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Two-Electron Reduction of $Fe_3(CO)_9(\mu_3\text{-}CCH_2R)(\mu_3\text{-}COC_2H_5)$ Complexes: Induction of an Alkylidyne–Alkylidyne Coupling Reaction and of a Subsequent Rearrangement to Acetylide or Allenyl Ligands. X-ray Structure of $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C(OC_2H_5){=}C{=}CHCHC(O)CH_3)]$ at 100 K

Joan Suades,† Françoise Dahan, and René Mathieu*

Laboratoire de Chimie de Coordination du CNRS, Unité Propre No. 8241 liée par convention à l'Université Paul Sabatier, 31077 Toulouse Cedex, France

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The synthesis of $Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}CCH_2R)$ complexes (R = $(CH_2)_2CH_3$, C_6H_5, $C(O)OCH_3$, $C(O)CH_3$) and their chemical reduction with $[Mn(CO)_5]^-$ are reported. The two-electron reduction always gives $[Fe_9(CO)_3(\mu_3\text{-}\eta^2\text{-}CCCH_2R)]^-$ compounds, but when R = $C(O)OCH_3$ or $C(O)CH_3$, the major products of the reaction are $[Fe_3(CO)_9(\mu_3\text{-}C(OC_2H_5)CC(CH_2R))]^-$ complexes. The structure of one of these anionic clusters with the $[PPh_4]$ counterion has been established for R = $C(O)CH_3$ at 100 K: monoclinic; space group $P2_1/c$; a = 11.890 (1) Å, b = 24.438 (2) Å, c = 12.978 (1) Å; β = 91.53 (2)°; Z = 4. The structure has been refined to R and R_w values of 0.019 and 0.020, respectively, by using 4994 reflections. Indirect evidence of the coupling of the two alkylidyne ligands induced by the two-electron reduction is presented, and a mechanism for the formation of the allenyl ligand is proposed.

Introduction

We have recently shown that chemical or electrochemical reduction of $[PPh_4][Fe_3(CO)_{10}(\mu_3\text{-}CCH_3)]$ and $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ complexes induces the coupling of the CCH_3 ligand with carbon monoxide[1] or with the COC_2H_5 ligand with subsequent eliminations of the ethoxy anion.[2] More recently, the same type of results have been observed by Shapley and co-workers on similar triosmium complexes.[3]

We have now extended the field of this study of the case of various $Fe_3(CO)_9(\mu_3\text{-}CCH_2R)(\mu_3\text{-}COC_2H_5)$ complexes to check the influence of the group R on the scope of the reaction. R has been chosen with varying electron-donating properties, viz, R = $(CH_2)_2CH_3$, C_6H_5, $C(O)OCH_3$, and $C(O)CH_3$. Here we report results showing that, while in all cases the same type of behavior is observed (i.e. two-electron reduction and subsequent elimination of the ethoxy anion to give a $\mu_3\text{-}\eta^2$-bonded acetylide ligand, $CCCH_2R$), in two cases (R = $C(O)OCH_3$ and $C(O)CH_3$) the major product of the reaction results from the elimination of a hydride ligand to give a $\mu_3\text{-}\eta^3$-bonded allenyl ligand, $C_2H_5OC{=}C{=}CHR$. The X-ray structure determination of the complex with R = $C(O)CH_3$ has been performed.

Results and Discussion

$Fe_3(CO)_9(\mu_3\text{-}CCH_2R)(\mu_3\text{-}COC_2H_5)$ complexes have been synthesized by the same pathway as $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$,[4] i.e. by the reaction of triethyloxonium tetrafluoroborate with $[PPh_4][Fe_3(CO)_{10}(\mu_3\text{-}CCH_2R)]$.[5] The yields are nearly quantitative, and the spectroscopic data of these complexes are gathered in Table I. They are very similar to that of the complex with R = H. The infrared stretching frequencies of the carbonyl group are nearly insensitive to the nature of the R group.

These complexes are reduced at room temperature by 2 equiv of $[Mn(CO)_5^-$ giving $Mn_2(CO)_{10}$ and anionic complexes of iron. When R = C_6H_5 and $(CH_2)_2CH_3$, these complexes have been identified by spectroscopic data as being of the $[Fe_3(CO)_9(\mu_3\text{-}CCCH_2R)]^-$ family. Actually, infrared spectra in the ν(CO) stretching region (Table I) closely resemble that of the $[Fe_3(CO)_9(\mu_3\text{-}CCCH_3)]^-$ complex.[2] ^1H and ^{13}C NMR spectra (Table I) provide confirmation giving good evidence of the presence of the CCH_2R fragment, especially as characteristic ^{13}C resonances[2,6] of the acetylide carbons are detected. Moreover as for the $[Fe_3(CO)_9(\mu_3\text{-}CCCH_3)]^-$ complex,[2] the carbonyl resonances appear as two singlets in an approximative 2/1 ratio, giving evidence of a localized rapid axial–radial exchange. The same phenomenon has been observed for the isoelectronic $[Ru_3(CO)_9(\mu_3\text{-}CC\text{-}t\text{-}Bu)]$ anion.[7] Thus, in both cases, the same behavior toward reduction as $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ is observed and is summarized by the equation $Fe_3(CO)_9(\mu_3\text{-}COEt)(\mu_3\text{-}CCH_2R) + 2\ Mn(CO)_5^- \rightarrow [Fe_3(CO)_9(\mu_3\text{-}CCCH_2R)]^- + OEt^- + Mn_2(CO)_{10}$. When R = $CH_3OC(O)$ or $CH_3C(O)$, the reduction is also carried out with 2 equiv of $[Mn(CO)_5]^-$. The infrared spectrum in the ν(CO) stretching region closely resembles that of $[Fe_3(CO)_9(\mu_3\text{-}CC\text{-}CH_2R)]^-$ compounds, but the purple color of the solution compared with the characteristic red color of solutions of the acetylide complexes suggests a different reaction.

Proton NMR studies of the crude products of the reactions confirm these observations and especially give evidence that the ethoxy group is retained in one of the products of the reaction. ^{13}C NMR spectra (Table I) show that the products of the reaction are a mixture of two types of complexes: the acetylide complex and another complex

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† On leave from the Universitat Autonoma de Barcelona, Facultat de Ciencies, Department de Quimica, Divisio Inorganica, Bellaterra, 08193 Barcelona, Spain.

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Table I. Spectroscopic Data for the Isolated Complexes

	IR, cm^{-1}	^1H NMR,^{c,d} δ	^{13}C NMR,^{c,d} δ
$Fe_3(CO)_9(C(CH_2)_3CH_3)(COC_2H_5)$	2085 w, 2035 s, 2012 s, 1997 m,^{a} 1986 m	4.79 (m, CH_2 + OCH_2), 2.36 (m, $C(CH_2)_2$), 1.84 t (*J* = 7.1 Hz ($OCH_2\mathit{CH_3}$) 1.14 (t, *J* = 6.7 Hz, CH_3)	
$Fe_3(CO)_9(CCH_2Ph)(COC_2H_5)$	2085 w, 2037 s, 2010 sh,^{a} 1995 sh	5.94 (CH_2), 4.84 (q, *J* = 7.1 Hz, OCH_2), 1.83 (t, *J* = 7.1 Hz, $OCH_2\mathit{CH_3}$)	356.2 ($\mathit{C}OC_2H_5$), 335.6 ($\mathit{C}CH_2Ph$), 210.4 (CO), 145.8, 129.6, 129.0, 127.6 (Ph), 83.9 (OCH_2), 63.2 ($\mathit{C}H_2Ph$), 14.8 ($OCH_2\mathit{C}H_3$)
$Fe_3(CO)_9(CCH_2C(O)CH_3)(COC_2H_5)$	2085 w, 2035 s, 2011 s,^{a} 2000 sh, 1980 m	5.50 (CH_2), 4.57 (q, *J* = 7 Hz, OCH_2), 2.02 (CH_3), 1.47 (t, *J* = 7 Hz, OCH_2-$\mathit{CH_3}$)	
$Fe_3(CO)_9(CCH_2C(O)OCH_3)(COC_2H_5)$	2086 w, 2040 s, 2015 s,^{a} 2000 sh, 1987 sh	5.58 (CH_2), 4.53 (q, *J* = 7 Hz, OCH_2), 3.61 (OCH_3), 1.45 (t, *J* = 7 Hz, $OCH_2\mathit{CH_3}$)	
$[PPh_4][Fe_3(CO)_9(CC(CH_2)_3CH_3)]$	2043 m, 1985 s, 1977 s, 1955 s,^{b} 1930 m	3.10 (t, *J* = 7 Hz, CH_2), 1.83 (m, CH_2CH_2), 1.09 (t, *J* = 7.4 Hz, CH_3)	217.2, 217.1 (CO), 186.2 ($\mathit{C}{\equiv}C$), 105.4 ($C{\equiv}\mathit{C}$), 35.4, 32.3, 22.5 (CH_2), 13.9 (CH_3)
$[PPh_4][Fe_3(CO)_9(CCCH_2Ph)]$	2045 m, 1987 s, 1980 s, 1957 s,^{b} 1933 m	4.44 (CH_2)	217.6, 217.5 (CO), 188.8 ($\mathit{C}{\equiv}C$), 104.5 ($C{\equiv}\mathit{C}$), 38.8 (CH_2)
$[PPh_4][Fe_3(CO)_9(CCCH_2COCH_3)]$		4.13 (CH_2), 1.70 (CH_3)	216.5, 216.4 (CO), 191.3, ($C{\equiv}C$), 96.0 ($C{\equiv}\mathit{C}$), 47.6 (CH_2), 28.3 (CH_3)
$[PPh_4][Fe_3(CO)_9(CCCH_2C(O)OCH_3]$		3.96 (CH_2), 3.72 (OCH_3)	216.6, 216.5 (CO), 191.2 ($\mathit{C}{\equiv}C$) 95.9 ($C{\equiv}\mathit{C}$), 51.9 (OCH_3)
$[PPh_4][Fe_3(CO)_9(C(OC_2H_5)CCHCOCH_3)]$	2044 m, 1988 s, 1975 s, 1960 s,^{b} 1937 m	4.19 (m, OCH_2), 3.11 (CH), 1.98 (CH_3), 1.42 (t, *J* = 7.1 Hz, $OCH_2\mathit{CH_3}$)	219.7, 218.6, 214.6 (CO), 201.9 ($\mathit{C}OC_2H_5$), 199.3 (C(O)), 145.3 ($C{=}\mathit{C}{=}C$), 67.5 (OCH_2), 38.1 (=CH), 25.8 (CH_3), 14.7 ($OCH_2\mathit{CH_3}$)
$[PPh_4][Fe_3(CO)_9(C(OC_2H_5)CCHC(O)OCH_3)]$	2045 m, 1985 s, 1975 s, 1960 s,^{b} 1935 m	4.21 (m, OCH_2), 3.52 (OCH_3), 2.94 (CH)	219.4, 219.0, 214.6 (CO), 200.1 ($\mathit{C}OC_2H_5$), 172 (C(O)O), 146.1 ($C{=}\mathit{C}{=}C$), 67.2 ($O\mathit{C}H_2$), 50.8 (OCH_3), 27.7 (CH), 14.9 ($OCH_2\mathit{C}H_3$)
$[PPh_4][Fe_3(CO)_9CCH]$	2047 m, 1989 s, 1985 s, 1960 s,^{b} 1935 m	5.47 (CH)	
$[HFe_3(CO)_9CCH$	2094 m, 2058 s, 2043 s, 2022 m,^{b} 2010 m	4.67 (d, *J* = 2 Hz), −27.8 (d, *J* = 2 Hz)	

^{a} In hexane solution. ^{b} In dichloromethane solution. ^{c} In CD_2Cl_2 solution. ^{d} Except $P[C_6H_5]_4$ resonances.

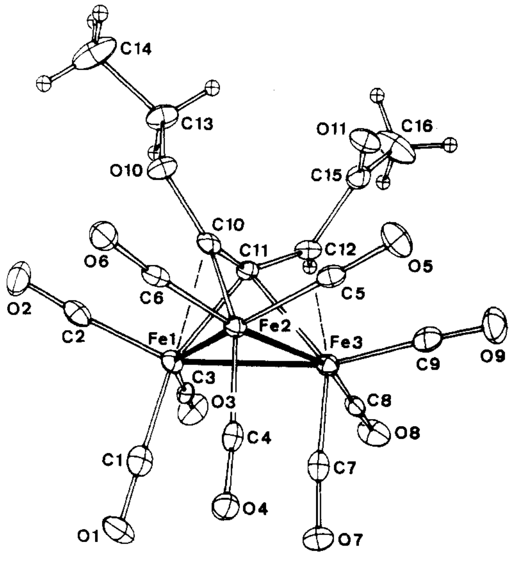


Figure 1. ORTEP drawing of $[Fe_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C(OC_2H_5)CCHC(O)CH_3)]$ showing the atom numbering scheme.

Table II. Selected Bond Lengths (Å) and Angles (deg) with Esd's in Parentheses

	Bond Lengths		
Fe(1)–Fe(2)	2.6060 (5)	Fe(3–)C(11)	2.045 (3)
Fe(1)–Fe(3)	2.6024 (6)	Fe(1)–C(10)	2.208 (3)
Fe(2)–Fe(3)	2.7460 (6)	Fe(3)–C(12)	2.194 (3)
Fe(1)–C(1)	1.792 (3)	C(10)–O(10)	1.372 (3)
Fe(1)–C(2)	1.779 (3)	O(10)–C(13)	1.454 (3)
Fe(1)–C(3)	1.758 (3)	C(13)–C(14)	1.494 (4)
Fe(2)–C(4)	1.817 (3)	C(10)–C(11)	1.378 (4)
Fe(2)–C(5)	1.765 (3)	C(12)–H(C12)	0.970 (9)
Fe(2)–C(6)	1.764 (3)	C(11)–C(12)	1.382 (4)
Fe(3)–C(7)	1.757 (3)	C(12)–C(15)	1.482 (4)
Fe(3)–C(8)	1.780 (3)	C(15)–O(11)	1.207 (3)
Fe(3)–C(9)	1.795 (3)	C(15)–C(16)	1.503 (4)
Fe(1)–C(11)	1.940 (3)	C–O(mean dist)	1.152 (3)
Fe(2)–C(10)	1.867 (3)		
	Bond Angles		
Fe(3)–Fe(1)–Fe(2)	63.64 (2)	C(7)–Fe(3)–C(8)	92.0 (1)
Fe(1)–Fe(2)–Fe(3)	58.12 (2)	C(7)–Fe(3)–C(9)	97.0 (1)
Fe(2)–Fe(3)–Fe(1)	58.24 (2)	C(8)–Fe(3)–C(9)	100.1 (1)
Fe(1)–C(1)–O(1)	175.0 (3)	C(11)–C(10)–O(10)	125.4 (2)
Fe(1)–C(2)–O(2)	176.4 (3)	C(10)–O(10)–C(13)	116.6 (2)
Fe(1)–C(3)–O(3)	177.8 (2)	O(10)–C(13)–C(14)	107.2 (2)
Fe(2)–C(4)–O(4)	173.9 (2)	C(10)–C(11)–C(12)	140.6 (2)
Fe(2)–C(5)–O(5)	178.5 (3)	C(11)–C(10)–Fe(2)	106.6 (2)
Fe(2)–C(6)–O(6)	175.9 (2)	C(11)–C(12)–H(C12)	123 (1)
Fe(3)–C(7)–O(7)	171.7 (2)	C(15)–C(12)–H(C12)	113 (1)
Fe(3)–C(8)–O(8)	176.9 (2)	C(11)–C(12)–C(15)	120.4 (2)
Fe(3)–C(9)–O(9)	176.7 (2)	C(12)–C(15)–O(11)	123.1 (3)
C(1)–Fe(1)–C(2)	98.3 (1)	C(12)–C(15)–C(16)	114.9 (2)
C(1)–Fe(1)–C(3)	98.6 (1)	O(11)–C(15)–C(16)	121.9 (3)
C(2)–Fe(1)–C(3)	99.6 (1)	C(12)–C(11)–Fe(1)	137.6 (2)
C(1)–Fe(1)–C(11)	149.6 (1)	C(10)–C(11)–Fe(3)	113.4 (2)
C(4)–Fe(2)–C(5)	99.8 (1)	Fe(1)–C(11)–Fe(3)	81.49 (9)
C(4)–Fe(2)–C(6)	91.1 (1)		
C(5)–Fe(2)–C(6)	96.9 (1)		
C(4)–Fe(2)–C(10)	159.5 (1)		

containing the $C(OC_2H_5)CCHR$ fragment. A careful analysis of the proton NMR spectra is consistent with these observations and, furthermore, shows that, when R = $CH_3OC(O)$, the acetylide complex represents 33% of the reduced compounds while, when R = $CH_3C(O)$, only 20% of the mixture is of the acetylide form.

By fractional crystallization, it has been possible to isolate the complexes containing the $C(OC_2H_5)CCHR$ fragment, and their chemical analysis was consistent with the $[PPh_4][Fe_3(CO)_9(COC_2H_5CCHR)]$ formulation, suggesting a trinuclear cluster with a metallaallenyl ligand. To confirm firmly this hypothesis, an X-ray structure determination was undertaken on the $[PPh_4][Fe_3(CO)_9\{C(OC_2H_5)CCHC(O)CH_3\}]$ complex. An ORTEP plot of the anionic part of the complex is shown in Figure 1, and bond distances and angles of interest are gathered in Table II.

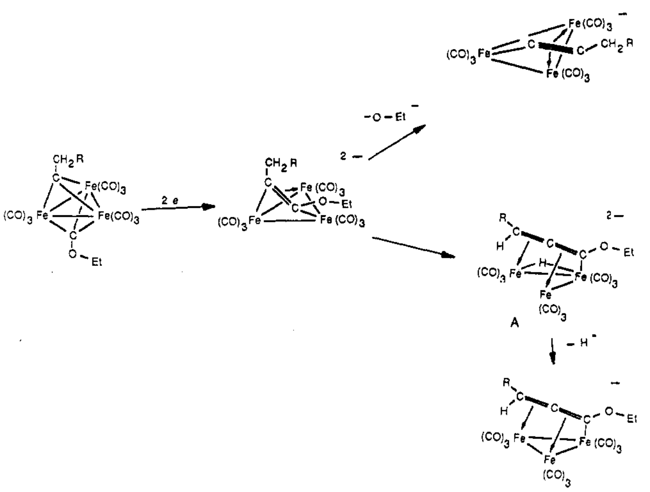
As expected, the anion consists of a trinuclear cluster with three iron atoms at each vertex of an isosceles triangle, each metal atom being bonded to three terminal carbonyl groups. The Fe(2)–Fe(3) bond is longer than the other two Fe–Fe bonds, but this seems to be a common feature of trinuclear clusters with an allenyl ligand.[8,9] The allenyl ligand results formally from the coupling of the two alkylidyne groups of the neutral precursor and from the elimination of one hydrogen ligand in the α-position to the ketonic group. It can be described as being σ-bonded to Fe(2) and π-bonded to Fe(1) and Fe(3). The Fe(1)–C(10) and Fe(3)–C(12) bonds are longer than the Fe(1)–C(11) and Fe(3)-C(11) bonds, which corresponds to the general mode of bonding of μ-η^3-bonded allenyl ligands where it is observed that the central carbon atom is closer to the metal atoms than the other complexed carbon atoms.[8-13] The C(10)–C(11) and C(11)–C(12) bonds are of the same order of magnitude, and the C(10)–C(11)–C(12) angle (140.6 (2)°) is slightly shorter than in the 1-methyl-3-ethyl-3-allenyl ligand bonded to a $HRu_3(CO)_9$ cluster (142.3 (6)°).[8] Finally, the Fe(2)–C(10) bond is the shortest of the Fe–C bonds for the allenyl ligand, suggesting a partial double-bond character. All the other bond distances in the allenyl units have normal order of magnitude for this mode of bonding.

To summarize, the two-electron reduction of $Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}CCH_2R)$ complexes leads, depending on the nature of R, to two types of complexes: (i) when R is n-C_3H_7 or C_6H_5, the only complexes formed are of the type $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CCCH_2R)]^-$ (i.e., formally the two-electron reduction induces the coupling of the two alkylidyne ligands with subsequent rearrangement to an acetylide ligand by ethoxide anion elimination); (ii) when R = $C(O)CH_3$ or $C(O)OCH_3$, the same initial behavior is observed but the acetylide clusters are minor products of the reaction. The major products of the rearrangement of the intermediate dianion result from hydride elimination from the CH_2R group, giving a $C(OC_2H_5)CCHR$ allenyl ligand. This is a quite unexpected result as the hydrogen atoms in the CCH_2R group have an acidic character when the R group has electron-withdrawing properties. We may thus suspect that this hydride elimination is metal-assisted.

At this stage, a question remains open: does the two-electron reduction induce first the coupling of the two alkylidyne fragments prior to the rearrangement toward acetylide or allenyl ligands? The coupling of the CCH_3 and CO ligands induced by one-electron reduction that we observed[1] during the reduction of $[Fe_3(CO)_{10}(\mu_3\text{-}CCH_3)]^-$ suggests that this could be the case.

We did not succeed in isolating the $[Fe_3(CO)_9(COC_2H_5)(CCH_2R)]^{2-}$ intermediate by low-temperature electrochemical reduction, but we have obtained indirect evidence of the coupling of the alkylidyne fragments in the dianionic intermediate. Indeed the reaction of ethoxyacetylene with $[Fe_3(CO)_{11}]^{2-}$ at room temperature leads to the isolation with a good yield of $[Fe_3(CO)_9(\mu_3\text{-}CCH)]^-$ which has been identified by spectroscopic techniques (Table I), the formulation being confirmed by mass spectrometry of the protonated form $HFe_3(CO)_9(\mu_3\text{-}CCH)$ (m/z 446). This result provides good support to our hypothesis and allows us to propose a mechanism for the reduction of $Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}CCH_2R)$ complexes shown in Scheme I.

Scheme I



In the first step, the two-electron reduction would induce the coupling of the two alkylidyne fragments to give a dianionic cluster containing an alkyne in a μ_3-η^2-$\|$ mode of coordination. This type of dianionic cluster has recently been observed in the reduction of $Fe_3(CO)_9(RC_2R)$ complexes.[14] Then, depending on the nature of the R group, two types of rearrangement occur: (i) when R = Ph or C_3H_7, ethoxide elimination gives the acetylide cluster; (ii) when R = $C(O)CH_3$ or $C(O)OCH_3$, ethoxide elimination may also occur, but the main product contains the allenyl ligand $C(OC_2H_5)CCHR$. This could result from hydride elimination by the intermediate of complex A (this type of rearrangement has been observed during the reaction of CH_3CCCH_2R alkynes with $Ru_3(CO)_{12}$[15]).

The occurrence of two negative charges in A would be accommodated by the opening of one Fe–Fe bond while the subsequent re-formation of this metal–metal bond would occur simultaneously with hydride ligand elimination. This proposed mechanism would be consistent with the acidic character of the CH_2 hydrogen atoms in the $CH_2C(O)$–CH_3 group and the elimination of a hydride ion to give the final product.

Experimental Section

All reactions were performed under a nitrogen atmosphere by using standard Schlenk tube techniques. Infrared spectra were recorded with a Perkin-Elmer 225 spectrometer in dichloromethane solution for ionic complexes and hexane solution for neutral complexes. ^1H NMR spectra were obtained with a Bruker WH90 machine and ^{13}C NMR spectra with a Bruker WH 250 instrument. Mass spectra were obtained on a Varian MAT 311-A instrument using 70-eV electron impact.

$[PPh_4][Fe_3(CO)_{10}(\mu_3\text{-}CCH_2R)]$ complexes were synthesized by published methods.[5] $[PPh_4][Mn(CO)_5]$ was obtained by sodium-amalgam reduction of $Mn_2(CO)_{10}$ and cation exchange with $[PPh_4]Br$ in methanol. $[PPh_4]_2[Fe_3(CO)_{11}]$ was prepared by a literature method.[16]

General Procedure for the Synthesis of $Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}CCH_2R)$ Complexes. To a solution of 1 g, (1.17

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Table III. Summary of Crystal and Intensity Data Collection

compd	$[P(C_6H_5)_4][Fe_3(CO)_9C(OC_2H_5)CCHC(O)CH_3]$
formula	$C_{40}Fe_3H_{29}O_{11}P$
fw	884.2
a, Å	11.890 (1)
b, Å	24.438 (2)
c, Å	12.978 (1)
β, deg	91.53 (2)
V, Å^3	3769.6 (9)
Z	4
C_{calcd}, g/cm^3	1.558
cryst system	monoclinic
space group	$C_{2h}^5P2_1/c$
radiatn	Mo Kα from graphite monochromator (λ = 0.71073 Å)
linear abs coeff, cm^{-1}	11.9
temp, K	100
receiving aperture, mm	3.0 × 3.5
takeoff angle, deg	3.5
scan mode	$\omega-2\theta$
scan range, deg	1.10 + 0.35 tan θ
2θ limits, deg	50

mmol (R = $CH_3(CH_2)_2$, $C(O)CH_3$); 1.16 mmol (R = $CH_3OC(O)$); 1.12 mmol (R = Ph)) of the $[PPh_4][Fe_3(CO)_{10}(\mu_3\text{-}CCH_2R)]$ complexes in dichloromethane was added 0.3 g (1,6 mmol) of $[(C_2H_5)_3O][BF_4]$ dissolved in dichloromethane, and the mixture was stirred for 15 min. The solvent then was evaporated under reduced pressure, and the residue was extracted with hexane until the solution was colorless. Except for the case when R = Ph, the products are red oils that were purified by filtration through a Florisil column and evaporation of hexane in vacuo. IR and proton NMR spectroscopies gave evidence of the purity of the complexes that were isolated in 80–90% yield.

$Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}CCH_2Ph)$: red crystals. Anal. Calcd for $C_{20}H_{12}Fe_3O_{10}$: C, 41,38; H, 2.06. Found: C, 41.22; H, 2.12.

$Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}C(CH_2)_3CH_3)$: red oil; mass spectrum, *m/z* 546 and successive loss of 9 CO.

$Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}CCH_2C(O)CH_3)$: red oil; mass spectrum, *m/z* 546 and successive loss of 9 CO.

$Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}CCH_2C(O)OCH_3)$: red oil; mass spectrum, *m/z* 562 and successive loss of 9 CO.

General Procedure for the Reduction of $Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}CCH_2R)$ Complexes. To a solution of 500 mg of $Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}CCH_2R)$ (1.83 mmol (R = $CH_3(CH_2)_2$, $CH_3C(O)$; 1.81 mmol (R = CH_3 OC(O)); 1.72 mmol (R = C_6H_5)) in dichloromethane was added 2 equiv of $[PPh_4][Mn(CO)_5]$ in dichloromethane, and the solution was stirred for 5 h. The solution then was evaporated to dryness in vacuo. The residue was extracted with hexane to remove the $Mn_2(CO)_{10}$ produced during the reaction. The recovered amount of $Mn_2(CO)_{10}$ was in all the cases of the order of 80% of the theoretical amount. The residual solid was dissolved in the minimum amount of methanol, and the solution was cooled to −20 °C. The following complexes have been isolated.

$[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CCCH_2Ph)]$: dark red crystals (58% yield). Anal. Calcd for $C_{42}H_{27}Fe_3O_9P$: C, 57.71; H, 3.08. Found: C, 57.52; H, 3.10.

$[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CC(CH_2)_3CH_3)]$: dark red crystals (43% yield). Anal. Calcd for $C_{39}H_{29}Fe_3O_9P$: C, 55.71; H, 3,45. Found: C, 55.88; H, 3.51.

$[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C(OC_2H_5)CCHC(O)CH_3)]$: dark brown crystals (48% yield). Anal. Calcd for $C_{40}H_{29}Fe_3O_{11}P$: C, 54.29; H, 3.28. Found: C, 53.92; H, 2.98.

$[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C(OC_2H_5)CCHCO(OCH_3))]$: dark brown crystals (52% yield). Anal. Calcd for $C_{40}H_{29}Fe_3O_{12}P$: C, 53.33; H, 3.22. Found: C, 53.30; H, 2.92.

It has not been possible to isolate the acetylide clusters with R = $C(O)CH_3$ and ($C(O)OCH_3$ in the pure state free from the allenyl clusters.

Reaction of $[PPh_4]_2[Fe_3(CO)_{11}]$ with Ethoxyacetylene. $[Pph_4]_2[Fe_3(CO)_{11}]$ (1 g, 0.9 mmol) was dissolved in dichloromethane, and a slight excess (1.5 mmol) of ethoxyacetylene (40% solution in hexane) was added. The solution was stirred for 5 h and then evaporated to dryness. Crystallization in methanol gave 0.3 g of $[PPh_4][Fe_3(CO)_9(CCH)]$ (44% yield) as red crystals. Anal. Calcd for $C_{35}H_{21}Fe_3O_9P$: C, 53.57; H, 2.67. Found: C, 53.38; H, 2.81.

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

atom	*x/a*	*y/b*	*z/c*
Fe(1)	0.65260 (3)	0.14540 (2)	0.10195 (3)
Fe(2)	0.83724 (3)	0.11914 (1)	0.20280 (3)
Fe(3)	0.64156 (3)	0.14212 (2)	0.30185 (3)
C(1)	0.7217 (2)	0.20902 (12)	0.0771 (2)
O(1)	0.7585 (2)	0.25158 (8)	0.0604 (2)
C(2)	0.6557 (2)	0.11766 (12)	−0.0247 (2)
O(2)	0.6549 (2)	0.09730 (8)	−0.1046 (2)
C(3)	0.5131 (2)	0.16920 (11)	0.1016 (2)
O(3)	0.4204 (2)	0.18326 (8)	0.1000 (2)
C(4)	0.9151 (2)	0.18289 (11)	0.2152 (2)
O(4)	0.9704 (2)	0.22094 (7)	0.2168 (1)
C(5)	0.8845 (2)	0.08590 (10)	0.3167 (2)
O(5)	0.9173 (2)	0.06336 (8)	0.3903 (2)
C(6)	0.9395 (2)	0.09185 (10)	0.1212 (2)
O(6)	1.0075 (2)	0.07181 (7)	0.0726 (1)
C(7)	0.7077 (2)	0.20641 (12)	0.3005 (2)
O(7)	0.7403 (2)	0.25107 (8)	0.3062 (1)
C(8)	0.5100 (2)	0.17176 (11)	0.3330 (2)
O(8)	0.4271 (2)	0.19260 (8)	0.3564 (2)
C(9)	0.6912 (2)	0.12159 (11)	0.4278 (2)
O(9)	0.7200 (2)	0.11053 (8)	0.5100 (2)
C(10)	0.7327 (2)	0.06808 (10)	0.1524 (2)
C(11)	0.6302 (2)	0.08278 (10)	0.1910 (2)
C(12)	0.5532 (2)	0.06583 (11)	0.2622 (2)
H(C12)	0.4744 (5)	0.0762 (9)	0.259 (2)
O(10)	0.7518 (1)	0.02334 (7)	0.0915 (1)
C(13)	0.6573 (2)	−0.01343 (11)	0.0730 (2)
C(14)	0.6872 (3)	−0.04997 (13)	−0.0143 (3)
C(15)	0.5744 (2)	0.01587 (11)	0.3245 (2)
O(11)	0.6663 (2)	−0.00459 (7)	0.3355 (2)
C(16)	0.4710 (3)	−0.01012 (13)	0.3673 (3)
P	0.16000 (5)	0.14535 (3)	0.58713 (5)
C(17)	0.0624 (1)	0.11778 (5)	0.6748 (1)
C(18)	−0.0438 (1)	0.14107 (5)	0.6856 (1)
C(19)	−0.1165 (1)	0.12052 (5)	0.7588 (1)
C(20)	−0.0830 (1)	0.07667 (5)	0.8212 (1)
C(21)	0.0231 (1)	0.05338 (5)	0.8105 (1)
C(22)	0.0958 (1)	0.07393 (5)	0.7373 (1)
C(23)	0.1732 (1)	0.10321 (5)	0.4762 (1)
C(24)	0.1948 (1)	0.12756 (5)	0.3816 (1)
C(25)	0.2041 (1)	0.09526 (5)	0.2936 (1)
C(26)	0.1917 (1)	0.03861 (5)	0.3002 (1)
C(27)	0.1701 (1)	0.01427 (5)	0.3949 (1)
C(28)	0.1609 (1)	0.04657 (5)	0.4829 (1)
C(29)	0.1184 (1)	0.21135 (6)	0.5426 (1)
C(30)	0.1860 (1)	0.25663 (6)	0.5655 (1)
C(31)	0.1571 (1)	0.30797 (6)	0.5259 (1)
C(32)	0.607 (1)	0.31402 (6)	0.4634 (1)
C(33)	−0.0069 (1)	0.26874 (6)	0.4405 (1)
C(34)	0.0220 (1)	0.21741 (6)	0.4800 (1)
C(35)	0.2912 (1)	0.15247 (7)	0.6554 (1)
C(36)	0.2924 (1)	0.16764 (7)	0.7590 (1)
C(37)	0.3940 (1)	0.18015 (7)	0.8098 (1)
C(38)	0.4945 (1)	0.17750 (7)	0.7570 (1)
C(39)	0.4934 (1)	0.16233 (7)	0.6533 (1)
C(40)	0.3917 (1)	0.14982 (7)	0.6025 (1)

X-ray Structure Analysis of $[PPh_4][Fe_3(CO)_9\{C(OC_2H_5)CCHC(O)CH_3\}]$. Collection and Reduction of X-ray Data. Crystals belong to the monoclinic system, space group $P2_1/c$. A black, approximately hexagonal, crystal (0.25 × 0.15 × 0.10 mm, thickness 0.20 mm) was sealed on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer equipped with a low-temperature device.[17] This device has been designed for routine low-temperature data collection: it uses low dry nitrogen (< 2 L min^{-1}) cooled in a liquid-nitrogen Dewar. The temperature (down to 93 K) is controlled at the nozzle by a fine low-power electronic regulator that allows a long-term temperature stability

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(17) Bonnet, J.-J.; Askenazy, S., commercially available as NJET from Soterem, Z.I. de Vic, 31320 Castanet Tolosan, France.

better than 0.3 K. At 100 K, cell constants were obtained from a least-squares fit of the setting angles of 25 reflections. A summary of crystal and intensity collection data is given in Table III. A total of 6626 reflections were recorded in two shells (1–20° and 20–25°) by procedures described elsewhere.[18] At the end of the second shell data collection, the crystal broke down and no attempt to collect the few missing reflections was made with a new crystal. Intensity standards, recorded periodically, showed only random, statistical fluctuations. Data reduction was then performed,[19] and empirical absorption corrections[20] were made ($\mu = 11.9$ cm^{-1}; calculated transmission range 0.95–1.00), psi scan having been made before registration of the data. A total of 4994 reflections with $I > 3\sigma(I)$ were considered as observed and used for structure resolution.

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

All non-hydrogen atoms were refined anisotropically, except phenyl rings which were refined as isotropic rigid groups (C–C = 1.395 Å). Hydrogen atoms were all located on a difference Fourier map and were included in calculations in constrained geometry (C–H = 0.97 Å) with fixed isotropic temperature factors, except for that bonded to C(12) which was allowed to vary.

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 refirement converged to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.019$ and $R_W = [\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.020$ with $w = 1/\sigma^2(F_o)$. The error in an observation of unit weight was $S = [\sum w(|F_o| - |Fc|)^2/(n - m)]^{1/2} = 1.0$ with $n = 4994$ observations and $m = 332$ variables. An analysis of variance showed no unusual trends. In the last cycle of refinement the shifts for all parameters but those for H(C12) were less than 0.05σ. A final difference Fourier showed a residual electron density of 0.3 e/Å^3. The final fractional atomic coordinates are listed in Table IV.

Registry No. $Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}CCH_2Ph)$, 110698-07-2; $Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}C(CH_2)_3CH_3)$, 110698-08-3; $Fe_3(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}CCH_2C(O)CH_3)$, 110698-09-4; $Fe(CO)_9(\mu_3\text{-}COC_2H_5)(\mu_3\text{-}CCH_2C(O)OCH_3)$, 110698-10-7; $[PPh_4][Fe_3(CO)_{10}(\mu_3\text{-}CCH_2Ph)]$, 109993-92-2; $[PPh_4][Fe_3(CO)_{10}(\mu_3\text{-}C(CH_2)_3CH_3)]$, 109993-94-4; $[PPh_4][Fe_3(CO)_{10}(\mu_3\text{-}CCH_2C(O)CH_3)]$, 109993-84-2; $[PPh_4][Fe_3(CO)_{10}(\mu_3\text{-}CCH_2C(O)OCH_3)]$, 109993-96-6; $[PPh_4][Mn(CO)_5]$, 67047-43-2; $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CCCH_2Ph)]$, 110698-12-9; $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CC(CH_2)_3CH_3)]$, 110698-14-1; $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C(OC_2H_5)CCHC(O)CH_3)]$, 110698-16-3; $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^3\text{-}C(OC_2H_5)CHC(O)OCH_3)]$, 110698-18-5; $[PPh_4]_2[Fe_3(CO)_{11}]$, 95765-17-6; $[PPh_4][Fe_3(CO)_9(CCH)]$, 110698-20-9; $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CCCH_2C(O)CH_3)]$, 110698-22-1; $[PPh_4][Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}CCCH_2C(O)OCH_3)]$, 110698-24-3; $Mn_2(CO)_{10}$, 10170-69-1; $HFe_3(CO)_9(\mu_3\text{-}CCH)$, 83802-15-7; Fe, 7439-89-6; ethoxyacetylene, 927-80-0.

Supplementary Material Available: Tables of atomic coordinates, hydrogen and thermal parameters, and bond lengths and angles (6 pages); a table of structure factors (24 pages). Ordering information is given on any current masthead page.

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Molecular Orbital Analysis of Dicarbido–Transition-Metal Cluster Compounds

Jean-François Halet[†] and D. Michael P. Mingos[*]

Inorganic Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QR, United Kingdom

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Molecular orbital calculations on dicarbido–transition-metal carbonyl cluster compounds have shown that the bonding between C_2 and the metal cage results primarily from electron donation from the C_2 σ_p- and π-bonding molecular orbitals and back donation from filled metallic molecular orbitals to the C_2 π^* orbitals. The bonding therefore follows closely the Chatt–Dewar–Ducanson model that has been established previously for ethyne and ethene complexes but not for interstitial moieties. The C–C separation in the dicarbido clusters depends critically on the geometric constraints imposed by the metal cage and the extent of forward and back donation. In these clusters where the carbon atoms are in adjacent trigonal-prismatic sites the calculated formal bond order is between 1.0 and 1.5, which agrees well with the observed C–C bond lengths.

Introduction

Carbido–transition-metal carbonyl clusters have been studied in some detail from both an experimental[1] and a theoretical[2] point of view because they are thought to be good models for intermediates in heterogeneous Fischer–Tropsch catalytic processes. The study of polycarbido compounds have received much less attention although examples of such compounds have been recognized in both cluster chemistry and solid-state chemistry. In solid-state chemistry the bonded carbon–carbon unit was characterized initially in the simple binary compounds[3] like CaC_2,

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[†] Permanent address: Laboratoire de Cristallochimie, U.A. 254, University of Rennes, Rennes, France.

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