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FURTHER STUDIES OF THE REACTIONS OF DITUNGSTEN HEXA-t-BUTOXIDE WITH ACETYLENES. ISOLATION AND CHARACTERIZATION OF $WO(OCMe_3)_4(THF)$, $[W_3(OCMe_3)_5(\mu\text{-}O)(\mu\text{-}CC_3H_7)O]_2$ AND $W(CPh)(OCMe_3)_3$ *

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Summary

Further studies of the reactions of $W_2(OCMe_3)_6$ with acetylenes at 70°C in toluene for up to 12 h are reported. All acetylenes of the type PhCCR afford $(Me_3CO)_2W(\mu\text{-}CPh)_2W(OCMe_3)_2$ (**1**) in high yield. Purely aliphatic acetylenes, RCCR, give complex products containing tritungsten cluster units, one example from the reaction with 4-octyne being the "dimer of trimers" $[W_3(OCMe_3)_5(\mu\text{-}O)(\mu\text{-}CC_3H_7)O]_2$ (**3b**), whose structure has been determined by X-ray crystallography. It forms monoclinic crystals ($P2_1/n$) with unit cell dimensions of *a* 12.838(1), *b* 14.440(1), *c* 18.465(1) Å, *β* 97.57(1)°, and $Z = 2$. One half of the centrosymmetric dimer is the crystallographic asymmetric unit and it contains an approximately isosceles triangle of metal atoms (W–W 2.892(1), 2.901(1), 2.418(1) Å) with one of the longer edges bridged by CC_3H_7 and the other by μ-O. There are then five terminal $OCMe_3$ groups and the two trinuclear units are united by a pair of bridging oxygen atoms. From the reaction of $W_2(OCMe_3)_6$ with 4-octyne it was also possible to isolate the mononuclear complex $WO(OCMe_3)_4(THF)$ (**4**) as colorless or pale yellow crystals. The structure, which is disordered, was determined by X-ray crystallography and contains molecules with apparent C_4 symmetry. The four Me_3CO groups form a planar set of W–O bonds (1.905(8) Å) and the W=O and $W\text{–}OC_4H_8$ bond lengths are 1.77(3) and 2.38(3) Å), respectively. The refinement was conducted in space group $I\bar{4}$ with $Z = 2$ and unit cell dimensions of *a* 11.707(1) and *c* 9.514(a) Å. Aliphatic carbynes, $(Me_3CO)_3W{\equiv}CR$ (R = Et, Pr), upon reactions with $W_2(OCMe_3)_6$ in 1/1 ratio gave the dimer of trimers product (**3**), but the aromatic carbyne, $(Me_3CO)_3W{\equiv}CPh$, did not give the dinuclear species **1**. The structure of $W(CPh)(OCMe_3)_3$ (**5**) was determined by X-ray crystallography. It forms monoclinic crystals ($P2_1/n$) with unit cell dimensions *a* 10.011(3), *b* 21.041(7), *c*

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* Dedicated to Professor Lamberto Malatesta in recognition of his important contributions to organometallic chemistry.

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10.064(2) Å, β 94.66(2)° and $Z = 4$. The tungsten atom has nearly regular tetrahedral coordination with W≡C 1.758(5), W–O(mean) 1.865(4) Å, O–W≡C(mean) 107.8(11), W–O–C(mean 141(1) and W≡C–C 175.8(4)°.

Introduction

In previous publications we have demonstrated that reactions between acetylenes and ditungsten hexa-t-butoxide, $W_2(OCMe_3)_6$, can lead to a variety of products, depending on the nature of the acetylene, the reaction conditions (especially temperature) and the mole ratio of the reactants [1,2]. Generally, under forcing conditions (70°C in toluene, for example) we obtain dinuclear and trinuclear products, in contrast to the mononuclear metathesis products, $RC{\equiv}W(OCMe_3)_3$, reported by Schrock and coworkers [3] for reactions of 1/1 mole ratios at room temperature. Specifically, we found that with diphenylacetylene [1] we could obtain **1** and **2** while with 3-hexyne [2] we obtained **3a**, where we reserve the number **3** for all compounds of the same general formula and use **3b** for the one (to be reported here) with $R = n\text{-}C_3H_7$.

$(Me_3CO)_2W(\mu\text{-}CPh)_2W(OCMe_3)_2$ **(1)** $(Me_3CO)_2W(\mu\text{-}PhCCPh)_2W(OCMe_3)_2$ **(2)**

$[W_3(OCMe_3)_5(\mu\text{-}O)(\mu\text{-}CR)O]_2$

(**3a**, $R = C_2H_5$; **3b**, $R = n\text{-}C_3H_7$)

We now report the results obtained in a study of several types of acetylenes, PhCCR, RCCR, and RCCH. It is found that the dinuclear molecule, $W_2(OCMe_3)_4(\mu\text{-}CPh_2)_2$ (**1**) is the major product from phenylacetylenes, PhC≡CR, whereas entirely aliphatic acetylenes, RC≡CR, yield trinuclear products, **3**. Terminal acetylenes, as well as 2-butyne, afforded only polymeric materials. All of the di- and tri-nuclear products we have prepared have a deficiency of alkoxide groups (i.e., a Me_3CO/W ratio of < 3) as compared to the starting material. We have now been able to isolate and characterize an alkoxide-rich byproduct, $WO(OCMe_3)_4(THF)$ (**4**) that seems always to occur. Its formation may account for the fate of some or all of the alkoxide groups "missing" from the other products.

For further studies of the reaction mechanism the carbynes, $W(CPh)(OCMe_3)_3$ (**5**) and $W(CC_3H_7)(OCMe_3)_3$ (**6**) were prepared. The former, **5**, has been shown to be a mononuclear species, while the second is probably a weakly associated dimer, as is the case for the $(Me_3CO)_3W{\equiv}CR$ compounds with $R = CH_3$ [4] and NMe_2 [5], according to studies by Chisholm and Huffman.

Experimental

Ditungsten hexa-t-butoxide was prepared by reducing WCl_4 in THF at −10°C with sodium amalgam in the presence of $LiOCMe_3$, followed by recrystallization from hexane at −20°C [3]. All reactions were carried out under argon.

Reaction of $W_2(OCMe_3)_6$ with 4-octyne. A weighed amount of $W_2(OCMe_3)_6$ (400 mg, 0.50 mmol) was dissolved in 20 ml of toluene. 4-Octyne (0.02 ml, 0.17 mmol) was added to the solution by syringe at room temperature. The reaction mixture was heated slowly to 70°C and then stirred at this temperature overnight. The solvent was removed and the residue was extracted with 10 ml of hexane. The extract was concentrated to ca. 3 ml. A homogeneous crop of dark tablets of **3b** (reddish brown by transmitted light) was harvested after 2 d at −20°C (40–45% yield), and the solution was then transferred to another flask. A few drops of THF were added to the solution which was then stored at −20°C. After 2 d colorless crystals of **4** were isolated in about 10% yield based on the $W_2(OCMe_3)_6$ used.

Reaction of $W_2(OCMe_3)_6$ with 1-phenyl-1-pentyne. A weighed amount of $W_2(OCMe_3)_6$ (400 mg, 0.50 mmol) was dissolved in 20 ml of toluene. 1-Phenyl-1-pentyne (0.15 ml, 1.0 mmol) was added to the solution at room temperature by syringe. The reaction mixture was heated slowly to 70°C and then stirred at this temperature overnight. The solvent was removed and the residue was extracted with 10 ml of hexane. The extract was concentrated to ca. 3 ml. Dark tablets of **1** (reddish purple by transmitted light) were isolated after 2 d at −10°C in 70–80% yield. Comparison of the unit cell dimensions identified the product as $W_2(OCMe_3)_4(\mu\text{-}CPh)_2$ (**1**).

Reaction of $W_2(OCMe_3)_6$ with 1-phenyl-1-heptyne. A weighed amount of $W_2(OCMe_3)_6$ (400 mg, 0.50 mmol) was dissolved in 20 ml of toluene and 0.18 ml (1.0 mmol) of 1-phenyl-1-heptyne was added at room temperature. The rest of the procedure was the same as that for the reaction with 1-phenyl-1-pentyne and again compound **1** was obtained in 70–80% yield.

Reaction of $W_2(OCMe_3)_6$ with 2-butyne. A weighted amount of $W_2(OCMe_3)_6$ (400 mg, 0.50 mmol) was dissolved in 20 ml of toluene. 2-Butyne (0.01 ml, 0.17 mmol) was added to the solution (10°C) by syringe. The reaction mixture was stirred at 10°C for 2 h and then was heated slowly to 60°C at which temperature it was stirred for 14 h. Polymeric products were obtained which were insoluble in THF, acetone, DMSO, and water. The polymer appeared to be air stable.

Reactions of $[W_3(OCMe_3)_5(\mu\text{-}O)(\mu\text{-}CC_3H_7)O]_2$ (3b) with Lewis bases such as pyridine and dimethylphenylphosphine. A weighed amount of **3b** (100 mg) was dissolved in 10 ml of freshly distilled pyridine. The reaction was run separately at temperatures 25, 50 and 85°C for 24 h. At the lower temperatures (25 and 50°C) starting material was recovered, but at 85°C the products obtained were insoluble in common organic solvents. Another attempt was made by dissolving 100 mg of **3b** in 15 ml of toluene. An amount of 1 ml of phenyldimethylphosphine was added to the solution by syringe. The solution was heated to ca. 60°C and then stirred overnight. The color of the solution changed from red brown to greenish but no defined products could be isolated.

Reaction of $W_2(OCMe_3)_6$ with 1-phenyl-1-propyne. A weighed amount of $W_2(OCMe_3)_6$ (806 mg, 1.0 mmol) was dissolved in 20 ml of hexane. 1-Phenyl-1-propyne (0.315 ml, 2.2 mmol) was syringed into the reaction mixture at 25°C at which temperature it was stirred for 4 h. The solvent was removed under vacuum and crystals of **5** were obtained by slow sublimation (10^{-4} torr, 24 h, 40°C) in ca. 10% yield based on $W_2(OCMe_3)_6$.

Reaction of $W_2(OCMe_3)_6$ with $W(CPh)(OCMe_3)_3$ (5). An equimolar mixture of the two compounds was dissolved in 15 ml of toluene. The solution was stirred for 4 h at 65°C. The color of the solution soon changed from red to dark brown, and insoluble brown products precipitated. The same products were obtained when a ratio of one mole $W_2(OCMe_3)_6$ to 50 of $W(CPh)(OCMe_3)_3$ was used.

Reaction of $W_2(OCMe_3)_6$ with $W(CPr)(OCMe_3)_3$. A one to one ratio of $W_2(OCMe_3)_3$ to carbyne (prepared according to Schrock's procedure [3]) was dissolved in 15 ml of toluene. The solution was stirred for 8 h at 65°C. The toluene was removed under vacuum, and the residue was extracted with 10 ml of hexane. The solution was concentrated to ca. 4 ml. Dark tablets of **1** were isolated at −10°C in ca. 62% yield based on the carbyne.

X-ray crystallographic procedures

The structures of compounds **3b**, **4** and **5** were determined by applying general procedures which we have described elsewhere [6]. The crystal parameters and basic

TABLE 1

CRYSTALLOGRAPHIC DATA FOR COMPOUNDS **3b**, **4** AND **5**

	$[W_3(OCMe_3)_5(\mu\text{-}O)(\mu\text{-}CC_3H_7)O]_2$ (**3b**)	$WO(OCMe_3)_4$(THF) (**4**)	$W(CPh)(OCMe_3)_3$ (**5**)
Formula weight	1908.4	564.4	492.3
Space group	$P2_1/n$	$I\bar{4}$	$P2_1/n$
a (Å)	12.838(1)	11.707(1)	10.011(3)
b (Å)	14.440(1)	11.707(1)	21.041(7)
c (Å)	18.465(1)	9.514(1)	10.064(2)
β, (°)	97.57(1)	–	94.66(2)
V (Å^3)	3393(2)	1304(4)	2113(4)
Z	2	2	4
d_{calc} (g/cm^3)	1.966	1.437	1.547
Crystal size (mm)	0.25×0.15×0.2	0.3×0.3×0.25	0.3×0.2×0.2
μ(Mo-K_α) (cm^{-1})	104.01	45.499	55.95
Data collection instrument	CAD-4	Syntex P$\bar{1}$	CAD-4
Radiation (monochromated in incident beam)	Mo-K_α	Mo-K_α	Mo-K_α
Orientation reflections, number, range (2θ)	25, 10–24	15, 20–30	25, 8–28
Temperature (°C)	25	25	−107
Scan method	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Data col. range, 2θ, (°)	4–46	5–50	4–50
No. unique data, total with $F_0^2 > 3\sigma(F_0^2)$	2880	624	2917
Number of parameters refined	227	60	337
Trans. factors, max., min (exp)	99.9%, 83.2%	99.88%, 89.5%	100%, 68.6%
R [a]	0.050	0.034	0.023
R_w [b]	0.061	0.041	0.030
Quality of fit indicator [c]	1.63	0.912	0.949
Largest shift/e.s.d., final cycle	0.05	1.21	0.54
Largest peak (e/Å^3)	0.85	0.75	0.4

[a] $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. [b] $R_w = [\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}$; $w = 1/\sigma^2(|F_0|^2)$. [c] Quality of fit $= [\Sigma w(|F_0| - |F_c|)^2/(N_{obs} - N_{parameters})]^{1/2}$.

information pertaining to data collection and structure refinement for the three compounds are summarized in Table 1.

For **3b** the dark tabular crystals appear red-brown by transmitted light. A crystal was mounted in a sealed Lindemann glass capillary. During 68.0 h of data collection the standards showed a 10% uniform decline and an appropriate correction was made. An empirical absorption correction was also made based on azimuthal scans of nine reflections. The unit cell dimensions are so similar to those of **3a** [2] that the metal atom positions were assumed to be the same and the remainder of the structure was soon located and refined. The methyl carbon atoms of the t-butoxy groups had high thermal parameters and there were indications of some disorder, but attempts to refine specific models failed. These carbon atoms were therefore assigned to single sets and refined isotropically.

For compound **4** a crystal was sealed in a capillary and preliminary examination on the diffractometer gave lattice vectors showing that it belonged to the tetragonal class. Axial photographs, however, raised a problem since two mirror planes (rather than one or three) were seen. A number of crystals, grown under a variety of conditions, consistently showed these characteristics. No indication of macroscopic twinning was seen under the polarizing microscope, nor did any of the X-ray photographs taken of various crystals indicate such twinning. A full set of data (i.e., a hemisphere) was then collected using a primitive triclinic unit cell. These data were then reduced to F_0 values with corrections for Lorentz factors and polarization, and also, based on ψ scans, for absorption. These data were then reindexed according to the tetragonal unit cell and equivalent reflections averaged. In this way 624 independent data points for each of which F_0^2 was $\geq$ 3 times its e.s.d. were obtained.

The data set so obtained indicated the existence of two, and only two, mirror planes and had no systematic absences other than $h+k+l=2n$. We therefore assumed that the space group had to be $I4/m$, $I4$ or $I\bar{4}$, and that the apparent mirror plane not perpendicular to c is non-rigorous. Trial solutions were developed in all three space groups, but those in $I4/m$ and $I4$ failed to refined satisfactorily. In the former, two-fold disorder of the Me_3CO groups, four-fold disorder of the THF and two-fold disorder of the oxo atom are all required. In $I4$ such extensive disorderings are not demanded but electron density maps seemed to indicate that disorder beyond that required was actually present, a situation that seemed suspicious. In $I\bar{4}$ the disorder required was minimal (two 1/2 THF and two 1/2 O) and refinement proceeded smoothly to give excellent figures of merit: $R=0.034$, $R_w=0.041$ and quality of fit 0.912.

The refined model can be used to explain the observed "superfluous" mirror plane by assuming a twinning pattern that arises from two-fold rotation about the b axis, which would cause mirror symmetry in a plane perpendicular to the a axis. As noted, all crystals we could make appeared to show this pattern of growth. We have also attempted to replace the THF with other donor molecules (e.g. pyridine, diethyl ether, several phosphines) in the hope of obtaining a crystallographically simpler compound, but no other crystalline compound could be obtained.

For compound **5**, the yellowish-orange crystals, a data set was collected over 28.1 h. The orientation matrix and unit cell parameters were derived from a least-squares fit to the goniometer settings of 25 accurately located reflections in the range of $15 < 2\theta < 39°$. An empirical absorption correction was made based on azimuthal scans of nine reflections. The position of the tungsten atom was derived from a

Patterson map. The remainder of the structure (including the hydrogen atoms which are omitted from the ORTEP view for clarity) was located and refined by an alternating sequence of least squares cycles and difference Fourier maps. The last cycle gave residuals of $R = 0.023$, $R_w = 0.030$ and a quality of fit index of 0.949 for a fit of 337 variables to 2917 observations.

Results and discussion

The positional parameters for the atoms in each of the three compounds and selected interatomic distances and angles are given in Tables 2–7, and drawings of each molecule, giving the atomic numbering schemes are shown in Figs. 1–3. We turn next to a discussion of each of the structures.

Structure of 3b

The structure of this "dimer of trimers", shown in Fig. 1, with $R = C_3H_7$ is very similar to that of **3a** ($R = C_2H_5$) which we have already reported [2]. Replacement of a bridging ethylidene unit by a propylidene, not surprisingly, has little effect on the size and shape of the molecule. The crystal packing in the two cases is so similar that it was possible to use the atomic coordinates of the tungsten atoms from **3a** to begin the solution and refinement of the structure of **3b**. Clearly, the periphery of the molecule as it affects the packing is dominated by the bulky t-butoxy groups and the addition of one methylene group to each ethylidene unit of **3a** scarcely alters the shape of the hexanuclear molecule.

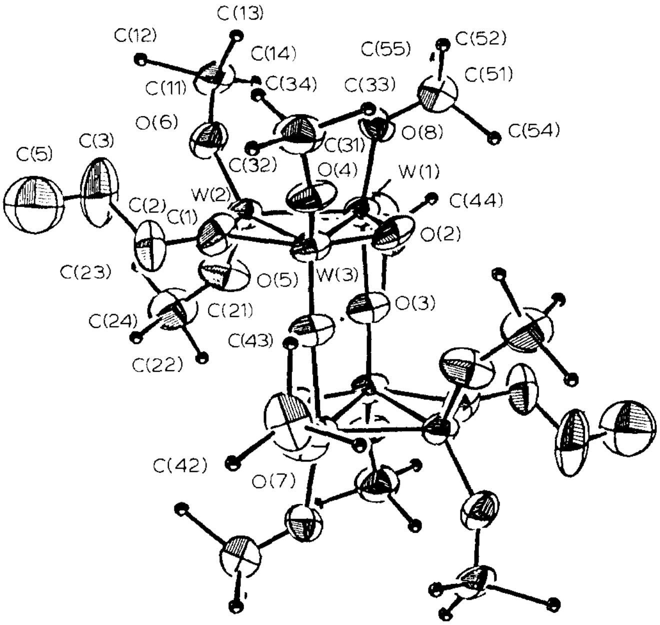


Fig. 1. An ORTEP drawing of the entire molecule, $[W_3(OCMe_3)_5(\mu\text{-}O)(\mu\text{-}CC_3H_7)O]_2$ (**3b**), giving the atomic labelling scheme. The methyl carbon atoms of the t-butyl groups are represented by arbitrarily small spheres to avoid covering up other atoms. All other atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

TABLE 2

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $[W_3(OCMe_3)_5(\mu\text{-}O)(\mu\text{-}CC_3H_7)O]_2$ (**3b**) [a,b]

Atom	x	y	z	B (Å^2)
W(1)	0.11400(7)	0.35265(5)	0.46597(4)	3.82(2)
W(2)	−0.01839(7)	0.36310(5)	0.36023(4)	3.88(2)
W(3)	−0.09636(7)	0.38691(5)	0.49955(4)	3.88(2)
O(2)	0.040(1)	0.3683(8)	0.5481(6)	4.5(3)
O(3)	−0.127(1)	0.5021(8)	0.5226(6)	4.5(3)
O(4)	−0.182(1)	0.3049(8)	0.5408(7)	5.0(3)
O(5)	0.027(1)	0.4643(9)	0.3086(7)	6.3(4)
O(6)	−0.022(1)	0.2581(9)	0.3018(7)	5.2(4)
O(7)	0.741(1)	0.1361(9)	0.9244(7)	5.5(3)
O(8)	0.626(1)	0.2797(9)	0.9751(6)	4.9(3)
C(1)	−0.158(2)	0.381(1)	0.3946(9)	5.0(5)
C(2)	−0.263(2)	0.396(2)	0.356(1)	6.7(6)
C(3)	−0.291(2)	0.325(2)	0.293(1)	9.5(9)
C(5)	0.600(3)	0.342(2)	0.260(2)	11(1)*
C(11)	0.014(2)	0.166(1)	0.2862(9)	4.8(5)
C(12)	0.130(2)	0.173(2)	0.286(1)	8.1(7)*
C(13)	−0.049(2)	0.144(2)	0.2061(1)	7.0(6)*
C(14)	0.472(2)	0.401(2)	0.840(1)	7.0(6)*
C(21)	0.505(2)	0.027(2)	0.253(1)	7.2(7)
C(22)	0.435(3)	0.108(2)	0.242(2)	9.4(8)*
C(23)	0.618(3)	0.059(2)	0.244(2)	10.3(9)*
C(24)	0.508(3)	0.029(2)	0.681(2)	11(1)*
C(31)	−0.232(2)	0.216(1)	0.545(1)	6.4(6)
C(32)	0.315(3)	0.326(2)	0.113(2)	12(1)*
C(33)	0.782(3)	0.167(2)	0.478(2)	12(1)*
C(34)	0.654(4)	0.231(3)	0.542(2)	16(1)*
C(41)	0.330(2)	0.404(2)	0.400(1)	6.4(6)
C(42)	0.310(3)	0.388(2)	0.314(2)	12(1)*
C(43)	0.670(3)	0.490(3)	0.597(2)	14(1)*
C(44)	0.421(3)	0.354(3)	0.425(2)	16(1)*
C(51)	0.700(2)	0.330(2)	0.026(1)	6.3(6)
C(52)	0.755(2)	0.267(2)	0.085(1)	7.7(7)*
C(54)	0.280(2)	0.122(2)	0.486(1)	7.5(6)*
C(55)	0.631(2)	0.404(2)	0.061(2)	8.9(8)*

[a] Starred atoms were refined isotropically. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

A discussion of the bonding in **3a** has been given [2] and pertains equally well to **3b**. One point we have checked further is the nature of the linkage between the two trinuclear halves of the hexanuclear molecule. If, as we proposed [2] there are two oppositely directed W=O→W′ bridges, it might be thought that these could be split by a suitable donor ligand, according to eq. 1. We have attempted to realize this

$$W{=}O{\to}W' + L \to W{=}O + L{\to}W' \qquad (1)$$

using both pyridine and $PhMe_2P$ as the ligand L, but without success. Under the milder conditions used there is no reaction and when more forcing conditions were used only intractable products were obtained. Most likely the W=O→W′ linkages are

TABLE 3

SOME BOND DISTANCES (Å) AND ANGLES (°) FOR $[W_3(OCMe_3)_5(\mu\text{-}O)(\mu\text{-}CC_3H_7)O]_2$ (**3b**)

W(1)–W(2)	2.418(1)	W(3)–O(4)	1.850(10)
W(1)–W(3)	2.892(1)	W(3)–C(1)	1.995(15)
W(2)–W(3)	2.901(1)	C(1)–C(2)	1.47(3)
W(1)–O(2)	1.906(9)	C(2)–C(3)	1.56(3)
W(1)–O(8)	1.924(10)	C(3)–C(5)	1.46(3)
W(1)–O(3)	2.113(9)	W(2)–O(6)	1.858(10)
W(1)–O(7)	1.903(11)	W(3)–O(2)	1.878(12)
W(2)–C(1)	1.99(2)	W(3)–O(3)	1.774(9)
W(2)–O(5)	1.881(11)		
W(2)–W(1)–W(3)	65.52(3)	W(3)–W(2)–C(1)	43.4(4)
W(2)–W(1)–O(2)	105.3(3)	W(3)–W(2)–O(5)	121.6(3)
W(2)–W(1)–O(3)	93.3(3)	W(3)–W(2)–O(6)	128.7(3)
W(2)–W(1)–O(7)	102.7(4)	W(1)–W(3)–W(2)	49.35(2)
W(3)–W(1)–O(7)	161.5(3)	W(1)–W(3)–O(2)	40.5(3)
W(3)–W(1)–O(8)	102.7(4)	W(1)–W(3)–O(4)	127.1(4)
W(3)–W(1)–O(3)	82.7(3)	W(1)–W(3)–O(3)	117.1(4)
W(3)–W(1)–O(2)	39.8(3)	W(2)–W(3)–O(3)	115.9(3)
W(1)–W(2)–W(3)	65.13(3)	W(2)–W(3)–O(4)	125.7(3)
W(1)–W(2)–O(5)	103.0(4)	W(2)–W(3)–C(1)	43.2(5)
W(1)–W(2)–O(6)	112.4(4)	W(2)–C(1)–W(3)	93.4(8)
W(1)–O(2)–W(3)	99.7(4)	W(1)–O(3)–W(3)	159.6(6)
W(2)–C(1)–C(2)	133.0(1)	W(3)–C(1)–C(2)	133.0(1)
W(1)–O(7)–C(41)	160.0(1)	W(1)–O(8)–C(51)	127.0(1)
W(2)–O(6)–C(11)	151.0(1)	W(2)–O(5)–C(21)	143.0(1)
W(3)–O(4)–C(31)	152.0(1)		

so sterically encumbered that they cannot be attacked except under conditions that are severe enough to favor other reactions as well.

Structure of WO(OCMe$_3$)$_4$(THF) (4)

The molecular structure is shown in Fig. 2. As described in detail in the

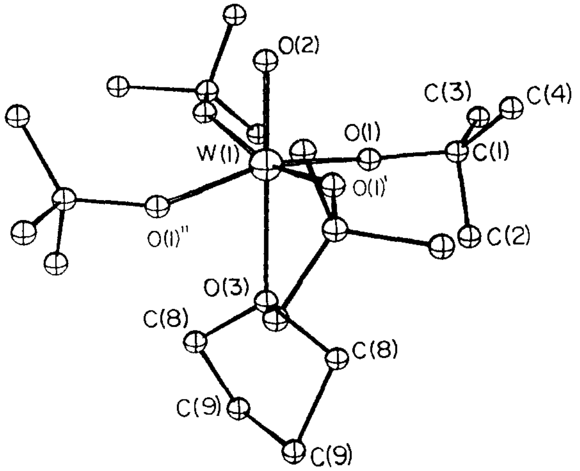


Fig. 2. An ORTEP drawing of the molecule, $WO(OCMe_3)_4(THF)$ (**4**), giving the atomic labelling scheme. All atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

TABLE 4

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $WO(OCMe_3)_3(THF)$ (**4**) [a,b]

Atom	x	y	z	B (Å^2)
W(1)	0.000	0.000	0.000	3.217(7)
O(1)	−0.1448(6)	0.0695(7)	0.0322(8)	4.6(2)
C(1)	−0.2625(9)	0.058(1)	0.018(2)	5.9(3)
C(2)	−0.313(1)	0.181(1)	0.011(6)	9.5(4)
C(3)	−0.318(2)	−0.018(2)	−0.095(4)	14.1(9)
C(4)	−0.275(2)	0.018(2)	0.155(2)	10.7(6)
O(2)	0.000	0.000	−0.185(3)	6.0(4)*
O(3)	0.000	0.000	−0.251(2)	5.6(4)*
C(8)	−0.093(4)	−0.037(4)	0.345(5)	7.9(9)*
C(9)	−0.031(4)	−0.063(3)	−0.45(2)	11(1)*

[a] Starred atoms were refined isotropically. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Experimental, the crystals of this compound exhibit a form of twinning which results in an apparent disordering of the O and THF ligands. Because of this, the accuracy of the W–O distances for these two ligands is poor, probably even worse than one would formally infer from the e.s.d. of 0.03 Å. However, the values obtained, 1.77(3) for W=O and 2.38(3) Å for $W–OC_4H_8$, are quite reasonable for such bonds. There is no disordering of the Me_3CO groups, however, and the W–O distance here, 1.905(8) Å, is reliable and about as expected. This distance, together with the W–O(1)–C(1) angle of 146.0(1)°, indicates that the amount of oxygen to tungsten $p_\pi \to d_\pi$ bonding is in the typical range. The t-butyl groups themselves have rather large amplitudes of vibration and thus the apparent O(1)–C(1) distance is a bit short and the O(1)–C(1)–C(2,3,4) angles are scattered. The O(1)–W–O(1)″ angle of 161.5(5)° shows clearly the puckering of the central set of $W–OMe_3$ bonds, in accord with the crystallographic $\bar{4}$ symmetry.

TABLE 5

SOME BOND DISTANCES (Å) AND ANGLES (°) FOR $WO(OCMe_3)_4(THF)$ (**4**)

W(1)–O(1)	1.905(8)
W(1)–O(2)	1.77(3)
W(1)–O(3)	2.38(3)
O(1)–C(1)	1.39(2)
W(1)–O(1)–C(1)	146.0(1)
O(1)–W(1)–O(3)	80.9(3)
O(1)–W(1)–O(3)	99.1(3)
O(1)–W(1)–O(2)	99.2(2)
O(1)–W(1)–O(2)	80.8(2)
O(2)–W(1)–O(3)	180.0(0)
O(1)–C(1)–C(4)	93.0(2)
O(1)–C(1)–C(2)	107.0(1)
O(1)–C(1)–C(3)	122.0(2)
O(1)–W(1)–O(1)″	161.5(5)
O(1)–W(1)–O(1)′	91.47(7)

TABLE 6

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS FOR $W(CPh)(OCMe_3)_3$ (**5**) [a,b]

Atom	x	y	z	B (Å)^2
W	0.26694(2)	0.09082(1)	0.19788(2)	1.544(3)
O(1)	0.4363(3)	0.0885(1)	0.1332(3)	2.02(6)
O(2)	0.8241(3)	−0.0141(2)	−0.1739(3)	2.09(6)
O(3)	0.1693(3)	0.1581(2)	0.1175(3)	2.37(7)
C(1)	0.2847(5)	0.1063(2)	0.3700(5)	1.97(9)
C(2)	0.3017(5)	0.1142(2)	0.5142(5)	2.07(9)
C(3)	0.4015(6)	0.0801(2)	0.5902(5)	2.8(1)
C(4)	0.4163(6)	0.0877(3)	0.7274(5)	3.4(1)
C(5)	0.3372(6)	0.1280(3)	0.7915(5)	3.7(1)
C(6)	0.2391(5)	0.1622(3)	0.7179(5)	3.1(1)
C(7)	0.2210(5)	0.1556(2)	0.5819(5)	2.4(1)
C(11)	0.5739(5)	0.1092(2)	0.1610(5)	2.28(9)
C(12)	0.6195(5)	0.0977(3)	0.3046(5)	3.0(1)
C(13)	0.5782(6)	0.1785(3)	0.1254(7)	4.3(1)
C(14)	0.6559(5)	0.0691(3)	0.0711(6)	3.9(1)
C(21)	0.9000(5)	0.0314(2)	−0.2477(5)	2.4(1)
C(22)	1.0191(5)	−0.0027(3)	−0.2952(6)	3.9(1)
C(23)	0.9406(6)	0.0845(3)	−0.1535(6)	4.2(1)
C(24)	0.8077(6)	0.0565(3)	−0.3629(7)	4.1(1)
C(31)	0.1004(5)	0.2150(2)	0.1565(5)	2.9(1)
C(32)	−0.0144(5)	0.1954(3)	0.2356(6)	3.8(1)
C(33)	0.0512(7)	0.2470(3)	0.0252(6)	4.8(1)
C(34)	0.1987(6)	0.2568(3)	0.2381(6)	3.8(1)
H(1)	0.449(4)	0.051(2)	0.551(4)	2(1)*
H(2)	0.470(5)	0.067(3)	0.770(5)	4(1)*
H(3)	0.351(5)	0.127(2)	0.894(5)	3(1)*
H(4)	0.188(5)	0.195(3)	0.756(6)	4(1)*
H(5)	0.155(5)	0.173(3)	0.531(5)	4(1)*
H(11)	0.708(5)	0.110(3)	0.325(5)	3(1)*
H(12)	0.609(5)	0.049(3)	0.321(5)	3(1)*
H(13)	0.563(5)	0.117(2)	0.363(5)	3(1)*
H(14)	0.520(4)	0.203(2)	0.172(4)	1.8(9)*
H(15)	0.680(6)	0.193(3)	0.135(6)	6(2)*
H(16)	0.542(6)	0.174(3)	0.023(6)	6(2)*
H(17)	0.620(8)	0.077(3)	−0.029(8)	9(2)*
H(18)	0.747(5)	0.076(2)	0.085(5)	3(1)*
H(19)	0.637(7)	0.024(3)	0.086(7)	8(2)*
H(21)	0.998(4)	0.063(2)	−0.084(4)	2(1)*
H(22)	0.845(6)	0.110(3)	−0.135(6)	5(1)*
H(23)	0.498(5)	0.382(3)	0.315(5)	4(1)*
H(24)	0.722(5)	0.082(2)	−0.340(5)	3(1)*
H(25)	0.727(6)	0.528(3)	0.908(6)	6(2)*
H(26)	0.875(5)	0.085(2)	−0.402(5)	3(1)*
H(27)	0.582(7)	0.513(3)	0.287(7)	8(2)*
H(28)	0.571(5)	0.474(2)	0.156(5)	3(1)*
H(29)	0.509(5)	0.463(2)	0.843(5)	3(1)*
H(31)	0.739(6)	0.256(4)	0.815(6)	8(2)*
H(32)	0.160(5)	0.299(2)	0.249(5)	4(1)*
H(33)	0.272(5)	0.270(3)	0.192(5)	5(2)*
H(34)	0.523(5)	0.329(3)	0.815(5)	4(1)*
H(35)	−0.060(5)	0.231(2)	0.256(5)	3(1)*
H(36)	−0.075(6)	0.163(3)	0.163(6)	7(2)*

TABLE 6 (continued)

Atom	x	y	z	B (Å)^2
H(37)	0.005(4)	0.286(2)	0.050(4)	2(1)*
H(38)	0.135(5)	0.262(3)	−0.022(5)	5(1)*
H(39)	−0.006(6)	0.222(3)	−0.023(7)	8(2)*

[a] Starred atoms were refined isotropically. [b] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)_{13} + bc(\cos\alpha)\beta_{23}]$.

Structure of $W(CPh)(OCMe_3)_3$ (5)

The crystals of the compound $W(CPh)(OCMe_3)_3$ consist of discrete mononuclear molecules, each having the structure shown in Fig. 3. The coordination geometry of the tungsten atom is almost ideally tetrahedral with all L–W–L bond angles in the range 107 to 111°. The average W–O distance is 1.865(4) Å and W–O–C angles from 139 to 143°. The W≡C bond length is 1.758(5) Å and W≡C–C bond angles is 175.8(4)°.

W=O bonds

It is interesting to compare the W=O bonds found here in **3a**, **3b** and in **4** with those found in the simpler compounds WX_4O (X = Cl, Br) [7]. In **4** where the oxygen atom of the W=O bond is not serving as a donor to any other metal atom, the bond length is 1.77(3) Å. In **3a** and **3b**, where there is an appreciable donor bond, with O→W′ equal to 2.12 Å, the W=O bond is still the same length within the experimental error at 1.774(9) Å. This seems to imply that the additional donation to another metal atom need not necessarily have a major weakening effect on the W=O

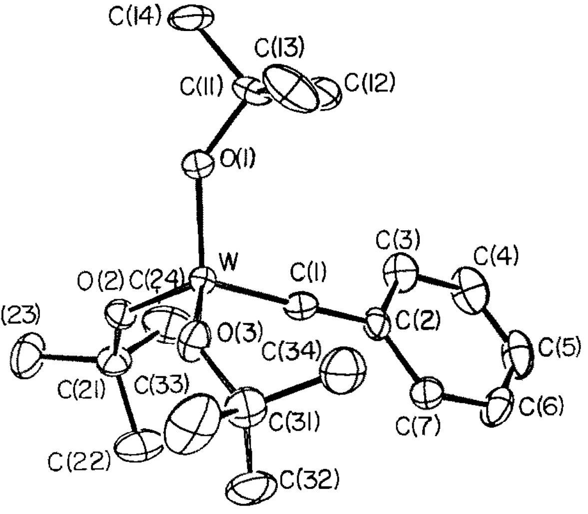


Fig. 3. An ORTEP drawing of the molecule, $W(CPh)(OCMe_3)_3$ (5), giving the atomic labelling scheme. The hydrogen atoms are eliminated to avoid covering of other atoms. All other atoms are represented by their ellipsoids of thermal vibration at the 40% probability level.

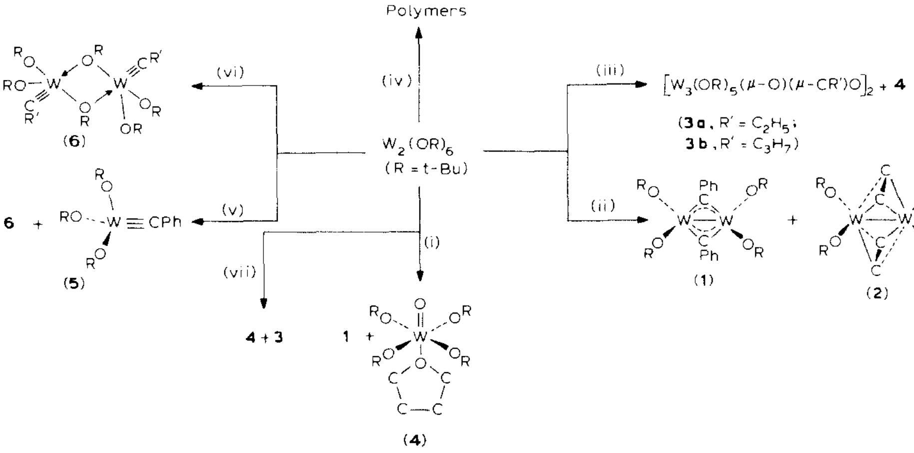
TABLE 7

SOME BOND DISTANCES (Å) AND ANGLES (°) FOR $W(CPh)(OCMe_3)_3$ (5)

W–O(1)	1.866(3)
W–O(2)	1.861(3)
W–O(3)	1.868(3)
W–C(1)	1.758(5)
O(1)–C(11)	1.450(5)
O(2)–C(21)	1.461(6)
O(3)–C(31)	1.451(6)
C(1)–C(2)	1.456(6)
C(1)–W–O(1)	109.1(2)
C(1)–W–O(2)	107.3(2)
C(1)–W–O(3)	107.1(2)
O(1)–W–O(2)	112.4(1)
O(1)–W–O(3)	109.1(1)
O(2)–W–O(3)	111.6(1)
W–C(1)–C(2)	175.8(4)
W–O(1)–C(11)	143.2(3)
W–O(2)–C(21)	140.5(3)
W–O(3)–C(31)	138.7(3)

bond. In WBr_4O there are chains of W=O→W=O→W=O bonds with lengths of 1.78(3) and 2.16(3) Å, for the double and donor bonds, respectively, which is very comparable to what we have found. However, it has been reported that gaseous WBr_4O has an appreciably shorter W=O distance, 1.70 Å. In view of the known uncertainties in all of the distances as well as the unspecified error in the gas-phase electron diffraction value for WBr_4O, we can probably not yet draw any firm conclusions as to the behavior of these bonds when W=O→W type association takes place.

SCHEME 1. (i) 70°C; toluene; PhC≡CR (R = Ph, C_3H_7), C_5H_{11}; W_2/C≡C = 1/2; (ii) 70°C; toluene; PhC≡CPh, W_2/C≡C = 1/3; (iii) 70°C; toluene; RC≡CR (R = C_2H_5, C_3H_8), W_2/C≡C = 1/3; (iv) 70°C; toluene; $CH_3C{\equiv}CCH_3$, terminal acetylenes; (v) 25°C; hexane; PhC≡CCH_3, W_2/C≡C = 1/2.2; (vi) 25°C; hexane; $CH_3C{\equiv}CCH$, W_2/C≡C = 1/1; (vii) 70°C; toluene; $(OCMe)_3W{\equiv}CC_2H_5$, W_2/W≡C = 1/1.



Chemical reactions

A summary of the various reactions we have observed is presented in Scheme 1. Reactions of $W_2(O\text{-}t\text{-}Bu)_6$ with PhCCR compounds in 1/2 mole ratio proceeded in the same way for $R = C_2H_5$, C_3H_7 and C_5H_{11}, namely, to produce in isolated yields of 70–80% the phenylidyne bridged dimer, **1**, plus traces of $WO(O\text{-}t\text{-}Bu)_4(THF)$. According to Schrock's observations [3], $W_2(O\text{-}t\text{-}Bu)_6$ reacts with PhCCR in 1/2 molar ratio to give the products shown in eq. 2. One might then be tempted to

$$W_2(O\text{-}t\text{-}Bu)_6 + 2PhCCR \rightarrow \underset{(\mathbf{5})}{2PhCW(O\text{-}t\text{-}Bu)_3} + RCCR \qquad (2)$$

believe that dimerization of the tungsten monomer, **5**, followed by extrusion of two t-butoxy radicals at 70°C, could lead to the formation of the phenylidyne bridging dimer as shown in eq. 3. However, reaction 3 has been shown not to take place on

$$2PhCW(O\text{-}t\text{-}Bu)_3 \xrightarrow{70^\circ C} W_2(\mu\text{-}CPh)_2(O\text{-}t\text{-}Bu)_4 + 2''BuO'' \qquad (3)$$

heating a freshly prepared solution of pure $(PhC)W(O\text{-}t\text{-}Bu)_3$ in toluene, neither in the presence nor in the absence of $W_2(O\text{-}t\text{-}Bu)_6$. Instead, other uncharacterized products, insoluble in common organic solvents, were obtained. Figure 3 shows that the bulky ligands on the metal atom might play a role in preventing the coupling of **5**. Furthermore, even to predict at what stage of the reaction the t-butoxy radicals are given off is risky. It is worth noting that the products actually obtained when attempting reaction 3 precipitate from toluene soon after the color of solution changes from red to dark brown.

The formation of the dimer of trimers, when dialkyl acetylenes are used, is also difficult to account for in detail. Again, according to Schrock [3], the facile reaction shown in eq. 4 will occur even at 25°C. It might be hypothesized that this would be

$$W_2(O\text{-}t\text{-}Bu)_6 + RCCR \rightarrow 2RCW(O\text{-}t\text{-}Bu)_3 \qquad (4)$$

followed by reaction 5 to give the isolated products. However, we have not been able

$$6RCW(O\text{-}t\text{-}Bu)_3 \xrightarrow{70^\circ C} [W_3O(CR)(O\text{-}t\text{-}Bu)_5(\mu\text{-}O)]_2 + 4\text{“}RC\text{”} + 2\text{“}BuO\text{”} \qquad (5)$$

to carry out reaction 5; it does not go as written, but when a 1/1 molar ratio of $RCW(O\text{-}t\text{-}Bu)_3$ and $W_2(O\text{-}t\text{-}Bu)_6$ are reacted at 70°C for 8–12 h, the dimer of trimers products were obtained in good yield (60–65%). This confirms the proposal, eq. 6, we have made in a previous publication [1] about the mechanism for the reaction pathway.

$$\begin{aligned} &W_2(OR')_6 + (R'O)_3W{\equiv}CR \rightarrow \text{“}W_3(OR')_5(\mu\text{-}O)(\mu\text{-}CR)O'' \rightarrow \\ &\qquad\qquad [W_3(OR')_5(\mu\text{-}O)(\mu\text{-}CR)O]_2 \qquad (6) \end{aligned}$$

Supplementary Data Available. Tables of thermal vibration parameters and structure factors are available from the senior author on request.

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References

1 F.A. Cotton, W. Schwotzer and E.S. Shamshoum, Organometallics, 2 (1983) 1167.

2 F.A. Cotton, W. Schwotzer and E.S. Shamshoum, Organometallics, 2 (1983) 1340.

3 R.R. Schrock, M.L. Listemann and L.G. Sturgeoff, J. Am. Chem. Soc., 104 (1982) 4291.

4 M.H. Chisholm, D.M. Hoffman and J.C. Huffman, Inorg. Chem., 22 (1983) 2903.

5 M.H. Chisholm, J.C. Huffman and N.S. Marchant, J. Am. Chem., Soc., 105 (1983) 6162.

6 (a) A. Bino, F.A. Cotton and P.E. Fanwick, Inorg. Chem., 18 (1979) 3558; (b) F.A. Cotton, B.A. Frenz, G. Degannello and A. Shaver, J. Organomet. Chem., 50 (1973) 227; (c) A.C.T. North, D.C. Phillips and F.S. Mathews, Acta Cryst., A24 (1968) 351.

7 U. Müller, Acta Cryst., C40 (1984) 915, and earlier references cited therein.