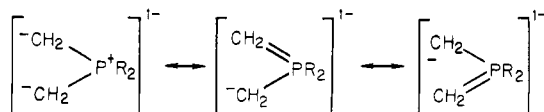


to permit a determination of whether lengthening of the C≡C bond occurs.

The idea of a multiple bond in $\text{Cp}_3\text{UC}\equiv\text{CR}$ is supported by the extended Hückel calculations of Tatsumi.³⁰ The calculated overlap population in this species is 0.5958, much higher than in the methyl compound and even a little higher than in $\text{Cp}_3\text{U}=\text{CHPh}_3$. In view of these structural and computational results, it will be interesting to see whether the uranium acetylides display any reactivity characteristic of metal-carbon multiple bonding.

The Nature of the Uranium-Carbon Bond. Structures of a number of $\text{Cp}_3\text{U}-\text{R}$ complexes have been determined; U-C(R) bond distances in these compounds plus data for two ylide complexes are summarized in Table VI. Obviously uranium-carbon distances show a wide variation. The 0.37-Å range spanned by the compounds in Table VI corresponds to 8.7 σ and is, thus, statistically highly significant. At least qualitatively this variation can be inversely correlated with the formal negative charge on the carbon atom bound to uranium.

Comparing the ligands $[\text{C}^-\text{H}^+\text{PR}_3]^- \leftrightarrow [\text{CH}=\text{PR}_3]^{1-}$, $[\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3]^{1-}$ and



the highest negative charge on the metal-bound carbon atom should occur in complexes of $[\text{CHPR}_3]^-$ and the smallest in those of $[(\text{CH}_2)(\text{CH}_2)\text{PR}_2]^-$, with $[\text{C}_4\text{H}_9]^-$ being intermediate. Correspondingly, the shortest U-C distance is found in $\text{Cp}_3\text{U}=\text{CHPMe}_2\text{Ph}$ and the longest in $\text{CpU}-[(\text{CH}_2)(\text{CH}_2)\text{PPh}_2]_3$, with a middle value in $\text{Cp}_3\text{U}-\text{C}_4\text{H}_9$. Within the $\text{Cp}_3\text{U}-\text{R}$ series, both 2-methylallyl and *p*-

methylbenzyl ligands possess resonance structures that can delocalize negative charge from the carbon atom that binds to the metal, and their uranium carbon distances exceed the one in the *n*-butyl derivative.

Such a correlation of bond length with α -carbon charge is also consistent with another observation. We have attempted to prepare complexes in which a free ylide, rather than an anion, is bound to uranium. Thus in the reaction of Cp_3UCl and $\text{H}_2\text{C}=\text{PPh}_3$ we observe a color change indicating product formation. However, the product is very unstable and we have been unable to characterize it. In this neutral ylide, charge on the α -carbon would be less than in $[(\text{CH}_2)(\text{CH}_2)\text{PPh}_2]^-$ and the uranium-carbon bond should be even longer than the very long ones in $\text{CpU}-[(\text{CH}_2)(\text{CH}_2)\text{PPh}_2]_3$. Presumably, this bond should be weak, probably leading to a marginally stable complex.

The variation in uranium-carbon distances with the negative charge on the α -carbon is consistent with an ionic component of the uranium carbon bond: as the charge on the carbon increases, electrostatic attraction increases and the bond shortens. In our view this correlation provides strong evidence that the uranium-carbon bond has an important ionic component.

Acknowledgment. R.E.C. and J.W.G. gratefully acknowledge the support of this work by the National Science Foundation, Grant No. CHE-8210244.

Registry No. $\text{Cp}_3\text{U}=\text{CHPMe}_2\text{Ph}$, 86584-33-0.

Supplementary Material Available: Table II, parameters for the rigid groups of $(\text{Cp}_3)\text{U}=\text{CHPMe}_2\text{Ph}$, Table III, derived parameters for the rigid group atoms, Table V, short nonbonded intramolecular contacts, and Table VII, listing of $10|F_o|$ vs. $10|F_c|$ (11 pages). Ordering information is given on any current masthead page.

A New Type of Triangular Tungsten Cluster Compound from Reaction of 3-Hexyne with Hexa-*tert*-butoxyditungsten

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The reaction of $\text{W}_2(\text{O}-t\text{-Bu})_6$ with $\text{EtC}\equiv\text{CEt}$ at 75–80 °C for about 3 days affords moderate yields of a remarkable hexanuclear product, $[\text{W}_3(\text{OCMe}_2)_5(\mu\text{-O})(\mu\text{-CEtO})_2]$. The molecule consists of two trinuclear subunits joined by a pair of bridging oxygen atoms and related by a crystallographic center of inversion. In each moiety there is an isosceles triangle of W atoms (W–W distances: 2.420 (1), 2.895 (1), 2.899 (1) Å). One long edge is bridged by an EtC group and the other by an oxygen atom. The short W–W bond is not bridged. There are only six electrons available for metal-metal bonding within the W_3 moiety, and it is suggested that these may best be allocated to provide one double bond and a three-center-two-electron bond. The compound forms monoclinic crystals in space group $P2_1/n$ with unit-cell dimensions of $a = 12.600$ (3) Å, $b = 14.415$ (5) Å, $c = 18.223$ (4) Å, $\beta = 97.02$ (2)°, $V = 3285$ (3) Å³, and $Z = 2$. The structure was refined to discrepancy indices of $R = 0.0366$ and $R_w = 0.0448$.

Introduction

Reactions between ditungsten hexaalkoxides and acetylenes have led to a remarkable variety of products, depending on the nature of the alkoxide, the acetylene, and

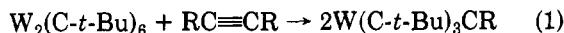
the reaction conditions. The general case, which applies to most of the sterically nondemanding alkoxides, was extensively probed by Chisholm's group, yielding 1:1 adducts in an oxidative addition reaction.¹ Reactions of

Table I

formula	$[\text{W}_3(\text{OCMe}_3)_5(\text{C}_3\text{H}_5)\text{O}_2]_2$
formula weight	1880.40
space group	$P2_1/n$
a , Å	12.600 (3)
b , Å	14.415 (5)
c , Å	18.223 (4)
β , deg	97.02 (2)
V , Å ³	3285 (3)
Z	2
d_{calcd} , g/cm ³	2.002
cryst size, mm	0.25 × 0.15 × 0.15
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	107.41
data collectn instrument	CAD-4
radiation	Mo K α
scan method	$\theta-2\theta$
data collectn range	$5.0 < 2\theta < 50.0^\circ$
no. of unique data, with $F_o^2 \geq 3\sigma(F_o^2)$	3537
no. of parameters refined	243
R^a	0.0366
R_w^b	0.0448
quality of fit indicator ^c	1.193
largest shift/esd, final cycle	0.02
decay during data collection	10.5% (corrected linearly)
abs correctn	samiempirical (ψ scan); min and max transmission factors 85.3% and 99.9%

^a $R = \sum |F_o| - |F_c| / \sum |F_o|$. ^b $R_w = \{\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2\}^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{obsd}} - N_{\text{parameters}})]^{1/2}$.

$\text{W}_2(\text{OCMe}_3)_6$ were investigated by Schrock, thus opening facile synthetic access to W^{VI} alkylidynes² via reaction 1.



This metathetic reaction was reported to fail for aromatic substituents, as in the case of diphenylacetylene. We have found, however, that aromatic acetylenes do react under more vigorous conditions, forming new dimeric products.³ If an aliphatic acetylene is now employed under the same conditions, yet another type of product is isolated. Thus 3-hexyne reacts with $\text{W}_2(\text{OCMe}_3)_6$ in a 1:1 molar ratio at ca. 75–80 °C in toluene to form a molecule that is a dimer of trimeric clusters $[\text{W}_3(\text{OCMe}_3)_5(\mu\text{-CCH}_2\text{CH}_3)(\mu\text{-O})(\text{O})_2]$ in moderate but reproducible yields. The composition suggests a formal addition of a carbyne species ($\text{W}\equiv\text{C}$) to a W_2 alkoxide species, as will be discussed later.

Experimental Section

Ditungsten hexa-*tert*-butoxide was prepared by Na/Hg reduction of WCl_4 in THF at –10 °C in the presence of LiOCMe_3 , followed by recrystallization from hexane at –20 °C.² All reactions were done under an argon atmosphere.

Reaction of $\text{W}_2(\text{OCMe}_3)_6$ with 3-Hexyne. A weighed amount of $\text{W}_2(\text{OCMe}_3)_6$ (400 mg, 0.50 mmol) was dissolved in 20 mL of toluene. 3-Hexyne (0.09 mL, 0.79 mmol) was added to the solution via a syringe at room temperature. The reaction mixture was heated slowly to approximately 79 °C and then stirred at this temperature for 60 h. The solvent was removed, and the residue

(1) (a) Bailey, W. I., Jr.; Chisholm, M. H.; Cotton, F. A.; Rankel, L. A. *J. Am. Chem. Soc.* 1978, 100, 5764. (b) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *Ibid.* 1982, 104, 4389. (c) Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C.; Leonelli, J. *J. Chem. Soc. Chem. Commun.*, in press.

(2) Schrock, R. R.; Listemann, M. L.; Sturgeooff, L. G. *J. Am. Chem. Soc.* 1982, 104, 4291.

(3) Cotton, F. A.; Schwotzer, W.; Shamsoum, E. S. *Organometallics*, 1983, 2, 1167.

Table II. Table of Positional Parameters and Their Estimated Standard Deviations^a

atom	x	y	z	B, Å ²
W(1)	0.10754 (4)	0.35111 (3)	0.46173 (3)	2.89 (1)
W(2)	–0.02998 (4)	0.36587 (3)	0.35740 (3)	2.98 (1)
W(3)	–0.10387 (4)	0.39038 (4)	0.50067 (3)	3.01 (1)
O(1)	0.2331 (7)	0.3527 (6)	0.4166 (5)	4.4 (2)
O(2)	0.1106 (7)	0.2179 (6)	0.4736 (5)	4.2 (2)
O(3)	–0.0396 (8)	0.2614 (6)	0.2965 (5)	4.4 (2)
O(4)	0.0155 (9)	0.4677 (7)	0.3056 (6)	5.8 (3)
O(5)	–0.1892 (8)	0.3076 (6)	0.5430 (5)	4.6 (2)
O(6)	0.0376 (7)	0.3709 (6)	0.5467 (5)	3.8 (2)
O(7)	0.1340 (8)	0.4956 (6)	0.4752 (5)	4.1 (2)
C(21)	–0.165 (1)	0.3856 (8)	0.3962 (7)	3.0 (3)
C(1)	0.326 (1)	0.390 (1)	0.391 (9)	5.1 (4)
C(2)	0.296 (3)	0.446 (2)	0.323 (2)	15 (1)*
C(3)	0.392 (2)	0.439 (2)	0.456 (1)	10.4 (7)*
C(4)	0.388 (2)	0.311 (2)	0.366 (1)	10.0 (7)*
C(6)	0.243 (2)	0.229 (1)	0.5839 (9)	7.9 (5)
C(8)	0.115 (2)	0.098 (2)	0.564 (1)	10.4 (7)*
C(9)	–0.000 (1)	0.173 (1)	0.2782 (8)	5.0 (4)
C(10)	–0.053 (2)	0.150 (1)	0.1982 (9)	6.9 (5)
C(11)	0.122 (1)	0.181 (1)	0.282 (1)	6.6 (5)
C(12)	–0.034 (2)	0.098 (1)	0.334 (1)	7.2 (5)
C(13)	–0.016 (2)	0.529 (1)	0.2459 (9)	6.3 (5)
C(14)	0.043 (2)	0.619 (2)	0.265 (1)	9.7 (6)*
C(15)	–0.135 (2)	0.554 (2)	0.251 (2)	13.2 (9)*
C(16)	0.005 (2)	0.488 (2)	0.177 (2)	11.5 (8)*
C(17)	–0.246 (1)	0.220 (1)	0.543 (1)	6.1 (4)
C(18)	–0.204 (2)	0.170 (2)	0.612 (1)	8.9 (6)*
C(19)	–0.222 (2)	0.168 (2)	0.474 (1)	9.5 (6)*
C(20)	–0.358 (2)	0.245 (2)	0.541 (1)	11.8 (8)*
C(22)	–0.279 (1)	0.405 (1)	0.363 (1)	5.9 (4)
C(23)	–0.314 (2)	0.343 (2)	0.296 (1)	8.9 (6)
C(7)	0.254 (2)	0.109 (2)	0.482 (1)	8.8 (6)*
C(5)	0.186 (2)	0.166 (1)	0.5247 (9)	5.8 (4)

^a Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a(1,1) + b(2,2) + c(3,3) + ab(\cos \gamma)(1,2) + ac(\cos \beta)(1,3) + bc(\cos \alpha)(2,3)]$.

Table III. Important Internuclear Distances and Angles

Bond Distances (Å)			
W(1)–W(2)	2.420 (1)	W(3)–O(5)	1.838 (8)
–W(3)	2.895 (1)	–O(6)	1.896 (9)
–O(1)	1.871 (8)	–O(7)	1.755 (8)
–O(2)	1.932 (8)	–C(21)	1.966 (12)
–O(6)	1.895 (8)	O(1)–C(1)	1.418 (15)
–O(7)	2.119 (8)	O(2)–C(5)	1.45 (2)
W(2)–W(3)	2.899 (1)	O(3)–C(9)	1.423 (15)
–O(3)	1.867 (8)	O(4)–C(13)	1.42 (2)
–O(4)	1.873 (9)	O(5)–C(17)	1.451 (15)
–C(21)	1.939 (11)		
Bond Angles (deg)			
W(1)–W(2)–W(3)	65.23 (2)	W(3)–W(1)–O(1)	163.4 (3)
–O(4)	103.3 (4)	–O(5)–C(17)	151.8 (9)
–O(3)	112.6 (3)	O(1)–W(1)–O(6)	149.4 (4)
–C(21)	107.6 (3)	–O(2)	93.2 (4)
W(1)–W(3)–W(2)	49.38 (2)	–O(7)	84.8 (4)
–O(5)	125.4 (3)	–W(3)	163.4 (3)
–O(7)	118.6 (3)	O(2)–W(1)–W(2)	100.2 (3)
–C(21)	91.0 (3)	O(5)–W(3)–O(6)	106.5 (4)
W(1)–O(1)–C(1)	157.6 (9)	–C(21)	101.8 (5)
–O(2)–C(5)	125.8 (8)	–O(7)	110.3 (4)
–O(6)–W(3)	99.6 (4)	O(3)–W(2)–C(21)	109.8 (4)
–O(7)–W(3)	156.0 (5)	–O(4)	109.6 (4)
W(2)–O(3)–C(9)	149.0 (9)	O(4)–W(2)–C(21)	109.8 (4)
–O(4)–C(13)	143.0 (1)	O(7)–W(1)–O(6)	80.8 (3)
–C(21)–W(3)	95.9 (5)	O(7)–W(3)–O(6)	104.4 (4)
W(3)–W(2)–O(3)	129.0 (3)		
–O(4)	120.7 (3)		
–C(21)	42.4 (3)		

was extracted with 2 × 10 mL portions of hexane. The extracts were concentrated to ca. 3.0 mL, and 2.5 mL of toluene was then

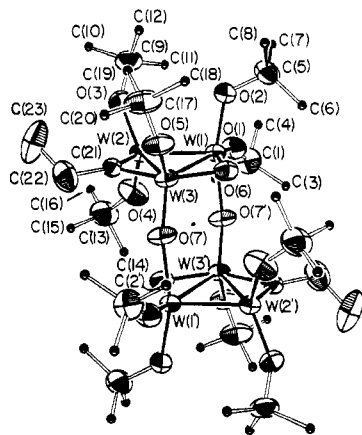


Figure 1. An ORTEP drawing of the entire molecule, giving the atomic labeling scheme. The methyl carbon atoms of the *tert*-butyl groups are represented by arbitrarily tiny spheres to avoid covering up other atoms. All other atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

added. Dark tablets (reddish brown by transmitted light) were isolated after 10 days of cooling at $-20\text{ }^{\circ}\text{C}$. The reaction is reproducible to give yields in the range of 40–60 mg (10% based on tungsten).

X-ray Crystallographic Procedures. The crystal used for X-ray study was immersed in epoxy cement inside a capillary tube. Data were collected on an Enraf-Nonius CAD-4F diffractometer at $25 \pm 1\text{ }^{\circ}\text{C}$. The general procedure used in determining the structure has already been described elsewhere.⁴ A detailed description pertinent to the present case is available as supplementary material. Key features of the data collection and refinement procedures are summarized in Table I.

Table II lists the positional parameters, and Table III gives important bond distances and angles. Tables of anisotropic thermal parameters and structure factors are available as supplementary material.

Results and Discussion

Chemical Considerations. We have earlier reported that while diphenylacetylene does not react with $\text{W}_2(\text{OCMe}_3)_6$ at room temperature, there is a reaction at 70–80 $^{\circ}\text{C}$ leading to several dinuclear products.³ Schrock et al., who also noted the failure of diphenylacetylene to react at 25 $^{\circ}\text{C}$, showed that aliphatic acetylenes in general do react at 25 $^{\circ}\text{C}$. The present work arose from our interest in how an aliphatic acetylene would react with $\text{W}_2(\text{OCMe}_3)_6$ at elevated temperatures. We have found that 3-hexyne affords a complicated product, consisting of a “dimer of trimers”; when reacted with $\text{W}_2(\text{OCMe}_3)_6$ at 75–80 $^{\circ}\text{C}$ for 60 h. The yields are small (ca. 10%) but reproducible.

On the basis of Schrock's observations we assume that some of the $\text{W}_2(\text{OCMe}_3)_6$ is first converted into the alkylidyne complex $(\text{Me}_3\text{CO})_3\text{W}\equiv\text{CEt}$, which can then react with $\text{W}_2(\text{OCMe}_3)_6$ irreversibly to form the trinuclear cluster, which subsequently dimerizes to give the isolated hexanuclear molecule. Scheme I summarizes our suggestions as to the course of the synthetic procedure. Doubtless the second step is in reality several steps, and it also involves a change in the number of OR' groups per W atom and the appearance of oxygen atoms. We have previously found that in the reactions of $\text{PhC}\equiv\text{CPh}$ with $\text{W}_2(\text{OCMe}_3)_6$ there is a loss of Me_3CO groups. Presumably

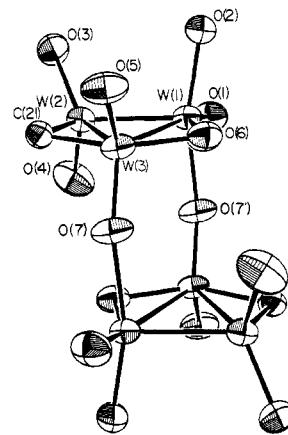
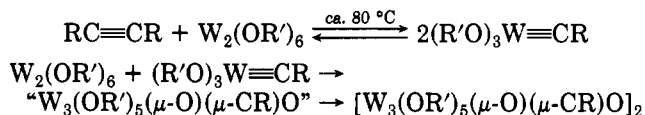


Figure 2. An ORTEP drawing of only the tungsten atoms and those ligand atoms bonded to them.

the oxygen atoms arise from decomposition of these, with hydrocarbons such as isobutylene being simultaneously produced. It has been observed that $\text{W}_2(\text{OCMe}_3)_6$ itself undergoes thermal decomposition to yield isobutylene, *tert*-butyl alcohol, and water.⁵

Scheme I



Structure and Bonding. The entire molecular unit is shown in Figure 1 where all methyl carbon atoms of the *tert*-butoxy groups have been drawn as very tiny spheres to minimize their tendency to obscure the other parts of the structure. The entire hexanuclear molecule resides on a crystallographic inversion center. In Figure 2 we have further simplified the structure by omitting all atoms other than the tungsten atoms and those bonded to them.

When we observe further that the two $\text{W}(1)\text{-O}(7)\text{-W}(3)$ type bridges are very unsymmetrical, with $\text{W}(1)\text{-O}(7) = 2.119(8)\text{ \AA}$ while $\text{W}(3)\text{-O}(7) = 1.775(8)\text{ \AA}$, we adopt the view that the structure and bonding can be discussed in terms of one $\text{W}_3\text{O}(\mu\text{-CC}_2\text{H}_5)(\mu\text{-O})(\text{O-}t\text{-Bu})_5$ unit. These two units can be regarded as joined by a pair of $\text{W}=\text{O}\rightarrow\text{W}$ bridges. Within a trinuclear unit the three tungsten atoms form an approximately isosceles triangle with two $\text{W}\text{-W}$ distances averaging $2.997(2)\text{ \AA}$ and a considerably shorter one of $2.420(1)\text{ \AA}$. The coordination spheres of the three individual tungsten atoms differ in the types of ligands involved as well as coordination numbers. $\text{W}(1)$ is bonded to two alkoxide groups, exhibits a weaker interaction with the oxygen atom on $\text{W}(3)$ (of the symmetry related trimer), and shares an oxo bridge, $\text{O}(6)$, with $\text{W}(3)$. $\text{W}(2)$ shares the $\mu\text{-CC}_2\text{H}_5$ group with $\text{W}(3)$ and has only two additional alkoxide groups in its coordination sphere. Apart from its bonds to the $\mu\text{-O}$ and $\mu\text{-C}$ ligands $\text{W}(3)$ is strongly bonded to the oxygen that is linking the two trimers ($\text{W}(3)\text{-O}(7) = 1.775(8)\text{ \AA}$) and to a terminal butoxide group.

The coordination spheres of the individual tungsten atoms are not easily described in terms of regular polyhedra. The four oxygen atoms around $\text{W}(1)$ have an arrangement that comes close to square planar. For $\text{W}(2)$, with two alkoxide oxygen atoms and one alkylidyne carbon atom, the arrangement is close to trigonal pyramidal whereas the three oxygen and one carbon atoms on $\text{W}(3)$ afford an approximation to a tetrahedron. Both the $\mu\text{-O}$

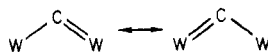
(4) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* 1979, 18, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* 1973, 50, 227. (c) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* 1968, A24, 351. Calculations were done on the PDP-11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX, with software from the Enraf-Nonius SDP-PLUS package.

(5) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Hatko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* 1979, 18, 2266.

and the μ -C bridging atoms lie essentially in the plane defined by the three tungsten atoms with deviations of 0.01 and 0.09 Å, respectively.

Turning now to the W(3)-O(7)-W(1)' type linkages in the complete hexanuclear molecule, we believe that the distances W(3)-O(7) = 1.755 (8) Å and W(1)'-O(7) = 2.119 (8) Å can be satisfactorily understood in terms of a W=O→W picture of the bonding. In support of this we may cite the W distances found in the $[W_4O_8Cl_8(H_2O)_4]^{2-}$ ion,⁶ where there are terminal W=O bonds with W—O = 1.711 (9) Å, W—OH₂ groups with W—O = 2.29 (1) Å, and essentially symmetrical, linear W—O—W bridge units in which the two W—O distances are 1.858 (2) Å. Using these as benchmarks for the different sorts of bonds, we think the W=O→W picture is quite plausible.

Within the trinuclear moiety there are two bridging ligands, O and C₂H₅C, and in each case essentially symmetrical bridges are formed. This is strictly the case for the oxygen bridge where the two distances are 1.896 (9) and 1.895 (8) Å. This bridging arrangement can reasonably be described as two W—O σ bonds with some O→W π bonding superimposed. The two W—C distances may differ slightly, but the existence of a real difference cannot be defended statistically, since it and its esd are 0.027 (17) Å, i.e., the difference itself is less than 2 σ . The entire C α -C—W—W group is essentially planar. Thus, it is reasonable to describe the electronic structure here in terms of a resonance-symmetrized combination of two σ and one π bond:



As in other di- and polynuclear alkoxide compounds of tungsten,³ we find here again that the W—O—C angles are relatively large, thus implying that there are O→W π interactions involving not just one but, to some extent, both pairs of oxygen lone-pair electrons. One of these angles, W(1)-O(2)-C(5), is only 125.8 (8)°, but the other four range from 143.01 (1)° to 157.6 (9)°.

Having considered all of these individual stereoelectronic components of the total molecule, we can now turn to the central question, which is how to formulate the metal-metal bonding in the W₃ cluster. There seems little hope

of convincingly assigning oxidation states to the individual metal atoms, nor any real need to do so. Instead, our approach is to deduce the total number of electrons available for bonding in the cluster and then consider how best to distribute them. Three tungsten atoms possess initially a total of 18 valence electrons. The metal electrons required to form all of the metal-ligand bonds can be counted up as follows:

W-O-W bonds	2
W-C(Et)-W bonds	3
five W-OR bonds	5
W=O bonds	$\frac{2}{2}$
total	$\frac{12}{12}$

This leaves six electrons for metal-metal bonding in the cluster.

While six electrons could be used to form three W—W single bonds, as in a variety of other W₃ cluster compounds,⁷ the great inequalities in W—W distances and W—W—W angles (the one at W(3) being only 49.38 (2)° while the other two are ca. 65°) rule this out. It seems clear that the W(1)-W(2) bond order (W—W = 2.420 Å) must be greater than one while the other two (W—W \approx 2.897 Å) bonds must be less than single bonds. We suggest that an appropriate simple description of the bonding is that there is one double bond (W(1)=W(2)) and a two-electron-three-center bonding arrangement linking W(3) to W(1) and W(2). Obviously some blurring of this picture so that the "double" bond may be somewhat less than double and more electron density may thereby be available for the other two bonds is possible. We suggest the $\frac{1}{2}$, $\frac{1}{2}$, 2 set of bond orders only as a convenient approximate description.

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Registry No. $[W_3(OCMe_3)_5(\mu-CCH_2CH_3)(\mu-O)(O)]_2$, 86747-57-1; $W_2(O-t-Bu)_6$, 57125-20-9; WCl_4 , 13470-13-8; $LiOCMe_3$, 1907-33-1; $EtC\equiv CEt$, 928-49-4; W , 7440-33-7.

Supplementary Material Available: A detailed description of the crystallographic procedure, a table of anisotropic thermal parameters, and a table of structure factors (26 pages). Ordering information is given on any current masthead page.

(6) Jeannin, Y.; Launay, J.-P.; Livage, J.; Nel, A. *Inorg. Chem.* **1978**, *17*, 374.

(7) Müller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 875.