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Study of the Reactivity of $[HFe_4(CO)_{13}]^-$ toward Acetylene and Monosubstituted Alkynes. X-ray Structure Determination of $[N(P(C_6H_5)_3)_2][Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)CHCH)(\mu\text{-}CO)_2(CO)_9]$

Mahmoud Kalam Alami, Françoise Dahan, and René Mathieu*

Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241 liée par convention à l'Université Paul Sabatier, 31400 Toulouse, France

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$[PPN][HFe_4(CO)_{13}]$ (1; PPN = $N(P(C_6H_5)_3)_2$) reacts with acetylene in boiling ethyl acetate to give $[PPN][Fe_4(\mu_3\text{-}CCH_3)(CO)_{12}]$ (2) in a first step. This cluster then reacts with a second molecule of acetylene in boiling 3-pentanone leading to $[PPN][Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)CHCH)(\mu\text{-}CO)_2(CO)_9]$ (3) whose structure has been determined by X-ray diffraction. 3 is monoclinic of space group C_{2h}^5—$P2_1/n$ with a = 23.014 (4) Å, b = 9.420 (1) Å, c = 22.166 (4) Å, β = 90.45 (1)°, and Z = 4. The structure has been solved and refined to R and R_w values of 0.026 and 0.030, respectively, using 4539 reflections. 3 contains an allylic ligand, resulting from the coupling of the ethylidyne ligand with one molecule of acetylene, $\mu_4\text{-}\eta^3$-bonded to a butterfly arrangement of the four iron atoms. Extension of the study to monosubstituted alkynes, RC≡CH, shows that the reaction is alkyne dependent and two types of reactions have been observed. If the substituents on the alkyne have electron-withdrawing properties like R = C_6H_5 or $CH_3OC(O)$, complexes of type 3 with the $C(CH_2R)CHC(R)$ allylic ligand are formed directly without observation of the alkylidyne intermediate. If the substituents R are electron-donating alkyl groups, fragmentation of the tetranuclear unit of the cluster is observed and trinuclear anionic clusters $[PPN][Fe_3(\mu_3\text{-}C{\equiv}CR)(CO)_9]$ are formed. The fluxionality of complexes with the structure of 3 is also discussed.

Introduction

We have shown recently that at room temperature the $HFe_3(CO)_{11}^-$ anion is very reactive toward substituted alkynes, acetylene,[1] and ethylene.[2] To pursue this study with the aim of comparing the reactivity of iron cluster anions with the well-known reactivity of ruthenium or osmium clusters,[3-6] we now have extended our work to the case of the tetranuclear hydrido cluster anion $[HFe_4(CO)_{13}]^-$ (with the $[N(P(C_6H_5)_3)_2]^+$ counterion (PPN)) (1). Actually, this tetranuclear cluster anion was far less reactive than the $[HFe_3(CO)_{11}]^-$ anion and a reaction with acetylene or monosubstituted alkynes was observed only if the reaction temperature was 78 °C or higher. Furthermore, the products of the reactions were alkyne dependent.

We report here the results during this study and the X-ray structure determination of $[PPN][Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)CHCH)(\mu\text{-}CO)_2(CO)_9]$, one of the products of the reaction of 1 with acetylene and monosubstituted alkynes RC≡CH (R = C_6H_5, $CH_3OC(O)$, $C(CH_3)_3$, C_3H_7).

Results and Discussion

Initially, we checked the reactivity of diphenylacetylene toward 1. No reaction occurred at room temperature. Extensive decomposition was observed in boiling acetone, but small amounts of $[HFe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_6H_5{\equiv}CC_6H_5)]^{-1}$ were detected. Taking into account this first result, the study of reactivity of 1 toward disubstituted alkynes was not pursued.

Reactivity of 1 toward Acetylene. In the case of acetylene, the reaction proceeds more cleanly in refluxing ethyl acetate. Two products have been isolated by fractional crystallization. In the ν(CO) stretching region, the infrared spectrum of the major compound 2 shows absorption characteristic of terminal carbonyl ligands. In the proton NMR spectrum, excluding resonances of the PPN cation, a 3 H singlet is observed at 4.18 ppm. By analogy with the reactivity of $[HFe_3(CO)_{11}]^-$ toward acetylene,[1] this suggests the $[PPN][Fe_4(\mu_3\text{-}CCH_3)(CO)_{12}]$ formulation for 2. This complex was first obtained by the action of CH_3^+ on the carbido cluster dianion $[PPN]_2[Fe_4C(CO)_{12}]$. Indeed, the infrared spectrum of 2 closely resembles the published data.[7] This identity has been confirmed by analysis and the ^{13}C NMR spectrum of 2 which was in good agreement with the published spectrum[7] (the CH_3 resonance that was observed at 43.9 ppm was not mentioned, but our assignment is confirmed by the proton-coupled spectrum which shows a quartet for this signal). The second product 3 was obtained with variable yields under these conditions. As suspected, it was a product of the reaction of more than one molecule of acetylene and, therefore, the reaction was performed with excess acetylene at higher temperature in refluxing 3-pentanone. Indeed, 3 was obtained in reasonable yield as the only isolable product.

In the infrared spectrum of 3 in the ν(CO) stretching region, except for absorptions due to terminal carbonyl groups, a weak broad unsymmetrical band was observed at 1795 cm^{-1} which is attributed to bridging carbonyl groups. In the solid state, two well-resolved bands are observed at 1800 and 1790 cm^{-1} which could explain the dissymmetry observed in solution for the band at 1795 cm^{-1}. The proton NMR spectrum, except for the phenyl resonances, shows two broad bands in the 1:3 intensity ratio at 9.27 and 2.47 ppm, suggesting the presence of CH and CH_3 groups. The proton-coupled ^{13}C NMR spectrum of 3 confirms the presence of a CH_3 group (δ 36.4 (J_{CH} = 129.2 Hz)), and, in addition to the phenyl resonances, we observed one doublet at 92.6 ppm (J_{CH} = 172.3 Hz), broad signals centered at 156.4, 159.1, 209.1, and 216.9 ppm, and a sharp resonance at 218.4 ppm. The proton-decoupled

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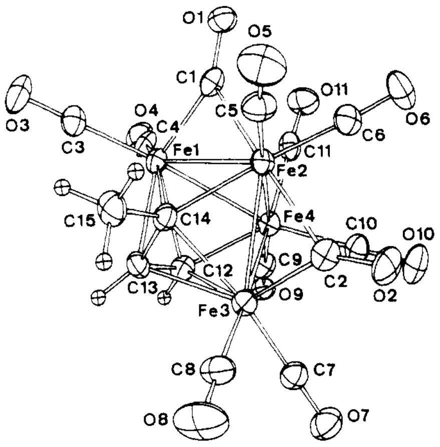

Figure 1. Structure of complex **3** showing the atomic numbering scheme with the ellipsoid at the 35% probability level.

^{13}C NMR spectrum gives evidence that the two resonances at 156.4 and 159.1 ppm are in fact a broad doublet centered at 157.9 ppm (J = 168 Hz).

From these spectroscopic data it appears that in **3** there are one CH$_3$ and two CH groups (one of the CH groups which was not detected in the proton NMR spectrum is certainly obscured by the phenyl resonances of the PPN cation). This suggests that the organic fragment in **3** is C(CH$_3$)CHCH resulting from the coupling of the ethylidyne group of **2** with one molecule of acetylene.

The exact formulation of **3** on the basis of chemical analysis was difficult to ascertain, and to have a better knowledge of the structure of **3** in the solid state, an X-ray structure determination was undertaken. An ORTEP plot of the anionic part of **3** is shown in Figure 1. Bond distances and angles of interest are gathered in Table I. The exact formulation of **3** is [PPN][Fe$_4$(μ_4-η^3-C(CH$_3$)CHCH)(μ-CO)$_2$(CO)$_9$]. The anionic part of **3** consists of a butterfly arrangement of iron atoms. The dihedral angle between the two "wings" is 97.9°. The two Fe(1) and Fe(3) iron atoms on each "wing tip" are bonded to two terminal carbonyl groups and two bridging carbonyl groups which span the Fe(1)–Fe(2) and Fe(2)–Fe(3) bonds.

The two C(1)O(1) and C(2)O(2) bridging groups are asymmetric, being more tightly bonded to Fe(1) and Fe(3). The Fe(2) iron atoms also is bonded to two terminal CO groups. The remaining Fe(4) iron atom is bonded to three terminal CO groups. Two types of Fe–Fe bond distances are observed, and as expected, the Fe–Fe bonds bridged by carbony ligands (Fe(1)–Fe(2) and Fe(2)–Fe(3)) are about 0.1 Å shorter than the other three. The nonbridged Fe–Fe bonds are of the same order of magnitude, but the hinge side of the cluster is significantly longer than the other two nonbridged bonds. The nonbonded Fe(1)···Fe(3) distance is 3.3234 (9) Å. The organic fragment CHCHC(CH$_3$) is a substituted allylic fragment resulting from the coupling of the ethylidyne ligand of **2** with acetylene. This fragment is bonded to all the iron atoms in a similar way to the allylic ligands bonded to the tetranuclear heterometallic cluster (η-C$_5$H$_5$)NiRu$_3$(CO)$_8$(C$_6$H$_9$)[8] or the homometallic cluster Ru$_4$(CO)$_{10}$(C$_{12}$H$_{16}$)[9] or even to the nonametallic cluster [Os$_9$(CO)$_{21}$(CHC(R)CH)]$^-$ (R = CH$_3$ or C$_2$H$_5$).[10]

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) with Esd's for 3

Bond Lengths			
Fe(1)–Fe(2)	2.5185 (7)	Fe(3)–C(2)	1.883 (5)
Fe(1)–Fe(4)	2.6204 (7)	C(2)–O(2)	1.165 (6)
Fe(2)–Fe(3)	2.5136 (9)	Fe(1)–C(3)	1.772 (5)
Fe(2)–Fe(4)	2.6477 (8)	Fe(1)–C(4)	1.797 (5)
Fe(3)–Fe(4)	2.6353 (8)	Fe(2)–C(5)	1.791 (5)
Fe(1)···Fe(3)	3.3234 (9)	Fe(2)–C(6)	1.777 (5)
Fe(1)–C(12)	2.129 (5)	Fe(3)–C(7)	1.755 (5)
Fe(1)–C(13)	2.112 (4)	Fe(3)–C(8)	1.748 (5)
Fe(1)–C(14)	2.109 (4)	Fe(4)–C(9)	1.808 (5)
Fe(2)–C(14)	2.014 (4)	Fe(4)–C(10)	1.776 (5)
Fe(3)–C(12)	2.155 (5)	Fe(4)–C(11)	1.811 (5)
Fe(3)–C(13)	2.124 (4)	C(3)–O(3)	1.142 (6)
Fe(3)–C(14)	2.101 (4)	C(4)–O(4)	1.125 (6)
Fe(4)–C(12)	1.960 (4)	C(5)–O(5)	1.134 (6)
C(12)–C(13)	1.425 (6)	C(6)–O(6)	1.142 (6)
C(13)–C(14)	1.446 (6)	C(7)–O(7)	1.153 (6)
C(14)–C(15)	1.537 (6)	C(8)–O(8)	1.150 (7)
Fe(1)–C(1)	1.872 (4)	C(9)–O(9)	1.125 (7)
Fe(2)–C(1)	2.048 (5)	C(10)–O(10)	1.146 (6)
C(1)–O(1)	1.178 (6)	C(11)–O(11)	1.145 (6)
Fe(2)–C(2)	2.036 (5)		
Bond Angles			
Fe(2)–Fe(1)–Fe(4)	61.99 (2)	Fe(3)–C(7)–O(7)	176.2 (4)
Fe(1)–Fe(2)–Fe(3)	82.67 (3)	Fe(3)–C(8)–O(8)	177.8 (4)
Fe(1)–Fe(2)–Fe(4)	60.90 (2)	Fe(4)–C(9)–O(9)	178.8 (5)
Fe(1)–Fe(4)–Fe(2)	57.11 (2)	Fe(4)–C(10)–O(10)	177.6 (4)
Fe(3)–Fe(2)–Fe(4)	61.34 (2)	Fe(4)–C(11)–0(11)	177.0 (4)
Fe(2)–Fe(3)–Fe(4)	61.84 (2)	Fe(4)–C(12)–C(13)	129.6 (3)
Fe(1)–Fe(4)–Fe(3)	78.44 (2)	C(12)–C(13)–C(14)	111.6 (4)
Fe(2)–Fe(4)–Fe(3)	56.82 (2)	C(13)–C(14)–Fe(2)	122.5 (3)
Fe(1)–C(1)–O(1)	145.5 (4)	C(15)–C(14)–Fe(2)	121.8 (3)
Fe(2)–C(1)–O(1)	134.7 (3)	C(13)–C(14)–C(15)	115.7 (3)
Fe(1)–C(1)–Fe(2)	79.8 (2)	C(12)–C(13)–H(C13)	123 (2)
Fe(2)–C(2)–O(2)	136.0 (4)	C(14)–C(13)–H(C13)	121 (3)
Fe(3)–C(2)–O(2)	144.3 (4)	Fe(4)–C(12)–H(C12)	119 (2)
Fe(2)-C(2)-Fe(3)	79.7 (2)	C(13)-C(12)-H(C12)	111 (2)
Fe(1)–C(3)–O(3)	179.7 (4)	Fe(1)–C(12)–Fe(3)	101.7 (2)
Fe(1)–C(4)–O(4)	178.4 (4)	Fe(1)–C(13)–Fe(3)	103.4 (2)
Fe(2)–C(5)–O(5)	175.8 (5)	Fe(1)–C(14)–Fe(3)	104.3 (2)
Fe(2)–C(6)–O(6)	176.8 (4)		

The allylic ligand can be described as being σ-bonded to the Fe(2)–Fe(4) iron atoms of the hinge but it is more tightly bonded to Fe(4), with the Fe(4)–C(12) distance of the same order as those found in a trinuclear iron cluster containing an allylic ligand.[11] The C(12)C(13)C(14) system is η-bonded to the Fe(1) and Fe(3) iron atoms. This organic fragment defines a plane from which Fe(2) and Fe(4) are only displaced by 0.0068 (6) and 0.0020 (6) Å, respectively. Fe(1) and Fe(3) are nearly equidistant on each side of this plane (1.6576 (4) and 1.6656 (7) Å, respectively), and the C(15) atom is displaced by 0.003 (5) Å from the same plane.

In this mode of bonding the allylic group is a five-electron donor and the [Fe$_4$(μ_4-η^3-C(CH$_3$)CHCH)(μ-CO)$_2$(CO)$_9$]$^-$ anion is a 60-valence-electron cluster, i.e., two less than required by the 18-valence-electron rule. According to Wade's theory,[12] this anion can be considered as a closo pentagonal-bipyramidal structure.

Having now a good knowledge of the structure of **3** allows us to assign the observed ^{13}C resonances at 92.6, 157.9, and 218.4 ppm to C(13), C(12), and C(14), respectively. The fact that for the carbonyl ligands only one broad resonance is observed at 209.1 ppm indicates also that **3** is a fluxional molecule. This phenomenon will be discussed later.

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To summarize, acetylene reacts with **1** in two steps, giving in the first step a cluster with an ethylidyne ligand (**2**) and then by coupling of a second molecule of acetylene and with departure of one molecule of carbon monoxide, a cluster with an allylic ligand (**3**). This provides a further example of the coupling of ethylidyne ligands with alkynes.[13]

To check if these observations are general reactions for monosubstituted alkynes, RC≡CH, we have extended the study to the cases where R = C_6H_5, $CH_3OC(O)$, *t*-Bu, and C_3H_7. Actually, depending on the nature of R, two types of reactivity have been observed which seem related to the electronic properties of the R group.

Reactivity of 1 toward Monosubstituted Alkynes RC≡CH. A. Case Where R Is an Electronegative Group, C_6H_5 or $CH_3OC(O)$. With the two alkynes the reaction in refluxing ethyl acetate or 3-pentanone leads to one type of product only, **4** (R = C_6H_5) or **5** (R = $CH_3OC(O)$), which can be isolated in reasonable yield in both cases if the reaction is conducted with 2 equiv of the alkyne.

The infrared spectra of **4** and **5** strongly resemble that of **3** suggesting similar structures. The proton NMR spectrum of **4**, in addition to the phenyl resonances of the cation and the alkyne, shows one signal at 6.72 ppm and a broad resonance at 4.06 ppm in the relative ratio of 1:2. The $^{13}C\{^1H\}$ NMR spectrum at room temperature gives evidences of signals at 56.5, 95.1, 156.4, 215.3, and 216.9 ppm, with broad resonances at 56.5, 156.4, and 215.3 ppm. The proton-coupled ^{13}C NMR spectrum shows that the 56.5 ppm resonance is a broad triplet ($J \approx 130$ Hz) and the 95.1 ppm resonance a doublet ($J = 176$ Hz). These results are very similar to the spectroscopic data of **3** and are consistent with a $C(CH_2C_6H_5)CHC(C_6H_5)$ ligand in **4**. Actually, the doublet observed at 95.1 ppm compares well with the resonance found for C(13) in **3** and allows us to assign this formulation for the allylic ligand. The resonances at 216.9 and 156.4 ppm are attributed to the $\mathit{C}(CH_2C_6H_5)$ and $\mathit{C}(C_6H_5)$ carbon atoms, respectively. The chemical analysis is consistent with the $[PPN][Fe_4(C(CH_2C_6H_5)CHC(C_6H_5))(CO)_{11}]$ formulation.

The NMR data for **5** are also in agreement with the formulation of the allylic fragment $C(CH_2C(O)OCH_3)CHC(C(O)OCH_3)$ as the proton NMR spectrum shows resonances at 3.72 and 3.85 ppm for the OCH_3 groups and a broad resonance centered at 4.29 ppm for the CH_2 group. The CH resonance is certainly obscured by the resonances of the cation. The ^{13}C NMR spectrum confirms the presence of the two OCH_3 groups (signals at 51.6 and 52 ppm) and of the CH_2 group (at 54.8 ppm) and shows the CH resonance at 92.9 ppm ($J = 175.8$ Hz).

Thus, monosubstituted alkynes with an electron-withdrawing substituent react with **1** to afford directly a cluster with the same structure as **3** in which the allylic fragment has the $C(CH_2R)CHCR$ formulation. This fragment results from the coupling of the carbyne $C(CH_2R)$ with a second molecule of alkyne. By analogy with the case of acetylene, we may presume that the carbyne ligand is formed in a first step by the reaction of the alkyne with **1** but the intermediate $[Fe_4(\mu_3\text{-}C(CH_2R))(CO)_{12}]^-$ has not been detected, even at lower temperature as in refluxing acetone. Perhaps the electronic properties of the R group facilitate the coupling with a second molecule of alkyne, making the carbyne intermediate too reactive to be isolated. Only one isomer is detected in these coupling reactions.

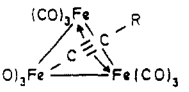

Figure 2. Proposed structure for complexes **6** (R = $(CH_3)_3C$) and **7** (R = C_3H_7).

B. Case Where R Is an Electron-Donating Group, $(CH_3)_3C$ or *n*-C_3H_7. Here again only one type of product has been isolated in the reaction of these two alkynes with **1**. The best yields have been obtained in refluxing ethyl acetate for R = $(CH_3)_3C$ and refluxing 3-pentanone for R = *n*-C_3H_7.

The infrared spectra of the two products **6** (R = $(CH_3)_3C$) and (**7**) (R = *n*-C_3H_7) in the ν(CO) stretching region are very similar and show the presence of only terminal carbonyl groups. Moreover, they closely resemble the infrared spectrum of the recently prepared $[Fe_3(\mu_3\text{-}C{\equiv}CCH_3)(CO)_9]^-$ (**8**) anion.[14] This hypothesis is confirmed by NMR data. Proton NMR spectra give evidence only of the resonances of the PPN cation and of the R group. The ^{13}C NMR spectrum, except the resonances due to the R group and the cation, shows two resonances in the 1:2 intensity ratio in the carbonyl region (216.8 and 217.8 ppm for **6** and 216.9 and 217.1 ppm for **7** and two resonances at 120.3 and 193.3 ppm for **6** and 104.8 and 186.3 ppm for **7**.

This agrees weil with the ^{13}C data for the anion **8** for which the resonances of carbonyl groups were observed with the same intensity ratio at 216.0 and 217.1 ppm and the resonance of the μ_3-bonded carbons of the triple bond at 99.5 and 184.7 ppm.[14] In this anion it has also been possible to attribute unambiguously the resonance at lower field to the carbon bonded to iron (C_α) and the other resonance to the C_β carbon of the triple bond, in good agreement with other authors' results.[15]

Finally, the chemical analysis confirms the $[PPN][Fe_3(CCR)(CO)_9]$ formulation and we propose for **6** and **7** the same structure as for **8** (Figure 2).

In summary, the terminal alkynes in which R is an alkyl group react with **1** to give a trinuclear cluster containing a μ_3-bonded acetylide group, RC≡C. Fragmentation of the cluster and C–H bond scission are observed in the reaction. The fate of the cluster fragment and of the hydrogen have not been determined but infrared spectra of the solution after isolation of **6** or **7** give evidence of unidentified carbonyl complexes.

Fluxional Behavior of Complexes 3 and 4. As already mentioned, ^1H and ^{13}C NMR data for complexes containing an allylic ligand (**3–5**) strongly suggest that these molecules are fluxional. This is particularly obvious from the ^{13}C resonance in the carbonyl region for which only a broad signal is observed at room temperature with no resonance observed in the bridging carbonyl region. This phenomenon has been more fully studied for complexes **3** and **4** by variable-temperature studies of the ^1H and ^{13}C NMR spectra.

The 250-MHz ^1H NMR spectrum of **3** at room temperature shows a broad resonance at 2.33 ppm for the CH_3 group, a broad doublet at 7.33 ppm ($J = 5$ Hz, C(13)H) and a very broad signal at 9.18 ppm attributed to the C(12)H group. On cooling to −100 °C, the 9.18 ppm resonance progressively sharpens to a doublet centered at 9.45 ppm ($J = 5$ Hz), and in a decoupling experiment it has been confirmed that it is coupling with the C(13)H proton. The 7.33 ppm resonance is only slightly affected by cooling,

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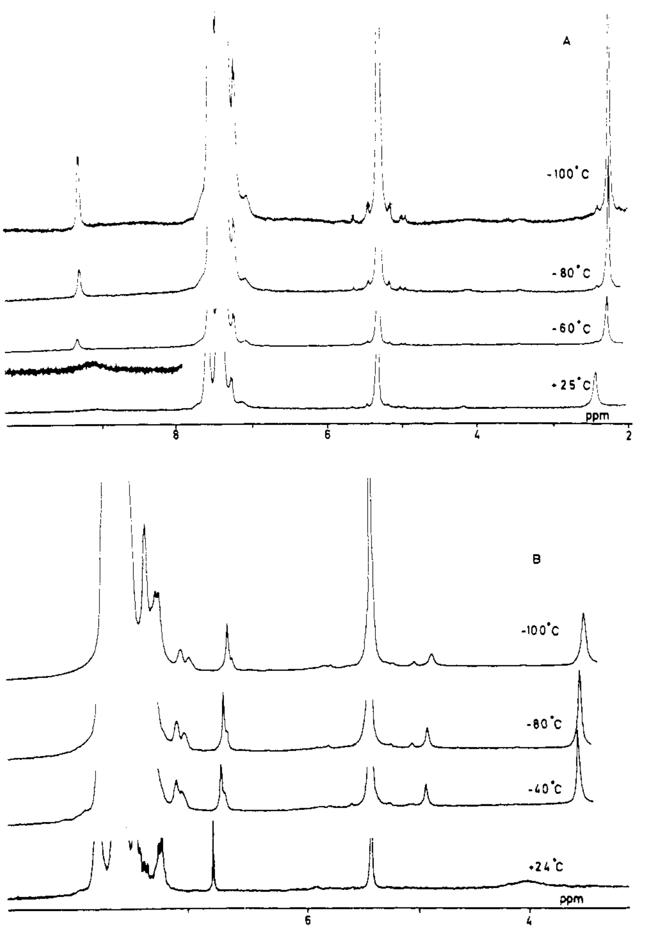

Figure 3. Variable-temperature ^1H NMR spectra of (A) complex 3 and (B) complex 4.

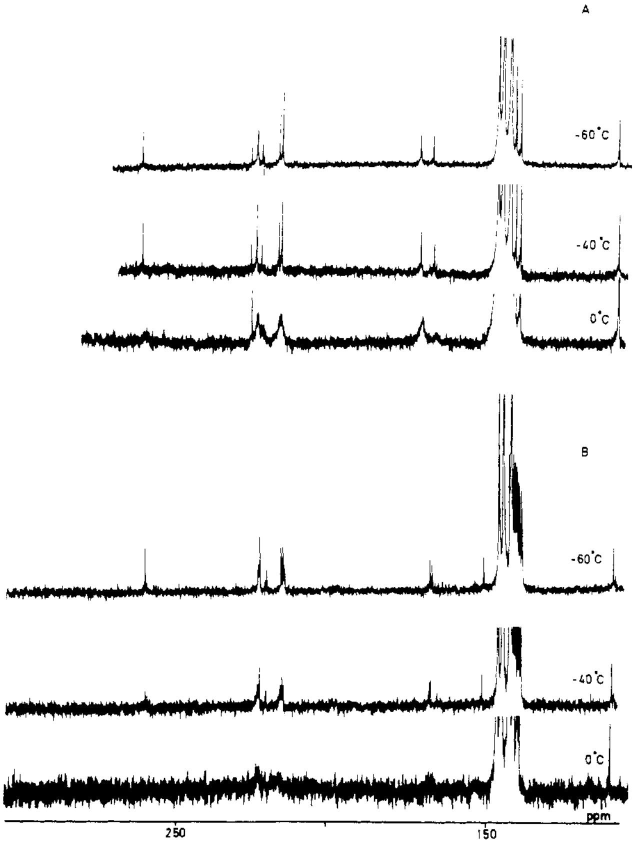

Figure 4. Variable-temperature $^{13}C\{^1H\}$ NMR spectra of (A) complex 3 and (B) complex 4.

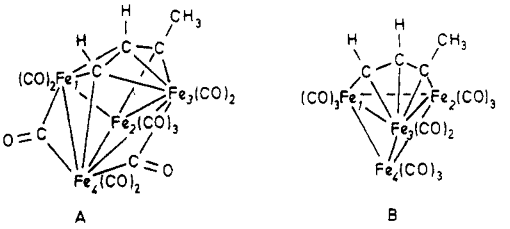

Figure 5. Two possible structures for the isomer of 3.

and the methyl resonances sharpens (Figure 3).

At room temperature the 250-MHz ^1H NMR spectrum of 4 gives evidence of a very broad signal centered at 4.00 ppm for the $CH_2(C_6H_5)$ protons and a sharp singlet at 6.68 ppm for the CH group. On cooling to −80 °C, the 4.00 ppm resonance progressively changes to two signals centered at 3.54 and 4.84 ppm in 3:1 relative ratio. During the same time the sharp singlet at 6.68 ppm is transformed into two singlets at 6.56 and 6.52 ppm in the same relative ratio (Figure 3).

While the variable-temperature ^1H NMR spectra of 3 are not very conclusive, the results obtained for 4 strongly suggest that complex 4 exists in two forms in equilibrium in solution.

The variable-temperature $^{13}\{^1H\}$ of 3 is more informative (Figure 4). On cooling to −60 °C, the 157.7 ppm resonance attributed to C(12) progressively changes to two nearly equal sharp resonances at 155.3 and 159.8 ppm, while the resonances at 92.5 (C(13)) and 36.2 ppm (C(15)) only sharpen upon cooling. In the CO resonance region, the room-temperature broad resonance is split at 0 °C into three broad resonances at 254.8, 216.3, and 208.7 ppm, the first being attributed to bridging carbonyl groups. At −40 °C further splitting occurs and resonances at 255.7, 216.0, 214.3, 208.5, and 207.4 ppm are observed. Cooling to −60 °C induces a broadening of the 216.0 ppm resonance, the other signals being unaffected. If we assign the intensity 2 to the 255.7 ppm resonance, the integrated intensities are 2, 4, 1, 2, and 3, moving upfield. The 218.4 ppm resonance attributed to C(14) remains sharp at all temperatures moving to 217.9 ppm at −60 °C.

A similar phenomenon is observed with 4 in the CO resonance region (Figure 4). At −60 °C resonances at 254.9, 215.6, 213.2, 208.4, 207.6, and 207.2 ppm are observed with the integrated intensities 2, 4, 1, 2, 2, and 1. The only difference is that the resonance at higher field for 3 of intensity 3 is split into two resonances of intensity 2 and 1, respectively. During the same time a broad band centered at 156.6 ppm splits into two resonances of nearly the same intensity at 157.3 and 156.4 ppm. By comparison with 3, these resonances can be attributed to the $C(C_6H_5)$ carbon of the allylic group. For the CH resonances two peaks are observed at −60 °C at 94.2 and 93.5 ppm, the first being the most intense, and two resonances are also detected for the $CH_2(C_6H_5)$ group at 57.7 and 56.4 ppm.

These ^{13}C NMR results firmly confirm the proton NMR data for 4; i.e., two species are in equilibrium in solution and show that the same phenomenon exists for 3. In particular, the ^{13}C NMR spectrum is very similar in the CO resonance region and the C(12) resonance gives rise to two signals at low temperature. Nevertheless, confirming the proton NMR data, the occurrence of two species is less apparent from the C(13) resonance and the CH_3 resonance for which only sharpenings of signals are observed upon cooling.

This information is not sufficient to establish the structure of the second isomer but two hypotheses are plausible. In the first (Figure 5A), the iron core butterfly structure would be preserved and the second isomer would

Table II. Summary of Crystal and Intensity Collection

compd	$[Fe_4(CO)_{11}CHCHCCH_3]$- $[N(P(C_6H_5)_3)_2]$
formula	$C_{51}H_{35}NO_{11}P_2Fe_4$
fw	1122.4
fw	1122.4
a, Å	23.014 (4)
b, Å	9.420 (1)
c, Å	22.166 (4)
β, deg	90.45 (1)
V, Å^3	4805.3
Z	4
F(000)	2280
D_{calcd}, g/cm^3	1.551
space group	C_{2h}^5—$P2_1/n$
radiation	Mo Kα from graphite monochromator (λ = 0.71069 Å)
linear abs coeff, cm^{-1}	μ = 13.1
temp, °C	20
receiving aperture, mm	4.0 × 4.0
takeoff angle, deg	4
scan mode	ω
scan range, deg	(0.75 + 0.35 tan θ)
2θ limits, deg	46

differ by the position of the CO bridges which would bridge Fe(1)–Fe(4) and Fe(3)–Fe(4) bonds. This type of isomerism has been found for the tetranuclear heterometallic cluster $(\eta$-$C_5H_5)NiRu_3(CO)_8(C_6H_9)$[8] but the isomers are not interconverting.

In the second hypothesis (Figure 5B), the iron core would be tetrahedral, the allylic ligand being μ_3-η^3-bonded to a triangle face. A same type of equilibrium between a butterfly and tetrahedral framework for a Fe_4 core has been detected for 1.[16] This structure would be fully consistent with a 60-valence-electron cluster.

Experimental Section

All reactions were performed under nitrogen atmosphere. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer. ^1H and ^{13}C NMR spectra were obtained with a Bruker WM 250 instrument. $[PPN][HFe_4(CO)_{13}]$ (1) was prepared by protonation of $[Fe(C_5H_5N)_6][Fe_4(CO)_{13}]$[17] with chlorohydric acid and cation exchange with PPNCl (Aldrich).

Preparation of $[PPN][Fe_4(\mu_3\text{-}CCH_3)(CO)_{12}]$ (2). 1 (1 g) was dissolved in ethyl acetate (30 mL), and the solution was saturated with acetylene at room temperature. Then the solution was heated to reflux under a slow stream of acetylene for 1.5 h in a fume hood. After being cooled, the solution was evaporated to dryness and the residue was dissolved in dichloromethane (5 mL). Methanol (20 mL) then was added and the solution cooled to −20 °C yielding 0.6 g of 2 as black crystals (60% yield): IR (CH_2Cl_2) ν(CO) 2050 (w), 1982 (vs), 1953 (m), 1947 (m) cm^{-1}; ^1H NMR (CD_2Cl_2) 7.52 (PPN), 4.16 ppm (CH_3); ^{13}C NMR (CD_2Cl_2) 359.6 (CCH_3), 218.6, 214.3 (CO), 43.9 ppm (CH_3). Anal. Calcd for $C_{50}H_{33}NO_{12}P_2Fe_4$: C, 53.33; H, 2.93. Found: C, 53.89; H, 2.30.

Preparation of $[PPN][Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_3)CHCH)(CO)_{11}]$ (3). 1 (1 g) was dissolved in 3-pentanone (30 mL), and the solution was saturated with acetylene at room temperature. Then the solution was refluxed for 4 h under a slow stream of acetylene. The solution then was evaporated to dryness, and the residue was dissolved in the minimum amount of dichloromethane. Adding methanol (20 mL) and cooling to −20 °C gave 0.4 g of 3 as black crystals (40% yield): IR (CH_2Cl_2) ν(CO) 2037 (m), 1976 (s), 1927 (m), 1795 (m, br) cm^{-1}; ^1H NMR (CD_2Cl_2) 9.27 (br), 7.53 (PPN), 2.47 ppm (br, CH_3). Anal. Calcd for $C_{51}H_{35}NO_{11}P_2Fe_4$: C, 54.49; H, 3.11. Found: C, 53.57; H, 2.96.[25]

Preparation of $[PPN][Fe_4(\mu_4\text{-}\eta^3\text{-}C(CH_2(C_6H_5))CHC(C_6H_5))(CO)_{11}]$ (4). To 1 (1 g) dissolved in ethyl acetate (30 mL) was added phenylacetylene (0.25 mL). The solution was refluxed for 3.5 h. The solution then was evaporated to dryness and the residue dissolved in dichloromethane (5 mL). Adding methanol (20 mL) and cooling to −20 °C gave 0.6 g of 4 (51% yield) as brown crystals: IR (CH_2Cl_2) ν(CO) 2035 (m), 1975 (s), 1927 (m), 1792 (m, br) cm^{-1}; ^1H NMR (CD_2Cl_2) 7.52 (PPN + C_6H_5), 6.72 (CH),

Table III. Fractional Atomic Coordinates with Esd's in Parentheses

atom	*x/a*	*y/b*	*z/c*
Fe(1)	0.43066 (2)	0.43178 (6)	0.28923 (3)
Fe(2)	0.51597 (2)	0.59282 (6)	0.27042 (3)
Fe(3)	0.48944 (3)	0.54753 (6)	0.16190 (3)
Fe(4)	0.51903 (2)	0.32880 (6)	0.22960 (3)
C(1)	0.4843 (2)	0.4983 (4)	0.3466 (2)
C(2)	0.5533 (2)	0.6522 (5)	0.1914 (2)
O(2)	0.5940 (1)	0.7176 (4)	0.1774 (2)
O(3)	0.3274 (2)	0.5355 (4)	0.3504 (2)
C(4)	0.4187 (2)	0.2549 (5)	0.3168 (2)
C(5)	0.5158 (2)	0.7678 (6)	0.3020 (2)
O(5)	0.5193 (2)	0.8781 (4)	0.3222 (2)
C(6)	0.5871 (2)	0.5615 (5)	0.2993 (2)
O(6)	0.6322 (2)	0.5457 (4)	0.3200 (2)
C(7)	0.5223 (2)	0.4645 (5)	0.1000 (2)
O(7)	0.5440 (2)	0.4173 (4)	0.0578 (2)
C(8)	0.4641 (2)	0.6796 (6)	0.1129 (2)
O(8)	0.4486 (2)	0.7650 (5)	0.0793 (2)
C(9)	0.5130 (2)	0.1534 (6)	0.1970 (2)
O(9)	0.5098 (2)	0.434 (4)	0.1775 (2)
C(10)	0.5898 (2)	0.3556 (5)	0.2004 (2)
O(10)	0.6360 (1)	0.3683 (4)	0.1822 (2)
C(11)	0.5467 (2)	0.2614 (5)	0.3007 (2)
O(11)	0.5649 (2)	0.2136 (4)	0.3444 (2)
C(12)	0.4413 (2)	0.3705 (5)	0.1975 (2)
H(C12)	0.421 (2)	0.300 (3)	0.175 (2)
C(13)	0.4080 (2)	0.4977 (5)	0.2011 (2)
H(C13)	0.3740 (11)	0.515 (5)	0.178 (2)
C(14)	0.4362 (2)	0.6124 (5)	0.2334 (2)
C(15)	0.4012 (2)	0.7509 (5)	0.2380 (2)
H1(C15)	0.4233 (2)	0.8190 (5)	0.2599 (2)
H2(C15)	0.3658 (2)	0.7332 (5)	0.2585 (2)
H3(C15)	0.3930 (2)	0.7863 (5)	0.1988 (2)
N	0.2733 (1)	0.5136 (3)	−0.0127 (1)
P(1)	0.23786 (4)	0.60885 (11)	−0.05849 (4)
C(16)	0.16556 (11)	0.6547 (2)	−0.03469 (11)
C(17)	0.11871 (11)	0.5705 (2)	−0.05117 (11)
C(18)	0.06427 (11)	0.5975 (2)	−0.02757 (11)
C(19)	0.05667 (11)	0.7086 (2)	0.1250 (11)
C(20)	0.10352 (11)	0.7928 (2)	0.02898 (11)
C(21)	0.15796 (11)	0.7658 (2)	0.00539 (11)
C(22)	0.27813 (11)	0.7692 (3)	−0.06863 (12)
C(23)	0.33521 (11)	0.7771 (3)	−0.04865 (12)
C(24)	0.36782 (11)	0.8976 (3)	−0.05995 (12)
C(25)	0.34334 (11)	1.0103 (3)	−0.09122 (12)
C(26)	0.28625 (11)	1.0024 (3)	−0.11120 (12)
C(27)	0.25365 (11)	0.8819 (3)	−0.09990 (12)
C(28)	0.23084 (10)	0.5234 (3)	−0.13060 (11)
C(29)	0.26672 (10)	0.4096 (3)	−0.14356 (11)
C(30)	0.26109 (10)	0.3392 (3)	−0.19816 (11)
C(31)	0.21959 (10)	0.3827 (3)	−0.23979 (11)
C(32)	0.18371 (10)	0.4966 (3)	−0.22683 (11)
C(33)	0.18934 (10)	0.5669 (3)	−0.17223 (11)
P(2)	0.25744 (4)	0.41240 (11)	0.04201 (5)
C(34)	0.25083 (12)	0.5098 (2)	0.11195 (12)
C(35)	0.23104 (12)	0.4445 (2)	0.16385 (12)
C(36)	0.22155 (12)	0.5240 (2)	0.21541 (12)
C(37)	0.23184 (12)	0.6688 (2)	0.21506 (12)
C(38)	0.25163 (12)	0.7342 (2)	0.16316 (12)
C(39)	0.26112 (12)	0.6547 (2)	0.11160 (12)
C(40)	0.31620 (10)	0.2884 (3)	0.0508 (1)
C(41)	0.30968 (10)	0.1649 (3)	0.0839 (1)
C(42)	0.35626 (10)	0.0733 (3)	0.0914 (1)
C(43)	0.40938 (10)	0.1053 (3)	0.0658 (1)
C(44)	0.41591 (10)	0.2289 (3)	0.0327 (1)
C(45)	0.36932 (10)	0.3204 (3)	0.0252 (1)
C(46)	0.19125 (11)	0.3129 (3)	0.03148 (10)
C(47)	0.14098 (11)	0.3382 (3)	0.06369 (10)
C(48)	0.09081 (11)	0.2630 (3)	0.05035 (10)
C(49)	0.09091 (11)	0.1623 (3)	0.00479 (10)
C(50)	0.14118 (11)	0.1370 (3)	−0.02742 (10)
C(51)	0.19135 (11)	0.2123 (3)	−0.01408 (10)

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4.06 ppm (br, CH_2). Anal. Calcd for $C_{63}H_{43}NO_{11}P_2Fe_4$: C, 59.33; H, 3.40. Found: C, 59.15; H, 3.52.

Preparation of [PPN][$Fe_4(\mu_4$-η^3-$C(CH_2(C(O)OCH_3))CHC(C(O)OCH_3))(CO)_{11}$] (5). To 1 (1 g) dissolved in 3-pentanone (30 mL) was added methyl propiolate (0.18 mL), and the solution was refluxed for 1.5 h. The solution then was evaporated to dryness, and the residue was dissolved in methanol (10 mL). Cooling to −20 °C gave 0.4 g of **5** (36% yield) as dark brown crystals: IR (CH_2Cl_2) ν(CO) 2037 (m), 1983 (s), 1952 (m), 1938 (m), 1920 (m), 1793 (m, br) cm^{-1}; ^1H NMR ($C(CD_3)_2CO$) 7.72 (PPN), 4.29 (br, CH_2), 2.85, 3.72 ppm (OCH_3). Anal. Calcd for $C_{55}H_{39}NO_{15}P_2Fe_4$: C, 53.31; H, 3.17. Found: C, 52.10; H, 3.21.[25]

Preparation of [PPN][$Fe_3(\mu_3$-$C{\equiv}CC(CH_3)_3)(CO)_9$] (6). To 1 (1 g) dissolved in 30 mL of ethyl acetate was added *tert*-butylacetylene (0.25 mL), and the solution was refluxed for 2 h. The solution was evaporated to dryness, and the residue was dissolved in a small amount of dichloromethane. Adding methanol (10 mL) and cooling to −20 °C gave 0.3 g of **6** (35% yield) as dark red crystals: IR (CH_2Cl_2) ν(CO) 2042 (m), 1983 (s), 1973 (s), 1955 (s), 1928 (m) cm^{-1}; ^1H NMR ($(CD_3)_2CO$) 7.70 (PPN), 1.61 ppm ($C(CH_3)_3$); ^{13}C NMR (CD_2Cl_2) 217.7, 216.8 (CO), 193.3 (FeC), 120.3 ($C{\equiv}C$–), 33.9 ppm (CH_3). Anal. Calcd for $C_{51}H_{39}NO_9P_2Fe_3$: C, 58.94; H, 3.78. Found: C, 58.2; H, 3.76.[25]

Preparation of [PPN][$Fe_3(\mu_3$-$C{\equiv}C(CH_2)_2CH_3)(CO)_9$] (7). To 1 (1 g) dissolved in 3-pentanone was added 1-pentyne (0.2 mL), and the solution was refluxed for 2.5 h. The solution was evaporated to dryness, and the residue was dissolved in methanol (10 mL) and cooled to −20 °C giving 0.35 g of 7 (32% yield) as dark red crystals: IR (CH_2Cl_2) ν(CO) 2042 (m), 1983 (s), 1975 (s), 1953 (s), 1938 (m) cm^{-1}; ^1H NMR ($(CD_3)_2CO$) 7.72 (PPN), 3.07 (t, J = 6.9 Hz, CH_2), 1.95 (complex multiplet, CH_2), 1.23 ppm (t, J = 7.1 Hz) (CH_3); ^{13}C NMR (CD_2Cl_2) 217.1, 216.9 (CO), 186.3 (FeC), 104.8 ($C{\equiv}C$–), 34.5 (t, J = 131 Hz, CH_2), 26.3 (t, J = 126 Hz), 13.7 ppm (q, J = 126 Hz). Anal. Calcd for $C_{50}H_{37}NO_9P_2Fe_3$: C, 58.7; H, 3.64. Found: C, 57.13; H, 3.64.[25]

Collection and Reduction of X-ray Data. Crystals belong to the monoclinic system, space group $P2_1/n$. The selected crystal was a black parallelepiped of 0.440 × 0.325 × 0.424 mm dimensions along direct axes. It was sealed on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. A summary of crystal and intensity collection data are given in Table II. A total of 6193 independent reflections were recorded to a 2θ(Mo) maximum of 46° by procedures described elsewhere.[18] Intensity standards, recorded periodically, showed only random, statistical fluctuations. Data reduction was then performed,[19] and absorption corrections[20] were made on 4539 reflections having $F_o^2 > 4\sigma(F_o^2)$ (μ = 13.1 cm^{-1}, calculated transmission range 0.58–0.69).

Structure Solution and Refinement. The structure was solved[21] by the heavy-atom method. Successive difference Fourier maps and least-squares refinement cycles processes revealed the positions of all nonhydrogen atoms.

All non-hydrogen atoms were refined anisotropically, except phenyl rings which were refined as isotropic rigid groups (C–C = 1.385 Å). Hydrogen atoms were located on a difference Fourier map. Methyl and phenyl hydrogen atoms were introduced in calculations in constrained geometry (C–H = 0.95 Å). Hydrogens bonded to C(12) and C(13) atoms were only imposed to stay at 0.95 Å from their atom of attachment. All hydrogens were assigned an isotropic temperature factor, U_H = 0.06 Å^2, kept fixed.

The atomic scattering factors used were those proposed by Cromer and Waber[22] with anomalous dispersion effects.[23] Scattering factors for the hydrogen atoms were taken from Stewart et al.[24]

The final full-matrix least-squares refinement converged to $R = \sum||F_o - F_c||/\sum|F_o| = 0.026$ and $R_w = \sum_w[(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.030$ with unit weights. The error in an observation of unit weight was $S = [\sum w(|F_o] - |F_c|)^2/(n - m)]^{1/2} = 1.8$ with n = 4539 observations and m = 376 variables. An analysis of variance showed no unusual trends. In the last cycle of refinement the shifts for all parameters were less than 0.04 σ. Maximum height in the final difference Fourier map was 0.3 e/Å^3.

All calculations were performed on a VAX-11/730 DEC computer.

The final fraction atomic coordinates are listed in Table III.

Registry No. **1**, 79795-91-8; **2**, 82865-65-4; **3**, 98705-13-6; **4**, 98705-15-8; **5**, 98705-17-0; **6**, 98705-19-2; **7**, 98705-21-6; acetylene, 74-86-2; phenylacetylene, 536-74-3; methyl propiolate, 922-67-8; *tert*-butylacetylene, 917-92-0; 1-pentyne, 627-19-0.

Supplementary Material Available: Tables of thermal parameters, hydrogen parameters, structure factors, and least-squares plane equations (25 pages). Ordering information is given on any current masthead page.

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[25] Systematic low carbon analyses were obtained for most of these samples, perhaps due to carbide formation. The values quoted are the best obtained on several samples from different syntheses.