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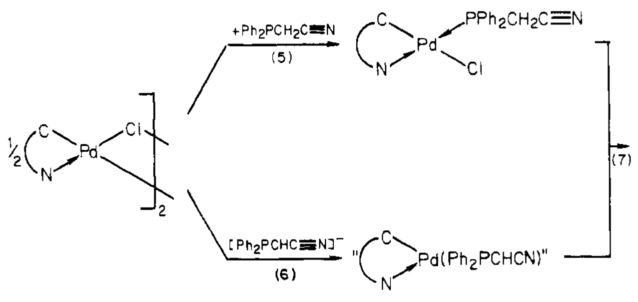
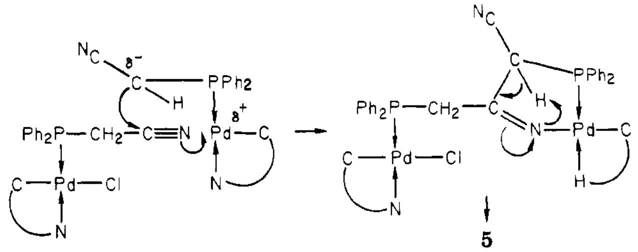
mediate **6** with the nitrile function of Pd($\overline{C\ N}$)ClL^1 results the formation of **5**. This reaction is strongly related to that described above between [L^1]$^-$ and the coordinated nitrile of PtCl$_2$(PhCN)$_2$ (eq 1). The differences reside in that (i) the carbanion is P coordinated in **6** (by contrast to (L^1)$^-$) and (ii) the attacked nitrile function is uncoordinated but connected to a metal via a phosphino group in Pd($\overline{C\ N}$)ClL^1. The sequence of reactions shown in eq 5–7 accounts for these observations.



6



5

The possible structures of intermediate **6** formed in (eq 6) have been discussed above (structures **6B** and **6C**). After nucleophilic attack on the nitrile has occurred (eq 7), the H shift from C(4) to N(3) follows the same pattern as in the reaction leading to **1**.[14] This gives rise in the IR to a ν(NH) vibration at 3285 cm^{-1}.

In conclusion, the reactions presented in this paper, namely, (i) nucleophilic attack of a carbanion on a coordinated organonitrile ligand and (ii) nucleophilic attack of a carbanionic metal complex on the free nitrile group of a functional phosphine complex, demonstrate the potential use of α-phosphino carbanions in synthetic coordination chemistry. They also illustrate the metal-assisted synthesis of new ligands since these reactions were performed within the coordination sphere of the metals involved.

Acknowledgment. Thanks are due to the CNRS for financial support and to A. Mitschler for collecting the X-ray data for **5**.

Registry No. **1**, 72910-27-1; **2**, 72910-26-0; **3**, 79079-79-1; **4**, 77063-83-3; **5**, 86632-51-1; **7**, 79110-94-4; PtCl$_2$(PhCN)$_2$, 14873-63-3; [Pd($\overline{C\ N}$)(M-Cl)]$_2$, 18987-59-2; Li[Ph$_2$PCHCN], 86632-52-2; Li[Ph$_2$PCHCOOC$_2$H$_5$], 86632-53-3.

Supplementary Material Available: Tables of least-squares planes (Tables IV and VI), anisotropic thermal parameters (Tables VIII and IX), and observed and calculated structure factors for **2** and **5**·2CH$_2$Cl$_2$ (Tables X and XI) and intra- and intermolecular contacts in **5**·CH$_2$Cl$_2$ (Table V) and stereoscopic view of **5** (Figure 3) (46 pages). Ordering information is given on any current masthead page.

Reactivity of [HFe$_3$(CO)$_{11}$]$^-$ toward Ethylene. Synthesis and Crystal Structure of Tetraphenylphosphonium [μ_3-Propionyl-*C*(*Fe*^{1},*Fe*^{2}),*O*(*Fe*^{1},*Fe*^{3})]nonacarbonyl-*triangulo*-triferrate. Study of Its Reactivity toward CO, P(C$_6$H$_5$)$_3$, H$_2$, and Proton

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Reaction of the cluster anion [HFe$_3$(CO)$_{11}$]$^-$ with ethylene at room temperature gives the trinuclear cluster anion [Fe$_3$(CO)$_9$(μ_3-COC$_2$H$_5$)]$^-$. The structure of this cluster anion has been determined by X-ray diffraction study of the tetraphenylphosphonium salt **1**. The latter is monoclinic of space group $C2/c$ with a = 18.813 (3) Å, b = 17.641 (4) Å, c = 22.551 (4) Å, β = 106.34 (2)°, and Z = 8. The structure has been solved and refined to R and R_w values of 0.054 and 0.060, respectively, using 3583 reflections. A μ_3 mode of bonding is shown for the acyl group. This is the first case where this mode of bonding results from the direct action of an alkene on a cluster unit. Reactivity of **1** toward CO and P(C$_6$H$_5$)$_3$ is attended by complete rupture of the cluster unit into Fe(CO)$_4$COC$_2$H$_5^-$ (CO case) or Fe(CO)$_{5-n}$[P(C$_6$H$_5$)$_3$]$_n$ (n = 1, 2). **1** gives a mixture of ethane and propanol under hydrogen pressure, which suggests an alkyl/acyl equilibrium in the cluster under the conditions of the reaction. Protonation of **1** gives HFe$_3$(CO)$_9$(μ_3-COC$_2$H$_5$).

Introduction

We have recently shown that the [HFe$_3$(CO)$_{11}$]$^-$ anion reacts readily with alkynes with preservation of trinuclear iron unit.[1] Furthermore, this anion has a reactivity that compares well with the known reactivity of ruthenium and osmium trinuclear clusters.[2] These results are quite unexpected with respect to the known lability of metal–metal bonds for the first-row period of transition metals.

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As an extension of this work, we have now studied the action of ethylene on $[HFe_3(CO)_{11}]^-$.

Ethylene is known to react with osmium[3] or ruthenium[4] trinuclear clusters with CH cleavage, leading to μ-vinyl or μ_3-vinylidene ligands. In this paper, we describe the action of ethylene on $[HFe_3(CO)_{11}]^-$ which does not lead to CH cleavage but gives a trinuclear complex containing the $[Fe_3(CO)_9(\mu_3\text{-}COC_2H_5]^-$ anion. The latter contains an unexpected propionyl group in which the CO group is μ_3 bonded as shown by an X-ray structure determination. This mode of bonding of an acyl group has been found recently in two other cases that do not involve the action of an alkene on an hydrido cluster complex.[5,6]

In an attempt to obtain a cluster with a terminal mode of bonding of the acyl group, we have reacted the Ph_4P^+ salt of this anion with carbon monoxide or triphenylphosphine. We have observed the rupture of the cluster unit leading to mononuclear species containing the acyl group (CO case) or no acyl unit ($P(C_6H_5)_3$ case). We report also the action of hydrogen and a protonic acid on $[Ph_4P][Fe_3(CO)_6(\mu_3\text{-}COC_2H_5)]$ (1).

Experimental Section

Synthetic Work. All reactions were performed under a nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer. The ^1H NMR spectra were obtained on a Bruker WH90 spectrometer and ^{13}C NMR spectra on a Bruker WM250 instrument. $[HFe_3(CO)_{11}][P(C_6H_5)_4]$ was prepared by published procedures.[7]

Preparation of $[Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)][P(C_6H_5)_4]$, 1. At Atmospheric Pressure. A 500-mg sample of $[HFe_3(CO)_{11}][P(C_6H_5)_4]$ dissolved in acetone was stirred at room temperature under an ethylene atmosphere for 1 week. Filtration and vacuum drying of the filtrate followed. Crystallization from dichloromethane/methanol gave 400 mg of 1 (80% yield), mp 120 °C. Anal. Calcd for $[Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)][P(C_6H_5)_4]$: C, 34.84, H, 3.08, Fe, 30.49. Found: C, 34.56, H, 3.07, Fe, 30.64.

Under Pressure. As the reaction at atmospheric pressure was time consuming, 1 was preferably prepared under a pressure of ethylene (5–10 atm) in a 100-mL stainless-steel autoclave at room temperature in acetone solution. This afforded up to 5 g of 1 in a 2-day experiment without affecting the yield.

Reaction of 1 with Carbon Monoxide. Synthesis of $[Fe(CO)_4COC_2H_5][P(C_6H_5)_4]$, 2. A 500-mg sample of 1 in dichloromethane was stirred overnight under a CO atmosphere at room temperature. The solution was filtered and the filtrate vacuum dried. Crystallization from dichloromethane/ether gave 200 mg of yellow $[Fe(CO)_4COC_2H_5][P(C_6H_5)_4]$ (57.8% yield), mp 64 °C. Anal. Calcd for $[Fe(CO)_4COC_2H_5][P(C_6H_5)_4]$: C, 65.95, H, 4.43, Fe, 9.93. Found: C, 65.55, H, 4.45, Fe, 10.41.

Reaction of 1 with Triphenylphosphine. To 500 mg of 1 dissolved in dichloromethane was added 350 mg of $P(C_6H_5)_3$ (2.2 equiv), and the reaction mixture was stirred for 16 h. IR spectra in the ν(CO) stretching region of the resulting solution gave evidence of $Fe(CO)_4P(C_6H_5)_3$ (ν(CO) in hexadecane solution 2052 (m), 1978 (m), 1946 (s) cm^{-1} (lit.[8] 2050.7, 1977.8, 1944.5 cm^{-1})) and $Fe(CO)_3[P(C_6H_5)_3]_2$ (ν(CO) 1893 cm^{-1} (lit.[8]) 1892 cm^{-1})) which were not isolated. Analysis of the solution by gas chromatography was performed on an Intersmat IGC 120M or IGC 16 instrument using a 2-m SiO_2 column (ethane/ethylene analysis) or a 6-ft column containing Carbowax 20M on Chromosorb WAW 80/100 (propanal/propanol analysis).

Table I. Crystal Data and Experimental Details of the X-ray Diffraction Study of $[Fe_3(CO)_{10}C_2H_5][P(C_6H_5)_4]$

(A) Crystal Parameters at 19 °C[a]

cryst system	monoclinic	V, Å^3	7181.9
a, Å	18.813 (3)	mol wt	815.5
b, Å	17.641 (4)	$F(000)$	3312
c, Å	22.551 (4)	Z	8
β, deg	106.34 (2)	ρ_{obsd}, g/cm^3	1.54
space group	$C2/c$	ρ_{calcd}, g/cm^3	1.508
cryst dimens, mm	0.50 × 0.45 × 0.25	μ, cm^{-1}	13.7

(B) Measurement of Intensity Data

instrument	Nonius CAD4
cryst detector dist, mm	210
detector window	
height, mm	4
width, mm	4
values	
determining the scan speed[b]	
SIGPRE	0.700
SIGMA	0.018
no. of reflctns collected	6081
stds	
intensity[c]	3 reflctns every 7200 s
orientatn	3 reflctns every 200 reflctns
radiatn	Mo Kα (λ = 0.710 69 Å) monochromatized graphite
takeoff angle, deg	2.6
scan mode	ω-2θ
scan range, deg	0.90 + 0.35 tan θ
VPRE, deg/m	10
TMAX, s	60
mas 2θ, deg	50.0

(C) Treatment of Intensity Data[d]

reduction to F_0^2 and $\sigma(F_0)^2$	corr for bkgd, attenuators, and Lorentz-polarization in the usual manner
unique data	$F_0 > 6\sigma(F_0)$
NO = 3583	3583
no. of variables	NV = 284
R[e]	0.054
R_w[f]	0.060
w	$1/[\sigma^2(F_o) + (pF_o)^2]$
p	0.038

[a] From a least-squares fitting of the setting angles of 25 reflections. [b] These parameters have been described: Mosset, A.; Bonnet, J. J.; Galy, J. *Acta Crystallogr. Sect. B* 1977, *B33*, 2639. [c] Showed only random, statistical fluctuations. [d] All calculations were performed on an Iris 80 CII computer. [e] $R = \Sigma|F_o| - |F_c||/\Sigma|F_o|$. [f] $R_w = [\Sigma w(F_o - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

Reaction of 1 with Hydrogen. A 300-mg sample of 1 dissolved in 10 mL of dichloromethane was pressurized with hydrogen (15 atm) in a 100-mL stainless-steel autoclave, and the solution was stirred for 16 h at 70 °C. At the end of the reaction, $[HFe_3(CO)_{11}]^-$ was identified by infrared spectrometry in the ν(CO) stretching region, and the solution was analyzed by gas chromatography following the preceding procedure.

Protonation of 1. Synthesis of $HFe_3(CO)_9(\mu_3\text{-}COC_2H_5)$, 3. To 500 mg of 1 dissolved in dichloromethane was added an excess of trifluoroacetic acid. The solution was stirred for 1 h and then was evaporated at reduced pressure. Extraction with pentane and crystallization at −20 °C yielded 90 mg of 3 (30% yield) as black crystals, mp 82 °C dec. Anal. Calcd for $HFe_3(CO)_9COC_2H_5$: C, 30.17, H, 1.26. Found: C, 30.19, H, 1.39.

X-ray Data Collection and Reduction (Compound 1). Preliminary Laue and precession photographs indicated the crystal to be monoclinic. Systematic extinctions were consistent with space groups C^6_{2h}—C/c and C^4_s—Cc. The structure was successfully solved in the space group $C2/c$. The crystal selected, mounted on a glass fiber for data collection, was a purple-brown parallelepiped, with boundary planes {001}, {110}, and {110}. The distances from these faces to an arbitrary origin were 0.25, 0.125, and 0.225 mm, respectively. Intensity data were collected by using an Enraf-Nonius CAD4 diffractometer. The details of the data

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[4] Deeming, A. J.; Hasso, S.; Underhill, M.; Canty, A. J.; Johnson, B. F. G.; Jackson, W. G.; Lewis, J.; Matheson, M. T. *J. Chem. Soc., Chem. Commun.* 1974, 807.

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Table II. Final Least-Squares Coordinates with Estimated Standard Deviations for [$Fe_3(CO)_{10}C_2H_5$][$P(C_6H_5)_4$]

atom	x/a	y/b	z/c
Fe(1)	0.72344 (5)	0.55396 (6)	0.69518 (4)
Fe(2)	0.78451 (5)	0.48769 (5)	0.62137 (4)
Fe(3)	0.82662 (5)	0.62004 (5)	0.66836 (4)
P	0.47716 (9)	0.75964 (9)	0.49690 (7)
C(1)	0.6808 (4)	0.5012 (4)	0.7429 (4)
O(1)	0.6520 (4)	0.4697 (4)	0.7734 (3)
C(2)	0.6897 (5)	0.6425 (5)	0.7120 (4)
O(2)	0.6647 (4)	0.6994 (4)	0.7237 (3)
C(3)	0.6584 (4)	0.5371 (6)	0.6230 (4)
O(3)	0.6073 (3)	0.5335 (6)	0.5810 (3)
C(4)	0.7409 (4)	0.5135 (4)	0.5414 (3)
O(4)	0.7120 (3)	0.5259 (3)	0.4908 (2)
C(5)	0.7541 (4)	0.3922 (5)	0.6133 (3)
O(5)	0.7359 (4)	0.3298 (4)	0.6066 (3)
C(6)	0.8725 (4)	0.4704 (5)	0.6136 (3)
O(6)	0.9304 (3)	0.4555 (4)	0.6086 (3)
C(7)	0.7830 (4)	0.6595 (4)	0.5948 (4)
O(7)	0.7574 (4)	0.6867 (3)	0.5477 (3)
C(8)	0.9197 (5)	0.6218 (5)	0.6651 (4)
O(8)	0.9786 (4)	0.6354 (5)	0.6614 (4)
C(9)	0.8338 (4)	0.7080 (5)	0.7095 (4)
O(9)	0.8372 (4)	0.7663 (4)	0.7332 (3)
O(10)	0.8326 (2)	0.5523 (3)	0.7372 (2)
C(10)	0.8128 (3)	0.4843 (4)	0.7101 (3)
C(11)	0.8308 (4)	0.4184 (4)	0.7535 (3)
C(12)	0.9085 (5)	0.3900 (6)	0.7620 (5)
H(1)	0.826	0.434	0.793
H(2)	0.796	0.377	0.737
H(3)	0.918	0.347	0.790
H(4)	0.943	0.430	0.779
H(5)	0.914	0.374	0.722

collection and reduction are given in Table I. Because of the dimensions of the crystal and of the absorption coefficient, corrections for absorptions were not useful.

Structure Solution and Refinement. The structure was solved[9] by the heavy-atom technique. A Patterson map yielded positions for the iron atoms. Subsequent Fourier maps revealed the positions of all non-hydrogen atoms, which were refined anisotropically, except the phenyl rings, which were refined as rigid groups. The ethyl hydrogen atoms were located from a difference electron density map. They were introduced in the last cycles of refinement with constraints C–H = 0.97 Å and H–C–H = 109.5°, with isotropic thermal parameters U equal to 0.08 and 0.10 Å^2 for methylene and methyl hydrogen atoms, respectively.

Neutral atom scattering factors for non-hydrogen atoms and corrections for anamalous dispersion effects for iron and phosphorus atoms were obtained from the tabulation of Cromer and Waber.[10] Scattering factors for the hydrogen atoms were those of Stewart et al.[11]

The final cycle of refinement leads to $R = 0.054$ and $R_w = 0.060$. The weighting scheme used in the minimization of the function $\sum w(F_o - |F_c|)^2$ is defined as $w = 1/[\sigma^2(F_o) + (pF_o)^2]$ where p is the factor to prevent overweighting of strong reflections. An analysis of variance according to F_o and $(\sin\theta)/\lambda$ showed satisfactory consistency. The largest peak on the final difference Fourier map was 1.0 e/Å^3 near one of the phenyl groups. Nongroup atomic positional parameters with their standard deviations are reported in Table II. Anisotropic thermal parameters and phenyl atomic parameters are listed in Tables IIS.A and IIS.B (supplementary material), respectively.

Results and Discussion

The [$HFe_3(CO)_{11}$]$^-$ anion reacts slowly with ethylene at atmospheric pressure at room temperature to give compound 1 in quantitative yield after 1 week. The reaction time was shortened to 2 days by carrying out the reaction under 5 atm of ethylene. The product anion, isolated as the $P(C_6H_5)_4^+$ salt, shows terminal carbonyl stretches in solution; no bridging carbonyl stretch is observed, even in the solid state (Table III). The proton NMR spectrum shows the presence of an ethyl group (Table III), and the chemical analysis is consistent with the [$Fe_3(CO)_{10}C_2H_5$][$P(C_6H_5)_4$] formula. The ^{13}C NMR spectrum of complex 1 shows the presence of an ethyl group, and, in the carbonyl region, two singlets at 215.8 and 213 ppm are assigned to terminal carbonyls. Another singlet is observed at 240 ppm, but this cannot be attributed to a bridging carbonyl. (The infrared spectra give no evidence of such a species).

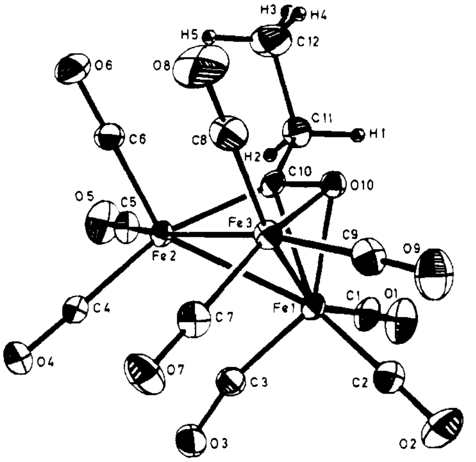

Figure 1. Structure of complex 1 showing the atomic numbering scheme. For the sake of clarity vibrational ellipsoids are given at the 15% probability level.

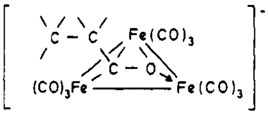

Figure 2. Mode of bonding of the μ_3-acyl group in 1.

In order to ascertain the exact nature of this CO group, we undertook an X-ray structure determination. As shown in Figure 1, the X-ray diffraction study gives evidence of a propionyl group μ_3 bonded to three iron atoms and lying above the surface defined by these three metal atoms. This unusual mode of bonding has been encountered earlier in two cases, namely, in the acetyl analogue of 1, the product of the reaction of methyl iodide with [$Fe_2(CO)_8$]$^{2-}$,[6] and in one of the products of the reaction of $H_2Os_3(CO)_{10}$ with $CpW(CO)_2CC_6H_4CH_3$:$CpWOs_3(CO)_{11}CH_2C_6H_4CH_3$.[5]

Selected interatomic distances and bond angles are collected in Tables IV and V together with the interatomic distances and bond angles found for [$Fe_3(CO)_9(\mu_3\text{-}COCH_3)$]$^-$ anion. They are of the same order within experimental error. The Fe_3 triangle is actually distorted, and the shortest distance is the one bridged by the oxygen atom of the acyl group.

Let us now consider the bonding of the propionyl group. The C(10) carbon atom is strongly bonded to the Fe(2) atom and the O(10) to the Fe(3) atom and Fe(1) is nearly equidistant from C(10) and O(10). The C(10)–O(10) bond length, 1.350 (27) Å, ranges between the values found for the acetyliron complex and those found for the acyl group bonded to the mixed osmium–tungsten cluster, 1.394 (27) Å, and indicates a considerable weakening of the CO bond. This supports the mode of bonding represented in Figure 2. In this mode of bonding, the oxygen atom is a three-

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Table III. Infrared and NMR Data of the Isolated Complexes

	IR ν(CO),[a] cm^{-1}	NMR,[b] δ (Me_4Si) ^1H	NMR,[b] δ (Me_4Si) ^{13}C
$[Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)][P(C_6H_5)_4]$ (1)	2040 w, 1977 s, 1947 m, 1930 sh	2.85 (q, J = 7 Hz), 1.23 (t, J = 7 Hz)	240 (COC_2H_5), 215.8, 213 (CO), 50.4 (CH_2), 13.6 (CH_3)
$[Fe(CO)_4COC_2H_5][P(C_6H_5)_4]$ (2)	2000 m, 1912 s, 1855 s, 1885 s, 1605 m	2.93 (q, J = 7.5 Hz), 0.80 (t, J = 7.5 Hz)	
$HFe_3(CO)_9(\mu_3\text{-}COC_2H_5)$ (3)	2093 m, 2055 s, 2030 s, 2018 s, 2010 m, 2001 m, 1995 m, 1982 w, 1961 w	2.79 (q, J = 7.3 Hz), 1.07 (t, J = 7.3 Hz), −24.70 (s)	247.5 (COC_2H_5), 207.4, 207 (CO), 50.2 (CH_2), 13.7 (CH_3)

[a] CH_2Cl_2 solution except 3, hexadecane solution. [b] In CD_2Cl_2 solution.

Table IV. Interatomic Distances (Å) with Esd's for $[Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)][P(C_6H_5)_4]$ (1) and $[Fe_3(CO)_9(\mu_3\text{-}COCH_3)][N(C_2H_5)_4]$[6]

	$[Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)]^-$	$[Fe_3(CO)_9(\mu_3\text{-}COCH_3)]^-$
	Iron-Iron	
Fe(1)-Fe(2)	2.556 (1)	2.541 (6)
Fe(1)-Fe(3)	2.481 (1)	2.478 (6)
Fe(2)-Fe(3)	2.594 (1)	2.592 (5)
	Acyl Group	
Fe(1)-C(10)	2.031 (6)	1.98 (1)
Fe(2)-C(10)	1.921 (6)	1.89 (1)
Fe(3)-O(10)	1.937 (4)	1.93 (1)
Fe(1)-O(10)	2.005 (4)	1.98 (1)
C(10)-C(11)	1.497 (9)	1.54 (2)
C(11)-C(12)	1.505 (10)	
	Iron-Carbon	
Fe(1)-C(1)	1.775 (7)	
Fe(1)-C(2)	1.767 (9)	
Fe(1)-C(3)	1.765 (9)	
Fe(2)-C(4)	1.816 (7)	
Fe(2)-C(5)	1.771 (8)	1.74 (2)-1.83 (2)
Fe(2)-C(6)	1.740 (7)	
Fe(3)-C(7)	1.773 (9)	
Fe(3)-C(8)	1.773 (8)	
Fe(3)-C(9)	1.793 (9)	
	Carbon-Oxygen	
C(1)-O(1)	1.135 (8)	
C(2)-O(2)	1.169 (9)	
C(3)-O(3)	1.145 (9)	
C(4)-O(4)	1.138 (7)	
C(5)-O(5)	1.150 (9)	
C(6)-O(6)	1.156 (8)	
C(7)-O(7)	1.142 (8)	
C(8)-O(8)	1.138 (9)	
C(9)-O(9)	1.153 (9)	
	$P(C_6H_5)_4$ Group	
P-C(13)	1.788 (4)	
P-C(19)	1.772 (5)	
P-C(25)	1.784 (4)	
P-C(31)	1.782 (4)	

Table V. Bond Angles (deg) with Esd's for $[Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)][P(C_6H_5)_4]$ (1) and $[Fe_3(CO)_9(\mu_3\text{-}COCH_3)][N(C_2H_5)_4]$[6]

	$[Fe_3(CO)_9\text{-}(\mu_3\text{-}COC_2H_5)]^-$	$[Fe_3(CO)_9\text{-}(\mu_3\text{-}COCH_3)]^-$
	Fe_3 Triangle	
Fe(2)-Fe(1)-Fe(3)	61.98 (4)	62.2 (2)
Fe(1)-Fe(2)-Fe(3)	57.58 (4)	57.7 (2)
Fe(1)-Fe(3)-Fe(2)	60.44 (4)	60.1 (2)
	Acyl Group	
Fe(1)-O(10)-Fe(3)	78.0 (1)	79 (1)
Fe(1)-O(10)-C(10)	71.5 (3)	71 (1)
Fe(1)-C(10)-Fe(2)	80.5 (2)	83 (1)
Fe(1)-C(10)-O(10)	69.4 (3)	71 (1)
Fe(1)-C(10)-C(11)	127.1 (4)	
Fe(2)-C(10)-C(11)	130.6 (4)	128 (1)
Fe(2)-C(10)-O(10)	113.9 (4)	117 (1)
Fe(3)-O(10)-C(10)	103.8 (3)	103 (1)
C(11)-C(10)-O(10)	114.3 (6)	114 (1)
C(10)-C(11)-C(12)	112.0 (6)	
C(10)-Fe(1)-O(10)	39.1 (2)	38.9 (4)
	Fe-C-O	
Fe(1)-C(1)-O(1)	177.6 (8)	
Fe(1)-C(2)-O(2)	176.9 (8)	
Fe(1)-C(3)-O(3)	167.1 (7)	
Fe(2)-C(4)-O(4)	176.3 (7)	
Fe(2)-C(5)-O(5)	177.5 (7)	
Fe(2)-C(6)-O(6)	177.0 (8)	
Fe(3)-C(7)-O(7)	177.2 (7)	
Fe(3)-C(8)-O(8)	177.2 (8)	
Fe(3)-C(9)-O(9)	176.6 (8)	
	$P(C_6H_5)_4$ Group	
C(13)-P-C(19)	109.8 (2)	
C(13)-P-C(25)	108.2 (2)	
C(13)-P-C(31)	111.4 (2)	
C(19)-P-C(25)	111.4 (2)	
C(19)-P-C(31)	107.9 (2)	
C(25)-P-C(31)	108.2 (2)	

electron ligand and the C(10) carbon atom is a two-electron ligand.

The ethyl group bond distances and angles are in the range of expected values. Bond angles and distances are normal for the $Fe(CO)_3$ units, except for the Fe(1)C(3)O(3) group. In the latter, the bond distances are normal but the bond angle Fe(1)C(3)O(3) is smaller, 167.1 (7)° (a similar anomalous value, 169.8°, as found in the acetyl complex)[6]. This anomaly seems to be due to a weak interaction with the Fe(2) iron atom as the Fe(2)–C(3) distance is 2.538 (8) Å. This is not really a semibridging interaction, as the normal criterion is a distance of 2.43–2.46 Å.[12] This is perhaps due to the fact that the anionic charge is fully localized on Fe(2) (the expected result of the 18-electron configuration counting) with the result of an increased charge density on this Fe(2) atom.

In summary, the action of ethylene on the anion $[HFe_3(CO)_{11}]^-$ leads to formation of an acyl group μ_3 bonded to the triangle of iron. In this mode of bonding, the acyl group is a five-electron donor such that each iron atom attains an 18-electron configuration. This is the third case of such a mode of bonding for an acyl group, but this is the first case in which it results directly from the interaction of an alkene with an hydrido cluster complex.

In Scheme I we have represented the mechanism proposed for the formation of 1. As in Shapley's proposal for the reaction of $H_2Os_3(CO)_{10}$ with ethylene,[13] the first step is a π complex of ethylene that in our case is made possible by the loss of one carbonyl ligand. Hydrogen transfer then

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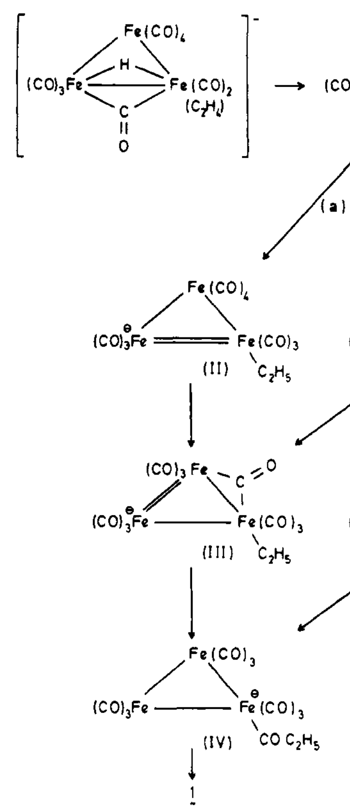
(12) Holt, E. M.; Whitmire, K. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 5621.

(13) Calvert, R. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

Scheme I



produces the 46-electron ethyl system (I) in which Fe(2) and Fe(3) are double bonded. Starting from I, we can postulate two pathways, a and b, leading to the final product. These two pathways differ in the localization of the negative charge of the cluster anion and in the redistribution of the CO ligand in the coordination sphere of the cluster.

In the path a, the bridged carbon monoxide migrates to Fe(2) leading to II in which the negative charge is located on Fe(3). A migration of a CO molecule from Fe(1) to Fe(2) then occurs by way of the intermediate structure III in which a CO bridges the Fe(1)Fe(2) bond and the double bond migrates to the Fe(1)Fe(3) edge. The migration of CO is concomitant with the formation of the acyl group leading to structure IV. In structure IV, Fe(1) and Fe(2) have a 16-electron configuration that explains why the acyl group becomes μ_3 bonded since in this way each iron atom attains an 18-electron configuration.

In the alternative path b, the migration of a terminal CO from Fe(1) to a bridged position precedes the migration of a CO to Fe(2). If the CO bridging the Fe(2)–Fe(3) edge migrates to Fe(2), a path a is encountered again. If the CO bridging the Fe(1)Fe(2) edge migrates to Fe(2), the intermediate IV is then attained through VI. In path b, the anionic charge is located on Fe(1). This scheme suggests the μ_3 mode of bonding of the acyl group may possibly encountered on the surface of heterogeneous metallic catalysts with a low-surface coverage of carbon monoxide.

Starting from 1, we found it of interest to check if the μ_3-acyl group could be brought to a terminal mode of bonding by adding ligands able to displace the acyl group from Fe(1) and Fe(3). Two ligands have been chosen: carbon monoxide and triphenylphosphine. 1 reacts with CO at atmosopheric pressure and at room temperature, yielding the yellow product 2 after crystallization. This product shows four terminal carbonyl stretches (Table III) and an acyl carbonyl stretch at 1605 cm^{-1}. The proton NMR spectrum shows the presence of an ethyl group with an integrated intensity of 5 compared to the intensity of $[P(C_6H_5)_4]^+$. The chemical analysis is consistent with the formula $[Fe(CO)_4COC_2H_5][P(C_6H_5)_4]$. This compound was prepared earlier by the action of C_2H_5COCl on $[Fe(CO)_4]^{2-}$ by Siegl and Collman[14] and isolated as the bis(triphenylphosphine)nitrogen(1+) salt. Thus, the action of carbon monoxide leads to the fragmentation of the cluster 1.

This result is a further proof that the $[HFe_3(CO)_{11}]^-$ anion is not the real catalyst in Reppe's synthesis of alcohols as postulated by Kutepow and Kindler.[15] Indeed, the occurrence of the reaction of the $[HFe_3(CXO)_{11}]^-$ anion with olefin and water at 100 °C to give an alcohol with one more carbon led these authors to the conclusion that $[HFe_3(CO)_{11}]^-$ was the catalyst and that an alkyl trinuclear cluster was the intermediate. Nevertheless, it has been shown that under catalysis conditions $[HFe_3(CO)_{11}]^-$ is not stable and only $[HFe(CO)_4]^-$ has been detected.[16] Furthermore, our results show that 1, which could be the intermediate postulated by Kutepow and Kindler, is not stable under a CO atmosphere and breaks down into mononuclear species.

At room temperature, 1 reacts slowly with 2 equiv of triphenylphosphine with complete fragmentation of the cluster unit. The complexes $(Fe(CO)_4P(C_6H_5)_3$ and $Fe(CO)_3[P(C_6H_5)_3]_2$ have been detected in the solution by infrared spectroscopy, by comparison with literature values in the CO stretching region.[8] Gas chromatographic analysis of the solution shows the presence of ethylene, ethane, and propanal. Consequently, the cluster unit cannot be preserved even with triphenylphosphine, and it is not possible to obtain a trinuclear complex in which an acyl group is terminally bonded.

In order to extend the study of the reactivity of 1 and particularly to see if the μ_3 mode of bonding of the acyl group induces a different behavior, we have allowed 1 to react with hydrogen. 1 in acetone solution reacts slowly with hydrogen at room temperature under pressure (15 atm), but the rate of the reaction may be increased by heating at 70 °C. At the end of the reaction $[HFe_3(CO)_{11}]^-$ is detected but extensive decomposition is also observed. Analysis by gas chromatography of the solution after an overnight experiment gives evidence of a mixture of ethane, propanal, and a small amount of propanol. Even though it was difficult to ascertain the exact ratio of ethane and propanal (ethane was present in the gas phase and in the solution), its total amount ranges between 30 and 40% of the products formed from 1. This strongly suggests the existence of a step during the course of the reaction with hydrogen, in which an equilibrium is reached between a propionyl and an alkyl form of the cluster. We tried to obtain evidence for this alkyl intermediate by heating 1 in refluxing acetone under nitrogen, but only $[HFe_3(CO)_{11}]^-$ has been detected.

We have also studied the reactivity toward a protonic acid. It was of interest to see if the μ_3 mode of bonding of the acyl group would be maintained in the protonated form. 1 reacts with an excess of trifluroacetic acid to give a neutral complex, 3, which is isolated in low yield by crystallization from pentane. The infrared spectrum of 3 in the CO stretching region is complex (Table III) but shows no bridging or acyl carbonyl. Comparison with the spectrum of 1 shows a shift of ca. 50 cm^{-1} toward higher frequency for the first carbonyl stretch. The proton NMR

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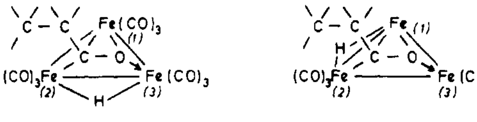

3a 3b

Figure 3. Proposed structures for 3.

spectrum shows an ethyl resonance that is slightly changed compared to 1 (Table III). In the high-field region, a hydride signal is observed at −24.70 ppm.

The same pattern as seen in 1 is observed in the ^{13}C NMR spectrum of 3. Especially in the CO region, the same type of spectrum is observed. Resonances at 247.5, 207.4, and 207.0 ppm compare well with those of 1, and the chemical shift is only slightly changed by protonation. Furthermore, the compound analyzes ae $HFe_3(CO)_9CO-C_2H_5$. From these observations, we can conclude that the core of the cluster is not affected by protonation and, in particular, that the μ_3 mode of bonding of the acyl group is preserved.

The spectroscopic data are consistent with the two structures presented in Figure 3. From the value of the chemical shift of the hydride, this ligand is clearly seen to bridge an iron–iron bond[17,18] and the two structures **3a** and **3b** are consistent with our data. However it is difficult to chose between these two forms. Nevertheless, the occurrence of the bonding of Fe(3) to the oxygen atom could favor structure **3a**.

Acknowledgment. This work has been supported by the CNRS (ATP Chimie Fine). We thank Renée Enjalbert for assistance in X-ray preliminary studies and Dr. Jean Galy for helpful comments.

Note Added in Proof. Our hypothesis has been confirmed by an X-ray structure determination of $HFe_3(CO)_9COCH_3$ which appeared when this paper was submitted for publication. Wong, W. K.; Wilkinson, G.; Galas, A. M. R.; Thornton-Pett, M. A.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 842.

Registry No. 1, 86508-04-5; 2, 86508-05-6; 3, 86508-06-7; $[HFe_3(CO)_{11}]^-$, 55188-22-2.

Supplementary Material Available: Tables of anisotropic thermal parameters (Table IIS.A), phenyl atomic parameters (Table IIS.B), and structure factors (22 pages). Ordering information is given on any current masthead page.

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Binuclear Phosphinothioylidene Complexes

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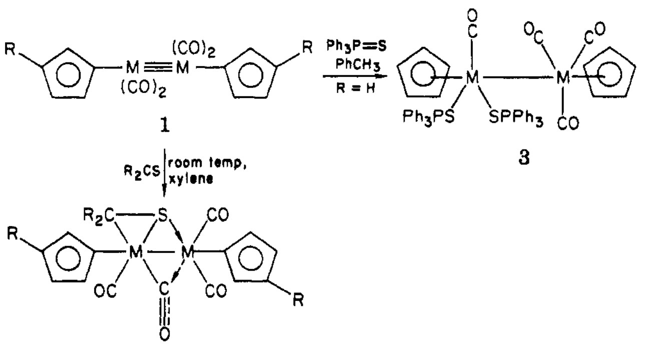
Lawesson's reagent (the dimer of (*p*-methoxyphenyl)thionophosphine sulfide) reacts with dicyclopentadienyltetracarbonyldimolybdenum or -ditungsten to give binuclear complexes containing a phosphinothioylidene ligand. These complexes were characterized on the basis of analytical and spectral data and a single-crystal X-ray analysis of the molybdenum complex. Crystal data of $[(C_5H_5)_2Mo_2(CO)_4(SPC_6H_4OCH_3)]$ are as follows: $a = 9.471$ (4) Å, $b = 9.119$ (3) Å, $c = 16.145$ (2) Å, $\alpha = 90.75$ (2)°, $\beta = 97.37$ (2)°, $\gamma = 126.89$ (3)°, $V = 1098.8$ Å,^{3} $Z = 2$, triclinic, space group $P\bar{1}$. Intensity data were collected by counter methods, Mo $K\alpha_1$ radiation. The structure was refined on 3541 reflections with $I > 2.30\sigma(I)$ to $R_F = 0.020$ and $R_{wF} = 0.028$. The P atom is σ bonded to Mo(1) and P═S π bonded to Mo(2): Mo—Mo = 3.245 (1) Å, Mo(1)—P = 2.326 (1) Å, Mo(2)—P = 2.451 (1) Å, Mo(2)—S = 2.567(1) Å, P═S = 2.022 (1) Å, Mo(1)–P–Mo(2) = 85.53 (3)°. One carbonyl attached to Mo(2) is semibridging: Mo(2)—C(21) = 1.968 (3) Å, Mo(1)···C(21) = 2.864 (3) Å, Mo(2)–C(21)–O(21) = 166.0 (2)°.

The reaction of metal–metal triple-bond complexes 1 with organosulfur compounds has been the subject of several investigations. Treatment of thioketones with 1 in xylene or toluene at room temperature gave a novel class of thione complexes 2 containing a semibridging carbonyl group.[2] These complexes undergo interesting ligand substitution and alkylation reactions on exposure to phosphites and alkoxyphosphines.[3]

A formal 1,1 addition to 1 occurs on reaction with triphenylphosphine sulfide to give 3.[4] In searching for other types of suitable substrates capable of undergoing analogous transformations, we examined the reaction of 1 with



1 3 2

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