Reactions of Hexa-*tert*-butoxyditungsten(*W*≡*W*) with Diphenylacetylene. Syntheses and Structures of $W_2(OCMe_3)_4(\mu\text{-}C_6H_5C)_2$ and $W_2(OCMe_3)_4(C_6H_5CCC_6H_5)_2$

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Reaction of $W_2(OCMe_3)_6$ with tolan, PhCCPh, at about 70 °C in nonpolar solvents produces $W_2(OCMe_3)_4(\mu\text{-}PhC)_2$ (1) and $W_2(OCMe_3)_4(PhCCPh)_2$ (2). Both of these new compounds have been characterized by X-ray crystallography. Compound 1 crystallizes in space group $P2_1/c$ with $a = 9.029$ (3) Å, $b = 19.769$ (11) Å, $c = 9.813$ (5) Å, $\beta = 107.67$ (2)°, $V = 1669$ (2) Å^3, and $Z = 2$. The molecule consists of two tetrahedra joined centrosymmetrically on a common edge formed by the μ-PhC groups. The tolan has been separated into two PhC units (C···C = 2.82 (2) Å), and the W–W distance is 2.665 (1) Å. There is structural evidence that the W–O bonds have appreciable O→W π character, and it is proposed that this is responsible for the rather long W–W bond. Compound 2 crystallizes in space group $P\bar{1}$ with $a = 10.206$ (6) Å, $b = 11.028$ (3) Å, $c = 20.763$ (9) Å, $\alpha = 92.16$ (3)°, $\beta = 90.91$ (5)°, $\gamma = 104.40$ (3)°, $V = 2261$ (2) Å^3, and $Z = 2$. The molecules are dinuclear with two terminal Me_3CO groups on each metal atom and two μ-η^2-tolan molecules. The O_2WWO_2 group is planar and the four alkyne carbon atoms define approximately a plane that is perpendicular to it; however, this second plane is not perpendicular to the W–W axis. Each alkyne carbon atom forms a short W–C bond, 1.99 ± 0.03 Å, and a long one, 2.34 ± 0.10 Å, and the W–W distance, 2.677 (1) Å, is consistent with a bond order between 1 and 2. A resonance description that accounts for the structure is presented.

Introduction

Metal–metal bonds represent a form of unsaturation and are thus centers of reactivity. Among the many manifestations of this reactivity is that of M–M triple bonds with carbon–carbon triple bonds.[1] Schrock, Listemann, and Sturgeoff[2] recently reported that internal alkynes react with the dimetal hexaalkoxide $W_2(OCMe_3)_6$ (but no others, so far as is known) according to eq 1, i.e., to yield the metal

$$W_2(OCMe_3)_6 + RC{\equiv}CR \rightarrow 2RCW(OCMe_3)_3 \quad (1)$$

alkylidynes. The one exception noted by Schrock et al. was the case where R = C_6H_5, i.e., the case of tolan, where neither reaction 1 nor any other reaction was observed under the conditions they used successfully with many other alkynes.

We now wish to report that interesting products can be obtained with tolan under different reaction conditions. With reaction temperatures in the range of 50–75 °C and $W_2(OCMe_3)_6$/tolan mole ratios greater than 1:1 and up to 3:1 we have isolated $W_2(OCMe_3)_4(\mu\text{-}PhC)_2$ (1) and $W_2(OCMe_3)_4(PhCCPh)_2$ (2) in moderate yields. Experiments monitored by ^{13}C NMR have shown that while 1 and 2 are the major reaction products, small amounts of $PhCW(OCMe_3)_3$ are also formed.

Experimental Section

Ditungsten hexa-*tert*-butoxide was prepared either by alcoholysis of $W_2(NMe_2)_6$[3] or, more conveniently, by Na/Hg reduction of WCl_4 in THF in the presence of $LiOCMe_3$,[2] followed by recrystallization from hexane.

Reactions of $W_2(OCMe_3)_6$ with Tolan. Various mole ratios of the alkoxide to the alkyne were used, but in all cases the general procedure was substantially the same. The case of a 3:1 ratio will be described in detail. A weighed amount of $W_2(OCMe_3)_6$ (400 mg, 0.5 mmol) was dissolved in 20 mL of toluene. Diphenylacetylene (31 mg, 0.17 mmol) was added at 0 °C from a side-arm tube. The reaction mixture was slowly heated to ca. 70 °C and then stirred at this temperature overnight. A small amount of a brownish precipitate was observed; it was insoluble in nonprotic solvents and has not been identified. The solvent was removed and the residue extracted with two 20-mL portions of hexane. The combined extracts were concentrated to ca. 5 mL. Dark tablets of 1 (reddish purple by transmitted light) were isolated after 72 h of cooling at −10 °C; yields 50–100 mg.

When a 2:1 mole ratio (i.e., more tolan) was used, at 70 °C it was found that the crystalline product 1 also contains a small amount of a second, black crystalline product (2). We have not yet found an efficient way to prepare 2 on a large scale, or to separate it from 1. The product ratio for the 2:1 reaction prior to isolation was determined by NMR, using spectral data separately measured for pure samples of 1, $W_2(OCMe_3)_6$, and $PhCW(OCMe_3)_3$ (3). After the reaction mixture was cooled and the solvent was removed, the solid residue was redissolved in the minimal quantity of toluene-d_8. The observed spectrum indicated that the yields were approximately as follows: 1, 50%; 2, 20%, $PhCW(OCMe_3)_3$ (3), 8%. The isolated yields of 1 and 2 were about 85 and 30 mg, respectively. However, no way of separating 2 from 1 has yet been found. Compound 1 free of 2 is, of course, obtainable from the reaction with a 3:1 mole ratio.

Decomposition of $CH_3CW(OCMe_3)_3$. A toluene solution of this compound was stirred at 60 °C for 14 h. The only product appeared to be a green precipitate insoluble in hexane and not identified. No hexane-soluble products were found.

Reactions of $W_2(OCMe_3)_6$ with PhCCMe and EtCCEt. These were carried out according to the general procedure described above. No products structurally similar to 1 or 2 were detected. In the case of 3-hexyne we have obtained a small amount of a very novel trinuclear compound that will be the subject of a future report.

X-ray Crystallographic Procedures. The structures of single crystals containing 1 and 2 were determined by applying the general procedures which we have already described elsewhere.[4] A detailed description is available as supplementary material. The

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Table I

	$W_2O_4C_{30}H_{46}$	$W_2O_4C_{48}H_{56}$
fw	838.4	1064.7
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	9.029 (3)	10.206 (6)
b, Å	19.769 (11)	11.028 (3)
c, Å	9.813 (5)	20.763 (9)
α, deg		92.16 (3)
β, deg	107.67 (2)	90.91 (5)
γ, deg		104.40 (3)
V, Å^3	1669 (2)	2261 (2)
Z	2	2
d_{calcd}, g/cm^3	1.67	1.56
cryst size, mm	0.5 × 0.4 × 0.2	0.4 × 0.4 × 0.2
μ(Mo Kα), cm^{-1}	70.65	52.09
data collectn instrument	Syntex P$\bar{1}$	CAD-4
radiatn	Mo Kα	Mo Kα
scan method	θ-2θ	θ-2θ
data collectn range, deg	4-50 (2θ)	5-50 (2θ)
no. of unique data, $F_o^2 \geqslant 3\sigma(F_o^2)$	1707	5085
no. of parameters refined	163	436
R^a	0.038	0.065
$R_w{}^b$	0.057	0.082
quality-of-fit indicator^c	1.35	1.82
largest shift/esd, final cycle	0.03	0.75
decay during data collection	4%	39% (corrected)
absorptn correctn	semiempirical (ψ scan)	
absorptn range (max-min)	99.9-77.3	99.7-63.9

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [b] Largest parameter shift in final refinement cycle. [c] Largest peak in a final difference Fourier, e/Å^3.

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

atom	x	y	z	B, Å^2
W(1)	0.94298 (4)	0.49866 (3)	0.35784 (4)	3.502 (8)
O(1)	0.2334 (7)	0.4549 (4)	0.7377 (7)	4.2 (2)
O(2)	0.9695 (8)	0.5499 (5)	0.7601 (8)	5.6 (2)
C(1)	0.367 (1)	0.4124 (7)	0.729 (1)	4.8 (3)
C(2)	0.510 (1)	0.5817 (9)	0.125 (1)	6.7 (4)
C(3)	0.420 (1)	0.4402 (8)	0.614 (1)	5.8 (3)
C(4)	0.298 (2)	0.3397 (8)	0.702 (2)	7.7 (4)
C(5)	0.071 (1)	0.3927 (7)	0.178 (1)	5.0 (3)
C(6)	0.101 (2)	0.3336 (8)	0.281 (2)	9.1 (5)
C(7)	0.226 (2)	0.413 (1)	0.139 (2)	13.8 (7)
C(8)	0.057 (2)	0.621 (1)	0.955 (2)	11.5 (7)
C(9)	0.093 (1)	0.5560 (5)	0.491 (1)	3.6 (2)
C(10)	0.185 (1)	0.6155 (6)	0.486 (1)	3.9 (2)
C(11)	0.165 (1)	0.6520 (7)	0.356 (1)	5.8 (3)
C(12)	0.252 (1)	0.7108 (7)	0.347 (2)	6.8 (4)
C(13)	0.375 (1)	0.7707 (7)	0.963 (2)	7.0 (4)
C(14)	0.408 (1)	0.6936 (7)	0.594 (1)	6.1 (3)
C(15)	0.315 (1)	0.6378 (7)	0.602 (1)	5.9 (3)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

crystal parameters and basic information pertaining to data collection and structure refinement for both compounds are summarized in Table I.

Tables II and III list the atomic coordinates for 1 and 2, respectively, while Tables IV and V give important bond distances and angles for the two structures. Complete tables of anisotropic thermal parameters and structure factor data are available as supplementary material. Figures 1 and 2 show the structures and atom numbering schemes.

Table III. Table of Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
W(1)	−0.00179 (7)	0.08589 (6)	0.23615 (3)	2.68 (1)
W(2)	0.20288 (7)	0.08802 (6)	0.31840 (3)	2.61 (1)
O(1)	−0.079 (2)	−0.054 (1)	0.1830 (7)	7.0 (4)
O(2)	0.314 (1)	−0.016 (1)	0.3418 (5)	3.5 (3)
O(3)	−0.114 (1)	0.188 (1)	0.2166 (5)	3.7 (3)
O(4)	0.268 (1)	0.218 (1)	0.3778 (7)	8.6 (4)
C(1)	0.181 (2)	0.206 (1)	0.2356 (7)	3.1 (4)
C(2)	0.226 (2)	0.093 (1)	0.2243 (8)	3.6 (4)
C(3)	0.019 (1)	−0.033 (1)	0.3253 (7)	2.4 (3)
C(4)	−0.037 (2)	0.076 (1)	0.3285 (7)	2.6 (3)*
C(5)	0.261 (2)	0.333 (2)	0.2257 (8)	3.9 (4)
C(6)	0.393 (2)	0.359 (2)	0.2112 (9)	4.5 (5)
C(7)	0.466 (2)	0.486 (2)	0.203 (1)	5.6 (6)
C(8)	0.402 (2)	0.583 (2)	0.211 (1)	6.0 (6)
C(9)	0.266 (2)	0.557 (2)	0.227 (1)	6.2 (6)
C(10)	0.197 (2)	0.431 (2)	0.234 (1)	4.5 (5)
C(11)	−0.092 (2)	0.129 (2)	0.3852 (8)	3.3 (4)
C(12)	−0.134 (2)	0.238 (2)	0.3799 (9)	4.0 (4)
C(13)	−0.180 (2)	0.295 (2)	0.4344 (8)	5.2 (5)
C(14)	−0.187 (2)	0.238 (2)	0.4913 (9)	5.4 (5)
C(15)	−0.146 (2)	0.131 (2)	0.4964 (8)	4.2 (4)
C(16)	−0.101 (2)	0.073 (2)	0.4418 (7)	3.5 (4)
C(17)	−0.042 (2)	−0.161 (1)	0.3366 (7)	3.0 (3)
C(18)	−0.183 (2)	−0.199 (2)	0.3372 (8)	4.0 (4)
C(19)	−0.252 (2)	−0.329 (2)	0.3396 (9)	5.0 (5)
C(20)	−0.040 (2)	−0.380 (2)	0.343 (1)	5.3 (5)
C(21)	−0.183 (2)	−0.417 (2)	0.3417 (9)	4.8 (5)
C(22)	0.028 (2)	−0.250 (2)	0.3406 (8)	3.9 (4)
C(23)	0.301 (2)	−0.082 (2)	0.1672 (8)	4.6 (5)
C(24)	0.344 (3)	−0.132 (2)	0.114 (1)	7.4 (7)
C(25)	0.363 (2)	−0.059 (2)	0.0537 (9)	6.2 (6)
C(26)	0.339 (2)	0.056 (2)	0.0540 (9)	6.4 (6)
C(27)	0.291 (2)	0.104 (2)	0.1066 (7)	4.2 (5)
C(28)	0.271 (2)	0.038 (2)	0.1641 (8)	3.6 (4)
C(29)	−0.169 (2)	0.252 (2)	0.1618 (9)	5.4 (4)
C(30)	−0.297 (2)	0.158 (3)	0.133 (1)	7.9 (7)
C(31)	−0.060 (3)	0.281 (3)	0.108 (1)	10.0 (8)
C(32)	−0.193 (3)	0.373 (2)	0.199 (1)	9.4 (7)
C(33)	−0.118 (2)	−0.159 (2)	0.1404 (8)	5.4 (6)
C(34)	−0.263 (2)	−0.196 (3)	0.143 (1)	7.5 (7)
C(35)	−0.068 (3)	−0.120 (2)	0.072 (1)	7.9 (8)
C(36)	−0.046 (3)	−0.258 (2)	0.162 (1)	6.5 (6)
C(37)	0.308 (2)	0.320 (2)	0.423 (1)	5.6 (6)
C(38)	0.296 (4)	0.260 (3)	0.487 (1)	12 (1)
C(39)	0.436 (4)	0.387 (4)	0.400 (2)	13 (1)*
C(40)	0.231 (3)	0.417 (2)	0.418 (2)	14 (1)
C(41)	0.453 (2)	−0.030 (2)	0.3487 (9)	4.7 (5)
C(42)	0.432 (2)	−0.178 (2)	0.334 (1)	8.1 (7)
C(43)	0.495 (2)	0.015 (2)	0.4158 (9)	6.9 (7)
C(44)	0.532 (3)	0.053 (2)	0.292 (1)	7.5 (6)*

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Other Physical Measurements. ^{13}C NMR spectra of a purified sample of 1 as well as of a mixture of 1 and 2 were measured on a VARIAN XL-200 PFT spectrometer in C_6D_6. The observed chemical shifts (in ppm relative to internal Me_4Si) are as follows: for 1, 351.3 (PhC), 81.4 (OC), 32.4 ($OC(CH_3)_3$), 125–129 (Ph); for 2, 82.1 (OC), 30.6 ((CCH_3). These data were used to assign resonances observed when entire reaction mixtures were examined to determine yields.

Results and Discussion

Synthetic Reactions. At the time we began this work we were aware, because of a private communication from Prof. R. R. Schrock, of the general reaction represented by eq 1. However, we knew none of the details and, in particular, we were unaware that it did not work with tolane. Our only objective, initially, was to have a convenient synthesis of $PhCW(OCMe_3)_3$ for use in other re-

Table IV. Some Bond Distances and Angles in $W_2(OCMe_3)_4(PhC)_2$

Bond Distances, Å

W(1)-W(1)′	2.665 (1)	C(5)-C(6)	1.51 (2)
-O(1)	1.831 (6)	-C(7)	1.61 (2)
-O(2)	1.855 (7)	-C(8)	1.49 (2)
-C(9)	1.935 (11)	C(9)-C(10)	1.451 (14)
-C(9)′	1.940 (10)	C(10)-C(11)	1.43 (2)
O(1)-C(1)	1.493 (12)	-C(15)	1.43 (2)
O(2)-C(5)	1.387 (13)	C(11)-C(12)	1.42 (2)
C(1)-C(2)	1.521 (15)	C(12)-C(13)	1.38 (2)
-C(3)	1.464 (15)	C(13)-C(14)	1.42 (2)
-C(4)	1.56 (2)	C(14)-C(15)	1.40 (2)

Bond Angles, deg

W(1)′-W(1)-O(1)	121.7 (2)	O(2)-W(1)-C(9)	112.4 (4)
-O(2)	124.1 (3)	-C(9)′	113.0 (4)
-C(9)	46.6 (3)	C(9)-W(1)-C(9)′	93.1 (4)
-C(9)′	46.5 (3)	W(1)-C(9)-W(1)′	86.9 (4)
O(1)-W(1)-O(2)	114.1 (4)	C(10)-C(9)-W(1)	138.1 (8)
-C(9)	111.9 (4)	-W(1)′	134.9 (9)
-C(9)′	110.5 (3)	W(1)-O(1)-C(1)	147.8 (7)
		W(1)-O(2)-C(5)	156.2 (8)

Table V. Some Bond Lengths and Angles for $W_2(O\text{-}t\text{-}Bu)_4(H_5C_6CCC_6H_5)_2$

Bond Lengths, Å

W(1)-W(2)	2.677 (1)	O(1)-C(33)	1.40 (2)
W(1)-O(1)	1.866 (9)	O(2)-C(41)	1.465 (15)
W(1)-O(3)	1.849 (8)	O(3)-C(29)	1.534 (13)
-C(1)	1.999 (12)	O(4)-C(37)	1.42 (2)
-C(2)	2.322 (13)	C(1)-C(2)	1.44 (2)
-C(3)	2.351 (12)	-C(5)	1.47 (2)
-C(4)	1.963 (10)	C(2)-C(28)	1.50 (2)
W(2)-O(2)	1.882 (8)	C(3)-C(4)	1.463 (15)
-O(4)	1.844 (10)	-C(17)	1.421 (15)
-C(1)	2.238 (12)	C(4)-C(11)	1.47 (2)
-C(2)	1.978 (12)		
-C(3)	2.023 (10)		
-C(4)	2.436 (12)		

Bond Angles, deg

W(2)-W(1)-O(1)	121.5 (3)	W(1)-C(1)-W(2)	78.1 (4)
-O(3)	137.9 (3)	W(1)-C(2)-W(2)	76.5 (4)
-C(1)	54.9 (3)	W(1)-C(3)-W(2)	75.0 (4)
-C(2)	45.9 (3)	W(1)-C(4)-W(2)	74.1 (4)
-C(3)	46.9 (3)	W(1)-C(1)-C(5)	148.0 (1)
-C(4)	61.1 (4)	W(1)-C(2)-C(28)	120.0 (1)
W(1)-W(2)-O(2)	139.1 (3)	W(1)-C(3)-C(17)	130.1 (8)
-O(4)	122.5 (3)	W(1)-C(4)-C(11)	147.1 (9)
-C(1)	47.0 (3)	W(2)-O(2)-C(41)	146.6 (9)
-C(2)	57.5 (4)	W(2)-O(4)-C(37)	175.0 (1)
-C(3)	58.1 (3)	W(2)-C(1)-C(5)	126.3 (9)
-C(4)	44.9 (2)	W(2)-C(2)-C(28)	148.5 (9)
W(1)-O(1)-C(33)	172.0 (1)	W(2)-C(3)-C(17)	141.4 (9)
W(1)-O(3)-C(29)	144.2 (9)	W(2)-C(4)-C(11)	122.3 (8)

actions. When we found, as Schrock and co-workers had already found and later reported,[2] that a facile reaction of this type fails for tolan, we persisted by changing the mole ratio and raising the reaction temperature. Thus, with use of the conditions reported in the Experimental Section, we found that compounds 1 and 2 could be formed, as indicated in reaction 2.

$$W_2(OCMe_3)_6 + PhCCPh \rightarrow W_2(OCMe_3)_4(\mu\text{-}PhC)_2 + W_2(OCMe_3)_4(PhCCPh)_2 + PhCW(OCBu_3)_3 \quad (2)$$

Having discovered that compounds 1 and 2 could be formed with tolan by using reaction conditions different from those used by Schrock et al., we examined the reactions of other symmetrical (RCCR) and unsymmetrical alkynes (RCCR′), but we have found no evidence for the formation of analogues of 1 and 2. The only products we have been able to isolate have been the alkylidynes $RCW(OCMe_3)_3$, and the optimum conditions for preparing them appear to be just those given by Schrock et al., i.e., 1:1 mole ratios and mild conditions. We also have looked at several possible reactions between $RCW(OCMe_3)_3$ compounds and $W_2(OMe_3)_6$ as well as thermal decomposition of the former, but we have never observed formation of 1 or 2, or analogues thereof.

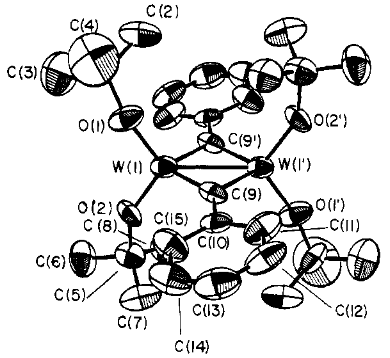

Figure 1. An ORTEP drawing of the $W_2(OCMe_3)_4(PhC)_2$ molecule. Atoms are represented by thermal vibration ellipsoids at the 40% level, and the atomic labeling scheme in this centrosymmetric molecule is defined.

We thus believe that processes leading to 1 and/or 2 diverge from those leading to alkylidyne products at an early stage. Moreover, our reactions seem to have higher activation energies and thus require higher temperatures and fairly long reaction times. It is thus not surprising that products of types 1 or 2 are not obtained in those cases where the metathesis reaction to give alkylidynes is efficient. Our reactions occur at a temperature which is close to where $W_2(OCMe_3)_6$ is known to decompose. At lower temperatures, 50–60 °C, we can reproducibly recover a large amount of starting material and we do not observe significant turnover at 20 °C over 10 h. A possible reaction mechanism might thus involve pyrolysis of $W_2(OCMe_3)_6$ and consecutive reaction of a highly reactive species thereby formed with one or two molecules of diphenylacetylene. The better yields obtained with substoichiometric amounts may be favored by additional $W_2(OCMe_3)_6$ trapping other fragmentation products. It is also to be noted that in the processes represented in eq 2 there is a loss of *tert*-butoxy groups. We do not know the fate of these.

Structures of $W_2(OCMe_3)_4(\mu\text{-}PhC)_2$, 1. Crystals of this compound consist of discrete molecules (Figure 1) residing on centers of inversion. Each tungsten atom is tetrahedrally coordinated by two *tert*-butoxide and two bridging phenylmethylidyne groups. Thus, the overall geometry of the dimer is that of two tetrahedra sharing an edge. The average W–O distance[5] is 1.84 [1] Å with W–O–C angles of 147.8 (7)° and 156.2 (8)°. Both the relatively short bond lengths and the large bond angles suggest considerable π interaction between oxygen and tungsten atoms. We shall find that this occurs also in 2. The two crystallographically independent W–C bond lengths are virtually identical with an avergae value of 1.937 (3) Å. The four oxygen atoms and the tungsten atoms are coplanar with deviations of less than 0.005 Å from the mean plane. Atoms W(1), W(1)′, C(9), and C(9)′ are rigorously coplanar. The dihedral angle between the two planes is 90.8°.

The $W_2(OCMe_3)_4(CPh)_2$ molecule has a substructure that can be compared to that of $W_2(CSiMe_3)_2(CH_2SiMe_3)_4$

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[5] The estimated deviation in square brackets is calculated as [ ] = $[\sum_n \Delta_i^2/n(n-1)]^{1/2}$ in which Δ_i is the deviation of the ith of n values from the arithmetic mean of the set.

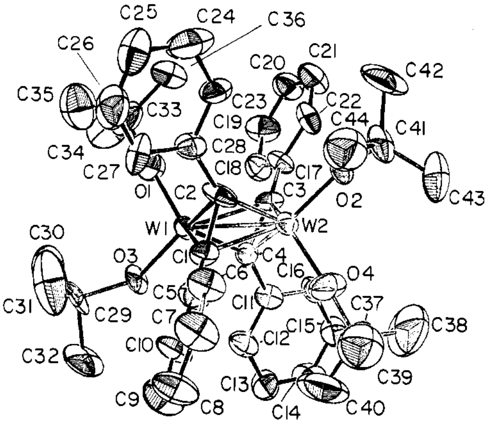

Figure 2. An ORTEP drawing of the $W_2(OCMe_3)_4(PhCCPh)_2$ molecule, with atoms represented by thermal vibration ellipsoids at the 40% level.

(4).[6] Despite the overall, qualitative similarity, there are several notable differences in detail. In crystals of 4 there are two crystallographically independent centrosymmetric molecules. In each one, the two independent W–C(br) distances differ, although the magnitudes of these differences are not large in view of the (rather large) esds. Thus, in one molecule the difference (with its esd) is 0.08 (4) Å while in the other the difference is 0.12 (4) Å. In 1 the difference is negligible, viz., 0.005 Å. Because of the large esd the average value of the W–C(br) distances in 4, 1.89 [3] Å, is not significantly different from that in 1, 1.937 (3) Å. The apparent inequalities within each of the molecules of 4 may result from a combination of packing forces and relatively large experimental uncertainties and may well not be intrinsic to the molecule.

A second difference, and one that certainly is significant, in both a statistical sense and a chemical sense, is that between the W–W distances in the two compounds. In 4 the two independent molecules have distances of 2.521 (2) and 2.549 (2) Å (an average value of 2.54 [1] Å) while in 1 the bond is much longer, 2.665 (1) Å. In both compounds the most natural, and doubtless correct, way to formulate the electronic structure is to consider that each metal atom has a formal oxidation number of V, that each has a formal 12-electron configuration, and that a single bond exists between them. We suggest that the cause for the difference of ca. 0.13 Å in the W–W distances is to be sought in the character of the bonds to the terminal ligands. In 1 there is an appreciable donation of π-electron density from the oxygen atoms to the tungsten atoms. This raises the effective electron count on the metal atoms above the formal value of 12. That this should result in an increase in the bond length is in keeping with the well-known fact that M–M bonds (both single ones and triple ones) between metal atoms with 18-electron configurations are always much longer than those between metal atoms with 12-electron configurations.

There are several structural indications that appreciable $O \rightarrow W$ π bonding occurs in 1. As already noted, the W–O–C angles are quite large (148° and 156°), and a very plausible reason for this would be to allow both pairs of oxygen π electrons, rather than only one pair to participate in π bonding. A more direct indication of $O \rightarrow W$ π bonding is provided by the W–O distances, which have a mean value of 1.84 [1] Å. In 4, the terminal W–C distances range from 2.05 (3) to 2.13 (3) Å. Thus, the W–O bonds are 0.21–0.29 Å shorter than the W–C bonds, whereas the difference between the commonly accepted single bond radii of C and O atoms is only 0.11 Å. The additional shortening is almost certainly the result of π bonding.

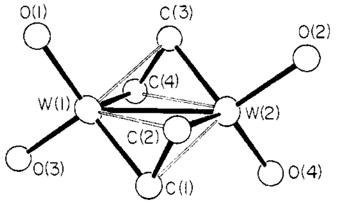

Figure 3. The central portion of the $W_2(OCMe_3)_4(PhCCPh)_2$ molecule. The shorter bonds are represented by solid lines and the longer W–C bonds by hollow lines.

Structure of $W_2(OCMe_3)_4(PhCCPh)_2$, 2. The entire molecule constitutes the crystallographic asymmetric unit and thus has no imposed symmetry. It is shown in its entirety in Figure 2, while the central core, consisting of the metal atoms and the eight atoms bound directly to them is shown in Figure 3. The symmetry in this central core is approximately C_{2h}, with the C_2 axis being a perpendicular bisector of the C(1)–C(2), C(3)–C(4), and W(1)–W(2) bonds and the plane of symmetry being defined by the two tungsten and four oxygen atoms, none of which deviate by more than 0.05 Å from their mean plane.

Although superficially the structure of 2 may seem to be comparable to some other structures of dinuclear molecules with bridging alkynes, close inspection suggests that the similarity may be more apparent than real. Previously there have been a number of compounds in which one alkyne, RCCR, lies above and projects perpendicular to an M–M bond, either single[1a,7] or double,[7,8] and can be thought of as supplying two electrons to each metal atom. Whether one chooses to look at the electronic structure of such an arrangement in more detail as two μ bonds or four C–M single bonds is of minor importance in the context of the present discussion. There is also at least one example of a metal–metal bond having two such crosswise alkyne bridges,[9] but, as noted at the end, this structure has much in common with the structure of 2. In some of the monoalkyne-bridged compounds, there are small distortions of the structure so that the alkyne C–C bond does not project exactly perpendicular to the M–M bond, but the strictly perpendicular structure seems to be an appropriate idealization. For our compound 2 this does not seem to be the case.

The two alkyne C–C bonds are practically parallel and define a plane that is far from perpendicular to the W–W bond (as is evident in Figure 2 and 3), although it is essentially perpendicular to the W_2O_4 plane. Each of the four alkyne carbon atoms forms one short C–W bond (in the range 1.96 (1)–2.02 (1) Å) and one long C–W bond (in the range 2.24 (1)–2.44 (1) Å). As shown in Figure 3, the inner coordination polyhedron of each metal atom can be regarded as a distorted tetrahedron, with two oxygen atoms at an averge distance of 1.86 [2] Å and two carbon atoms at an average distance of 1.99 [3] Å. These two tetrahedra have no common edge or vertex, and their only common symmetry element is the W_2O_4 plane. They are held together by the C–C bonds in the alkyne units and the W–W bond, which is very similar in length, 2.677 (1) Å, to that in compound 1. Overall, the arrangement of the metal

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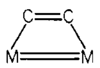
[6] Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1978**, *17*, 696.

[7] Cotton, F. A.; Jamerson, J. D.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 1774.

[8] Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2354.

[9] Nesmeyanov, A. N.; Gusev, A. I.; Pasynskii, A. A.; Anisimov, K. N.; Kolobova, N. E.; Struchkov, Y. T. *Chem. Commun.* **1968**, 1365.

atoms and the alkyne carbon atoms seems to be intermediate between exteme limiting structures[10] **a** and **b**, but closer to **b**. The alkyne C–C distances, which average 1.45 [1] Å, are consistent with such a view.

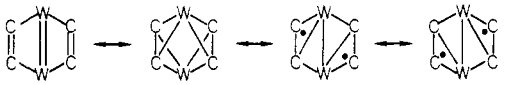


a

b

The alkyne moieties are extremely distorted from their "native" linear configurations. Thus, the C–C–C(phenyl) angles have an average value of 128 [2]°. This much is not surprising. However, the distortion from linearity is not merely a simple bending, as is usually the case, to give a planar ethane-like unit; there is also a twist so that the (phenyl)C–C–C–C(phenyl) chains have an average torsional angle of 61 [1]°.

We believe that a useful way, qualitatively, to formulate the bonding in this unusual molecule may be in terms of the resonance represented by **c**–**f**, where **c** and **d** are most important and, indeed, **e** and **f** (singlet diradicals) might be omitted altogether. This picture seems to account for all of the intermediate bond lengths and somewhat unusual angles mentioned above. In effect, there is a six-center, eight-electron bonding system in addition to the peripheral set of six two-electron single bonds defining the six-membered ring with its severely buckled chair conformation.



c **d** **e** **f**

Finally, as in compound 1, and to an even greater extent, we find evidence of extensive O→W π bonding. In 2 the average W–O distance, 1.86 [2] Å, is similar to that in 1, and two of the W–O–C groups are nearly linear, 173 (1)°, while the other two also have fairly large angles, viz., 145 (1)°. However, the remarkably large difference between these two W–O–C angles requires some comment. It does not seem reasonable to attribute it to packing forces since the alkoxide groups with the large bond angle occupy pseudoaxial positions in the central "dimetallocyclohexane ring" and would thus be inclined to bend away from the phenyl groups if steric crowding were severe. The W–O bond vectors associated with the large W–O–C angles are almost orthogonal to the long W–C bond vectors, so that the oxygen p orbitals are parallel to some of the bonding orbitals in the central six-center, eight-electron system.

A very similar structure, as far as the metal–carbon bonding is concerned, has been reported for $Cp_2(CO)_2Nb_2(PhCCPh)_2$.[9] Here, too, there are two short (2.11 Å) and two long (2.40 Å) bonds between a niobium atom and the central atom of the tolan group. The PhC–CPh bond length (1.39 (2) Å) appears to be somewhat shorter than in our case, going along with a smaller Ph–C–C–Ph dihedral angle (28°) and larger Ph–C–C bond angles (139 (2)°).

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Registry No. 1, 86260-95-9; 2, 86260-96-0; 3, 82228-87-3; W, 7440-33-7; $W_2(OCMe_3)_6$, 57125-20-9; tolan, 501-65-5.

Supplementary Material Available: Tables of anisotropic thermal vibration parameters, additional bond distance and angles, and structure factors for both compounds and a detailed description of the crystallographic procedures (51 pages). Ordering information is given on any current masthead page.

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[10] Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Chem. Soc.* **1982**, *104*, 3858.