucl. Chem., 9 (1959) 204; for a review see E. Sappa, A. Tiripicchio and P. Braunstein, Chem. Rev., 83 (1983) 203.

[10] J.F. Blount, L.F. Dahl, C. Hoogzand and W. Hübel, J. Am. Chem. Soc., 88 (1966) 292.

[11] D. Nuel, F. Dahan and R. Mathieu, J. Am. Chem. Soc., 107 (1985) 1658; M. Lourdichi and R. Mathieu, Organometallics, 5 (1986) 2067; J. Suades, F. Dahan and R. Mathieu, Organometallics, 7 (1988) 47; **3a** has been mentioned earlier in a short communication but no details of its preparation have been given [63].

[12] J.A. Hriljac and D.F. Shriver, J. Am. Chem. Soc., 109 (1987) 6010.

[13] A.A. Aradi, F.-W. Grevels, C. Krüger and E. Raabe, Organometallics, 7 (1988) 812.

[14] D. Nuel, F. Dahan and R. Mathieu, Organometallics, 4 (1985) 1436.

[15] E. Cabrera, J.C. Daran and Y. Jeannin, J. Chem. Soc., Chem. Comm., (1988) 607.

[16] D. Nuel and R. Mathieu, Organometallics, 7 (1988) 16.

[17] C.J. Cardin, D.J. Cardin, N.B. Kelly, G.A. Lawless and M.B. Power, J. Organomet. Chem., 341 (1988) 447.

[18] D. Lentz and M. Reuter, Chem. Ber., 124 (1991) 773; D. Lentz and M. Reuter, Z. Anorg. Allg. Chem., 614 (1992) 121.

[19] S. Rivomanana, G. Lavigne, N. Lugan, J.J. Bonnet, R. Yanez and R. Mathieu, J. Am. Chem. Soc.,

111 (1989) 8959; S. Rivomanana, G. Lavigne, N. Lugan and J.J. Bonnet, Organometallics, 10 (1991) 2285.

[20] E. Rosenberg, J. Bracker-Novak, R.W. Gellert, S. Aime, R. Gobetto and D. Osella, J. Organomet. Chem., 365 (1989) 163.

[21] M.A. Gallop, B.F.G. Johnson, R. Khattar, J. Lewis and P.R. Raithby, J. Organomet. Chem., 386 (1990) 121.

[22] C.G. Pierpont, Inorg. Chem., 16 (1977) 636.

[23] W.-Y. Yeh, J.R. Shapley, J.W. Ziller and M.R. Churchill, Organometallics, 5 (1986) 1757.

[24] W.-Y. Yeh, S.R. Wilson and J.R. Shapley, J. Organomet. Chem., 371 (1989) 257.

[25] W.-Y. Yeh and J.R. Shapley, J. Organomet. Chem., 315 (1986) C29.

[26] D. Lentz and M. Reuter, unpublished results, 1992.

[27] S. Aime, R. Gobetto, L. Milone, D. Osella, L. Violano, A.J. Arce and Y. De Sanctis, Organometallics, 10 (1991) 2854.

[28] D. Lentz and H. Michael, J. Organomet. Chem., 346 (1988) C37.

[29] D.L. Reger and M.D. Dukes, J. Organomet. Chem., 153 (1978) 67.

[30] T.G. Richmond and D.F. Shriver, Organometallics, 2 (1983) 1061; T.G. Richmond, A.M. Crespi and D.F. Shriver, Organometallics, 3 (1984) 314.

[31] J.D. Koola and D.M. Roddick, Organometallics, 10 (1991) 591; A.M. Crespi, M. Sabat and D.F. Shriver, Inorg. Chem., 27 (1988) 812; A.M. Crespi and D.F. Shriver, Organometallics, 4 (1985) 1830.

[32] D. Lentz and H. Michael, Inorg. Chem., 28 (1989) 3396.

[33] D. Lentz and H. Michael, Chem. Ber., 123 (1990) 1481.

[34] M.J. Went, M.J. Sailor, P.L. Bodgan, C.P. Brock and D.F. Shriver, J. Am. Chem. Soc., 109 (1987) 6023.

[35] D. Seyferth, J.E. Hallgren and C.S. Eschbach, J. Am. Chem. Soc., 96 (1974) 1730.

[36] D. Seyferth, G.H. Williams and C.L. Nivert, Inorg. Chem., 16 (1977) 758.

[37] J.B. Keister and T.L. Horling, Inorg. Chem., 19 (1980) 2304.

[38] A.C. Sievert, D.S. Strickland, J.R. Shapley, G.R. Steinmetz and G.L. Geoffroy, Organometallics, 1 (1982) 214; D.A. Strickland and J.R. Shapley, J. Orgamomet. Chem., 401 (1991) 187; J.B. Keister, Polyhedron, 7 (1988) 847.

[39] D. Lentz and M. Reuter, unpublished results, 1992.

[40] D. Lentz and H. Michael-Schulz, Z. Anorg. Allg. Chem., 618 (1992) 111.

[41] M. Casarin, A. Gulino, D. Lentz, H. Michael-Schulz and A. Vittadini, Inorg. Chem., 32 (1993) 1383.

[42] M. Casarin, D. Ajò, D. Lentz, R. Bertoncello and G. Granozzi, Inorg. Chem., 26 (1987) 465.

[43] R.T. Boere, V. Klassen, D. Lentz, H. Michael-Schulz, K.H. Mook and J. Weaver, manuscript in preparation.

[44] D. Osella, R. Gobetto, P. Montangero, P. Zanello and A. Cinquantini, Organometallics, 5 (1986) 1247.

[45] E.L. Mutterties and J. Stein, Chem. Rev., 79 (1979) 479; C.K. Rofer-De-Poorter, Chem. Rev., 81 (1981) 447; W.A. Herrmann, Angew. Chem., 94 (1982) 118; Angew. Chem., Int. Edn. Engl., 21 (1982) 117.

[46] D. Lentz and H. Michael, Chem. Ber., 121 (1988) 1413.

[47] D. Lentz and H. Michael-Schulz, Inorg. Chem., 29 (1990) 4396.

[48] D. Lentz, H. Michael-Schulz and M. Reuter, Organometallics, 11 (1992) 2916.

[49] C.A. Mirkin, K.-L. Lu, G.L. Geffroy and A.L. Rheingold, J. Am. Chem. Soc., 112 (1990) 461, 6155.

[50] D. Lentz and H. Michael-Schulz, unpublished results, 1990; H. Michael-Schulz, PhD thesis, Freie Universität Berlin, 1990.

[51] J.C.T.R. Burckett-St. Laurent, M.A. King, H.W. Kroto, J.F. Nixon and R.J. Suffolk, J. Chem. Soc., Dalton Trans., (1983) 755; B. Souliki, H. Bock, R. Appel, A. Westerhaus, G. Becker and G. Uhl, Chem. Ber., 115 (1982) 3747.

[52] M. Regitz, in M. Regitz and O. Scherer (eds.), Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme, Stuttgart, 1990; P. Binger, in M. Regitz and O. Scherer (eds.), Multiple Bonds and Low Coordination in Phosphorus Chemistry, Thieme, Stuttgart, 1990; M. Regitz, Chem. Rev., 90 (1990) 191; M. Regitz, Angew. Chem., 100 (1988) 1541; J.F. Nixon, Chem. Rev., 88 (1988) 1327.

[53] D. Lentz and H. Michael, Angew. Chem., 101 (1989) 330; Angew. Chem., Int. Edn. Engl., 28 (1989) 321.

[54] D. Lentz, M. Reuter and H. Michael-Schulz, unpublished results, 1992.

[55] G. Viehe (ed.), The Chemistry of Acetylenes, Marcel Dekker, New York, 1969; L. Brandsma, Preparative Acetylenic Chemistry, Studies in Organic Chemistry, Vol. 34, Elsevier, Amsterdam, 1988.

[56] W.J. Middleton, US Pat. 2 831 835, 1958; Chem. Abstr., 52 (1958) 14658f; J. Heicklen and V. Knight, J. Phys. Chem., 69 (1965) 2484; L. Kevan and P. Hamlet, Chem. Phys., 42 (1965) 2255; G. Bieri, J.-P. Stadelmann, F. Thommen and J. Vogt, Helv. Chem. Acta, 61 (1978) 357; G. Bieri, A. Schmelzer, L. Asbrink and V. Jonsson, Chem. Phys., 49 (1980) 213; J.C. Brahms and W.P. Dailey, J. Am. Chem. Soc., 111 (1989) 8940.

[57] H. Bürger, S. Sommer, J. Chem. Soc., Chem. Commun. (1991) 456.

[58] D. Lentz and H. Michael, Angew. Chem., 100 (1988) 871; Angew. Chem., Int. Edn. Engl., 27 (1988) 845; D. Lentz and H. Michael-Schulz, unpublished results, 1992.

[59] H. Bantel, A.K. Powell and H. Vahrenkamp, Chem. Ber., 123 (1990) 677.

[60] D. Lentz and D. Preugschat, Angew. Chem., 102 (1990) 308; Angew. Chem., Int. Edn. Engl., 29 (1990) 315.

[61] W.P. Griffith and G. Wilkinson, J. Chem. Soc. (1959) 1629; K.D. Grande, A.J. Kunin, L.S. Stuhl and B.V. Foxman, Inorg. Chem., 22 (1983) 1791; J.A.J. Jarvis, A. Johnson and R.J. Puddephatt, J. Chem. Soc., Chem. Commun. (1973) 373; J. Cleemens, M. Green, M.-C. Kuo, C.J. Fritchie Jr., J.T. Mague and F.G.A. Stone, J. Chem. Soc., Chem. Commun. (1972) 53; R.S. Dickson, S.H. Johnson, H.P. Kirsch and D.J. Lloyd, Acta Crystallogr., Sect. B, 33 (1977) 2057; J.W. Bixler, A.M. Bond, R.S. Dickson, G.D. Fallon, R.S. Nesbit and H. Pateras, Organometallics, 6 (1987) 2508; W. Beck, M.U. Schweiger and G. Müller, Chem. Ber., 120 (1987) 889.

[62] D. Nuel, F. Dahan and R. Mathieu, Organometallics, 5 (1986) 1278.

[63] D. de Montauzon and R. Mathieu, J. Orgamomet. Chem., 252 (1983) C83.