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Clusters containing fluorocarbons

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Abstract

Nonacarbonylbis(μ_3-fluoromethylidyne)triiron, $Fe_3(CO)_9(\mu_3\text{-}CF)_2$, and tetrafluoroferrole, $(CO)_3Fe\overline{FeCF{=}CFCF{=}C}F(CO)_3$, are obtained by the reaction of $Fe(CO)_5$ with $CFBr_3$. $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ was found to be a versatile starting material for the synthesis of other new clusters.

Clusters containing a diferra-allylligand are formed by regioselective attack of alkynes on one μ_3-CF ligand of $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ from the sterically less-hindered side. Replacement of fluorine by chlorine in $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ using aluminium chloride yields nonacarbonylbis(μ_3-chloromethylidyne)triiron at ambient temperature. At elevated temperature or with aluminium bromide further attack of the cluster and substitution of three carbonyl ligands by benzene occurs, forming a cationic cluster, which reacts with nucleophiles such as alcohols, forming $Fe_3(CO)_6(\eta^6\text{-}C_6H_6)(\mu_3\text{-}CX)(\mu_3\text{-}CCOOR)$.

The reaction of $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ with the phosphaalkyne $t\text{-}C_4H_9C{\equiv}P$ results in the formation of a pentagonal bipyramidal cluster $Fe_2(CO)_8[\overline{FeCFC(C_4H_9)PC}F]$, that contains a perfect planar FeCPCC five-membered ring system.

In the cluster expansion reaction of $Fe_3(CO)_9(\mu_3\text{-}CF)_2$ with $Cp^{\star}Co(CO)_2$, carbon–carbon bond formation with formation of a coordinated difluoroethyne ligand occurs. To our knowledge $Cp^{\star}CoFe_3(CO)_9(\mu_4\text{-}\eta^2\text{-}FC{\equiv}CF)$ is the first example of a coordinated difluoroethyne ligand.

Results and discussion

In 1985, when we published the synthesis of nonacarbonylbis(μ_3-fluoromethylidyne)triiron [1], the chemistry of fluoromethylidyne clusters was limited to nonacarbonyl(μ_3-fluoromethylidyne)tricobalt [2] and some derivatives obtained by ligand exchange and metal exchange reactions [3] (Scheme 1).

In order to study the chemistry of nonacarbonylbis(fluoromethylidyne)triiron we required larger amounts of this compound. In an optimized work up procedure for

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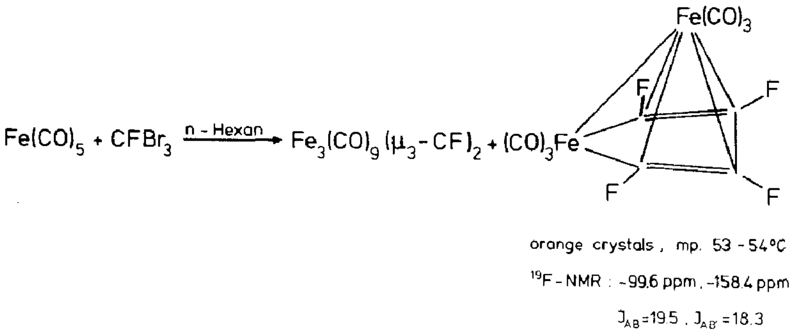
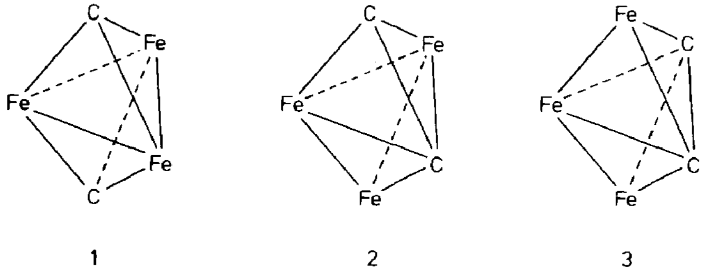


Scheme 1.

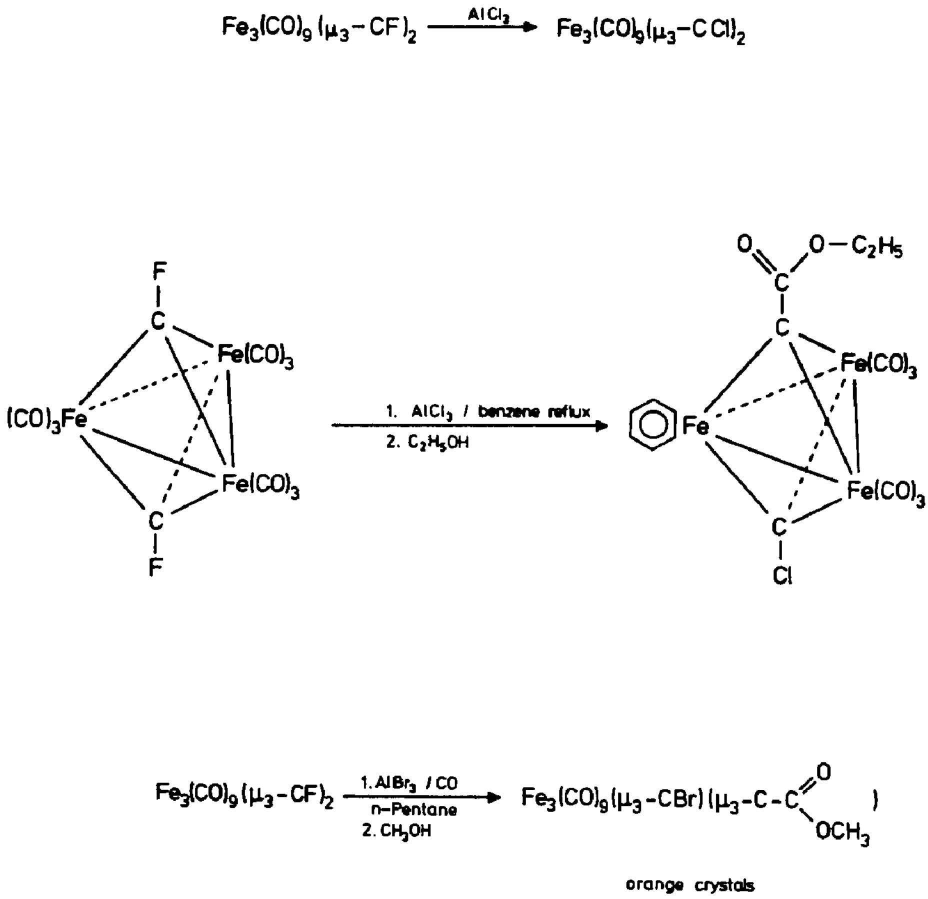
the synthesis of this compound from $Fe(CO)_5$ and $CFBr_3$ the solvent is removed from the hexane extract and the residue is sublimed under vacuum. In a search for possible reaction intermediates we observed that during this sublimation a more volatile yellow to orange compound formed in the liquid nitrogen trap. After recrystallisation of this product from pentane orange crystals were obtained. The spectroscopic properties of this compound, especially the NMR spectra, indicated it to be a tetrafluoroferrole (Scheme 1) [4]. In view of all the unsuccessful attempts to prepare η^5-pentafluorocyclopentadienyl complexes [5] the unexpected formation and high stability of such a tetrafluoroferrole derivative is very suprising. In addition, until very recently there existed only a few bis(alkylidyne)iron clusters [6–11], such as $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COCH_3)$ [6], which was prepared by Wilkinson et al. by a completely different method.

On the basis of the Wade rules [12] these clusters possess $2n + 2$ skeletal electrons and thus should form a trigonal bipyramidal closo cluster (Scheme 2). However, Wade rules do not predict which arrangement of the skeletal atoms is the thermodynamically most stable one, and indeed, an other possible arrangement is observed, which corresponds to the well known alkyne cluster of nonacarbonyl triiron [13]. This leads to the question, which substituents stabilize the bisalkylidyne form and which stabilize the alkyne form? Because Robinson et al. prepared $Co_3(CO)_9(\mu_3\text{-}CAr)$ by Friedel–Crafts alkylation of $Co_3(CO)_9(\mu_3\text{-}CCl)$ [14], we assumed that nonacarbonylbis(fluoromethylidyne)triiron can serve as a starting material for the synthesis of further bis(alkylidyne) clusters (Scheme 3).

The reaction of nonacarbonylbis(μ_3-fluoromethylidyne)triiron with benzene in the presence of aluminium chloride yields an orange crystalline product, whose



Scheme 2.



Scheme 3.

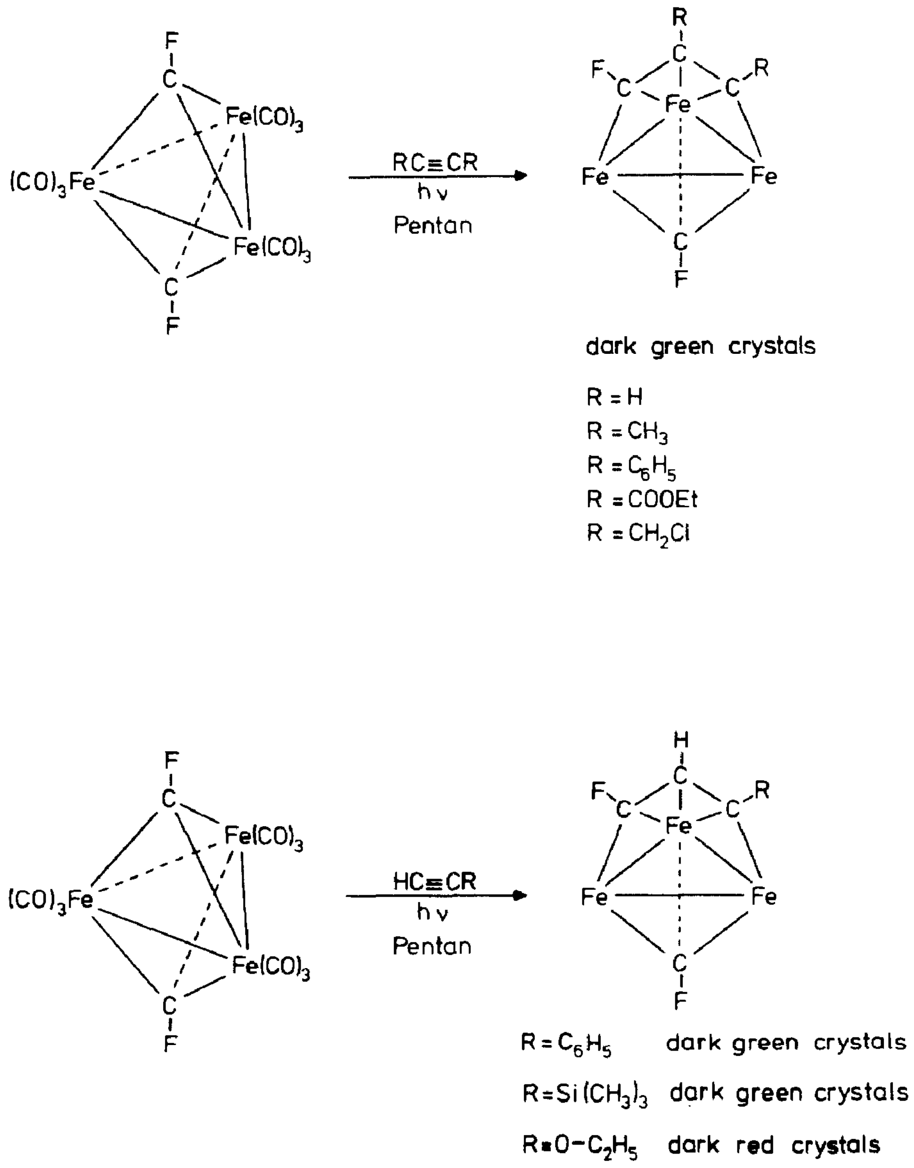
spectroscopic data revealed the presence of nonacarbonylbis(μ_3-chloromethylidyne)-triiron, a further halogenated bis(alkylidyne) cluster [15].

Heating the reaction mixture to force the formation of a Friedel–Crafts product, however, results in the formation of a precipitate, which is insoluble in non polar solvents. Nevertheless, it reacts with alcohols yielding a red soluble product, which after chromatographic work-up and crystallisation can be obtained as dark red crystals. The crystal structure determination proves that we obtained another bis(alkylidyne) cluster, now bearing a μ_3-chloromethylidyne and a μ_3-CCOOEt bridge. In addition three carbonyl ligands are substituted by an η^6-benzene ligand [15].

The formation of this product can be explained by the following mechanism. Abstraction of chloride by the Lewis acid aluminium chloride results in formation of a carbocation. This carbocation stabilizes itself by migration of a coordinated carbonyl group to the carbocationic alkylidyne carbon atom creating a new carbocationic species and a vacant site in the coordination sphere of one iron atom. This vacant site can now be occupied by the benzene ring resulting in further displacement of two carbonyl groups. Obviously the electrophilicity of the cation is too low for electrophilic attack of a benzene ring. Nevertheless, reaction with alcohols yields the ester, obtained as the final product [15].

Although we were not able to isolate any of the cationic intermediates, this reaction mechanism is supported by the fact that in the absence of a coordinating solvent and in the presence of carbon monoxide the corresponding nonacarbonyl cluster was formed [15]. An analogous carbocation of the nonacarbonylcobalt system was isolated by Seyferth et al. [16]. Applying our method we were able to vary the substituents at the alkylidyne carbon atom. We hope that we can get further data about the limits of stability of the bis-alkylidyne clusters vs. the alkyne clusters.

Very important reactions of organometallic compounds are the carbon–carbon bond formation with unsaturated substrates. Mathieu and coworkers have observed



Scheme 4.

the formation of a ferrole type five-membered ring system by treatment of their bis(alkylidyne) cluster with alkynes [7]. Except for special alkynes a mixture of several isomers is obtained, the formation of which has been explained by a complicated reaction mechanism, that offers several different reaction pathways [7].

In order to study the fluorine substitution effect on this reaction we have allowed nonacarbonylbis(μ_3-fluoromethylidyne)triiron to react with various alkynes. Our experiments have shown that a photolytic reaction is much cleaner than a thermal one. Only a single product is formed, which is the same product obtained by a thermal reaction in lower yields [17].

The analysis of the spectroscopic data has shown unambigiously that our product cannot have the expected ferrole type structure. First of all there are no bands in the infrared spectrum that can be assigned to carbonyl bridges typical for these ferrole type species.

The ^{19}F NMR spectra of all of these compounds show a very low field signal and one signal around zero ppm, which do not show significant coupling. The ^{13}C NMR spectra of these compounds obtained with various alkynes all exhibit a downfield signal ($\approx$ 350 ppm) with a large fluorine-carbon coupling constant (480 Hz), typical for a μ_3 bridging fluoromethylidyne ligand. Two additional low-field signals between 200 and 250 ppm are observed, one showing a CF coupling constant typical for a directly bonded fluorine atom. Apart from the signals of the substituents, there exists only one further high field signal that exhibits a small CF coupling constant.

From the spectroscopic data a structure containing a μ_3-CF and μ_3-CFCRCR ligand seems to be the most likely.

These findings were proved by the crystal structure determinations of two of these products, which in addition revealed that carbon–carbon bond formation occurs strictly regiospecifically at the sterically less hindered site of the alkyne [17,18]. These structures are in accord with the Wade rules, although they possess the less-common capped nido structure [12b].

Our success in the reactions with alkynes encouraged us to extend this reaction to heteroalkynes like the phosphaalkyne, t-C_4H_9-C≡P [19] (Scheme 5). We were very surprised that the spectroscopic data of the products do not fit a structure containing a μ_3-CF and a diferraphosphaallyl ligand. In contrast they strongly suggest a phosphaferrole type cluster, which was subsquently confirmed by X-ray crystal structure analysis [19]. This cluster obeys the Wade rules as long as the phosphorus atom posseses a lone pair and thus contributes three skeletal electrons. If this is correct, the cluster should be able to act as a ligand and should coordinate to 16 electron fragments.

Reaction of the cluster with the chromium and manganese complexes $(CO)_5Cr(\eta^2\text{-}C_8H_4)$ and $CpMn(CO)_2(\eta^2\text{-}C_8H_{14})$ containing the labile *cis*-cyclooctene ligand gave the expected products in a straightforward reaction [14]. According to a crystal structure determination the coordination of a $CpMn(CO)_2$ fragment has only minor effects on the bond lengths and angles of the cluster justifying the above description of the compound as a closo-cluster system [19].

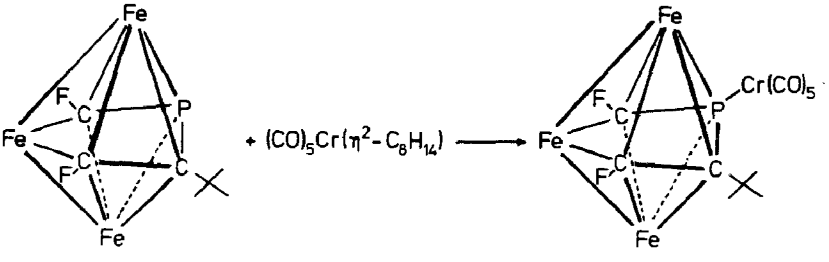
The reaction of nonacarbonylbis(μ_3-fluoromethylidyne)triiron with acetonitrile or benzonitrile, however, results in simple substitution of one carbonyl ligand by a nitrile ligand [20].

There are two further important reactions in cluster chemistry: metal exchange reactions and cluster expansion reactions. In a metal exchange reaction one metal

$$Fe_3(CO)_9(\mu_3\text{-}CF)_2 + {+}C{\equiv}P \longrightarrow Fe_3(CO)_8({+}C_3F_2P)$$

black crystals, mp. 142 °C

IR: 2078 (s)
2033 (vs)
1994 (s)
1877 (m)
1861 (m)



yellow green crystals dec. >70°C

^{19}F-NMR:
-68.7 $^3J_{PF}$ = 24 Hz
-99.5 $^2J_{PF}$ = 61 Hz

^{31}P-NMR:
2.9 ppm

^{19}F-NMR:
-67.6 $^3J_{PF}$ = 17 Hz
-100.3 $^2J_{PF}$ = 34 Hz

^{31}P-NMR:
74.0

Scheme 5.

fragment is replaced by an isolobal fragment whereas in a cluster expansion reaction the cluster grows by one or more fragments (Scheme 6). We have allowed nonacarbonylbis(μ_3-fluoromethylidyne)triiron to react with dicarbonyl(pentamethylcyclopentadienyl)cobalt in order to replace a tricarbonyliron unit by an isolobal pentamethylcyhclopentadienylcobalt fragment. However, a cluster expansion reaction by the CpCo fragment takes place [21]. Three possible isomers exist for this octahedral cluster. Two of them contain a difluoroethyne ligand and the other one contains μ_4-fluoromethylidyne ligands.

$$Fe_3(CO)_9(\mu_3\text{-}CF)_2 \xrightarrow[\substack{h\nu \\ \text{Pentan}}]{Cp^*Co(CO)_2} Cp^*CoFe_3(CO)_9(C_2F_2)$$

dark brown crystals

decomp. >142 °C

^{19}F-NMR: δ = -22.3 ppm

IR(n-Pentan): 2061 (m)
2016 (s)
1998 (vs)
1959 (w)
1901 (w)

Scheme 6.

The crystal structure determination of the compound readily revealed that the cluster contains the first example of a coordinated difluoroethyne ligand. However, the difluoroethyne has lost its idendity due to coordination to four metal centers as can be seen from the C–C bond length of 145 pm and a strongly bent C–C–F moiety. Thus, the difluoroethyne carbon atoms might better be regarded as a part of a $CoFe_3C_2$ closo cluster [21]. A similar cluster expansion reaction of $Fe_3(CO)_9(\mu_3\text{-}RC{\equiv}CR)$ has been described by Vahrenkamp et al. [22]

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