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“Deoxygenation” of $HC\equiv CC(Me)(OH)Ph$ by $Fe_3(CO)_{12}$. Crystal and Molecular Structure of $Fe_2(CO)_6[HCCHC(Me)Ph]$, a Complex Showing an Uncommon Coordination Arrangement

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Summary: The title complex is obtained by reaction of $Fe_3(CO)_{12}$ with 3-phenyl-1-butyn-3-ol in toluene. It has been characterized by spectroscopy, and its structure has been determined by X-ray analysis. Crystals are triclinic with space group $P\bar{1}$ and $a = 7.152(1)$ Å, $b = 8.494(2)$ Å, $c = 13.465(3)$ Å, $\alpha = 81.94(3)°$, $\beta = 81.33(3)°$, $\gamma = 86.85(3)°$, $V = 800.1(4)$ Å^3, and $Z = 2$. The structure was solved by direct methods and refined to $R = 0.0278$, $R_w = 0.0370$ for 2960 observed reflections ($F > 4.0\sigma(F)$). The hydrogen atoms were located on the final difference maps and refined. During the formation of the complex, deoxygenation and rearrangement of the alkyne occurs with formation of an HC·CH·C{(Me)(Ph)} moiety. The molecule contains a $Fe_2(CO)_6$ unit to which the residual of the alkyne is bonded via a chain of five C atoms, three belonging to the butyne and two to the phenyl ring.

Introduction

We are currently interested in the synthesis and reactivity of chiral metal carbonyl derivatives.[1] We have synthesized chiral complexes by substituting phosphines or diphosphines for CO ligands in ruthenium acetylide clusters[2] or $Co_2(CO)_6(RC\equiv CR')$ derivatives.[3] Another possible approach is the use of chiral acetylenes as ligands. Therefore, we investigated the reactions of iron, ruthenium, and cobalt carbonyls with $HC\equiv CC(Me)(OH)Ph$, 3-phenyl-1-butyn-3-ol (PBO).

Here we report on the results of the reaction of PBO with $Fe_3(CO)_{12}$. Besides tri- and dinuclear acetylene derivatives isostructural with complexes already described in the literature,[4] we could obtain a new molecule, $Fe_2(CO)_6[HCCHC\{(Me)Ph\}]$ (complex 1), whose formation formally involves “deoxygenation” of the alkyne and shift of the OH hydrogen to an acetylene carbon. Complex 1 has been characterized by X-ray diffraction analysis, by elemental analysis, and by spectroscopy.

Experimental Section

Preparation of Complex 1. The reaction of $Fe_3(CO)_{12}$ with a 3:1 molar excess of commercial racemic PBO, (±)-3-phenyl-1-butyn-3-ol, in refluxing toluene (previously dried over sodium) under N_2 for 5 min, followed by reduction to a small volume under vacuum and tlc purification (Kieselgel PF Merck, petroleum ether 40–70 °C and diethyl ether, 3/1 vol), yielded a yellow and a green product identified as *nido*-$Fe_2(CO)_6(PBO)_2$[4] and pentagonal-bipyramidal *closo*-$Fe_3(CO)_6(\mu\text{-}CO)_2(PBO)_2$ “green isomer”.[5] A deep red complex 1 was also isolated in about 10% yield. The yields of the latter increase to 15–20% (based on iron) after 10-min reflux or by increasing the PBO concentration. The use of CO_2 as reaction atmosphere under the same conditions resulted in lower yields of 1. The air-stable complex 1 crystallizes from heptane at −20 °C under N_2 after some hours.

Table I. Crystal Data

empirical formula	$C_{16}H_{10}Fe_2O_6$
color; habit	deep red, lamina
cryst size (mm)	0.1 × 0.4 × 0.7
cryst syst	triclinic
space group	$P\bar{1}$
unit cell dimens	
a (Å)	7.1520(10)
b (Å)	8.494(2)
c (Å)	13.465(3)
α (deg)	81.94(3)
β (deg)	81.33(3)
γ (deg)	86.85(3)
vol (Å^3)	800.1(4)
Z	2
fw	409.9
density (calc) (Mg/m^3)	1.702
abs coeff (mm^{-1})	1.841
F(000)	412

Anal. Calcd (Found) for 1: C, 46.87 (47.03); Fe, 27.25 (27.0); H, 2.46 (2.55). IR (ν_{CO}, C_7H_{16}): 2076 (ms), 2035 (vs), 2014 (ms) 1994 (vs) cm^{-1}. ^{1}H NMR ($CDCl_3$, room temperature): δ 7.79 (d, 1 H, J = 8.42 Hz) (H on C(10)); 7.28 (t, J = 7.33), 7.07 (t, J = 7.30), 6.98 (t, J = 7.31) (all 1 H; C(9), C(8), C(7)); 4.73 (d, 1 H, J = 6.22 Hz) (C(6)); 7.86 (d, 1 H, J = 5.86 Hz) (C(1)); 4.30 (d, 1 H, J = 5.86 Hz) (C(2)); 1.92 (s, 3 H, CH_3). (The assignment of the hydrogens on C(6) and C(10) can be reversed.) $^{13}C\{^1H\}$ NMR ($CDCl_3$, room temperature 14.0 (s) (C(4)); 72.91 (s) (C(3)); 87.86 (s), 90.15 (s) (C(1), C(2)); 126.82 (s), 128.67 (s), 129.98 (s), 133.64 (s), 133.37 (s), 145.31 (s) (C, Ph); 209.97 (s), 212.74 (s) (COs).

Crystallography. Crystal data are listed in Table I. Parameters of data collection solution and refinement are listed in Table II. The hydrogen atoms were clearly located on the last Fourier difference maps and refined with fixed thermal parameters. The fractional non-hydrogen atomic coordinates are listed in Table III.

Results and Discussion

The reaction of $Fe_3(CO)_{12}$ with PBO (eq 1) yields the complexes shown in Chart I and some CO_2.[6] The structural, spectroscopic, and analytical results indicate for

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[1] See for example: Mani, D.; Schacht, H. T.; Powell, A.; Vahrenkamp, H.; *Organometallics* 1987, *6*, 1360.

[2] (a) Predieri, G.; Tiripicchio, A.; Vignali, C.; Sappa, E. *J. Organomet. Chem.* 1988, *342*, C33. (b) Sappa, E.; Predieri, G., Tiripicchio, A.; Vignali, C. *J. Organomet. Chem.* 1989, *378*, 109.

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[6] In one experience, the mercury check valve was replaced by a bubbler filled with a water solution of $Ba(OH)_2$; a white precipitate was formed in small amounts. This was identified as $BaCO_3$.

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Table II. Data Collection, Solution, and Refinement

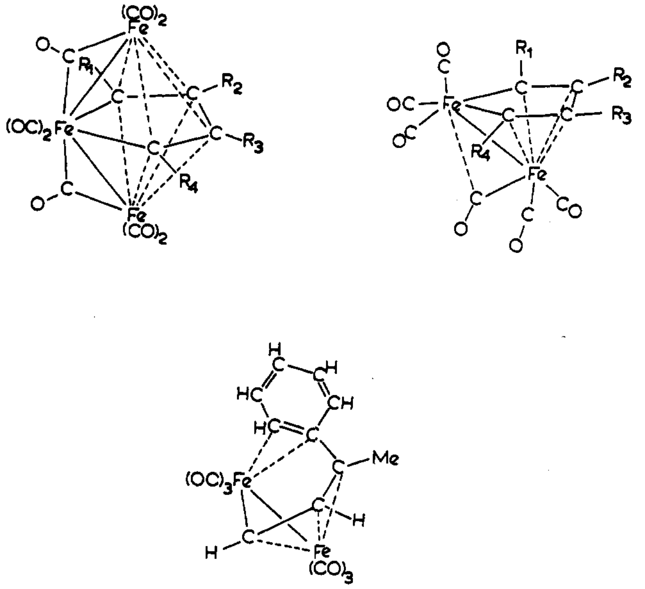
diffractometer used	Siemens P4
radiation	Mo Kα (λ = 0.710 73 Å)
temp (K)	293
monochromator	highly oriented graphite crystal
2θ range (deg)	2.0–50.0
scan type	θ–2θ
scan speed (deg/min)	variable; 4.00–20.00 (in θ)
scan range (θ) (deg)	2.00
background measurement	stationary crystal and stationary counter at beginning and end of scan, each for 0.5% of total scan time
no. of std reflns	2 measd every 50 reflns
index ranges	$-9 \le h \le 9, -10 \le k \le 11, -15 \le l \le 17$
no. of reflns collcd	5310
no. of ind reflns	3684 (R_{int} = 1.24%)
no. of obsd reflns	2960 ($F > 4.0\sigma(F)$)
abs corr	semiempirical
min/max transm	0.1104/0.1549
system used	Siemens SHELXTL PLUS (PC Version)
soln	direct methods
refinement method	full-matrix least squares
quantity minimized	$\sum w(F_o - F_c)^2$
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
no. of params refined	247
final R indices (obsd data)	R = 2.78%, R_w = 3.70%
R indices (all data)	R = 3.74%, R_w = 4.05%
goodness-of-fit	0.95
largest and mean Δ/σ	0.180, 0.012
data-to-param ratio	12.0:1
largest diff peak (e Å^{-3})	0.46
largest diff hole (e Å^{-3})	0.00

Table III. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 10^3$)

	x	y	z	U(eq)[a]
Fe(1)	824(1)	9231(1)	7659(1)	38(1)
Fe(2)	2486(1)	7141(1)	6498(1)	33(1)
C(1)	2842(3)	9429(2)	6393(2)	38(1)
C(2)	3574(3)	9931(3)	7193(2)	40(1)
C(3)	3563(3)	8808(3)	8089(2)	39(1)
C(4)	4112(4)	9341(4)	9032(2)	56(1)
C(5)	4074(3)	7120(2)	7972(2)	37(1)
C(6)	5430(3)	6733(3)	7169(2)	39(1)
C(7)	6198(3)	5152(3)	7171(2)	49(1)
C(8)	5656(4)	4011(3)	7966(2)	57(1)
C(9)	4327(4)	4384(3)	8777(2)	56(1)
C(10)	3548(3)	5879(3)	8785(2)	46(1)
C(11)	−379(3)	7561(3)	8399(2)	48(1)
O(11)	−1185(3)	6546(3)	8883(2)	72(1)
C(12)	−936(3)	10121(3)	6916(2)	55(1)
O(12)	−2058(3)	10744(3)	6464(2)	84(1)
C(13)	209(4)	10621(3)	8543(2)	53(1)
O(13)	−202(4)	11514(3)	9102(2)	84(1)
C(21)	1771(3)	5092(3)	6923(2)	45(1)
O(21)	1272(3)	3838(2)	7144(2)	73(1)
C(22)	4087(3)	6934(3)	5354(2)	40(1)
O(22)	5072(3)	6881(2)	4612(1)	60(1)
C(23)	507(3)	7482(3)	5863(2)	47(1)
O(23)	−731(3)	7658(3)	5410(2)	71(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Chart I. Structures of the Complexes Obtained from the Reaction of $Fe_2(CO)_{12}$ with PBO[a]



[a] The derivatives $Fe_3(CO)_6(\mu\text{-}CO)_2(PBO)_2$ and $Fe_2(CO)_6(PBO)_2$ may give substitutional isomers (e.g. $R_1 = R_4$ = H, $R_2 = R_3$ = C(OH)MePh; $R_1 = R_3$ = H, $R_2 = R_4$ = C(OH)MePh).

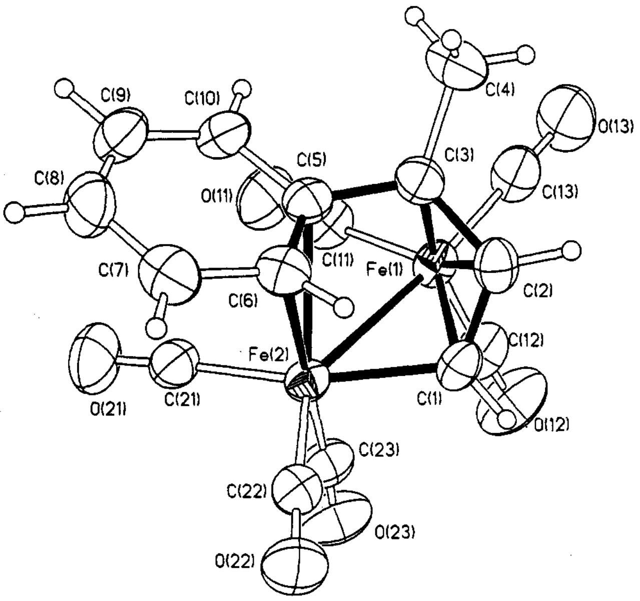


Figure 1. ORTEP view of the molecule (50% probability) with the atom labeling scheme.

$$Fe_3(CO)_{12} + HC{\equiv}C{\cdot}C(Me)(OH)Ph \rightarrow Fe_3(CO)_6(\mu_2\text{-}CO)_2(PBO)_2\ (30\%) + Fe_2(CO)_6(PBO)_2\ (20\%) + Fe_2(CO)_6[HC{\cdot}CHC(Me)Ph]\ (1)\ (10\%) + Fe(CO)_5 + CO_2 \quad (1)$$

complex 1 a formula $Fe_2C_{16}H_{10}O_6$. The molecular structure of the complex is shown in Figure 1. Selected bond distances and angles are given in Table IV.

Complex 1 has no symmetry elements and is formed by a $Fe_2(CO)_6$ framework with a Fe–Fe distance of 2.645(1) Å and three terminal carbonyls coordinated to each metal. The Fe–Fe distance is in the normal range of values found in diiron carbonyl compounds (2.50–2.74 Å). The PBO ligand has undergone chemical transformations during the reaction; one hydrogen is now on C(2) and the OH group has disappeared. The organic ligand bonds Fe(1) via C(1)–C(2)–C(3), with C(1) bridging the Fe–Fe bond, and interacts with Fe(2) via the phenyl C(5)–C(6) bond. The ensemble C(1)–C(3) is characterized by C–C distances of 1.393(3) and 1.429(3) Å, intermediate between a double and a single bond. The C(3)–C(5) distance [1.484(3) Å] is nearer to that of a single bond, and the C(5)–C(6) distance [1.402(3) Å] corresponds exactly to a phenyl value. The angle between the C(1)C(2)C(3) plane and the C(3)C(5)C(6)

Table IV. Bond Lengths (Å) and Bond Angles (deg)

Fe(1)–Fe(2)	2.645(1)	Fe(1)–C(1)	2.055(2)	C(4)–H(4B)	0.958(35)	C(4)–H(4C)	0.994(31)
Fe(1)–C(2)	2.066(2)	Fe(1)–C(3)	2.123(2)	C(5)–C(6)	1.402(3)	C(5)–C(10)	1.431(3)
Fe(1)–C(11)	1.796 (2)	Fe(1)–C(12)	1.794(3)	C(6)–C(7)	1.423(3)	C(6)–H(6)	0.960(30)
Fe(1)–C(13)	1.784(3)	Fe(2)–C(1)	1.957(2)	C(7)–C(8)	1.364(4)	C(7)–H(7)	0.917(32)
Fe(2)–C(5)	2.429(2)	Fe(2)–C(6)	2.403(2)	C(8)–C(9)	1.396(4)	C(8)–H(8)	0.931(34)
Fe(2)–C(21)	1.830(2)	Fe(2)–C(22)	1.799(2)	C(9)–C(10)	1.359(4)	C(9)–H(9)	1.026(30)
Fe(2)–C(23)	1.751(2)	C(1)–C(2)	1.393(3)	C(10)–H(10)	0.912(32)	C(11)–O(11)	1.133(3)
C(1)–H(1)	0.916(26)	C(2)–C(3)	1.429(3)	C(12)–O(12)	1.142(3)	C(13)–O(13)	1.139(4)
C(2)–H(2)	0.950(29)	C(3)–C(4)	1.517(4)	C(21)–O(21)	1.127(3)	C(22)–O(22)	1.137(3)
C(3)–C(5)	1.484(3)	C(4)–H(4A)	1.013(34)	C(23)–O(23)	1.140(3)		

Fe(2)–Fe(1)–C(1)	47.2(1)	Fe(2)–Fe(1)–C(2)	73.4(1)	Fe(1)–C(1)–Fe(2)	82.4(1)	Fe(1)–C(1)–C(2)	70.7(1)
C(1)–Fe(1)–C(2)	39.5(1)	Fe(2)–Fe(1)–C(3)	75.3(1)	Fe(2)–C(1)–C(2)	115.8(1)	Fe(1)–C(1)–H(1)	119.3(16)
C(1)–Fe(1)–C(3)	70.0(1)	C(2)–Fe(1)–C(3)	39.9(1)	Fe(2)–C(1)–H(1)	124.4(19)	C(2)–C(1)–H(1)	119.6(19)
Fe(2)–Fe(1)–C(11)	85.5(1)	C(1)–Fe(1)–C(11)	132.6(1)	Fe(1)–C(2)–C(1)	69.8(1)	Fe(1)–C(2)–C(3)	72.2(1)
C(2)–Fe(1)–C(11)	138.0(1)	C(3)–Fe(1)–C(11)	100.3(1)	C(1)–C(2)–C(3)	116.3(2)	Fe(1)–C(2)–H(2)	118.3(16)
Fe(2)–Fe(1)–C(12)	100.9(1)	C(1)–Fe(1)–C(12)	90.5(1)	C(1)–C(2)–H(2)	121.6(17)	C(3)–C(2)–H(2)	121.1(17)
C(2)–Fe(1)–C(12)	117.1(1)	C(3)–Fe(1)–C(12)	156.9(1)	Fe(1)–C(3)–C(2)	67.9(1)	Fe(1)–C(3)–C(4)	123.2(2)
C(11)–Fe(1)–C(12)	102.2(1)	Fe(2)–Fe(1)–C(13)	167.0(1)	C(2)–C(3)–C(4)	119.0(2)	Fe(1)–C(3)–C(5)	105.8(1)
C(1)–Fe(1)–C(13)	128.0(1)	C(2)–Fe(1)–C(13)	96.3(1)	C(2)–C(3)–C(5)	118.2(2)	C(4)–C(3)–C(5)	114.5(2)
C(3)–Fe(1)–C(13)	91.7(1)	C(11)–Fe(1)–C(13)	97.6(1)	Fe(2)–C(5)–C(3)	94.4(1)	Fe(2)–C(5)–C(6)	72.1(1)
C(12)–Fe(1)–C(13)	90.8(1)	Fe(1)–Fe(2)–C(1)	50.4(1)	C(3)–C(5)–C(6)	120.5(2)	Fe(2)–C(5)–C(10)	115.2(2)
Fe(1)–Fe(2)–C(5)	69.6(1)	C(1)–Fe(2)–C(5)	81.7(1)	C(3)–C(5)–C(10)	120.6(2)	C(6)–C(5)–C(10)	117.3(2)
Fe(1)–Fe(2)–C(6)	99.0(1)	C(1)–Fe(2)–C(6)	87.6(1)	Fe(2)–C(6)–C(5)	74.1(1)	Fe(2)–C(6)–C(7)	113.5(2)
C(5)–Fe(2)–C(6)	33.7(1)	Fe(1)–Fe(2)–C(21)	114.2(1)	C(5)–C(6)–C(7)	120.2(2)	Fe(2)–C(6)–H(6)	93.4(21)
C(1)–Fe(2)–C(21)	164.4(1)	C(5)–Fe(2)–C(21)	90.8(1)	C(5)–C(6)–H(6)	120.3(20)	C(7)–C(6)–H(6)	118.3(20)
C(6)–Fe(2)–C(21)	93.7(1)	Fe(1)–Fe(2)–C(22)	143.7(1)	C(6)–C(7)–C(8)	120.3(2)	C(7)–C(8)–C(9)	120.1(2)
C(1)–Fe(2)–C(22)	93.5(1)	C(5)–Fe(2)–C(22)	113.3(1)	C(8)–C(9)–C(10)	120.7(2)	C(5)–C(10)–C(9)	121.3(2)
C(6)–Fe(2)–C(22)	79.9(1)	C(21)–Fe(2)–C(22)	102.0(1)	Fe(1)–C(11)–O(11)	177.4(2)	Fe(1)–C(12)–O(12)	177.1(3)
Fe(1)–Fe(2)–C(23)	85.4(1)	C(1)–Fe(2)–C(23)	91.1(1)	Fe(1)–C(13)–O(13)	179.2(3)	Fe(2)–C(21)–O(21)	176.2(2)
C(5)–Fe(2)–C(23)	152.6(1)	C(6)–Fe(2)–C(23)	173.0(1)	Fe(2)–C(22)–O(22)	176.4(2)	Fe(2)–C(23)–O(23)	176.3(2)
C(21)–Fe(2)–C(23)	89.4(1)	C(22)–Fe(2)–C(23)	93.3(1)				

plane is 63°. The contact distances and the angles around the carbon atoms suggest an electron delocalization principally in the C(1)–C(3) fragment. The phenyl ring forms an angle of 71° with the Fe(2)C(5)C(6) plane, with Fe(2) at a distance of 2.403(2) and 2.429(2) Å from C(5) and C(6), respectively. Therefore, the ligand is a formal six-electron donor and gives rise to two types of π bonding: an allyl interaction with Fe(1) and an interaction of the phenyl ring with Fe(2).

This bonding mode can be compared with that found in $Fe_2(CO)_6[\mu\text{-}C(OEt)C(Ph){\cdot}C(Ph)H]$,[7] in $Fe_2(CO)_6[C_3Ph_3H]$,[8] and in $Fe_2(CO)_6[(EtO)CCH{=}CHC{\cdot}C(OEt)]$.[9] Another example of a three (allenyl) plus two (ethylene) carbon atom system is ref 10.

The interaction between Fe(2) and the phenyl C(5)–C(6) carbons is rare. Besides the binuclear derivatives reported above,[7,8] two more examples have been reported respectively for the electronically unsaturated ruthenium[13] and iron[14] phosphido-bridged $(\mu\text{-}H)M_3(CO)_9(\mu\text{-}PRR')$ clusters in which one phenyl on phosphorus interacts with one metal center. The use of propargyl derivatives for the synthesis of allenyl derivatives has been described by Wojcicki and Schuchart.[11] However, in these derivatives, as for example $CpWFe(CO)_5(RC{=}C{=}CH_2)$,[12] a different geometry has been found.

The NMR results are in accord with the X-ray structure and confirm the presence of hydrogens on the C(1), C(2), C(6), and phenyl C(7)–C(10) carbon atoms of the organic moiety, in particular, the ^1H NMR signals at 7.86 (d) and 4.30 (d) can be attributed to the hydrogens of the allyl system. This is supported by the same J value of 5.86 Hz. The signals at 7.79 (d) and 4.73 (d) (different value of J) can be attributed to C(6) and C(10), and the triplets, to the remaining phenyl hydrogens. The ^{13}C NMR spectrum provides also evidence for the presence of two differrent sets of three CO's each and probably localized scrambling of the carbonyls at room temperature in solution.

Finally, the X-ray and ^1H NMR show the presence of the hydrogen on C(6). Therefore, the above discussed interaction of the phenyl ring with Fe(2) is not the consequence of an ortho-metalation. The source of hydrogen on C(2) should hence be the OH originally present in PBO.

The unprecedented deoxygenation of PBO to form complex 1 is worthy of note. Some reports on the reactivity of PBO and related ligands have appeared. The acetylene $(OH)Ph(Me)C{\cdot}C{\equiv}C{\cdot}C(Me)PhOH)$ reacts with $Ru_3(CO)_{12}$ to form the hydride $(\mu\text{-}H)Ru_3(CO)_9\{\mu_3\text{-}\eta^2\text{-}\perp\text{-}C{\equiv}C{\cdot}C(Me)Ph(OH)\}$ (complex 2) and the ketone $Ph{\cdot}C({=}O)Me$ with the shift of one OH hydrogen to the cluster metals.[15] A shift of hydrogen from OH to N in cluster-bound nitrobenzene residuals has been observed; this occurs in reductive carbonylation experiments,[13] a reaction related with the water gas shift reaction discussed below. Complex 2 is also formed directly from $Ru_3(CO)_{12}$ and PBO. The

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ligand can be dehydrated to cluster-bound $\{\mu_3\text{-}\eta^2\text{-}\perp\text{-}C{\equiv}C{\cdot}C({=}CH_2)Ph\}$ with acetic acid.[17]

We have no direct evidence for the mechanism of formation of complex 1, as other complexes and decomposition products are obtained in the same reaction. A tempting hypothesis could be formation of CO_2 from a coordinated carbonyl and the PBO oxygen as a consequence of the attack of the OH group of alkyne on a carbonyl on iron in a fashion similar to that proposed for the water gas shift reaction homogeneous catalysis,[18] eq 2. The observation of some CO_2 in the reaction effluents and the lower yields of 1 under CO_2 could be indirect evidence for this hypothesis.

$$\text{R–OH} + \text{(OC)–ML}_n \rightarrow \text{(R)(H)–ML}_n + \text{CO}_2 \qquad (2)$$

$$\text{R} = \text{HC}{\equiv}\text{C}{\cdot}\text{C(Me)Ph}$$

Related reactions between $Fe_3(CO)_{12}$ and organolithium reactants are known.[19]

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Supplementary Material Available: Full lists of bond angles, anisotropic displacement coefficients, and H-atom coordinates (2 pages). Ordering information is given on any current masthead page.

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