thanks the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant Award.

Registry No. 2, 90967-69-4; 3, 96898-11-2; 4b, 96898-12-3; 5, 96898-13-4; Cp_2ZrCl_2, 1291-32-3; $(C_5Me_5)_2ZrCl_2$, 54039-38-2; Me_2PCH_2Li, 64065-06-1.

Supplementary Material Available: Listings of bond lengths (Tables X and XI), bond angles (Tables VI and XII), temperature factors (Tables VII and XIII), derived hydrogen coordinates (Tables VIII and XIV), and structure factors (Tables IX and XV) (36 pages). Ordering information is given on any current masthead page.

Alkylidyne–Alkylidyne Coupling Induced by Carbon Monoxide Addition to the Bis(alkylidyne) Cluster $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$: An Unexpected Reversible Reaction. X-ray Structure of $Fe_3(CO)_9[P(C_6H_5)_3](\mu_3\text{-}\eta^2\text{-}CH_3C{\equiv}COC_2H_5)$

Didier Nuel, Françoise Dahan, and René Mathieu*

Laboratoire de Chimie de Coordination du CNRS, Associé à l'Université Paul Sabatier, 31400 Toulouse, France

Received January 7, 1985

The bis(alkylidyne) cluster $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ reacts with carbon monoxide, at room temperature and under 20 atm, leading quantitatively to $Fe_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}CH_3C{\equiv}COC_2H_5)$ (1). Coupling of the two alkylidynes is established from ^{13}C NMR data. Unexpectedly, this reaction is easily reversible and 1 reverts back to the bis(alkylidyne) starting material in solution at room temperature or, more slowly, in the solid state at room temperature. Coupling of the two alkylidyne ligands is confirmed by an X-ray diffraction study of the more stable complex $Fe_3(CO)_9[P(C_6H_5)_3](\mu_3\text{-}\eta^2\text{-}CH_3C{\equiv}COC_2H_5)$ (2). 2 crystallizes in the triclinic space group C_i^1—$P\bar{1}$, with cell dimensions a = 9.667 (1) Å, b = 18.335 (3) Å, c = 9.329 (1) Å, α = 98.02 (1)°, β = 100.62 (1)°, γ = 78.74 (1)°, and Z = 2. The structure was solved and refined to R and R_w values of 0.035 and 0.036, respectively, using 4273 reflections. Coupling of the two alkylidynes into the $CH_3C{\equiv}COC_2H_5$ alkyne $\mu_3\text{-}\eta^2$-bonded to an iron triangle is confirmed. The overall geometry of the molecule gives evidence of extensive electron delocalization which is discussed. Possible reasons for the easy cleavage of the carbon–carbon triple bond also are discussed.

Introduction

Carbon–carbon bond formation between alkylidene ligands bonded to polynuclear complexes and unsaturated organic molecules has received much study,[1] but similar reactions of alkylidyne ligands bonded to polynuclear clusters have attracted much less attention.[2]

Continuing our investigation into the possibility of carbon–carbon bond formation starting with alkylidyne ligands bonded to trinuclear iron clusters,[3] we were interested in the study of possible coupling of these ligands with carbon monoxide. We report here the study of the reaction of carbon monoxide with the $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ cluster.[3c]

Experimental Section

All reactions were performed under a nitrogen atmosphere. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer. ^1H NMR spectra were obtained with a Bruker WH90 spectrometer and ^{13}C NMR spectra with a Bruker WM250 instrument. $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ was prepared by the action of $[(C_2H_5)_3O]BF_4$ on $[Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}CO)][P(C_6H_5)_4]$.[4]

Preparation of $Fe_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}CH_3C{\equiv}COC_2H_5)$ (1). $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (0.5 g), dissolved in 20 mL of pentane, was introduced into a 100-mL stainless-steel autoclave and pressurized under 20 atm of carbon monoxide. The solution was stirred for 48 h. After depressurization, the solution was cooled to −78 °C, yielding 0.5 g of a green powder (1). Low stability prevented good chemical analysis of this product, but a parent ion was detected in the mass spectrum (m/z 532) with fragment ions corresponding to successive loss of 10 CO ligands: IR ν(CO) (hexadecane) 2088 (m), 2045 (s), 2028 (s), 2003 (m), 1989 (m), 1979 (m), 1977 (m), 1962 (m), 1925 (w, br) cm^{-1}; ^1H NMR (C_6D_6) 3.94 (q, J = 7.3 Hz, OCH_2), 2.32 (CH_3), 1.10 ppm (t, J = 7.3 Hz, OCH_2CH_3); ^{13}C NMR (CD_2Cl_2, −20 °C) 224.8 ($FeCOC_2H_5$), 208.7 (CO), 155.6 ($FeCCH_3$), 69.4 (OCH_2CH_3), 32.2 (CCH_3), 14.2 ppm (OCH_2CH_3).

Preparation of $Fe_3(CO)_9[P(C_6H_5)_3](\mu_3\text{-}\eta^2\text{-}CH_3C{\equiv}COC_2H_5)$ (2). $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (0.5 g) was treated as for 1. To the solution of 1 then was added $P(C_6H_5)_3$ (0.3 g) dissolved in a small amount of pentane, and the solution was allowed to

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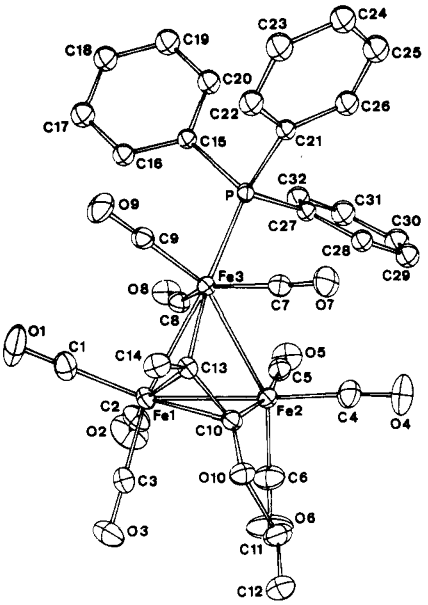

Figure 1. Structure of complex 2 showing the atomic numbering scheme with the ellipsoids at the 40% probability level.

stand at room temperature. Black crystals slowly deposited. After 5 h, the supernatant solution was discarded, giving 0.4 g (52.6%) of 2. Suitable crystals for X-ray analysis were obtained by crystallization from CH_2Cl_2/CH_3OH (1/1 mixture): IR ν(CO) (hexadecane) 2060 (m), 2019 (s), 1994 (s), 1985 (s), 1970 (m), 1956 (m), 1875 (w, br) cm^{-1}; ^{13}C NMR (CD_2Cl_2, except phenyl resonances) 221.8 ($FeCOC_2H_5$), 210.2 (CO), 209.2 (CO), 147.3 ($FeCCH_3$), 69.1 (OCH_2CH_3), 30.5 (CCH_3), 14.7 ppm (OCH_2CH_3). Anal. Calcd for $C_{32}H_{23}O_{10}PFe_3$: C, 50.13; H, 3.00. Found: C, 49.92; H, 2.82.

Preparation of $Fe_3(CO)_8[P(C_6H_5)_3](\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (3). 2 (0.1 g) was heated in refluxing dichloromethane for 2 h. The solution was cooled and evaporated to dryness in vacuo. Dissolution in 10 mL of pentane and cooling to −20 °C gave 0.05 g (52%) of 3. Concentration of the mother solution to 5 mL and cooling to −20 °C gave 0.03 g (45.6%) of $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ (3): IR (hexadecane) ν(CO) 2059 (m), 2022 (s), 1999 (s), 1988 (s), 1964 (m), 1945 (w) cm^{-1}; ^{13}C NMR (CD_2Cl_2, except phenyl resonances) 354 (COC_2H_5), 329.5 (CCH_3), 215.6 (d, $J_{P\text{-}CO}$ = 14.4 Hz, CO), 211.8 (CO), 82.3 (OCH_2CH_3), 45.8 (CCH_3), 14.2 ppm (OCH_2CH_3). Anal. Calcd for $C_{31}H_{23}O_9PFe_3$: C, 50.40; H, 3.11. Found: C, 50.32; H, 2.99.

Collection and Reduction of X-ray Data. Preliminary Weissenberg photographs failed to reveal any symmetry. Crystals belong to the triclinic system, space group $P1$ or $P\bar{1}$. The structure was successfully solved in the C_i^1—$P\bar{1}$ space group. The selected crystal was a black prism (section 0.150 × 0.100 × 0.050 mm; height 0.25 mm). The crystal 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. The summary of crystal and intensity collection data are given in Table I. A total of 6204 independent reflections were recorded out to 2θ(Mo) = 52° by procedures described elsewhere.[5] Intensity standards, recorded periodically, showed only random, statistical fluctuations. Intensity data were corrected for Lorentz, polarization, and absorption (μ = 14.6 cm^{-1}, calculated[6] transmission range 0.81–0.94). A total of 4273 reflections having $F_o^2 > 4\sigma(F_o^2)$ were used in structure determination.

Table I. Summary of Crystal and Intensity Collection Data

formula: $C_{32}H_{23}O_{10}PFe_3$
fw: 765.55
a = 9.667 (1) Å
b = 18.335 (3) Å
c = 9.329 (1) Å
α = 98.02 (1)°
β = 100.62 (1)°
γ = 78.74 (1)°
V = 1584.7 Å^3
$F(000)$ = 776
D_{calcd} = 1.604 g/cm^3
space group: C_i^1—$P\bar{1}$
radiation: Mo Kα from graphite monochromator (λ = 0.71069 Å)
linear abs coeff: μ = 14.6 cm^{-1}
temp: 20 °C
receiving aperture: 4.0 × 4.0 mm
takeoff angle: 2.8°
scan mode: θ–2θ
scan range: $(0.75 + 0.35 \tan\theta)$°
2θ limits: 52°

Table II. Fractional Atomic Coordinates with Estimated Standard Deviations in Parentheses

atom	x/a	y/b	z/c
Fe(1)	0.43082 (6)	0.34730 (3)	0.60076 (6)
Fe(2)	0.27474 (6)	0.33634 (3)	0.78758 (6)
Fe(3)	0.21149 (5)	0.28058 (3)	0.50126 (5)
C(1)	0.4943 (5)	0.3339 (2)	0.4279 (5)
O(1)	0.5297 (5)	0.3275 (2)	0.3169 (5)
C(2)	0.5817 (5)	0.2974 (3)	0.7149 (6)
O(2)	0.6793 (4)	0.2680 (2)	0.7863 (5)
C(3)	0.4968 (5)	0.4325 (3)	0.6503 (5)
O(3)	0.5384 (4)	0.4875 (2)	0.6799 (5)
C(4)	0.1089 (5)	0.3612 (3)	0.8536 (5)
O(4)	0.0044 (4)	0.3803 (3)	0.8983 (5)
C(5)	0.3373 (4)	0.2485 (3)	0.8671 (4)
O(5)	0.3854 (4)	0.1963 (2)	0.9254 (4)
C(6)	0.3828 (6)	0.3779 (3)	0.9383 (5)
O(6)	0.4552 (5)	0.4020 (2)	0.0363 (4)
C(7)	0.0857 (4)	0.3259 (2)	0.5358 (4)
O(7)	−0.0790 (3)	0.3541 (2)	0.5477 (4)
C(8)	0.3774 (4)	0.2245 (2)	0.5805 (4)
O(8)	0.4606 (3)	0.1716 (2)	0.6110 (3)
C(9)	0.2080 (4)	0.2754 (2)	0.3073 (4)
O(9)	0.2062 (4)	0.2736 (2)	0.1838 (3)
C(10)	0.2334 (4)	0.4180 (2)	0.6663 (4)
O(10)	0.2053 (3)	0.4933 (2)	0.6961 (3)
C(11)	0.2290 (6)	0.5285 (2)	0.8445 (5)
C(12)	0.1883 (5)	0.6108 (2)	0.8387 (5)
C(13)	0.2287 (4)	0.3908 (2)	0.5179 (4)
C(14)	0.1779 (5)	0.4415 (2)	0.3970 (4)
P	0.1286 (1)	0.17081 (5)	0.4760 (1)
C(15)	0.2206 (3)	0.0899 (1)	0.3660 (3)
C(16)	0.3389 (3)	0.8957 (1)	0.3070 (3)
C(17)	0.4054 (3)	0.0348 (1)	0.2242 (3)
C(18)	0.3535 (3)	−0.0319 (1)	0.2006 (3)
C(19)	0.2352 (3)	−0.0377 (1)	0.2597 (3)
C(20)	0.1688 (3)	0.0232 (1)	0.3424 (3)
C(21)	−0.0579 (2)	0.1717 (2)	0.3812 (3)
C(22)	−0.0949 (2)	0.1963 (2)	0.2433 (3)
C(23)	−0.2297 (2)	0.1928 (2)	0.1636 (3)
C(24)	−0.3276 (2)	0.1646 (2)	0.2219 (3)
C(25)	−0.2907 (2)	0.1399 (2)	0.3598 (3)
C(26)	−0.1559 (2)	0.1435 (2)	0.4395 (3)
C(27)	0.1269 (3)	0.1380 (1)	0.6529 (3)
C(28)	0.0402 (3)	0.1837 (1)	0.7441 (3)
C(29)	0.0343 (3)	0.1629 (1)	0.8797 (3)
C(30)	0.1151 (3)	0.0964 (1)	0.9241 (3)
C(31)	0.2019 (3)	0.0507 (1)	0.8329 (3)
C(32)	0.2077 (3)	0.0715 (1)	0.6973 (3)

Structure Solution and Refinement. The structure was solved[7] by the heavy-atom method and difference Fourier maps. The hydrogen atoms were localized and included in calculations in idealized positions (C–H = 0.95 Å) with an isotropic temperature factor, U = 0.05 Å^2, kept fixed. Other atoms were refined anisotropically, except phenyl rings which were refined as isotropic rigid groups.

The atomic scattering factors used were those proposed by Cromer and Waber[8] with anomalous dispersion effects.[9] Scat-

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(5) Mosset, A.; Bonnet, J.-J.; Galy, J. *Acta Crystallogr., Sect. B: Cryst. Crystallogr. Cryst. Chem.* **1977**, *B33*, 2639.

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tering factors for the hydrogen atoms were taken from Stewart et al.[10]

The final full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$, converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.035$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.036$ with unit weights. The error in an observation of unit weight was $S = [\sum w(|F_o| - |F_c|)^2/n - m]^{1/2} = 1.2$ with $n = 4273$ observations and $m = 289$ variables. In the last cycle of refinement the shifts for all parameters were less than 0.05σ. A final difference Fourier map showed no excursion of electron density greater than 0.5 e/Å^3.

The final fractional coordinates for non-hydrogen atoms are listed in Table II. An ORTEP plot[11] of the molecule with atomic labeling scheme is shown in Figure 1.

Results and Discussion

The red $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ cluster reacts slowly at room temperature with carbon monoxide under a pressure of 20 atm. After 2 days, the solution had turned green, evidence for the formation of a new complex. Infrared spectra in the ν(CO) stretching region confirmed the disappearance of the starting cluster. New bands appeared in the ν(CO) stretching region of terminal carbonyl groups and one weak and broad band at 1925 cm^{-1} suggested the presence of a semibridging carbonyl group.[12] Furthermore, when the solution was left in the infrared beam, the ν(CO) stretching frequencies of the starting material slowly appeared. This seems to indicate that the observed reaction is reversible. Actually, if the green solution is left at room temperature, it slowly turns red, giving back the starting material.

For these reasons, compound **1** can be isolated in good yield only by cooling to −78 °C and quickly precipitating it from the solution. The infrared spectrum of the isolated compound is the same as that observed in solution. Furthermore, even in the solid state the reaction is reversible at room temperature: the green solid slowly turns red. The parent ion in the mass spectrum is detected at m/z 532, with fragment ions corresponding to the successive loss of 10 CO's. The proton NMR spectrum of **1** shows that the CCH_3 and COC_2H_5 groups are preserved, which is confirmed by the proton-coupled ^{13}C NMR, but the ^{13}C NMR spectrum gives strong evidence of the change of mode of bonding of the $C(CH_3)$ and $C(OC_2H_5)$ fragments. The low-field resonance of the carbyne carbon atoms of the starting material (333 (COC_2H_5) and 292.8 ppm (CCH_3)) have disappeared and have been replaced by two resonances at 224.8 and 155.6 ppm. These values suggest that the two carbyne ligands are bonded, giving an alkyne μ_3-η^2 bonded.[13]

An X-ray structure determination of **1** was not possible because of its instability, but replacement of one CO ligand by Ph_3P gave a stable product, $Fe_3(CO)_9[P(C_6H_5)_3][C(CH_3)C(OC_2H_5)]$ (**2**), according to the equation $Fe_3(CO)_{10}[C(CH_3)C(OC_2H_5)] + P(C_6H_5)_3 \rightarrow Fe_3(CO)_9[P(C_6H_5)_3][C(CH_3)C(OC_2H_5)] + CO$. The infrared spectrum of **2** shows the presence of a weak and broad band at 1875 cm^{-1} which could be attributed to a semibridging carbonyl ligand.[12] Furthermore, the ^{13}C NMR spectrum of **2** shows that the substitution of one carbon monoxide by triphenylphosphine has not changed the mode of bonding of the $C(CH_3)C(OC_2H_5)$ fragment. The ^{13}C resonances of these groups are only slightly affected. Moreover, **2** readily rearranges to a bis(alkylidyne) cluster, at relatively low temperature, in refluxing dichloromethane. Two products have been isolated in about the same yield, one that results from loss of CO (compound **3**) and the other from loss of triphenylphosphine, i.e., the $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ starting material. The equation of the reaction can be written as $2Fe_3(CO)_9[P(C_6H_5)_3][C(CH_3)C(OC_2H_5)] \rightarrow Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5) + Fe_3(CO)_8[P(C_6H_5)_3](\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5) + CO + P(C_6H_5)_3$. This means that triphenylphosphine and carbon monoxide have similar labilities in **2**. In compound **3**, the ^{13}C NMR spectrum confirms the bis(alkylidyne) structure since two resonances at 354 and 329.5 ppm characteristic of COC_2H_5 and CCH_3 carbons are present. Since **2** is more stable than **1** in the solid state, its X-ray structure determination was undertaken.

Table III. Interatomic Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for $Fe_3(CO)_9P(C_6H_5)_3(\mu_3\text{-}\eta^2\text{-}CH_3C{\equiv}COC_2H_5)$ (2)

Bond Distances

Fe(1)–Fe(2)	2.5573 (9)	Fe(3)–C(9)	1.793 (4)
Fe(1)–Fe(3)	2.6123 (9)	Fe(3)–P	2.275 (1)
Fe(2)–Fe(3)	2.7265 (8)	C(1)–O(1)	1.133 (7)
Fe(1)–C(10)	2.226 (4)	C(3)–O(3)	1.137 (7)
Fe(1)–C(13)	2.015 (3)	C(4)–O(4)	1.137 (7)
Fe(2)–C(10)	1.938 (4)	C(5)–O(5)	1.140 (6)
Fe(3)–C(13)	2.043 (4)	C(6)–O(6)	1.137 (6)
Fe(1)–C(1)	1.798 (5)	C(7)–O(7)	1.146 (5)
Fe(1)–C(2)	1.810 (5)	C(8)–O(8)	1.164 (5)
Fe(1)–C(3)	1.773 (5)	C(9)–O(9)	1.146 (5)
Fe(1)...C(8)	2.382 (5)	C(10)–O(10)	1.354 (4)
Fe(2)–C(4)	1.777 (5)	O(10)–C(11)	1.441 (5)
Fe(2)–C(5)	1.818 (5)	C(11)–C(12)	1.488 (6)
Fe(2)–C(6)	1.766 (5)	C(10)–C(13)	1.399 (5)
Fe(3)–C(7)	1.805 (4)	C(13)–C(14)	1.512 (6)
Fe(3)–C(8)	1.818 (4)		

Bond Angles

Fe(3)–Fe(1)–Fe(2)	63.65 (2)	C(5)–Fe(2)–C(10)	166.0 (2)
Fe(1)–Fe(2)–Fe(3)	59.16 (2)	C(6)–Fe(2)–Fe(1)	94.6 (2)
Fe(2)–Fe(2)–Fe(3)	57.19 (2)	C(6)–Fe(2)–Fe(3)	153.6 (2)
C(1)–Fe(1)–C(2)	101.2 (2)	C(6)–Fe(2)–C(10)	98.0 (2)
C(1)–Fe(1)–C(3)	91.4 (2)	Fe(3)–Fe(2)–C(10)	71.1 (1)
C(10)–Fe(1)–C(13)	38.2 (1)	Fe(1)–C(10)–O(10)	128.1 (3)
Fe(3)–Fe(1)–C(13)	50.4 (1)	Fe(2)–C(10)–O(10)	133.3 (3)
C(4)–Fe(2)–C(5)	98.5 (2)	Fe(2)–C(10)–C(13)	110.8 (3)
C(4)–Fe(2)–C(6)	98.5 (2)	Fe(1)–C(13)–C(14)	128.4 (3)
C(5)–Fe(2)–C(6)	87.1 (2)	Fe(3)–C(13)–C(10)	106.6 (3)
C(7)–Fe(3)–C(8)	143.6 (2)	Fe(3)–C(13)–C(14)	125.7 (2)
C(7)–Fe(3)–C(9)	106.7 (2)	Fe(1)–C(1)–O(1)	177.2 (4)
C(7)–Fe(3)–P	86.6 (1)	Fe(1)–C(2)–O(2)	177.6 (5)
C(8)–Fe(3)–C(9)	108.4 (2)	Fe(1)–C(3)–O(3)	179.0 (4)
C(8)–Fe(3)–p	83.1 (1)	Fe(2)–C(4)–O(4)	176.7 (5)
C(9)–Fe(3)–P	91.5 (1)	Fe(2)–C(5)–O(5)	174.8 (4)
C(13)–C(10)–O(10)	115.9 (3)	Fe(2)–C(6)–O(6)	177.4 (4)
C(10)–O(10)–C(11)	121.1 (3)	Fe(3)–C(7)–O(7)	175.4 (4)
O(10)–C(11)–c(12)	107.4 (4)	Fe(3)–C(8)–O(8)	159.2 (4)
C(10)–C(13)–C(14)	122.2 (3)	Fe(3)–C(9)–O(9)	178.5 (4)
Fe(1)–C(10)–Fe(2)	75.5 (1)		

As shown in Figure 1, the X-ray diffraction study confirms that the two carbyne fragments are coupled, giving an alkyne ligand which is μ_3-η^2 bonded. This mode of bonding is quite common for alkynes bonded to trinuclear clusters.[14] Selected interatomic distances and bond angles are collected in Table III. The molecule has an asymmetric structure closely resembling the $Os_3(CO)_{10}(C_6H_5C{\equiv}CC_6H_5)$ molecule.[15] Three terminal carbonyl ligands

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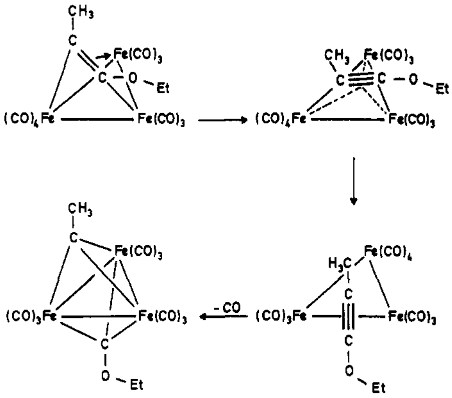
Scheme I



are bonded to each of the two iron atoms, Fe(1) and Fe(2). The Fe(2) iron atom is bonded to three carbonyl groups and the triphenylphosphine ligand. The 1-ethoxy-1-propyne ligand is σ-bonded to Fe(2) and Fe(3) and π-bonded to Fe(1). A conventional electron count including the metal–metal bond shows that Fe(1) is electronically saturated but Fe(3) has 19-valence electrons and Fe(2) 17-valence electrons. In the osmium cluster, the same situation exists and it has been suggested that the metal–metal bond between the electron-rich and the electron-poor centers can be viewed as a donor–acceptor bond.[17] In our case, the situation seems to be more subtle and the electronic equilibrium in the molecule appears to result from more delocalized interactions. For instance, the shortest iron–iron distance is that between Fe(1) and Fe(2), i.e., between the 18- and the 17-valence electron center and not between Fe(3) and Fe(2), i.e., between the electron-rich Fe(3) center and the electron-deficient Fe(2) center.

Such asymmetry in electron distribution is further evident when considering the bonding of the alkyne fragment: the Fe(1)–C(13) bond distance is 0.2 Å shorter than the Fe(1)–C(10) bond distance, the latter being quite long for an iron bonded with a π system.[16] Moreover, the Fe(3)–C(13) and Fe(2)–C(10) bond distances are quite different, the short Fe(2)–C(10) distance suggesting a partial multiple-bond order. This seems substantiated by the fact already mentioned that the Fe(1)–C(10) bond is long.

The carbonyl ligands around the iron centers further show the dissymmetry in electron distribution. For instance, even though the Fe(3) atom is bonded to the phosphine ligand, the Fe(3)–carbon distances for the carbonyl groups are generally longer than that of the iron–carbon distance in the other $Fe(CO)_3$ groups. Also, carbonyl ligands approximately trans to C(13), i.e., C(2)–O(2), and C(10), i.e., C(5)–O(5), have Fe–C bonds slightly longer than the others.

The most significant feature concerns the C(8)–O(8) carbonyl group. The Fe(3)–C(8)–O(8) bond angle of 159.2 (4)° and the Fe(1)–C(8) distance of 2.382(5) Å indicate that this ligand is in a semibridging position.[17] The occurrence of this mode of bonding for a carbonyl group was suggested by the presence of a broad and weak band at 1925 cm^{-1} for (1) and 1875 cm^{-1} for (2), but what is unexpected is that this semibriding group occurs between the two electron-rich iron centers, Fe(3) and Fe(1), and not, as could be expected, between Fe(3) and the electron-poor Fe(2) center. Nevertheless, this confirms the fact that semibridging carbonyl ligands are generally encountered in molecules containing electronically dissimilar metal centers.[12,17]

To summarize, the X-ray structure determination of **2** firmly establishes that on reaction of carbon monoxide with $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ one molecule of carbon monoxide is added to the cluster inducing the coupling of the two carbyne ligands to give an alkyne which is μ-η^3 bonded. This mode of coupling of two carbyne ligands has been encountered in the reaction of $Cp(CO)_2W{\equiv}CC_6H_4Me$ with $H_2Os_3(CO)_{10}$.[18] But in our case, the most novel feature is that this reaction is easily reversible. The reversibility is observed at room temperature for **1** and at the boiling point of dichloromethane for **2**. Indeed, known cases of C≡C bond scission observed during the reaction of alkynes with mononuclear[19] or polynuclear[20] complexes required more forcing conditions (reaction temperatures between 100 and 500 °C).

This ease of carbon–carbon bond breaking in our case is clearly not due to a weak C(10)–C(13) bond as the bond length observed, 1.399 (5) Å, is in the normal range for alkyne μ_3-η^2 bonded.[21] In a recent experimental and theoretical study of alkyne scission in the isoelectronic trinuclear $Cp_3Rh_3(CO)C_2(C_6H_5)_2$ complexes,[20b] a scheme was proposed that was substantiated by theoretical calculations, in which the alkyne rotates from the μ^3-(η^2-$\|$) to the μ^3-(η^2-$\perp$) position over the triangle of the metals. Then through an intermediate with edge coordination of the alkyne and after final loss of carbon monoxide, the final bis(alkylidyne) complex is formed. In the light of these observations, it could be suggested (Scheme I) that in our case the first step, i.e., the rotation of the alkyne over the triangle of the metals, would be facilitated by the weak Fe(1)–C(10) bond. A second factor would be the ease of CO loss since the loss of one molecule of carbon monoxide from the cluster is very easy, even with triphenylphosphine substitution of one carbon monoxide. All these facts are perhaps the consequence of the presence of the electronegative OC_2H_5 group on one alkylidyne ligand.

Acknowledgment. This work has been supported by the CNRS (GRECO-CO).

Registry No. 1, 96666-11-4; 2, 96666-12-5; 3, 96666-13-6; $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$, 88055-72-5; CO, 630-08-0.

Supplementary Material Available: Tables of thermal parameters, hydrogen parameters, and structure factors (23 pages). Ordering information is given on any current masthead page.

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