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Study of Ethylidyne–Alkyne Coupling on the Trinuclear Iron Cluster, $Fe_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}CCH_3)$

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Received February 11, 1987

The reaction of $HFe_3(\mu\text{-}CCH_3)(CO)_{10}$ with alkynes is highly dependent on the nature of the alkyne. With monosubstituted alkynes, $RC{\equiv}CH$, three types of complexes have been isolated from refluxing hexane: $Fe_3(\mu_3\text{-}\eta^2\text{-}\perp\text{-}CH_3CCCH_2R)(CO)_9$ (R = H (**2**) or $C(CH_3)_3$ (**5**)), $Fe_3(\mu^3\text{-}CCH_3)(\mu_3\text{-}CCH_2R)(CO)_9$ ($R = C(CH_3)_3$) (**6**), and $HFe_3[\mu_3\text{-}\eta^3\text{-}C(CH_3)C(R)CH](CO)_9$ ($R = C_6H_5$) (**8**). It has been shown that complexes **5** and **6** cannot be interconverted under the reaction conditions used for their synthesis and a mechanism for their formation is proposed. Complex **8** with $R = C_6H_5$ shows an interesting thermal evolution leading to $Fe_3(CO)_6(\mu\text{-}CO)_2[CHC(C_2H_5)C(CH)_4C]$ (**9**) through an $Fe_2(CO)_6[CHC(C_2H_5)C(CH)_4C][\mu\text{-}Fe(CO)_3]$ (**10**) intermediate, which implies the breaking of two Fe–Fe bonds and the formation of one Fe–Fe bond facilitated by coordination of a $Fe(CO)_3$ fragment to the phenyl ring. The ferracyclopentadiene ring of these two compounds results from the hydrogenation of the CCH_3 group, the hydrogen atom being provided by the orthometalation of the phenyl ring and hydride ligand. In the case of RCCR alkynes, fragmentation of the cluster is observed and two types of dinuclear complexes are isolated: $Fe_2(CO)_6(CRCRCCH_3CRCRH)$ ($R = CH_3$ or C_6H_5) and $Fe_2(CO)_6(CCH_3CRCRH)$ ($R = C_6H_5$).

Introduction

Pursuing our investigation about the reactivity of alkylidyne ligands bonded to trinuclear iron clusters,[1] we have now extended our study to the case when a hydride ligand is present in the cluster frame as well. The readily available $HFe_3(CO)_{10}(\mu\text{-}CCH_3)$, **1**,[2] has been selected for this purpose. This should lead to interesting comparisons with the chemistry of alkylidyne ligands bonded to trinuclear ruthenium clusters, $HRu_3(\mu\text{-}CX)(CO)_{10}$ or $H_3Ru(\mu_3\text{-}CX)(CO)_9$, reported by Keister et al.[3]

Here we describe the results of the study of the reactivity of $HFe_3(\mu\text{-}CCH_3)(CO)_{10}$ toward alkynes, $RC{\equiv}CR'$ ($R = R' = H$, CH_3, or C_6H_5; $R = H$, $R' = (CH_3)_3C$, C_6H_5), which shows that, contrary to the case of ruthenium, the products formed are highly alkyne-dependent.

Results and Discussion

Reactivity of 1 toward Acetylene. **1** reacts with acetylene in refluxing hexane to give several products, which have been separated by chromatography. Except for $Fe_3(CO)_{10}(\mu\text{-}CCH_2)$ which is a product of the thermal rearrangement of **1**,[2] only one product, **2**, was obtained in sufficient quantity to be isolated and identified. Mass spectrometry and chemical analysis are consistent with the $Fe_3(CO)_9(CH_3C)_2$ formulation and the proton NMR spectra show two singlets of the same intensity for the CH_3 groups. This observation is consistent with **2** being assumed to belong to the family of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}RC{\equiv}CR)$ compounds.[4] At this point, a question remained open about the origin of the second CCH_3 fragment, as it could equally come from a fragmentation of a CCH_3 of the starting material or from the reaction of acetylene with the hydride ligand on the trinuclear frame, as observed with the $[HFe_3(CO)_{11}]^-$ cluster anion.[2]

To solve this problem, we have used a cluster with a slightly different alkylidyne ligand, $HFe(\mu\text{-}CCH_2Ph)(CO)_{10}$, **3**.[5] Under the same conditions as for **1**, **3** reacts with acetylene to give a new product, **4**, which shows a similar infrared spectrum to that of **2** in the ν(CO) stretching region (Table I). Moreover, the mass spectrum and chemical analysis are consistent with the $Fe_3(CO)_9(CH_3CCCH_2Ph)$ formulation. In the proton NMR spectrum, except for the phenyl resonances, four singlets are observed, the intensities of which are consistent with the occurrence of two isomers of the $C_6H_5CH_2CCCH_3$ group in 65% (4.93 ppm, 1.31 ppm singlets) and 35% (3.55 ppm, 2.84 ppm singlets) ratio. These data support a $\mu_3\text{-}\eta^2\text{-}\perp$ mode of bonding of the $C_6H_5CH_2CCCH_3$ fragment and we propose for the two isomers of **4** the structures shown in Figure 1, but it is difficult on the sole basis of proton NMR data to attribute the structure of the main isomer to A or B form.

The formation of **4** starting from **3** gives evidence that the CCH_3 fragment is provided by the interaction of acetylene with the hydride ligand on the trinuclear iron unit.

To get insight into the reaction mechanism, we have studied the reaction of **1** with the more bulky alkyne 3,3-dimethyl-1-butyne hoping to trap some intermediate.

Reactivity of 1 toward 3,3-Dimethyl-1-butyne. Two main products, **5** and **6**, have been isolated by chromatography after the reaction in refluxing hexane, in 8% and 25% yield, respectively. Infrared and mass spectrometry of **5** are consistent with the $Fe_3(CO)_9[\mu_3\text{-}\eta^2\text{-}\perp\text{-}(CH_3CCCH_2C(CH_3)_3]$ formulation indicative of a similar structure to that of **2** and **4**. Contrary to **4**, only one isomer has been detected in this case by proton NMR (Table I).

The mass spectrometry of the second product, **6**, shows the same parent ion as **5**, with the successive loss of nine CO, but the infrared spectrum (Table I) in the ν(CO) stretching region is very different from that of **5** and closely resembles that of $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$.[2] The presence of the CH_3 and $CH_2C(CH_3)_3$ groups is confirmed

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Table I. Spectroscopic Data for the Isolated Complexes

compounds	IR (ν(CO)),[a] cm^{-1}	^{1}H NMR,[b] ppm	^{13}C NMR,[bc] ppm
$Fe_3(CO)_9(CH_3CCCH_3)$ (**2**)	2080 (m), 2032, (s), 2023 (s), 2007 (m), 1997 (m), 1992 (m), 1972 (w)	CH_3: 1.15, 3.34	
$Fe_3(CO)_9(CH_3CCCH_2Ph)$ (**4**)	2078 (m), 2032 (s), 2024 (s), 2007 (m), 1994 (m), 1973 (w)	C_6H_5: 7.44, 7.23, 6.71 CH_3: 3.55 CH_2: 2.84 CH_2: 4.93 CH_3: 1.31	
$Fe_3(CO)_9(CH_3CCCH_2\text{-}t\text{-}Bu)$ (**5**)	2070 (m), 2036 (s), 2022 (s), 2010 (s), 1996 (m), 1992 (m), 1967 (w)	CH_3: 3.53 CH_2: 1.29 $C(CH_3)_3$: 0.67	
$Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}CCH_2\text{-}t\text{-}Bu)$ (**6**)	2080 (w), 2040 (s), 2033 (s), 2015 (m), 2005 (sh), 1989 (m)	CH_3: 4.71 CH_2: 4.98 $C(CH_3)_3$: 1.43	μ_3-CR: 350.3, 347.4 CO: 210.6 CH_2: 72.4 (t, J_{CH} = 125 Hz) CCH_3: 48.7 (qt, J_{CH} = 128 Hz) $C(CH_3)_3$: 35.6 $C(CH_3)_3$: 30.3 (qt, J_{CH} = 127 Hz)
$Fe_3(CO)_{10}(CH_3CCCH_2\text{-}t\text{-}Bu)$ (**7**)	2087 (m), 2044 (s), 2029 (s), 2001 (m), 1977 (m), 1962 (m), 1937 (w and br)		
$HFe_3(CO)_9[C(CH_3)C(Ph)CH]$ (**8**)	2088 (m), 2053 (s), 2029 (s), 2018 (s), 2009 (m), 2001 (m), 1987 (m), 1911 (w and br)	CH: 8.55 C_6H_5: 7.3 (m) CH_3: 2.63 H: −28.78	CO: 213.2, 212.0, 211.5 CCH_3: 195.5 CH: 173.5 (d, J_{CH} = 154 Hz) CPh: 140.5 CH_3: 36.0 (qt, J_{CH} = 129 Hz)
$Fe_3(CO)_8[C(H)C(C_2H_5)CC(H)C(H)C(H)C(H)Cl$ (**9**)	2059 (m), 2019 (s), 1994 (s), 1978 (s), 1876 (m), 1866 (m)	H^1: 8.56 (m)[d] H^2: 7.34 (m) H^3,H^4: 6.6 (m) CH_2: 1.29 CH: 2.61 CH_3: 1.65 (t, J = 7.6 Hz)	
$Fe_3(CO)_9[C(H)C(C_2H_5)CC(H)C(H)C(H)C(H)C]$ (**10**)	2074 (m), 2054 (s), 2027 (s), 2008 (s), 1997 (s), 1987 (s), 1952 (w and br)	H^1: 6.72 (m)[d] CH: 6.55 H^4: 6.50 (m) H^3: 3.86 (dd) H^2: 3.46 (dd) CH_2: 2.33 (AB dd) CH_3: 1.23 (t)	
$Fe_2(CO)_6[HC(Ph)C(Ph)C(CH_3)C(Ph)C(Ph)]$ (**11**)	2059 (m), 2021 (s), 2001 (m), 1986 (s), 1974 (w), 1965 (w)	C_6H_5: 7.39 (m) CH: 3.84 CH_3: 2.17	
$Fe_2(CO)_6[HC(Ph)C(Ph)C(CH_3)]$ (**12**)	2060 (m), 2019 (s), 1992 (s), 1977 (m), 1965 (w), 1959 (w)	9 H phenyl: 7.15 (m) 1 H phenyl: 5.12 (m) CH: 4.49 CH_3: 2.98	
$Fe_2(CO)_6[C(CH_3)]_5H$ (**13**)	2055 (m), 2012 (s), 1983 (m), 1977 (m), 1962 (w and br)	CH_3: 2.67, 2.11, 1.94, 1.51 CH_3: 1.45 (d, J = 6.3 Hz) CH: 2.03 (qt, J = 6.3 Hz)	

[a] In hexane solution. [b] In CD_2Cl_2. [c] Except phenyl resonances. [d] For coupling constants, see text.

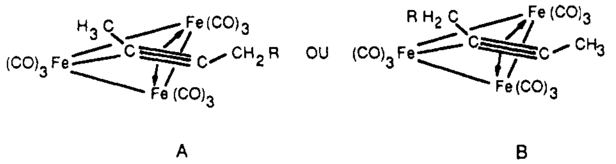

Figure 1. The two possible isomers for the $Fe_3(CO)_9(CH_3CCH_2R)$ complexes.

by proton NMR, and the ^{13}C NMR is consistent with the $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}CCH_2C(CH_3)_3)$ formulation: two signals characteristic of the carbon of an alkylidyne ligand's μ_3-bond are detected at 347.4 and 350.3 ppm.

To summarize, two isomers have been isolated in this reaction: one with two alkylidyne fragments μ_3-bonded, **6**, and one with an alkyne ligand, **5**, which results from the coupling of the two alkylidyne ligands.

As we[1c] and others[6-8] have shown that the interconversion between the dialkylidyne and the related alkyne complexes may be a facile reaction, we have checked if the two isomers **5** and **6** could be in equilibrium under the reaction conditions used for their synthesis. Thus, we have heated **5** in refluxing hexane but no conversion into **6** has been observed and **5** was recovered after this reaction.

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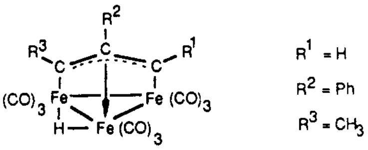


Figure 2. Structure of complex 8.

We also suspected the formation of $Fe^3(CO)_{10}[\mu_3-\eta^2-CH_3CCCH_2C(CH_3)_3]$, which could give 6 by decarbonylation, as observed for $Fe_3(CO)_{10}(\mu_3-\eta^2-CH_3CCOC_2H_5)$.[1c] To check this hypothesis, a 40-atm pressure of carbon monoxide was applied to 5. Indeed, we observed the formation of a new complex, 7, whose infrared spectrum in the ν(CO) stretching region (Table I) suggests, by comparison with that of $Fe_3(CO)_{10}(\mu_3-\eta^2-CH_3CCOC_2H_5)$, the $Fe_3(CO)_{10}[\mu_3-\eta^2-CH_3CCCH_2C(CH_3)_3]$ formulation. Nevertheless, 7 rapidly reverted to 5 at atmospheric pressure without any trace of 6 being detected.

Both results suggest that 5 and 6 are obtained through independent pathways, and, for further confirmation, we submitted 6 to reaction with carbon monoxide. Contrary to the case of $Fe_3(CO)_9(\mu_3-CCH_3)(\mu_3-COC_2H_5)$, 6 remains unchanged even under a 40-atm pressure of carbon monoxide.

To summarize, the study of the reactivity of 3,3-dimethylbutyne toward 1 has not allowed the observation of intermediates in the formation of complexes of type 5, but it has shown that the reaction is highly alkyne-dependent, and for this reason we have extended our study to the case of another monosubstituted alkyne, viz. phenylacetylene.

Reactivity of 1 toward Phenylacetylene. In refluxing hexane, 1 reacts with phenylacetylene to give only one new product, 8, which could be neither purified, as it decomposes on the chromatography column, nor crystallized. Nevertheless, it has been identified by mass spectrometry and spectroscopic data (Table I) which show that the sole impurity in the reaction mixture is 1. The mass spectrum of 8 shows a parent ion with m/z 550 and the successive loss of nine carbonyl groups. The proton NMR spectrum indicates the presence of one phenyl, one methyl, one hydrogen group, and one hydride ligand. Both observations agree with the $HFe_3(CO)_9(CCH_3CHCPh)$ formulation. Furthermore, the ^{13}C NMR spectrum shows the disappearance of the CCH_3 resonance in 1 and the presence of three new resonances at 195.5, 173.5, and 140.5, ppm attributed to the CCH_3, CH, and CPh carbons, respectively. All these data are consistent with the structure shown in Figure 2 for 8, a type of complex generally observed during the reaction of $H_3Ru_3(\mu_3-CX)(CO)_9$ or $HRu_3(\mu_3-CX)(CO)_{10}$ compounds with alkynes.[3b] Moreover, the comparison of chemical shifts in ^1H NMR with those of $HRu_3(CO)_9(\mu_3-\eta^3-CXCRCH)$ complexes allows us to attribute the R_1, R_2, and R_3 position to the H, Ph, and CH_3 group, respectively.

In an attempt to improve the synthesis of 8, we have run the reaction at higher temperature, and we have observed that, in refluxing methylcyclohexane, a new compound, 9, was formed, which is different from 8.

This green compound shows a parent ion in the mass spectrum at m/z 522 with the successive loss of eight carbonyl groups, which is consistent with the $Fe_3(CO)_8(C_{10}H_{10})$ formulation. The infrared spectrum in the ν(CO) stretching region (Table I) closely resembles the infrared spectrum of $Fe_3(CO)_6(\mu-CO)_2(RCCR)_2$ complexes,[1b] including two absorptions observed in the bridging carbonyl region. The true nature of the $Fe(RCCR)_2$ cycle has been inferred from proton NMR data (Table I). These data give evidence of the presence of four aromatic hydrogen atoms, one ethyl group, and one CH group. The ethyl group is presumably provided by the hydrogenation of the CCH_3 group, while the chemical shift of the CH group suggests that it is directly bonded to the iron atom.[1b] All these data are consistent with the ferracyclopentadiene ring shown in Figure 3. Moreover, decoupling experiments have allowed us to assign all the coupling constants (J_{1-2} = 8.9 Hz; J_{1-3} = 1.2 Hz; J_{1-4} = 1.2 Hz; J_{2-3} = 6 Hz; J_{2-4} = 2 Hz; J_{3-4} = 9 Hz) and the chemical shifts for the four aromatic protons.

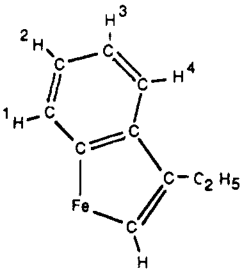


Figure 3. Structure of the ferracyclopentadiene ring in 9.

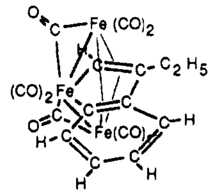


Figure 4. Structure of complex 9.

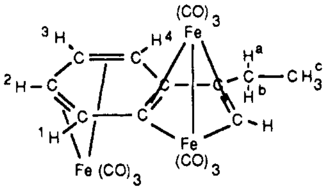


Figure 5. Structure of complex 10.

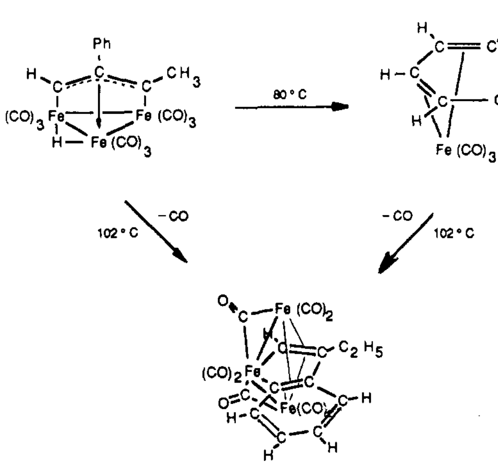
The structure proposed for complex 9 appears in Figure 4. The organic fragment of the ferracyclopentadienyl ring results from the intramolecular rearrangement of the allylic fragment of 8 by orthometalation of the phenyl ring and hydrogenation of the CCH_3 group by the hydrogen liberated by the orthometalation and the hydride ligand of 8 (we have checked that 9 is also obtained by thermal rearrangement of 8).

To get insight into this unusual intramolecular rearrangement of a dimetalloallylic fragment, we have run an experiment at lower temperature (80 °C) and indeed a new compound, 10, is formed. The parent ion in the mass spectrum of 10 is detected at m/z 550 with the successive loss of nine carbonyl groups, which is consistent with the $Fe_3(CO)_9(C_{10}H_{10})$ formulation.

So, it appears that 10 is an isomer of 8. Its infrared spectrum in the ν(CO) stretching region gives only evidence of terminal carbonyl groups, while the proton NMR spectrum shows the presence of a CH resonance at low field, an ethyl group, and four CH resonances in an area characteristic of olefinic hydrogens (Table I). The latter results suggest that the organic fragment in 10 is the same as in 9 but show that the mode of bonding to iron centers is not the same.

The true nature of 10 has been determined by comparison of spectroscopic data with data published for 1,1,1-tricarbonylferraindene-π-bis(tricarbonyl)iron, one of the products of the photochemical reaction of o-bromo-

Scheme I



styrene with pentacarbonyl iron,[9] and we propose the same type of structure as shown in Figure 5. It can be described as a ferrole-type structure with a third $Fe(CO)_3$ group π-bonded to the two C=C bonds of the aromatic cycle that is not engaged in the ferracyclopentadienyl ring. Homo decoupling experiments have allowed us to attribute all coupling constants and chemical shifts (J_{ab} = 14.5 Hz; J_{ac} = 7.4 Hz; J_{bc} = 7.6 Hz; J_{12} = 6.2 Hz; J_{13} = J_{24} = 1.6 Hz; J_{23} = 4.4 Hz; J_{34} = 6.3 Hz).

The fact that **10** was an intermediate in the formation of **9** has been checked and indeed, **10** generates **9** in refluxing methylcyclohexane. All these observations are summarized in Scheme I.

It has to be pointed out that the transformation **8** → **10** → **9** implies the breaking of two metal–metal bonds, the orthometalation of the phenyl ring, and the hydrogenation of the CCH_3 fragment to give a ferracyclopentadiene ring (**8** → **10**) and the formation of one metal–metal bond (**10** → **9**), the aromatic cycle driving these changes. A similar type of phenomenon (metal–metal bond breaking and bond forming assisted by an organic bridge) has been encountered in the trinuclear ferracyclobutene complex, $Fe_3(CO)_8[Ph_2PC_4(CF_3)_2](PPh_2)$.[10]

Mechanism of the Reaction of Acetylene and Monosubstituted Alkynes with 1. In the three experiments with the three RC≡CH alkynes used, three types of complexes have been isolated:

(i) With R = H, $C(CH_3)_3$, the compounds $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}CH_3CCCH_2R)$ are formed.

(ii) With R = $C(CH_3)_3$, the isomeric compound $Fe_3(CO)_9(\mu_3\text{-}CCH_3)[\mu_3\text{-}CCH_2C(CH_3)_3]$ is the main product of the reaction. Furthermore, we have shown that the interconversion of the two isomers is not possible in the conditions of the reaction, which suggests that they are formed through two independent pathways.

(iii) With R = C_6H_5, the first step of the reaction is a compound with a dimetallaallylic ligand resulting from the coupling of the alkyne with the ethylidyne ligand. At higher temperature, the ethylidyne ligand is hydrogenated to an ethyl group, the hydrogen being provided by the hydride ligand and the orthometalation of the aromatic cycle.

To rationalize these observations, two paths can be proposed, subsequent to the entering of the alkyne in the coordination sphere of the cluster (Scheme II).

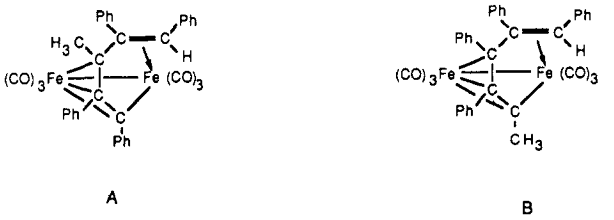


Figure 6. Proposed structures for complex **11**.

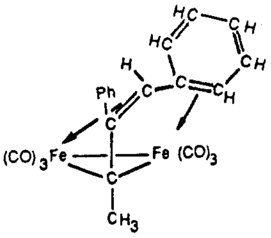


Figure 7. Structure of complex **12**.

In the *first path*, the ethylidyne–alkyne coupling leads to a dimetallaallylic ligand, as observed for R = Ph and for $HRu_3(\mu\text{-}CX)(CO)_{10}$ complexes.[3a,b] Then, the migration of the hydride ligand and hydrogen of the CH group should give the $Fe_3(CO)_9$(alkyne) complexes, possibly through an intermediate with a M_3–allenyl ligand.

A similar mechanism has been proposed for the conversion of $(\mu\text{-}H)Ru_3(\mu_3\text{-}\eta_2\text{-}HCCHCOMe)(CO)_9$ into $(\mu\text{-}H)_2Ru_3(\mu_3\text{-}\eta^2MeCCOMe)(CO)_9$ under hydrogen atmosphere.[3d] This proposal deserves some comments:

(i) In the intermediate with a dimetallaallylic ligand, the structure proposed is different from that observed for R = C_6H_5, with the CH group at the center of the ligand, but this is consistent with $C(CH_3)_3$ being a bulky group.

(ii) When R = $C(CH_3)_3$, only one alkyne is formed which corresponds to the hydrogenation of the $CC(CH_3)_3$ end of the allylic ligand. This is consistent with the results of Keister et al., who have observed that hydrogenation of allylic fragments is sterically accelerated in the case of ruthenium complexes.[3b]

(iii) In the case of trinuclear ruthenium complexes, the reaction of $Ru_3(CO)_{12}$ with the $RCCCH_2R'$ alkyne has shown that the $HRu_3(CO)_9(\mu_3\text{-}\eta^3RCCHCR')$ form is the thermodynamically stable form,[11] i.e. the reverse of what we observed in the iron case. This is presumably the consequence of a more stable metal–hydrogen bond in the case of ruthenium.

In the *second path*, the alkyne reacts with the hydride ligand to give an intermediate with an alkylidyne and an alkenyl ligand. The alkenyl ligand should then give the μ_3-bonded alkylidyne ligand by hydrogen migration. This hypothesis seems substantiated by the numerous examples of conversion of alkenyl ligands to alkylidyne ligands on di- or trinuclear complexes of iron[2,6,12] or ruthenium[13] and the isolation of a $Ru_3(CO)_9(\mu_3\text{-}CSEt)(\mu\text{-}CR'CR''H)$ complex during the reaction of $H_3Ru_3(\mu_3\text{-}CSEt)(CO)_9$ with alkynes.[3c]

Reactivity of 1 toward Disubstituted Alkynes. A. Case of Diphenylacetylene. Two compounds, **11** and **12**, have been isolated by chromatography and identified by spectroscopic techniques. In the mass spectrum of **11**, the parent ion has been detected (m/z 664) with the

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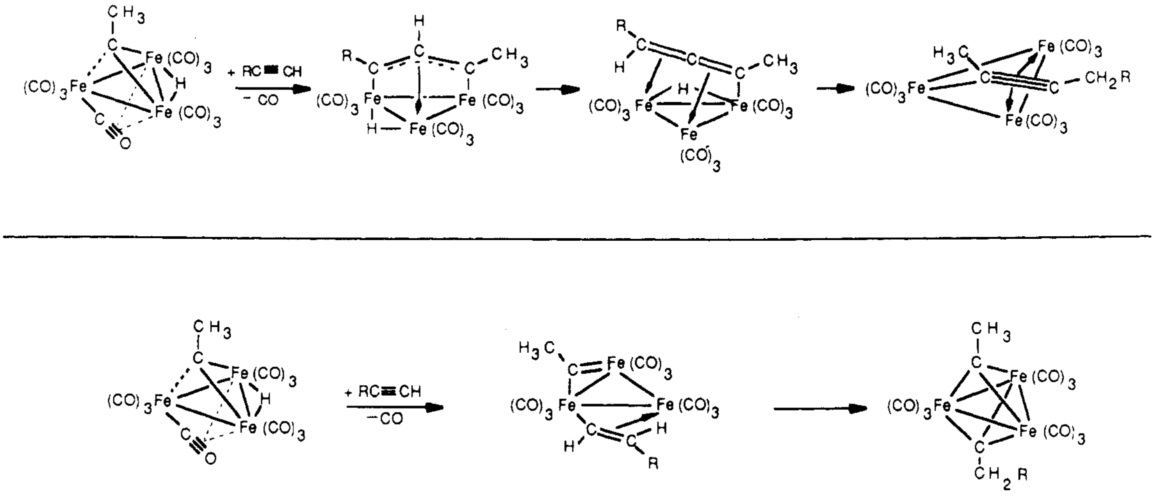
Scheme II



successive loss of six carbonyl groups. These data are consistent with the $Fe_2(CO)_6(C_{30}H_{24})$ formulation.

Infrared spectra give only evidence of terminal carbonyl groups.

The proton NMR spectrum (Table I) shows the presence of one CH_3, one H, and four phenyl groups. Furthermore, the H and CH_3 groups are not coupled.

All these results are consistent with the $Fe_2(CO)_6(CCH_3CPhCPhCPhCPhH)$ formulation and we propose two structures for **11**, shown in Figure 6, structure A being the most likely by comparison with the known complexes $Fe_2(CO)_6[C(CF_3)C(CF_3)CHCHCH(OEt)]$ and $Fe_2(CO)_6[C(C(O)OMe)C(C(O)OMe)C(OEt)CHCH_2]$, which result from the reaction of alkynes with the compound $Fe_2(CO)_6(\mu\text{-}COEt)(\mu\text{-}CHCH_2)$.[14]

Complex **12** has a mass spectrum consistent with the $Fe_2(CO)_6(C_{16}H_{14})$ formula (m/z 486 and successive loss of six CO). The proton NMR spectrum shows the presence of the CH_3 and H groups, a broad signal centered at 5.12 ppm with the intensity of 1 H, and a multiplet centered at 7.15 ppm with the relative intensity of 9 H. These data closely resemble the proton NMR data of the $Fe_2(CO)_6[\mu\text{-}C(OEt)C(Ph)C(Ph)H]$ complex (5.51 ppm for the aromatic CH, 4.81 ppm for the vinyl CH) for which an X-ray structure determination has shown that one of the phenyl rings is π-bonded to one of the iron centers.[15] Consequently, we propose for **12** the same type of structure as shown in Figure 7.

B. Case of 2-Butyne. In this case, two products have been isolated and identified. The first one, which is the less abundant, is identical with **2** but we have not checked if the 2-butyne present in the complex comes from the added alkyne or from the ethylidyne ligand of **1**. The second product, **13**, has a mass spectrum consistent with the $Fe_2(CO)_6(C_{10}H_{16})$ formulation (m/z 416 with the successive loss of six CO) and the proton NMR spectrum (Table I) shows the presence of five CH_3 groups, one of which is coupled with one hydrogen detected at 2.03 ppm. Moreover, the infrared spectrum in the ν(CO) stretching region is very similar to that of **11** and we propose for **13** the same type of structure.

To summarize, in the reaction of disubstituted alkynes with **1**, all the products isolated result from the fragmentation of the cluster into dinuclear species. These are bridged by organic fragments, which result formally from the coupling of an alkenyl ligand formed by the interaction of the alkyne with the hydride ligand, with the ethylidyne ligand, and eventually with a second molecule of alkyne.

As fragmentation occurs during these reactions, a mechanism is difficult to establish. Still, in the first step of the reaction, two intermediates can be equally considered: one of the type $HFe_3(\mu_3\text{-}\eta^3\text{-}CCH_3CRCR)(CO)_9$ (A), as exemplified by the case of phenylacetylene, the other of the type $Fe_3(\mu\text{-}CCH_3)(\mu\text{-}CRCRH)(CO)_9$ (B), as exemplified by the case of the reactivity of $H_3Ru_3(\mu\text{-}CSEt)(CO)_9$ toward alkynes.[3c] Both intermediates could lead either to complex **12** by migration of hydrogen and fragmentation (A) or by coupling of the two organic ligands and fragmentation (B) or to complexes **11** and **13** by reaction with a second molecule of the alkyne.

As a conclusion, this work provides some fair evidence of the difference of reactivity toward alkynes among related clusters of iron and ruthenium $M_3(\mu\text{-}H)(\mu\text{-}CX)(CO)_{10}$ under similar conditions. In the case of ruthenium, the dimetalloallyl complexes $HRu_3(\mu_3\text{-}\eta^3\text{-}CXCRCR')(CO)_9$ are always observed. In the case of the iron cluster studied here, this type of compound has only been observed in the case where R = Ph and R' = H and is supposed to be an intermediate if R = H and R' = t-Bu, H. These intermediates are not stable at the reaction temperature and generate $Fe_3(CO)_9(\mu_3\text{-}\eta^2XC{\equiv}CCH_2R')$ compounds by hydrogen shift. Furthermore, in the case of disubstituted alkynes, fragmentation of the iron cluster is observed. All these observations illustrate further the influence of the weakest metal–metal and metal–hydrogen bond in the case of iron compounds.

Experimental Section

All reactions were performed under nitrogen atmosphere by using standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer while using hexane solutions. ^1H NMR spectra were obtained with a Bruker WH90 instrument and ^{13}C NMR data with a Bruker WM250. Mass spectra were recorded on a Varian MAT 311-A with 70-eV electron impact. Elemental analyses were performed in our laboratory. $HFe_3(CO)_{10}(CCH_3)$,[2] **1**, and $HFe_3(CO)_{10}(CCH_2Ph)$,[5] **3**, have been synthesized by published procedures.

Synthesis of Complexes 2 and 4. **1** (500 mg) was dissolved in hexane and the solution was saturated with acetylene. The solution was refluxed under acetylene atmosphere for $^1/_2$ h and then evaporated to dryness. The residue was then chromatographed on a Florisil column. Elution with hexane gave successively $Fe_3(CO)_{10}(\mu\text{-}CCH_2)$[2] and **2** as a brown band. Crystallization in hexane at −20 °C gave 50 mg of **2** (10% yield) as brown crystals. Anal. Calcd for $C_{13}H_6Fe_3O_9$: C, 32.91; H, 1.26. Found: C, 32.81; H, 1.15.

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[14] Ros. J.; Commenges, G.; Mathieu, R.; Solans, X.; Font-Altaba, M. *J. Chem. Soc., Dalton Trans.* **1985**, 1087–1094, and unpublished results.

[15] Ros. J.; Mathieu, R.; Solans, X.; Font-Altaba, M. *J. Organomet. Chem.* **1984**, *260*, C40–C42.

The same experiment starting with 500 mg of 3 gave 70 mg of 4 (12% yield) as brown crystals. Anal. Calcd for $C_{19}H_{10}Fe_3O_9$: C, 41.51; H, 1.83. Found: C, 41.58; H, 1.69.

Synthesis of 5 and 6. To 1 (500 mg) dissolved in hexane was added 3-3-dimethyl-1-butyne (130 μL) and the solution was refluxed for $^1/_2$ h. The solution was evaporated to dryness and the residue chromatographed on a Florisil column. Elution with hexane/toluene with increasing toluene content gave successively an orange fraction of 6 and a brown fraction of 5.

6 was an orange oil, which was purified by elimination of the solvents under vacuum (140 mg, 25% yield). Anal. Calcd for $C_{17}H_{14}Fe_3O_9$: C, 38.54; H, 2.66. Found: C, 38.95; H, 2.95.

5 was crystallized in hexane at −20 °C as brown crystals (50 mg, 8% yield). Anal. Calcd for $C_{17}H_{14}Fe_3O_9$: C, 38.54; H, 2.66. Found: C, 38.32; H, 2.53.

Reaction of 5 with Carbon Monoxide under Pressure. A 20-mg sample of 5 was dissolved in 20 mL of hexane; the solution was the transferred to a stainless steel autoclave and pressurized to 40 atm with carbon monoxide. The solution was stirred for 24 h. After depressurization infrared spectra of the solution gave evidence of the formation of 7, which reverted back to 5 after 1 h at atmospheric pressure under nitrogen atmosphere.

Reaction of 6 with Carbon Monoxide under Pressure. A 50-mg sample of 6 was dissolved in 20 mL of hexane and the solution was pressurized to 40 atm in the same way as for 5. After the solution was stirred for 48 h, infrared spectroscopy gave only evidence of 6, which was recovered in nearly quantitative yield.

Synthesis of 8. It was synthesized under the same experimental conditions as 5 and 6 but it was not purified (see text).

Synthesis of 9. To 1 (350 mg) dissolved in methylcyclohexane was added phenylacetylene (81 μL) and the solution was refluxed for 2 h. The solution was then evaporated to dryness and chromatographed on a Florisil column. Elution with hexane/toluene with increasing toluene content gave successively $Fe_3(CO)_{10}(\mu\text{-}CCH_2)$, an unidentified yellow band, and a green band of 9.

Crystallization in hexane at −20 °C gave 93 mg of 9 as green crystals (31% yield). Anal. Calcd for $C_{17}H_{10}Fe_3O_8$: C, 40.0; H, 1.96. Found: C, 39.82; H, 1.76.

Synthesis of 10. The synthesis was carried out according to the same procedure as for 9 but in refluxing benzene. Chromatography on a Florisil column and crystallization in hexane gave 11 mg of 10 as orange crystals (28% yield). Anal. Calcd for $C_{18}H_{10}Fe_3O_9$: C, 40.14; H, 1.85. Found: C, 39.90; H, 1.73.

Synthesis of 11 and 12. 1 (500 mg) and diphenylacetylene (200 mg) were dissolved in methylcyclohexane and the solution was refluxed for $^1/_2$ h. The solution was then evaporated to dryness and the residue was chromatographed on a Florisil column. Elution with hexane/toluene with an increasing content of toluene gave successively $Fe_3(CO)_{10}(\mu\text{-}CCH_2)$, a red band of 12, and an orange band of 11.

11 was crystallized in hexane and gave 195 mg of orange crystals (28% yield). Anal. Calcd for $C_{36}H_{24}Fe_2O_6$: C, 65.09; H, 3.64. Found: C, 65.40; H, 3.74.

12 was a red oil, which was dried in vacuo to give 0.100 mg of product (19% yield). Anal. Calcd for $C_{22}H_{14}Fe_2O_6$: C, 54.32; H, 2.88. Found: C, 54.02; H, 2.92.

Synthesis of 13. To 1 (400 mg) dissolved in methylcyclohexane was added 2-butyne (70 μL) and the solution was refluxed for $^1/_2$ h. The solution was evaporated to dryness and the residue was chromatographed on a Florisil column. Elution with hexane gave successively $Fe_3(CO)_{10}(\mu\text{-}CCH_2)$, the complex 2, and an orange fraction containing 13.

Crystallization in hexane gave 75 mg of 13 as orange crystals (25% yield). Anal. Calcd for $C_{16}H_{16}Fe_2O_6$: C, 46.15; H, 3.84. Found: C, 45.78; H, 3.79.

Registry No. 1, 88610-52-0; 2, 101315-98-4; 3, 102774-28-7; 4A, 110935-08-5; 4B, 110935-09-6; 5, 110935-10-9; 6, 110935-11-0; 7, 110935-12-1; 8, 110935-13-2; 9, 110935-14-3; 10, 110970-98-4; 11, 110935-15-4; 12, 110935-17-6; 13, 110935-16-5; $Fe_3(CO)_{10}(\mu\text{-}CCH_2)$, 103751-58-2; acetylene, 74-86-2; 3,3-dimethyl-1-butyne, 917-92-0; phenylacetylene, 536-74-3; diphenylacetylene, 501-65-5; 2-butyne, 503-17-3.

Studies on Olefin-Coordinating Transition-Metal Carbene Complexes. 9. Synthesis, Structure, and Reactivities of Novel Chelated (η^4-Styrene)dicarbonyl[ethoxy(amino)carbene]iron Complexes†

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Received March 31, 1987

The three title compounds $[(\eta^4\text{-}C_6H_5CH{=}CH)CH(Ar)N(C_6H_5)C(OC_2H_5){=}]Fe(CO)_2$ (2, Ar = C_6H_5; 3, Ar = $m\text{-}CH_3C_6H_4$; 4, Ar = $p\text{-}CF_3C_6H_4$) have been prepared by the reaction of (cinnamaldehyde anil)iron tricarbonyl, $(\eta^4\text{-}C_6H_5CH{=}CHCH{=}NC_6H_5)Fe(CO)_3$ (1), with an aryllithium reagent in ether at low temperature, followed by the alkylation of the adducts formed with Et_3OBF_4 in aqueous solution at 0 °C. Compound 2 reacted with the Lewis bases PPh_3, $P(OPh)_3$, $AsPh_3$, CH_3CN, $PhCH_2NH_2$, and 4-vinylpyridine to give six chelated η^2-olefin carbene complexes (5–10). These new compounds are characterized by elemental analyses and IR, ^1H NMR, and mass spectra; one has been characterized by X-ray diffraction: $[(\eta^4\text{-}C_6H_5CH{=}CH)CH(m\text{-}CH_3C_6H_4)N(C_6H_5)C(OC_2H_5){=}]Fe(CO)_2{\cdot}{}^1/_2C_6H_5CH_3$, monoclinic, space group $C_{2h}^5\text{–}P2_1/c$ with unit cell constants $a = 12.457$ (3) Å, $b = 10.560$ (2) Å, $c = 20.072(4)$Å, $\beta = 96.63$ (2)°, $V = 2622.71$ Å^3, and $Z = 4$; $R = 0.047$ for 3239 reflections with $F_o^2 \geq 3\sigma(F_o)^2$. The ^1H NMR spectral data of 2–4 and the results of an X-ray structure analysis for 3 show that the benzene ring of the styrene is coordinated to the iron atom with a double bond in the complexes 2–4 and shows alternating long and short bond lengths.

Introduction

Transition-metal carbene alkene complexes have been postulated to exist as important intermediates in the reaction of olefin metathesis,[2] cyclopropanation of alkenes,[3] and Ziegler–Natta polymerization of alkenes.[4] As model compounds, some η^2-olefin metal carbene complexes have

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† Part 8, to be submitted for publication in *Acta Chim. Sin.*

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0276-7333/88/2307-0021$01.50/0