The monobridging bonding mode of the halogen has no significant influence on the Cu-X bond distances, which agree with those found in mononuclear, singly or doubly bridged copper(I) complexes.[19] Distances and angles within tmen and BPh_4^- units (Tables V and VI and Tables SVII-SIX available as supplementary material) fall in the usual range.[18]

Acknowledgment. We thank CNR, Rome, for financial support.

Registry No. I, 53513-40-9; III, X = Cl, 72840-12-1; III, X = Br, 72840-14-3; III, X = I, 72840-10-9; CuCl, 7758-89-6; CuBr, 7787-70-4; CuI, 7681-65-4; CO, 630-08-0.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes for all compounds and Tables SI-SIII listing anisotropic thermal parameters, SIV-SVI listing atomic coordinates for hydrogen atoms, SVII-SIX listing distances and angles in BPh_4^- anions, and SX-SXII for least-squares planes (65 pages). Ordering information is given on any current masthead page.

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(19) Baker, E. N.; Garrick, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 416. Bräuden, C. I. *Acta Chem. Scand.* **1967**, *21*, 1000. Baenziger, N. C.; Richards, G. F.; Doyle, J. R. *Inorg. Chem.* **1964**, *11*, 1529. Gill, J. T.; Mayerle, J. J.; Welcker, P. S.; Lewis, D. F.; Ucko, D. A.; Barton, D. J.; Stowens, D.; Lippard, S. J. *Ibid.* **1976**, *15*, 1155. Churchill, M. R.; Rotella, F. J. *Ibid.* **1979**, *18*, 166 and references cited therein. Jardine, F. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 115. Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shalzly, M. F.; Hutchinson, J. P.; Rupich, M. W.; Watkins, K. O. *Inorg. Chem.* **1979**, *18*, 2296. Van de Leemput, P. J. H. A. M.; Willemse, J.; Cras, J. A.; Groen, L. *Recl. Trav. Chim. Pays*-Bas **1979**, *98*, 413. Eller, P. G.; Kubas, G. J.; Ryan, R. R. *Inorg. Chem.* **1977**, *16*, 2454.

(20) Johnson, C. K. "ORTEP", Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

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Crystal Structure and Molecular Geometry of a Trigonal-Bipyramidal Oxo-Alkylidene Complex of Tungsten(VI), $W(=O)(=CHCMe_3)(PEt_3)Cl_2$

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The complex $W(=O)(=CHCMe_3)(PEt_3)Cl_2$, a catalyst for the metathesis of terminal and internal olefins, crystallizes in the centrosymmetric orthorhombic space group *Pbca* with $a = 9.111$ (2) Å, $b = 15.709$ (4) Å, $c = 24.207$ (6) Å, $V = 3465$ (1) Å^3, and $Z = 8$. Diffraction data ($2\theta = 4.0$–$50.0°$, Mo Kα radiation) were collected on a Syntex $P2_1$ automated four-circle diffractometer, and the structure was solved by conventional methods. All nonhydrogen atoms were located. The tungsten atom lies on a pseudospecial position ($\sim^1/_2$, $\sim^1/_2$, $\sim^1/_8$), and half of the data are systematically weak. Discrepancy indices are $R_F = 0.147$ and $R_{wF} = 0.068$ for all 3055 data and $R_F = 0.073$ and $R_{wF} = 0.055$ for those 1582 data with $|F_o| > 5.0\sigma(F_o)$. The tungsten(VI) atom has a distorted trigonal-bipyramidal coordination geometry with the oxo ligand (W=O = 1.661 (11) Å), the neopentylidene ligand (W=C(1) = 1.882 (14) Å), and a chloride ligand (W—Cl(1) = 2.389 (5) Å) in equatorial sites; the phosphine ligand (W—P = 2.518 (4) Å and the second chloride ligand (W—Cl(2) = 2.379 (5) Å) occupy the two axial sites.

Introduction

Although alkylidene derivatives of tantalum and niobium are now well characterized,[1] there are few such complexes known for the other transition metals. Recently, alkylidene *transfer* from tantalum has been shown[2] to yield alkylidene complexes of tungsten (via eq 1).

$$Ta(=CHCMe_3)(PR_3)_2Cl_3 + W(=O)(OCMe_3)_4 \rightarrow Ta(OCMe_3)_4Cl + W(=O)(=CHCMe_3)(PR_3)_2Cl_2 \quad (1)$$

The resulting products are octahedral oxo–alkylidene complexes of tungsten(VI) and are catalysts for the metathesis of both terminal and internal olefins.[3]

One PR_3 ligand can be removed from the octahedral oxo–alkylidene complexes by adding transition-metal complexes which will scavenge phosphines.[3] (See eq 2.)

$$W(=O)(=CHCMe_3)(PR_3)_2Cl_2 + {}^1/_2Pd(PhCN)_2Cl_2 \rightarrow W(=O)(=CHCMe_3)(PR_3)Cl_2 + {}^1/_2Pd(PR_3)_2Cl_2 + PhCN \quad (2)$$

We have undertaken a single-crystal X-ray diffraction study of the pentacoordinate complex $W(=O)(=CHCMe_3)(PEt_3)Cl_2$, prepared in this manner. A preliminary report has appeared.[3]

We have also attempted to solve the structure of the related octahedral species $W(=O)(=CHCMe_3)(PEt_3)_2Cl_2$ but have been frustrated by a severe disorder problem.[4a] Further studies on this class of complexes are being undertaken.[4b]

We now report the details of a structural study on $W(=O)(=CHCMe_3)(PEt_3)Cl_2$.

Experimental Section

(A) Collection and Processing of the X-ray Diffraction Data. Yellow, rectangular crystals of $W(=O)(=CHCMe_3)(PEt_3)Cl_2$ were provided by Professor R. R. Schrock of the Massachusetts Institute of Technology. The material is slightly air sensitive.

A well-formed crystal of approximate dimensions 0.3 × 0.2 × 0.2 mm was wedged and sealed in a thin-walled glass capillary of appropriate size in an inert-atmosphere drybox. The capillary was then flame sealed, fixed into an aluminum pin with beeswax, and mounted into an eucentric goniometer. Preliminary photographs indicated an orthorhombic unit cell. The crystal was centered on our Syntex $P2_1$ automated diffractometer. Determination of the crystal class, the

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(1) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

(2) Schrock, R. R.; Rocklage, S.; Wengrovius, J. H.; Rupprecht, G. A.; Fellman, J. D. *J. Mol. Catal.* **1980**, *8*, 73.

(3) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515.

(4) (a) This complex crystallizes in the space group *Pbcn* with $Z = 4$ and lies on a crystallographic C_2 axis. The oxo and one chloride ligand are disordered, and there is further rotational disorder of the $CHCMe_3$ and PEt_3 ligands. (b) Since the submission of this article we have succeeded in determining the molecular structure of the related trimethylphosphine complex $W(=O)(=CHCMe_3)(PMe_3)_2Cl_2$. See: Churchill, M. R.; Rheingold, A. L.; Youngs, W. J.; Schrock, R. R.; Wengrovius, J. H. *J. Organomet. Chem.* **1981**, *204*, C17–C20.

Table I. Experimental Data for the Diffraction Study on W(=O)(=CHCMe$_3$)(PEt$_3$)Cl$_2$

(A) Crystal Parameters at 24 °C[a]

crystal class: orthorhombic
space group: *Pbca*
$a = 9.111$ (2) Å
$b = 15.709$ (4) Å
$c = 24.207$ (6) Å
$V = 3465$ (1) Å^3
$Z = 8$
mol wt = 459.0
$\rho_{\text{calcd}} = 1.76$ g cm^{-3}

(B) Measurement of Intensity Data

diffractometer: syntex P2$_1$
radiation: Mo K$\bar{\alpha}$ ($\lambda = 0.710\,730$ Å); graphite monochromator
scan type: coupled θ(crystal)–2θ(counter)
scan speed: 3.0°/min in 2θ
scan width: $[2.0 + \Delta(\alpha_1 - \alpha_2)]°$
bkgd measurement: stationary-crystal, stationary-counter at beginning and end of each scan, each for one-fourth of the time taken for the scan
reflctns measd: $+h,-k,+l$
2θ range: 4.0–50.0°
std reflctns: 502; 0,10,0; 0,0,12; these were measured after each 97 reflections
reflctns collected: 3477 total, yielding 3055 symmetry-independent data
abs coeff: $\mu = 74.3$ cm^{-1}

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo Kα components of 24 reflections of the forms {640}, {611}, {397}, {1,11,3}, and {3,3,15}, all with 2θ between 25 and 30°.

orientation matrix, and accurate unit cell dimensions were carried out as described previously.[5] A survey of the portion of the data set with 2θ between 20 and 30° revealed the systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h = 2n + 1$. The orthorhombic space group *Pbca* is thereby strongly indicated. Details of data collection are given in Table I.

All crystallographic computations were carried out on our in-house Syntex XTL system (NOVA 1200 computer; Diablo disk; Versatec printer/plotter), including the XTL interactive program package[6] as modified by our research group at SUNY—Buffalo.

Data were corrected for absorption ($\mu = 74.3$ cm^{-1}) by an empirical method based upon a set of ψ scans of carefully selected reflections. The reflections used to obtain the normalized absorption curves, their 2θ values, and their maximum to minimum intensity ratios were as follows: $3\bar{3}1$, $2\theta = 15.61°$, max/min = 1.26; $4\bar{4}0$, $2\theta = 20.74°$, max/min = 1.30; $7\bar{4}2$, $2\theta = 33.54°$, max/min = 1.15.

Equivalent data were averaged, and all data were converted to unscaled $|F_o|$ values following correction for Lorentz and polarization effects. Any reflection with $I < 0$ was assigned a value of $|F_o| = 0$.

(B) Solution and Refinement of the Structure. Data were placed on an approximately absolute scale via a Wilson plot that also provided the average overall thermal parameter ($\bar{B} = 4.20$ Å^2). The location of the tungsten atom was determined from a three-dimensional (unsharpened) Patterson synthesis. Refinement of the scale factor and positional and isotropic thermal parameters for the tungsten atom led to $R_F = 23.8\%$ and $R_{wF} = 31.1\%$.

All other nonhydrogen atoms were located from two successive Fourier syntheses. Refinement of positional and isotropic thermal parameters for all nonhydrogen atoms (65 parameters in all) led to $R_F = 9.9\%$ and $R_{wF} = 8.7\%$ for those data with $|F_o| > 3.0\sigma(F_o)$.

A comparison of $|F_o|$ vs. $|F_c|$ for 34 reflections with intensity greater than 10^5 showed strong evidence for secondary extinction, and a correction was applied as shown in eq 3. The value determined for k was 5.8×10^{-6} e^{-2}.

$$F_o^{\text{cor}} = (1.0 + kI_o)F_o^{\text{uncor}} \tag{3}$$

At this stage all nonhydrogen atoms except C(1) were refined anisotropically. (Anisotropic refinement of C(1) gave an unrealistic shaped thermal ellipsoid.) Hydrogen atoms could not be located from a difference-Fourier synthesis but were included in the model in calculated idealized positions with d(C–H) = 0.95 Å[7] and with the appropriate geometry.

Table II. Discrepancy Indices for Final Model

data restriction(s)	R_F	R_{wF}	no. of data
none	14.7%	6.8%	3055
$\|F_o\| > 1.0\sigma(F_o)$	10.8%	6.4%	2256
$\|F_o\| > 3.0\sigma(F_o)$	8.2%	6.0%	1769
$\|F_o\| > 5.0\sigma(F_o)$	7.3%	5.5%	1582
$\|F_o\| > 5.0\sigma(F_o)$ *and* $(\sin\theta)/\lambda < 0.48$	4.6%	4.6%	932

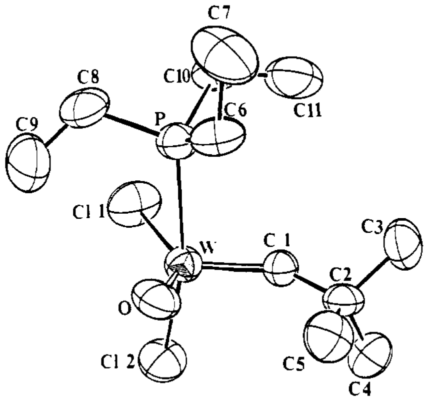

Figure 1. Labeling of nonhydrogen atoms in the W(=O)(=CH-CMe$_3$)(PEt$_3$)Cl$_2$ molecule.

Three cycles of full-matrix refinement led to final convergence. Discrepancy indices are collected in Table II. The large value for R_F for all data (14.7%) is an indication of the artificiality of this index and results from two factors. (i) The pseudospecial position of the tungsten atom ($\sim^1/_2$, $\sim^1/_2$, $\sim^1/_8$) causes it to contribute to only half of the data. (ii) There is much thermal motion in the molecule with B_{equ} (W) ~ 4 Å^2. Much of the higher angle data (2θ = 40–50°) is also very weak. The usual tests of the residual $[\sum w(|F_o| - |F_c|)^2$ vs. $|F_o|$, $(\sin\theta)/\lambda$, sequence number, and identity or parity of Miller indices] showed no unusual trends and suggested that the weighting scheme was satisfactory.

A final difference-Fourier synthesis showed peaks up to ~3.0 e Å^{-3} in height close to the tungsten atom, but there was no significant residual anywhere else. Final positional and thermal parameters are collected in Table III.

Thoughout the analysis, the analytical scattering factors for[8a] neutral W, P, Cl, O, C, and H were used; both the real and imaginary components of anomalous dispersion[8b] were applied to all nonhydrogen atoms. The function $\sum w(|F_o| - |F_c|)^2$ was minimized during the least-squares refinement; here $w = [(\sigma(F_o))^2 + (pF_o)^2]^{-1}$, and the ignorance factor (p) was 0.015.

Description of the Structure

Intramolecular distances and their estimated standard deviations (esd's) are shown in Table IV; interatomic angles and their esd's are given in Table V. Least-squares planes (and deviations of atoms therefrom) appear in Table VI.

The crystal consists of discrete molecular units of W(=O)(=CHCMe$_3$)(PEt$_3$)Cl$_2$, separated by normal van der Waals distances. There are no abnormally short intermolecular contacts. The scheme used for numbering the nonhydrogen atoms is shown in Figure 1. A stereoview of the molecule (with all hydrogen atoms included in idealized positions) appears as Figure 2. The geometry of the equatorial coordination plane is shown in Figure 3.

The molecule consists of a central tungsten(VI) atom which has a slightly distorted trigonal-bipyramidal coordination geometry. The equatorial ligands include both of the doubly bonded ligands, as expected from simple VSEPR (valence-shell

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(5) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

(6) "Syntex XTL Operations Manual", 2nd ed.; Syntex Analytical Instruments (now Nicolet XRD Division): Cupertino, CA, 1976.

(7) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(8) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4: (a) pp 99–101; (b) pp 149–150.

Table III. Final Positional and Thermal Parameters (in Å^2) for W(=O)(=CHCMe$_3$)(PEt$_3$)Cl$_2$[a,b]

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	0.47973 (6)	0.50286 (4)	0.12896 (2)	3.69 (3)	3.87 (3)	4.52 (3)	0.16 (4)	0.06 (3)	0.24 (4)
P	0.7531 (4)	0.4860 (3)	0.1398 (2)	3.6 (2)	6.0 (3)	4.5 (2)	−0.2 (2)	−0.01 (15)	−0.5 (2)
Cl(1)	0.5614 (6)	0.6249 (3)	0.0786 (2)	7.0 (3)	5.8 (3)	9.5 (4)	−0.5 (2)	0.1 (3)	2.9 (2)
Cl(2)	0.2410 (5)	0.5609 (3)	0.1160 (2)	4.6 (2)	6.1 (2)	9.8 (3)	1.6 (2)	−0.6 (2)	0.3 (3)
O	0.4629 (11)	0.4768 (6)	0.1952 (5)	4.2 (5)	5.8 (7)	7.8 (7)	1.2 (5)	1.3 (5)	−0.3 (5)
C(1)	0.456 (2)	0.4018 (9)	0.0881 (6)	B_{iso} = 3.7 (3)					
C(2)	0.409 (2)	0.3115 (11)	0.0954 (7)	2.7 (7)	6.2 (9)	4.8 (9)	−0.3 (7)	0.3 (6)	−1.4 (7)
C(3)	0.515 (2)	0.2501 (10)	0.0670 (8)	7.0 (11)	4.3 (8)	7.4 (11)	0.8 (8)	0.0 (9)	−0.9 (7)
C(4)	0.262 (2)	0.3037 (11)	0.0649 (7)	6.5 (10)	5.2 (10)	7.3 (11)	−1.1 (8)	0.5 (10)	0.4 (9)
C(5)	0.388 (2)	0.2855 (11)	0.1543 (8)	6.5 (11)	5.4 (9)	6.3 (10)	0.5 (9)	−0.0 (9)	0.7 (8)
C(6)	0.795 (2)	0.3908 (12)	0.1791 (8)	3.3 (8)	7.2 (11)	6.5 (11)	−0.3 (8)	−0.4 (8)	0.5 (9)
C(7)	0.956 (2)	0.3684 (15)	0.1847 (9)	6.4 (12)	14.4 (19)	6.7 (12)	4.1 (12)	−2.3 (10)	−2.5 (12)
C(8)	0.837 (2)	0.5753 (12)	0.1763 (9)	3.2 (8)	6.8 (11)	9.2 (14)	−0.0 (8)	−1.5 (9)	−0.7 (10)
C(9)	0.749 (2)	0.6110 (14)	0.2239 (9)	7.9 (13)	10.4 (16)	9.0 (13)	0.6 (12)	−1.6 (13)	−4.7 (12)
C(10)	0.866 (2)	0.4822 (12)	0.0772 (7)	4.5 (8)	7.8 (13)	5.7 (9)	−1.2 (9)	0.5 (7)	1.0 (9)
C(11)	0.838 (2)	0.408 (2)	0.0413 (10)	5.5 (12)	13.4 (19)	8.9 (15)	−0.8 (12)	2.0 (11)	−2.5 (14)

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
H2	0.483	0.193	0.072	H14	0.997	0.359	0.149
H3	0.610	0.256	0.082	H15	1.006	0.413	0.202
H4	0.519	0.262	0.028	H16	0.929	0.557	0.190
H5	0.226	0.247	0.068	H17	0.852	0.619	0.150
H6	0.275	0.317	0.027	H18	0.801	0.656	0.240
H7	0.193	0.342	0.080	H19	0.656	0.630	0.210
H8	0.357	0.227	0.155	H20	0.733	0.567	0.250
H9	0.314	0.320	0.170	H21	0.848	0.532	0.056
H10	0.477	0.292	0.173	H22	0.966	0.480	0.088
H11	0.756	0.398	0.215	H23	0.900	0.410	0.009
H12	0.747	0.344	0.161	H24	0.855	0.356	0.061
H13	0.965	0.317	0.205	H25	0.738	0.408	0.029

[a] The anisotropic thermal parameters enter the expression for the calculated structure factor in the form $\exp[-\frac{1}{4}(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$. [b] For the H atoms, B_{iso} = 5.0 Å^2.

Table IV. Intramolecular Distances with Esd's for W(=O)(=CHCMe$_3$)(PEt$_3$)Cl$_2$

atoms	dist, Å	atoms	dist, Å
(a) Distances from the Tungsten Atom			
W-C(1)	1.882 (14)	W-Cl(1)	2.389 (5)
W-O	1.661 (11)	W-Cl(2)	2.379 (5)
W-P	2.518 (4)		
(b) Distances within the Neopentylidene Ligand			
C(1)-C(2)	1.493 (21)	C(2)-C(4)	1.530 (24)
C(2)-C(3)	1.534 (23)	C(2)-C(5)	1.494 (24)
(c) Distances within the Phosphine Ligand			
P-C(6)	1.814 (19)	C(6)-C(7)	1.509 (26)
P-C(8)	1.826 (20)	C(8)-C(9)	1.510 (30)
P-C(10)	1.832 (18)	C(10)-C(11)	1.482 (31)

Table V. Interatomic Angles (Deg) with Esd's for W(=O)(=CHCMe$_3$)(PEt$_3$)Cl$_2$

atoms	angle	atoms	angle
(a) Angles around the Tungsten Atom			
P-W-Cl(2)	163.37 (16)		
P-W-Cl(1)	80.17 (16)	Cl(2)-W-Cl(1)	84.85 (17)
P-W-O	88.0 (4)	Cl(2)-W-O	97.9 (4)
P-W-C(1)	94.6 (4)	Cl(2)-W-C(1)	98.6 (4)
O-W-C(1)	106.7 (6)	O-W-Cl(1)	135.9 (4)
Cl(1)-W-C(1)	116.4 (4)		
(b) Angles within the Neopentylidene Ligand			
W-C(1)-C(2)	140.6 (11)	C(3)-C(2)-C(4)	106.6 (13)
C(1)-C(2)-C(3)	111.2 (13)	C(3)-C(2)-C(5)	109.7 (14)
C(1)-C(2)-C(4)	105.6 (13)	C(4)-C(2)-C(5)	109.1 (14)
C(1)-C(2)-C(5)	114.2 (14)		
(c) Angles within the Phosphine Ligand			
W-P-C(6)	110.5 (6)	P-C(6)-C(7)	116.4 (14)
W-P-C(8)	112.5 (6)	P-C(8)-C(9)	115.7 (14)
W-P-C(10)	118.4 (6)	P-C(10)-C(11)	114.3 (14)
C(6)-P-C(8)	106.9 (9)		
C(6)-P-C(10)	106.7 (8)		
C(8)-P-C(10)	100.9 (8)		

Table VI. Least-Squares Plane[a] and Atomic Deviations Therefrom

Equatorial Plane: $-0.9616X + 0.2566Y - 0.0973Z = -2.5601$

W*	0.0804 (5)	P	−2.408 (4)
C(1)*	−0.023 (14)	Cl(2)	2.436 (4)
O*	−0.033 (10)	C(2)	0.011 (15)
Cl(1)*	−0.025 (5)		

[a] Atoms used to calculate the plane are marked with an asterisk.

electron-pair repulsion) arguments. The W=O bond length is 1.661 (11) Å, the W=CHCMe$_3$ bond length is 1.882 (14) Å, and the third equatorial site is occupied by a chloride ligand (W—Cl(1) = 2.389 (5) Å). Rather surprisingly, the diequatorial O=W=C(1) bond angle is only 106.7 (6)°—i.e., it is reduced by ~13° from the ideal trigonal angle of 120°. The other two diequatorial angles are inequivalent with C(1)=W—Cl(1) = 116.4 (4)° and O=W—Cl(1) = 135.9 (4)°. The reasons for these variations are not clear. As is indicated by Table VI, the tungsten atom is displaced by about 0.1 Å from the C(1)···O(1)···Cl(1) plane in a direction toward atom Cl(2).

The triethylphosphine ligand and the second chloride ligand take up the two axial sites, with W-P = 2.518 (4) Å and W-Cl(2) = 2.379 (5) Å; the diaxial angle P-W-Cl(2) is only 163.37 (16)°.

Axial-equatorial angles from the PEt$_3$ ligand are P—W—Cl(1) = 80.17 (16)°, P—W=O = 88.0 (4)°, and P—W=C(1) = 94.6 (4)°; the analogous angles from Cl(2) show a similar direction of irregularity with Cl(2)—W—Cl(1) = 84.85 (17)°, Cl(2)—W=O = 97.9(4)°, and Cl(2)—W=C(1) = 98.6 (4)°.

The W=C(1)—C(2) system lies in the equatorial plane. The W=C(1) distance of 1.882 (14) Å is clearly compatible with its being designated a double bond—in fact this bond length is intermediate between the tungsten-neopentylidene and tungsten-neopentylidyne bond lengths found in the only

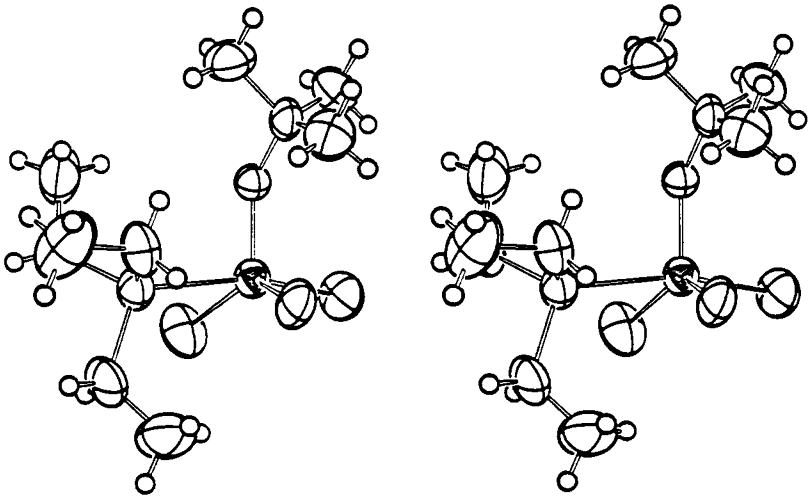

Figure 2. Stereoview of the W(=O)(=CHCMe$_3$)(PEt$_3$)Cl$_2$ molecule, with hydrogen atoms in idealized positions.

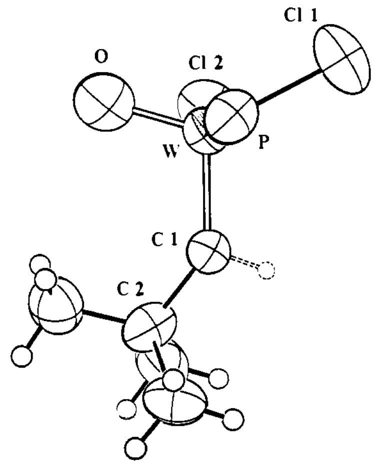

Figure 3. The equatorial coordination plane. (Only the phosphorus atom of the PEt$_3$ group is shown.)

previously examined primary alkylidene derivative of tungsten, W(≡CCMe$_3$)(=CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe)[9,10] (W≡C = 1.785 (8) Å and W=C = 1.942 (9) Å).

Another point of interest concerns the W=C(1)—C(2) bond angle of 140.6 (11)°. Although this angle (in common with all M=C(α)—C(β) angles for primary alkylidenes) is drastically increased from the idealized sp^2 angle of 120°, it is, nonetheless, the *smallest* of any observed so far in neopentylidene complexes of tantalum or tungsten[10-14] (see Table VII).

Table VII. M=C(α)–C(β) Angles (Deg) in Neopentylidene Complexes

complex	angle	ref
Ta(=CHCMe$_3$)(η^5-C$_5$Me$_5$)(η^2-C$_2$H$_4$)(PMe$_3$)	170.2 (2)	11
Ta(=CHCMe$_3$)$_2$(η^1-mesityl)(PMe$_3$)$_2$	168.9 (6), 150.0 (6)	12
[Ta(=CHCMe$_3$)(PMe$_3$)Cl$_3$]$_2$	161.2 (1)	13
Ta(=CHCMe$_3$)(η^5-C$_5$H$_5$)$_2$Cl	150.4 (5)	14
W(≡CCMe$_3$)(=CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe)	150.4 (8)	10
W(=O)(=CHCMe$_3$)(PEt$_3$)Cl$_2$	140.6 (11)	this work

There thus are some indications[3] that alkylidene ligand conformations may be more normal in electron deficient (i.e., 16- or 14-valence electron) tantalum or tungsten complexes which contain "hard" ligands than in those complexes which contain only "soft" ligands such as η^5-C$_5$Me$_5$, PR$_3$, Cl, Br, etc. Furthermore, the more "normal" M–C(α)–C(β) angles of ~140° appear to provide a positive correlation with the efficiency of the complex as an catalyst for olefin methasis.

Finally, we observe that the chemical nature of the complex studied is closely related to that of certain heterogeneous W(VI) and Mo(VI) catalysts used industrially for olefin metathesis reactions.[15]

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Registry No. W(=O)(=CHCMe$_3$)(PEt$_3$)Cl$_2$, 74658-29-0.

Supplementary Material Available: Listings of observed and calculated structure factors and data-processing formulas (18 pages). Ordering information is given on any current masthead page.

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(9) Churchill, M. R.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1979**, 321.

(10) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.

(11) Schultz, A. J.; Williams, J. M.; Brown, R. K.; Schrock, R. R. "Abstracts of Papers", Second Chemical Congress of the North American Continent, San Francisco, CA, Aug 1980; American Chemical Society: Washington, DC, 1980; INOR-133.

(12) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1930.

(13) Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, G. A.; Fellman, J. D. *J. Am. Chem. Soc.* **1979**, *101*, 1593.

(14) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957.

(15) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449 and references therein.