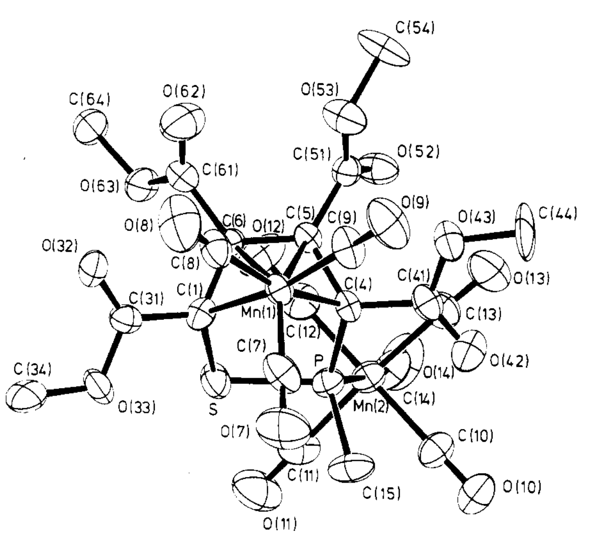


Figure 1. ORTEP plot of **6a**.

The dihedral angle between the least-squares planes C(1), C(6), C(5), C(4) and C(1), S, P, C(4) is 50.4°. The bonding of the cyclic ligand to the metal Mn(1) is identical with that observed.[18] Mn(1) is π-bonded to C(5)–C(6) and σ-bonded to C(1) und C(4), which explains the bond sequence long–short–long for C(4)–C(5), C(5)–C(6), and C(1)–C(6). The angles between the planes C(6)–C(61)–O(62) and C(1)–C(6)–C(5), and C(5)–C(51)–O(52) and C(4)–C(5)–C(6) are 59.9° and 63.4°, respectively. These values provide a satisfactory explanation for the observed single bonds C(5)–C(51) and C(6)–C(61), as there is no possibility for π-conjugation between C(5)–C(51) and C(6)–C(61).

The deviations of C(1) and C(4) from the planes S–C(6)–C(31) and P–C(5)–C(41) are 0.35 and 0.33 Å, respectively, which is consistent with sp^3-hybridized carbon atoms C(1) and C(4).

Acknowledgment. Support of this work by Deutsche Forschungsgemeinschaft, Bonn/Bad Godesberg, by Fonds der Chemischen Industrie, Frankfurt/Main, by BASF Aktiengesellschaft, by Consortium für elektrochemische Industrie GmbH, München, and by Schering AG is gratefully acknowledged. Thanks are also due to Prof. Dr. J. Strähle for providing the facilities for the X-ray investigations.

Registry No. **3**, 89509-61-5; **4a**, 762-42-5; **4b**, 762-21-0; **4c**, 79866-97-0; **5b**, 111290-91-6; **6a**, 111290-92-7; **6b**, 111290-93-8; **6c**, 111290-94-9.

Supplementary Material Available: Tables of least-squares planes, final positional and anisotropic thermal parameters, and interatomic distances and angles for **6a** (13 pages); a listing of observed and calculated structure factors for **6a** (15 pages). Ordering information is given on any current masthead page.

An Accurate Determination of the Molecular Structure of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_2Et_2)$: A Seminal Type of Acetylene Complex

Arthur J. Carty* and Nicholas J. Taylor

Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

Enrico Sappa*

Istituto di Chimica Generale ed Inorganica, Università di Torino, 10125 Corso Massimo d'Azeglio 48, Torino, Italy

Received June 16, 1987

A precise single-crystal X-ray structure determination of the $\perp$-diethylacetylene complex $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}EtC{\equiv}CEt)$ has been carried out. This molecule is one of a very small number of alkyne cluster complexes in which one carbon atom of the alkyne is coordinated to all three metal atoms with the triple bond perpendicular to one M–M vector. Such molecules are thought to be important intermediates in alkyne triple-bond scission reactions leading to bis(alkylidyne) species. Crystals of the title compound are triclinic, space group $P\bar{1}$, with $a = 9.446$ (1) Å, $b = 9.644$ (1) Å, $c = 10.022$ (1) Å, $\alpha = 87.84$ (1)°, $\beta = 85.96$ (1)°, $\gamma = 89.58$ (1)°, $V = 910.2$ Å^3, and $Z = 2$. The solution and refinement were based on 2560 observed reflections ($I \geqslant 3\sigma(I)$). Final R and R_w values with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic were 0.027 and 0.031. Key features of the accurate structure are as follows: (i) one carbon atom of the alkyne is bonded symmetrically to the Fe framework resembling a μ_3-alkylidyne; (ii) one Fe–Fe bond (Fe(1)–Fe(3) of 2.5666 (5) Å), that bridged perpendicularly by the alkyne is 0.1 Å longer than the two remaining, equivalent Fe–Fe bonds; (iii) the substituents on the alkyne have an anti disposition across the plane of the alkyne. Possible structural implications for the conversion of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}RC_2R')$ to $Fe_3(CO)_9(\mu_3\text{-}CR)(\mu_3\text{-}CR')$ are discussed.

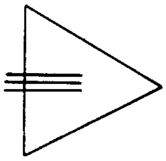
Of the many transition-metal–acetylene complexes which have been characterized,[1] one of the most interesting is $M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}RC_2R')$ (M = iron group metal) where the alkyne triple bond is disposed above the plane of the three metal atoms and perpendicular to one of the M–M bonds as shown in **1**.[2] The unusual bonding in these molecules, in which one alkyne carbon atom interacts with all three metals, has been the subject of theoretical studies by CNDO[3] and EHMO[4] methods. Apart from the fact that

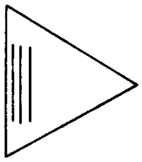
---

[1] For recent reviews see: (a) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203. (b) Einstein, F. W. B.; Tyers, K. G.; Tracey, A. S.; Sutton, D. *Inorg. Chem.* **1986**, *25*, 1631. (c) Bruce, M. I. *J. Organomet. Chem.* **1983**, *257*, 417.

[2] Blount, J. F.; Dahl, L. F.; Hoogzand, C.; Hübel, W. *J. Am. Chem. Soc.* **1966**, *88*, 292.

these molecules are known to be intermediates en route to more complex organometallic complexes,[5] there are two other aspects of their chemistry which are of current interest: (a) the relative stabilities and interrelationships between 46-electron $M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}RC_2R')$, 47-electron $[M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\|\text{-}RC_2O]^{2-}$, and 48-electron $M_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}\|\text{-}RC_2R')$[6-11] (in fact EHMO calculations[4] show that the $\mu^3\text{-}\eta^2\text{-}\perp$ configuration is favored by 15 kcal mol^{-1} for 46 electrons but that the $\mu_3\text{-}\eta^2\text{-}\|$ mode is preferred by 9 kcal mol^{-1} for 47 electrons and by 33 kcal mol^{-1} for 48 electrons); (b) the possible interconversion of 46-electron $M_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}RC_2R')$ to the isomeric alkylidyne complexes $M_3(CO)_9(\mu_3\text{-}CR)(\mu_3\text{-}CR')$, a reaction which, if intramolecular, would represent a skeletal isomerism based on the Wade–Mingos PSEP theory.[12] Although there is experimental evidence for reversible conversion of 46-electron (or closo) $Fe_3(CO)_9(\mu_3\text{-}CCH_3)(\mu_3\text{-}COC_2H_5)$ to 48-electron (or nido) $Fe_3(CO)_{10}(\mu_3\text{-}\eta^2\text{-}\|\text{-}CH_3C_2COC_2H_5)$ under CO,[9] isomers of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}MeC_2Ph)$ do not interconvert on the NMR time scale up to 100 °C.[7] However, Shriver has recently presented evidence for the existence of an unstable complex $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}HC_2OEt)$ which yields a bis(alkylidyne), $Fe_3(CO)_9(\mu_3\text{-}CH)(\mu_3\text{-}COEt)$, at room temperature.[10] Theoretical work suggests that the $\mu_3\text{-}\eta^2\text{-}\perp$-alkyne configuration 1 lies along the reaction pathway between $\mu_3\text{-}\eta^2\text{-}\|$-acetylene complexes 2 and bis(alkylidynes).[13]


1


2

Surprisingly, in view of the interest in $\mu_3\text{-}\eta^2\text{-}\perp$-alkyne complexes of type 1, few have been characterized. Only compounds with R = R' = Ph, Me, Et[2,5,6] R = Me, R' = Ph (two isomers),[6] and unstable R = H, R' = OC(O)Me, OEt are known for iron,[10] and two mixed-metal compounds, $Fe_2Ru(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}PhC_2Ph)$ and $Fe_2Ru(CO)_9(EtC_2Et)$, have been prepared.[6] Only two X-ray structures have been reported for iron triad compounds, the original work by Dahl and co-workers[2] in 1966 on $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}PhC_2Ph)$ using film data and a later study of the Fe_2Ru analogue by Busetti et al.[6] Neither of these structure determinations was of high accuracy by contemporary standards. We now report a highly precise X-ray crystal structure of a derivative of type 1, $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}EtC_2Et)$. The molecular parameters provide new data pertinent to alkyne–bis(alkylidyne) transformations.

Table I. Summary of Crystal Data and Experimental Parameters for Intensity Collection, Reduction, and Refinement

mol formula	$Fe_3O_9C_{15}H_{10}$
mol wt	501.78
crystal color and habit	brown-black rhombic prisms
crystal system	triclinic
a, Å	9.446 (1)
b, Å	9.644 (1)
c, Å	10.022 (1)
α, deg	87.84 (1)
β, deg	85.96 (1)
γ, deg	89.58 (1)
V, Å^3	910.2 (2)
Z	2
d_{calcd}, g·cm^{-3}	1.831
diffractometer	Syntex $P2_1$
space group	$P\bar{1}$
radiation	graphite-monochromated Mo Kα
F(000)	500
μ(Mo Kα), cm^{-1}	24.65
transmissn factors	0.58–0.75
scan method	θ–2θ
scan speed, deg/min	2.93–29.3
scan width, deg	0.9 below $K\alpha_1$ to 0.9 above $K\alpha_2$
2θ range, deg	3.2–50
temp, K	293 ± 1
reflctns collected	+*h*, ±*k*, ±*l*
std reflctns (every 100 measurements)	050, 412
stds variatn, %	−4
independent reflctns	3222
obsd reflctns	2560
R (anisotropic)	0.027
R_w	0.031
max residuals about Fe atoms, e Å^{-3}	0.5
weighting scheme $w^{-1} = A - B\|F_o\| + C\|F_o\|^2$	
A	1.41
B	0.019
C	0.00075

Experimental Section

The most convenient route to the title complex involves refluxing $Fe_3(CO)_{12}$ (0.5 g) with 2 equiv of 3-hexyne in *n*-hexane (100 mL) under dinitrogen for ~20 min. Separation by silica gel TLC, eluting with a petroleum ether/diethyl ether (10:1) mixture gave a green band of $Fe_3(CO)_{12}$ followed by a brown band of the product. Yields up to 35% were achieved. Spectroscopic features were identical with those reported elsewhere.[6]

X-ray Crystal Structure Analysis: Collection and Reduction of X-ray Data. A suitable brown-black crystal of dimensions 0.15 × 0.18 × 0.19 mm was chosen from a batch recrystallized from *n*-heptane at −15 °C, attached to a glass fiber and mounted on a goniometer head for X-ray measurements using a Data General Nova automated Syntex $P2_1$ diffractometer. After centering, polaroid rotation photographs were used to locate 15 reflections of appropriate intensity widely dispersed in reciprocal space. The Syntex autoindexing and cell refinement package was then used to refine accurate cell parameters from the setting angles of these reflections and to define the orientation matrix. There were no systematic absences thus the crystal belonged to the triclinic system, space group $P1$ or $P\bar{1}$. Solution and refinement of the structure confirmed the latter as the correct choice. Crystal data and details pertinent to the collection of intensities are listed in Table I. Diffraction data were collected in the θ–2θ mode, with variable scan speeds, using Mo K_α (λ = 0.71069 Å) graphite-monochromated radiation. Background counts were made at the beginning and end of each scan for a time of one-half of the total scan time. Standard reflections monitored after every 100 measurements decreased in intensity by 4% over the course of the data collection. These were used to scale the data to a common level. Intensities were corrected for Lorentz and polarization

---

[3] Granozzi, G.; Tondello, E.; Casarin, M.; Aime, S.; Osella, D. *Organometallics* **1983**, *2*, 430.

[4] Halet, J. F.; Saillard, J. Y.; Lissillour, R.; McGlinchey, M. J.; Jaouen, G. *Inorg. Chem.* **1985**, *24*, 218.

[5] Hübel, W. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley-Interscience: New York, 1968; Vol. 1.

[6] Busetti, V.; Granozzi, G.; Aime, S.; Gobetto, R.; Osella, D. *Organometallics* **1984**, *38*, 1510.

[7] Osella, D.; Gobetto, G.; Montangero, P.; Zanello, P.; Cinquantini, A. *Organometallics* **1986**, *5*, 1247.

[8] Dahan, F.; Mathieu, R. *J. Chem. Soc., Chem. Commun.* **1984**, 432.

[9] Nuel, D. P. Dahan, F.; Mathieu, R. *Organometallics* **1985**, *4*, 1436.

[10] (a) Hriljac, J. A.; Shriver, D. F. *Organometallics* **1985**, *4*, 2225. (b) Hriljac, J. A.; Shriver, D. F. *J. Am. Chem. Soc.* **1987**, *109*, 6010.

[11] Sappa, E. *J. Organomet. Chem.* **1987**, in press.

[12] (a) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (b) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.

[13] Clauss, A. D.; Shapley, J. R.; Wilker, C. W.; Hoffmann, R. *Organometallics* **1984**, *3*, 619.

Table II. Atomic Positions (Fractional × 10^4 Except for Hydrogen Atoms × 10^3) and $U_{eq}{}^a$ or U_{iso} for $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}EtC_2Et)$

atom	*x*	*y*	*z*	U_{eq} or U_{iso}, Å^2
Fe(1)	1376.4 (4)	1602.8 (4)	1680.2 (4)	43.3
Fe(2)	3871.3 (4)	2153.7 (4)	2039.2 (5)	45.1
Fe(3)	2141.0 (4)	4093.8 (4)	2075.5 (4)	40.9
O(1)	870 (4)	−1326 (3)	2395 (3)	89
O(2)	2651 (3)	1099 (3)	−996 (3)	81
O(3)	−1420 (3)	2215 (4)	754 (3)	88
O(4)	4631 (3)	−587 (3)	3132 (3)	85
O(5)	5770 (3)	1934 (4)	−372 (3)	81
O(6)	5978 (3)	3730 (3)	3332 (3)	75
O(7)	3585 (3)	6323 (3)	3349 (3)	82
O(8)	3528 (3)	4538 (3)	−610 (3)	75
O(9)	−332 (3)	5802 (3)	1536 (3)	76
C(1)	1079 (4)	−193 (4)	2117 (4)	60
C(2)	2252 (4)	1322 (4)	69 (4)	58
C(3)	−338 (4)	1941 (4)	1089 (4)	58
C(4)	4335 (4)	457 (4)	2660 (4)	59
C(5)	5042 (4)	2015 (4)	560 (4)	59
C(6)	5147 (3)	3131 (3)	2832 (4)	52
C(7)	3036 (4)	5455 (3)	2863 (4)	54
C(8)	3048 (4)	4301 (3)	454 (4)	54
C(9)	645 (4)	5163 (3)	1739 (4)	52
C(10)	−1352 (5)	1719 (4)	4314 (5)	65
C(11)	−549 (4)	3058 (4)	3966 (4)	53
C(12)	805 (3)	2869 (3)	3098 (3)	42
C(13)	2144 (3)	2386 (3)	3390 (3)	40
C(14)	2415 (4)	1988 (4)	4840 (3)	53
C(15)	2783 (6)	3212 (5)	5645 (5)	74
H(10A)	−75 (4)	106 (4)	474 (4)	81 (13)
H(10B)	−171 (5)	129 (5)	352 (5)	99 (15)
H(10C)	−215 (4)	188 (4)	501 (4)	79 (12)
H(11A)	−111 (4)	367 (4)	349 (4)	68 (11)
H(11B)	−32 (4)	352 (4)	479 (4)	89 (14)
H(14A)	149 (5)	149 (5)	529 (4)	106 (15)
H(14B)	319 (4)	131 (4)	490 (4)	77 (12)
H(15A)	282 (4)	290 (4)	657 (4)	78 (12)
H(15B)	207 (5)	388 (5)	554 (5)	111 (18)
H(15C)	362 (6)	367 (6)	524 (6)	133 (20)

[a] $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

effects but not for absorption [μ(Mo K$_\alpha$) = 24.65 cm^{-1}]. From 3222 measured diffraction intensities 2560 had $I \geqslant 3\sigma(I)$ and were used in the solution and refinement of the structure.

Solution and Refinement of the Structure. A Patterson map revealed the positions of all three iron atoms. Full-matrix least-squares refinement, Fourier, and difference Fourier techniques were used to locate the remaining non-hydrogen atoms. Several cycles of refinement of positions and isotropic thermal parameters followed by conversion to anisotropic coefficients and refinement to convergence gave an R value ($R = \sum||F_o| - |F_c||/\sum|F_o|$) of 0.034. All ten hydrogen atoms on the ethyl groups of the acetylene were then unambiguously located in a difference Fourier map. These were included in the refinement with positional and isotropic thermal parameters varying. Convergence was achieved with R and R_w ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$) values of 0.027 and 0.031, respectively. An appropriate weighting scheme (Table I) was used in the final cycles. A final difference map was quite featureless with maximum residual electron density of 0.5 e Å^{-3}. Scattering factors were taken from ref 14 and for hydrogen atoms from the compilation of Stewart et al.[15] Both real and imaginary components of anomalous dispersion were applied to corrections for the iron atoms. The function minimized in least-squares refinements was $\sum w(|F_o| - |F_c|)^2$. Computer programs have been described elsewhere.[15] A listing of observed and calculated structure factors is available as supplementary material (Table S2). Table II contains a listing of atomic positions and Table III a compilation of pertinent bond lengths and angles.

Table III. A Compilation of Bond Lengths (Å) and Angles (deg) for $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}EtC_2Et)$

(A) Bond Lengths

Fe(1)–Fe(2)	2.4734 (5)	Fe(1)–Fe(3)	2.5666 (5)
Fe(2)–Fe(3)	2.4749 (5)	Fe(1)–C(1)	1.789 (4)
Fe(1)–C(2)	1.791 (4)	Fe(1)–C(3)	1.787 (4)
Fe(2)–C(4)	1.791 (4)	Fe(2)–C(5)	1.794 (4)
Fe(2)–C(6)	1.783 (3)	Fe(3)–C(7)	1.802 (3)
Fe(3)–C(8)	1.788 (3)	Fe(3)–C(9)	1.787 (3)
Fe(1)–C(12)	1.953 (3)	Fe(3)–C(12)	1.947 (3)
Fe(1)–C(13)	2.077 (3)	Fe(2)–C(13)	2.062 (3)
Fe(3)–C(13)	2.070 (3)	C(1)–O(1)	1.133 (4)
C(2)–O(2)	1.135 (5)	C(3)–O(3)	1.125 (5)
C(4)–O(4)	1.137 (5)	C(5)–O(5)	1.126 (5)
C(6)–O(6)	1.133 (4)	C(7)–O(7)	1.131 (4)
C(8)–O(8)	1.145 (4)	C(9)–O(9)	1.132 (4)
C(10)–C(11)	1.519 (6)	C(11)–C(12)	1.509 (5)
C(12)–C(13)	1.391 (4)	C(13)–C(14)	1.528 (5)
C(14)–C(15)	1.511 (6)		
Fe(2)···C(2)	2.728 (4)	Fe(2)···C(8)	2.706 (3)
C(10)–H(10A)	0.96 (4)	C(10)–H(10B)	0.99 (5)
C(10)–H(10C)	1.01 (4)	C(11)–H(11A)	0.94 (4)
C(11)–H(11B)	0.99 (5)	C(14)–H(14A)	1.07 (5)
C(14)–H(14B)	0.98 (4)	C(15)–H(15A)	0.97 (4)
C(15)–H(15B)	0.93 (5)	C(15)–H(15C)	0.97 (6)

(B) Bond Angles

Fe(2)–Fe(1)–Fe(3)	58.78 (1)	Fe(2)–Fe(1)–C(1)	108.5 (1)
Fe(2)–Fe(1)–C(2)	77.7 (1)	Fe(2)–Fe(1)–C(3)	154.9 (1)
Fe(2)–Fe(1)–C(12)	87.95 (8)	Fe(2)–Fe(1)–C(13)	53.03 (8)
Fe(3)–Fe(1)–C(1)	155.4 (1)	Fe(3)–Fe(1)–C(2)	101.1 (1)
Fe(3)–Fe(1)–C(3)	99.7 (1)	Fe(3)–Fe(1)–C(12)	48.73 (8)
Fe(3)–Fe(1)–C(13)	51.64 (7)	C(1)–Fe(1)–C(2)	95.8 (2)
C(1)–Fe(1)–C(3)	96.2 (2)	C(1)–Fe(1)–C(12)	114.6 (1)
C(1)–Fe(1)–C(13)	103.8 (1)	C(2)–Fe(1)–C(3)	95.9 (2)
C(2)–Fe(1)–C(12)	149.3 (1)	C(2)–Fe(1)–C(13)	130.5 (1)
C(3)–Fe(1)–C(12)	85.6 (1)	C(3)–Fe(1)–C(13)	125.8 (1)
C(12)–Fe(1)–C(13)	40.2 (1)	Fe(1)–Fe(2)–Fe(3)	62.49 (1)
Fe(1)–Fe(2)–C(4)	96.0 (1)	Fe(1)–Fe(2)–C(5)	113.3 (1)
Fe(1)–Fe(2)–C(6)	150.5 (1)	Fe(1)–Fe(2)–C(13)	53.57 (8)
Fe(3)–Fe(2)–C(4)	148.0 (1)	Fe(3)–Fe(2)–C(5)	117.1 (1)
Fe(3)–Fe(2)–C(6)	92.6 (1)	Fe(3)–Fe(2)–C(13)	53.35 (8)
C(4)–Fe(2)–C(5)	92.5 (2)	C(4)–Fe(2)–C(6)	98.7 (2)
C(4)—Fe(2)–C(13)	95.1 (1)	C(5)–Fe(2)–C(6)	91.5 (2)
C(5)–Fe(2)–C(13)	165.4 (1)	C(6)–Fe(2)–C(13)	99.6 (1)
Fe(1)–Fe(3)–Fe(2)	58.73 (1)	Fe(1)–Fe(3)–C(7)	156.9 (1)
Fe(1)–Fe(3)–C(8)	93.4 (1)	Fe(1)–Fe(3)–C(9)	105.6 (1)
Fe(1)–Fe(3)–C(12)	48.95 (8)	Fe(1)–Fe(3)–C(13)	51.87 (8)
Fe(2)–Fe(3)–C(7)	103.9 (1)	Fe(2)–Fe(3)–C(8)	76.9 (1)
Fe(2)–Fe(3)–C(9)	162.1 (1)	Fe(2)–Fe(3)–C(12)	88.05 (8)
Fe(2)–Fe(3)–C(13)	53.06 (8)	C(7)–Fe(3)–C(8)	97.3 (2)
C(7)–Fe(3)–C(9)	93.5 (2)	C(7)–Fe(3)–C(12)	121.3 (1)
C(7)–Fe(3)–C(13)	106.1 (1)	C(8)–Fe(3)–C(9)	96.8 (2)
C(8)–Fe(3)–C(12)	141.1 (1)	C(8)–Fe(3)–C(13)	128.2 (1)
C(9)–Fe(3)–C(12)	86.6 (1)	C(9)–Fe(3)–C(13)	126.3 (1)
C(12)–Fe(3)–C(13)	40.4 (1)	Fe(1)–C(1)–O(1)	179.0 (2)
Fe(1)–C(2)–O(2)	171.7 (2)	Fe(1)–C(3)–O(3)	176.4 (2)
Fe(2)–C(4)–O(4)	175.6 (2)	Fe(2)–C(5)–O(5)	179.6 (2)
Fe(2)–C(6)–O(6)	178.6 (1)	Fe(3)–C(7)–O(7)	179.0 (2)
Fe(3)–C(8)–O(8)	173.0 (1)	Fe(3)–C(9)–O(9)	177.6 (1)
C(10)–C(11)–C(12)	114.0 (2)	Fe(1)–C(12)–Fe(3)	82.32 (8)
Fe(1)–C(12)–C(11)	133.4 (1)	Fe(1)–C(12)–C(13)	74.7 (1)
Fe(3)–C(12)–C(11)	135.6 (1)	Fe(3)–C(12)–C(13)	74.6 (1)
C(11)–C(12)–C(13)	132.0 (2)	Fe(1)–C(13)–Fe(2)	73.40 (8)
Fe(1)–C(13)–Fe(3)	76.49 (8)	Fe(1)–C(13)–C(12)	65.1 (1)
Fe(1)–C(13)–C(14)	142.2 (1)	Fe(2)–C(13)–Fe(3)	73.59 (8)
Fe(2)–C(13)–C(12)	126.3 (1)	Fe(2)–C(13)–C(14)	114.7 (1)
Fe(3)–C(13)–C(12)	65.0 (1)	Fe(3)–C(13)–C(14)	141.0 (1)
C(12)–C(13)–C(14)	118.9 (2)	C(13)–C(14)–C(15)	113.3 (2)

Table S1 gives anisotropic thermal parameters and hydrogen atom positions.

Results and Discussion

The crystal structure of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}EtC_2Et)$ consists of discrete molecules with no significant intermolecular contacts. A perspective view of the molecule, drawn to illustrate the skeletal stereochemistry and with

---

(14) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(15) Stewart, R. F.; Davidson, E. R. Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

Table IV. Selected Structural Parameters for Complexes of Type 1 Containing Iron

complex	M–M dist, Å	M–C(σ), Å	M–C(π)[C(α)], Å	M–C(π)[C(β)], Å	C–C(alkyne), Å	bend back angles, deg	ref
$Fe_3(CO)_9(C_2Ph_2)$	2.501 (9), 2.480 (10), $\underline{2.579\ (11)}^a$	2.048 (16)	2.098 (15), 2.043 (15) (2.070)^b	1.947 (16), 1.945 (15) (1.946)	1.409 (22)	118.3 (1.3),^{c} 130.8 (1.3)^d	2
$Fe_3(CO)_9(C_2Et_2)$	2.4749 (5), 2.4734 (5), $\underline{2.5666\ (5)}$	2.062 (3)	2.070 (3), 2.062 (3) (2.066)	1.953 (3), 1.947 (3) (1.950)	1.391 (4)	118.9 (2),^{c} 132.0 (2)^d	this work
$RuFe_2(CO)_9$-(C_2Ph_2)	2.564 (2),^{e} 2.582 (3),^{e} $\underline{2.588\ (3)}^f$	2.198 (17)^g	2.088 (12),^{h} 2.052 (13)^h (2.070)	1.941 (16),^{h} 1.961 (12)^h (1.951)	1.413 (20)	NR	6
$(Cp)_2W_2Fe(CO)_6$-(C_2R_2)	2.745 (1), 2.747 (1),^{k} $\underline{2.731\ (1)}$	2.264 (7)^l	2.011 (5),^{h} 2.289 (5)^l (2.150)	2.052 (5),^{h} 2.040 (6)^l (2.046)	1.399 (9)	133.1 (5)	18
$(Cp)_2W_2Fe(CO)_5$-$(O)(C_2R_2)$	2.677 (1), 2.848 (1),^{k} $\underline{2.747\ (2)}$	2.259 (8)^l	2.027 (9),^{h} 2.480 (10)^l (2.253)	2.017 (9),^{h} 2.046 (10)^l	1.441 (11)	131.0 (8)	18

[a] M–M "bridged" distance underlined. [b] Mean values in parentheses. [c] Angle at C_α. [d] Angle at C_β. [e] Fe–Ru. [f] Fe–Fe. [g] Ru–C. [h] Fe–C. [k] W–W. [i] R = C_6H_4Me. [l] W–C.

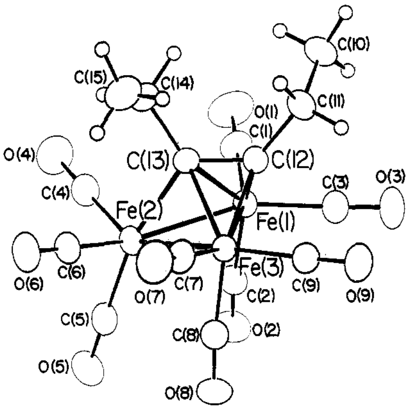


Figure 1. A perspective view of the molecular structure of $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_2Et_2)$ showing the atomic numbering.

atomic numbering, is shown in Figure 1. The orientation of the acetylene with respect to the Fe_3 triangle is better illustrated in Figure 2 from which it is apparent that the alkyne triple bond lies perpendicular to the Fe(1)–Fe(3) vector. The molecule, like its diphenylacetylene analogue,[2] is thus a classical example of a $\mu_3\text{-}\eta^2\text{-}\perp$-alkyne complex; the dihedral angle between the two planes defined by Fe(1), Fe(2), and Fe(3) and the alkyne carbon atoms C(12), C(13), their substituent atoms C(11), C(14), and Fe(2)[16] is 90°. The remaining methyl groups on the alkyne are disposed anti to one another relative to the C(11)–C(12)–C(13)–C(14) plane.

A closer inspection of Figure 1 reveals that the Fe_3C_2 core stereochemistry is that of a closo trigonal bipyramid with one of the alkyne carbon atoms C(13) occupying a five-connected equatorial vertex and the other C(12) a four-connected apical position. Distortions from a regular trigonal bipyramid are largely the result of bond length differences in the polyhedron (vide infra). An alternate description of the molecule is as an $Fe(CO)_3$ face-capped Fe_2C_2 tetrahedron. This view of the cluster serves to illustrate the relationship to binuclear alkyne complexes $M_2(CO)_6(\mu_2\text{-}\eta^2\text{-}\perp\text{-}RC_2R')$ typified by the classical, electron-precise cobalt derivatives (M = Co)[5] and the 32-electron $Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}\perp\text{-}t\text{-}BuC{\equiv}C\text{-}t\text{-}Bu)$.[17] On the basis of Wade–Mingos PSEPT counting, the latter, a five skeletal pair closo structure would afford a closo trigonal bipyramid on capping with a two-electron donor $Fe(CO)_3$ group. Whether $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}RCR')$ complexes are indeed formed via $Fe(CO)_3$ face-capping closo-$Fe_2(CO)_6(\mu_2\text{-}\eta^2\text{-}\perp\text{-}RC_2R')$ remains to be demonstrated.

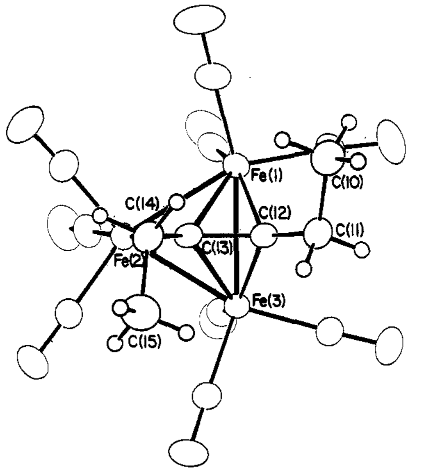


Figure 2. The orientation of the $\mu_3\text{-}\eta^2\text{-}\perp$-diethylacetylene ligand in $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}C_2Et_2)$.

Structural parameters for the known $M_3(\mu_3\text{-}\eta^2\text{-}\perp$-alkyne) complexes are compared in Table IV. Of the two other iron group compounds, one is heteronuclear $FeRu_2(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}PhC_2Ph)$. The remaining two examples contain $(\eta^5\text{-}C_5H_5)W$ fragments. The present stucture is easily the most precise, but detailed comparisons of bond distances are compromised by the high estimated standard deviations (esd's) on M–C and C–C distances particularly for the other iron triad species. Nevertheless some significant features emerge. One alkyne carbon atom [C(13) in $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}EtC_2Et)$] can now be seen to be essentially symmetrically μ_3-bonded on the triangular Fe_3 face. The Fe–C(13) distances lie in the narrow range of 2.062 (3)–2.077 (3) Å with the average 2.069 Å. Thus this carbon atom could essentially be regarded as a symmetrical μ_3-alkylidyne unit. The Fe–C_β, i.e. Fe(1)–C(12) and Fe(3)–C(12), bond lengths are equal (average 1.950 Å) and closely similar to those in $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}PhC_2Ph)$ (average 1.946 Å) and $Fe_2Ru(CO)_9(\mu_3\text{-}\eta^2\text{-}\perp\text{-}EtC_2Et)$ (average 1.951 Å) and ~0.1 Å shorter than the average Fe–C(13) distance (2.069 Å). Thus C(13) is significantly less strongly bound to the cluster than C(12). The alkyne triple bond length is remarkably invariant in all five $\mu_3\text{-}\eta^2\text{-}\perp$ compounds in Table IV, the only two values which are significantly different being 1.391 (4) Å in $Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}EtC_2Et)$ and 1.441 (11) Å in $Cp_2W_2Fe(CO)_5(O)(\mu_3\text{-}\eta^2\text{-}PhC_2Ph)$[18] where the difference lies within 5 esd's. Bend back angles at C_β are also virtually constant. Thus it does not appear that

---

[16] The equation of the best plane through C(12), C(13), C(11), and C(14) is given by $0.2871X + 0.9456Y - 0.1528Z - 3.4759 = 0$, where (X, Y, Z) refer to an orthogonal coordinate system in Å. Deviations from this plane are as follows: C(12), 0.009; C(13), −0.008; C(11), −0.004; C(14), 0.003; Fe(2), −0.034 Å.

[17] Cotton, F. A.; Frenz, B. A.; Troup, J. M.; Deganello, G. *J. Organomet. Chem.* **1975**, *94*, C53.

[18] Busetto, L.; Jeffery, J. C.; Mills, R. M.; Stone, F. G. A.; Went, M. J.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1983**, 101.

either a change in alkyne substituents or metal fragments has much influence on the perturbation of the alkyne. This structure analysis also confirms that the metal–metal bond bridged perpendicularly by the acetylene (Fe(1)–Fe(3) = 2.5666 (5) Å) is quite significantly longer than either of the other Fe–Fe bonds (Fe(1)–Fe(2) = 2.4734 (5), Fe(2)–Fe(3) = 2.4749 (5) Å).

A theoretical model[13] for the cleavage of the alkyne triple bond in the related trirhodium cluster $Cp_3Rh_3(CO)(\mu_3$-η^2-$\|$-$PhC_2Ph)$ to generate a bis(alkyidyne) species suggests that rotation of the acetylene from a μ_3-η^2-$\|$- to a μ_3-η^2-$\perp$-position occurs, followed by edge coordination of the alkyne, CO loss, and alkylidyne formation. It is interesting to compare this postulate with the structure of the present complex since the $C(13)$–C_2H_5 group is already "alkylidyne-like" structurally and C(12) is much more "edge coordinated". Figure 2 shows however that scission of the C(12)–C(13) bond and rotation of the $C(12)$–C_2H_5 group around the Fe(1)–Fe(3) bond to bridge the bottom face of the cluster might be impaired by steric interactions between the substituent ethyl group on C(12) and the equatorial carbonyls of the $Fe(CO)_3$ units unless significant Fe(1)–Fe(3) bond lengthening and/or reorientation of the alkyl groups to slide between the equatorial CO's occurred in the transition state. On the other hand, such a rotation leading to skeletal isomerism might be more favorable with an alkyne bearing hydrogen or a smaller group than Et on C(12). CNDO calculations on $Fe_3(CO)_9(\mu_3$-η^2-$\perp$-$EtC_2H)]$ suggest that the site C_α [C(13) in $Fe_3(CO)_9(\mu_3$-η^2-$\perp$-$EtC_2Et)]$ should be positively charged and hence favored by electron-releasing substituents. Keeping this in mind a particularly favorable situation for conversion of $Fe_3(CO)_9(\mu_3$-η^2-$\perp$-$RC_2R')$ to $Fe_3(CO)_9(\mu_3$-$CR)(\mu_3$-$CR')$ might be found for monosubstituted alkynes with an electron-releasing substituent at C_α and unsubstituted at C_β. Interestingly, Shriver[10] has recently prepared an unstable complex of this type in solution and found a smooth conversion to a bis(alkylidyne) cluster at room temperature.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

Registry No. $Fe_3(CO)_9(\mu_3$-η^2-$\perp$-$C_2Et_2)$, 69402-19-3; $Fe_3(CO)_{12}$, 17685-52-8; Fe, 7439-89-6.

Supplementary Material Available: A table of anisotropic thermal parameters (Table S1) (1 page); a listing of structure factors (Table S2) (15 pages). Ordering information is given in any current masthead page.

Sterically Hindered Aryloxide-Substituted Alkylaluminum Compounds

Andrew P. Shreve,[†] Rolf Mulhaupt,[†] William Fultz,[†] Joseph Calabrese, Wayne Robbins, and
Steven D. Ittel*

Central Research & Development Department,[‡] *E. I. du Pont de Nemours & Company,*
Wilmington Delaware 19898

Received June 25, 1987

Aluminum alkyl reagents react with sterically hindered phenols such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) to liberate alkane and generate alkylaluminum phenoxides. This substitution chemistry has been followed by NMR techniques, and the products of the reactions have been characterized by NMR and by X-ray crystallography. In the reaction with trimethylaluminum, observed species are Al_2Me_6, Al_2Me_5BHT, $AlMe_2BHT$, and $AlMeBHT_2$. At intermediate stages of reaction, all four species are observed in dynamic equilibrium. In the $AlEt_3$ system, the corresponding Al_2Et_5BHT is not observed. In the $Al(i$-$Bu)_3$ system, the two monomeric products are formed sequentially. The alkylaluminum phenoxides react with Lewis bases to form four-coordinate molecules of relevance to Ziegler–Natta catalysts that display both high activity and high stereospecificity. The compound $AlMeBHT_2$ crystallizes in the triclinic space group $P\bar{1}$ with unit-cell dimensions a = 12.108 (2) Å, b = 12.793 (2) Å, c = 10.981 (1) Å, α = 102.65 (1)°, β = 110.54 (1)°, and γ = 68.16 (1)°. The methyl toluate adduct $AlEt_2BHT(MeC_6H_4CO_2Me)$ crystallizes in the monoclinic space group $C2/c$ with unit-cell dimensions a = 24.554 (4) Å, b = 14.924 (2) Å, c = 15.216 (2) Å, and β = 91.01 (1)°.

Introduction

The early work of Jeffery and Mole[1] demonstrated that aluminum alkyl reagents could be modified readily by reaction with phenols. This approach has been the subject of considerable subsequent work in a number of laboratories.[2-4] While simple phenols give compounds that are bridged through the oxygen atoms of the resulting phenoxide group, sterically hindered phenols give products that are monomeric in nature. These monomeric species, usually synthesized from 2,6-di-*tert*-butyl-substituted phenols, have found application in organic synthesis[5,6] and

---

[†] Current addresses: A.P.S., Department of Chemistry, Cornell University, Ithaca, NY; R.M., Ciba Geigy AG, Forschungszentrum KA/Marly, CH-1701 Fribourg, Switzerland; W.F., J. M. Huber Corp., P.O. Box 310, Havre de Grace, MD 21078.

[‡] Contribution No. 4414.

(1) Jeffrey, E. A.; Mole, T. *Aust. J. Chem.* **1968**, *21*, 2683.

(2) (a) Pasynkiewicz, S.; Starowieyski, K. B.; Skowronska-Ptasinska, M. *J. Organomet. Chem.* **1973**, *52*, 269. (b) Starowieyski, K. B.; Pasynkiewicz, S.; Skowronska-Ptasinska, M. *J. Organomet. Chem.* **1974**, *65*, 155. (c) Starowieyski, K. B.; Pasynkiewicz, S.; Skowronska-Ptasinska, M. *J. Organomet. Chem.* **1975**, *90*, C43–44. (d) Pasynkiewicz, S.; Starowieyski, K. B.; Peregudov, A. S.; Kravtsov, D. N. *J. Organomet. Chem.* **1977**, *132*, 191. (e) Skowronska-Ptasinska, M.; Starowieyski, K. B.; Pasynkiewicz, S. *J. Organomet. Chem.* **1977**, *141*, 149. (f) Starowieyski, K. B.; Skowronska-Ptasinska, M.; Muszynski, J. *J. Organomet. Chem.* **1978**, *157*, 379. (g) Skowronska-Ptasinska, M.; Starowieyski, K. B.; Pasynkiewicz, S.; Carewska, M. *J. Organomet. Chem.* **1978**, *160*, 403.

(3) Panasenko, A. A.; Khalilov, L. M.; Kuchin, A. V.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 2652.

(4) Yoon, N. M.; Gyoung, Y. S. *J. Org. Chem.* **1985**, *50*, 2443.

0276-7333/88/2307-0409$01.50/0