Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

X-ray Structural Study of an Alkylidene-Carbonyl Complex of Tungsten(IV): $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$

MELVYN ROWEN CHURCHILL* and HARVEY J. WASSERMAN

Received July 16, 1982

Bis(trimethylphosphine)dichloroneopentylidenecarbonyltungsten(IV), $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$, previously prepared by Schrock and Wengrovius, has been subjected to a single-crystal X-ray structural analysis. Crystals are monoclinic, space group $P2_1/c$, with $a = 15.460$ (3) Å, $b = 9.795$ (1) Å, $c = 12.923$ (2) Å, $\beta = 90.66$ (1)°, $V = 1956.8$ (5) Å^3, and ρ(calcd) = 1.71 g cm^{-3} for $Z = 4$ and mol wt = 503.8. Final discrepancy indices for all 3471 automated diffractometer intensity data are $R_F = 2.6\%$ and $R_{wF} = 2.3\%$ (Mo Kα; $3.5° \leq 2\theta \leq 50°$; *none* rejected). All atoms, including all hydrogen atoms, were located and refined. The molecule has a highly distorted octahedral geometry, with PMe_3 ligands in mutally trans sites [W-P(1) = 2.522 (1) Å; W-P(2) = 2.506 (1) Å] and the chloride ligands in mutually cis sites [W-Cl(1) = 2.458 (1) Å; W-Cl(2) = 2.478 (1) Å]. The neopentylidene ligand [W-C(2) = 1.859 (4) Å] is highly distorted [$W-C_\alpha-C_\beta$ = 168.7 (3)°] and is oriented cis to the carbonyl ligand [W-C(1) = 1.968 (4) Å, C(1)-O(1) = 1.154 (5) Å, W-C(1)-O(1) = 179.2 (3)°] with an interligand angle of 80.30 (16)°. The neopentylidene H_α occupies a capping position on a $P-Cl-C_\alpha$ face of the octahedron. The severe neopentylidene distortion as well as the capping orientation of H_α is discussed in terms of the "reduced" nature of the complex and a unique π-donor/π-acceptor relationship between the neopentylidene and carbonyl ligands.

Introduction

Although primary alkylidene complexes of tantalum have been well characterized by structural methods,[1] the corresponding alkylidene complexes of tungsten have not been studied as extensively. Only three tungsten-neopentylidene structures have been reported, two of which are the oxo-neopentylidene species $W(=O)(=CHCMe_3)(PEt_3)Cl_2$[2] and $W(=O)(=CHCMe_3)(PMe_3)_2Cl_2$,[3] while the third is the unusual compound $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$.[4] A structural report has also appeared on the *secondary* alkylidene complex $W(=CPh_2)(CO)_5$.[5]

In the oxo complexes the neopentylidene ligands are less distorted than any encountered in tantalum or niobium chemistry, presumably due to the presence of the "hard", strongly π-donating, oxo ligand.[6] Neopentylidene complexes containing imido ligands display similar properties;[1,7] both oxo- and imido-neopentylidene compounds are active olefin metathesis catalyst.[8,9]

In an effort to prepare neopentylidene complexes of tungsten in which no strong π-donor ligands are present, Schrock and co-workers have carried out the reaction sequence shown in Scheme I, from which two new neopentylidene complexes, **1** and **2**, were isolated.[10] Complex **2** seemed to merit a single-crystal X-ray diffraction analysis for the following reasons: (1) The spectroscopic data available for this species ($^1J_{^{13}C-^1H_\alpha}$ = 84 Hz) indicate that it is the most severely distorted alkylidene complex of tungsten yet isolated. (2) It is the first neopentylidene complex off W(IV). Studies of "reduced" *tantalum* neopentylidene compounds[11] have indicated unusually large alkylidene distortion, leading eventually to alkylidyne-hydride complexes.[12] (3) A carbon monoxide ligand is present in the coordination sphere of a relatively high oxidation state metal, and further, it does not react with the alkylidene ligand to form a ketene ligand, as is commonly the case in tantalum and niobium chemistry.[1]

Table I. Experimental Data for the X-ray Diffraction Study of $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$

A. Crystal Parameters[a] at 22 °C

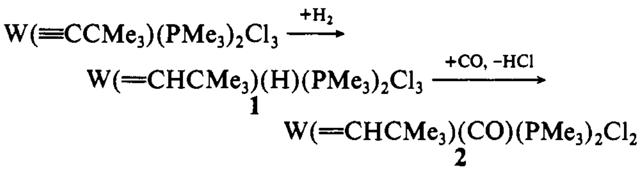
cryst syst: monoclinic
$a = 15.4604$ (26) Å
$b = 9.7948$ (14) Å
$c = 12.9230$ (22) Å
$\beta = 90.657$ (14)°
space group: $P2_1/c$
$V = 1956.8$ (5) Å^3
mol wt = 503.8
$\rho_{(calcd)} = 1.71$ g cm^{-3}
$Z = 4$

B. Data Collection

radiation: Mo Kα ($\bar{\lambda} = 0.710\,73$ Å); graphite monochromator
reflctns measd: $\pm h, +k, +l$
2θ range: 3.5-50.0°
scan type: θ(crystal)-2θ(counter)
scan speed: 2.5° min^{-1}
scan range: $[2\theta(K\alpha_1) - 1.0]-[2\theta(K\alpha_2) + 1.0]°$
abs coeff: 66.7 cm^{-1}

[a] Based on a least-squares refinement of setting angles of the unresolved Mo Kα peaks of 25 reflections with $25° < 2\theta < 30°$.

Scheme I



$$W(\equiv CCMe_3)(PMe_3)_2Cl_3 \xrightarrow{+H_2} \underset{\mathbf{1}}{W(=CHCMe_3)(H)(PMe_3)_2Cl_3} \xrightarrow{+CO,\ -HCl} \underset{\mathbf{2}}{W(=CHCMe_3)(CO)(PMe_3)_2Cl_2}$$

Experimental Section

Data Collection. Professor R. R. Schrock, of the Massachusetts Institute of Technology, kindly provided a quantity of the air/moisture-sensitive material. A well-formed crystal measuring approximately 0.25 × 0.30 × 0.35 mm was wedged into a 0.3 mm diameter capillary while inside a specially modified inert-atmosphere drybox.[13] Table I lists unit cell and data collection parameters; the technique by which these data are obtained in our laboratory has been previously published.[14] Lorentz and polarization factors,[15] as well

---

[1] Schrock, R. R. In "Reactions of Coordinated Ligands"; Braterman, P. S., Ed.; Plenum Press: New York, in press.

[2] Churchill, M. R.; Missert, J. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 3388.

[3] Churchill, M. R.; Rheingold, A. L. *Inorg. Chem.* **1982**, *21*, 1357-1359.

[4] (a) Churchill, M. R.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1979**, 321. (b) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.

[5] Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.

[6] Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148-155.

[7] Rocklage, S. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7808-7809.

[8] Schrock, R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73-83.

[9] Rappé, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 448-456 and references therein.

[10] Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 1739.

[11] Fellman, J. D.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6608-6609.

[12] Churchill, M. R.; Wasserman, H. J.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 1710-1716.

[13] Youngs, W. J. Ph.D. Thesis, State University of New York, Buffalo, 1981.

[14] Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265-271.

0020-1669/83/1322-1574$01.50/0

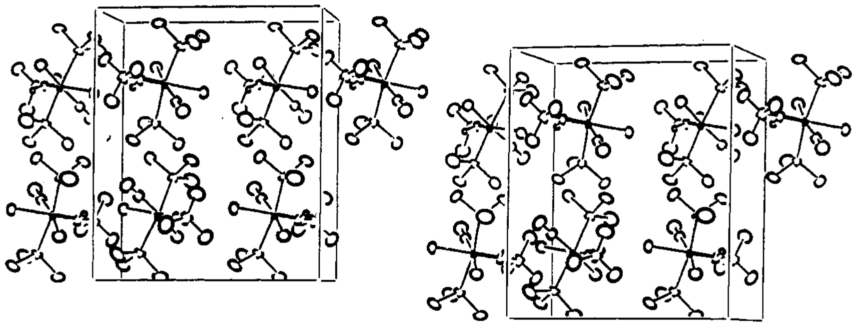


Figure 1. Stereoscopic view of unit cell packing of $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$ molecules (30% ellipsoids; ORTEP II diagram).

Table II. Final Positional Parameters (with Esd's) for $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$

atom	*x*	*y*	*z*	B_{iso}, Å
W	0.24867 (1)	0.33113 (1)	0.22986 (1)	
Cl(1)	0.27370 (7)	0.22548 (12)	0.40015 (8)	
Cl(2)	0.17041 (7)	0.12498 (10)	0.16880 (8)	
P(1)	0.38948 (7)	0.22129 (12)	0.17898 (8)	
P(2)	0.10492 (6)	0.38634 (10)	0.30715 (8)	
O(1)	0.35566 (22)	0.55789 (35)	0.34294 (25)	
C(1)	0.31610 (25)	0.47350 (40)	0.30182 (28)	
C(2)	0.23559 (23)	0.47334 (36)	0.13568 (27)	
C(3)	0.23197 (27)	0.60534 (39)	0.07657 (32)	
C(4)	0.32030 (42)	0.63356 (68)	0.02921 (61)	
C(5)	0.20754 (50)	0.72137 (56)	0.15148 (50)	
C(6)	0.16263 (38)	0.59620 (56)	−0.00844 (44)	
C(11)	0.45335 (37)	0.31756 (76)	0.08843 (49)	
C(12)	0.46584 (46)	0.1998 (12)	0.28495 (49)	
C(13)	0.38312 (50)	0.05498 (69)	0.11636 (72)	
C(21)	0.06133 (33)	0.26040 (58)	0.39640 (44)	
C(22)	0.09943 (45)	0.53967 (58)	0.38510 (55)	
C(23)	0.01938 (31)	0.40528 (70)	0.21130 (47)	
H(2)	0.2562 (23)	0.3865 (37)	0.0946 (28)	2.86 (74)
H(4A)	0.3325 (30)	0.5626 (52)	−0.0182 (36)	4.8 (12)
H(4B)	0.3209 (31)	0.7139 (52)	−0.0025 (38)	5.4 (12)
H(4C)	0.3607 (41)	0.6475 (56)	0.0881 (51)	7.4 (17)
H(5A)	0.2508 (24)	0.7258 (40)	0.1975 (32)	2.63 (85)
H(5B)	0.2014 (37)	0.8070 (58)	0.1142 (47)	7.1 (14)
H(5C)	0.1466 (47)	0.7095 (66)	0.1930 (54)	9.9 (20)
H(6A)	0.1561 (33)	0.6845 (52)	−0.0462 (40)	6.0 (12)
H(6B)	0.0994 (33)	0.5746 (52)	0.0134 (37)	6.3 (13)
H(6C)	0.1774 (31)	0.5339 (53)	−0.0595 (36)	5.3 (12)
H(11A)	0.5070 (42)	0.2790 (61)	0.0756 (44)	7.3 (15)
H(11B)	0.4188 (48)	0.3256 (64)	0.0191 (59)	10.2 (22)
H(11C)	0.4682 (43)	0.4092 (73)	0.1217 (53)	9.5 (21)
H(12A)	0.5127 (34)	0.1663 (48)	0.2637 (39)	5.2 (12)
H(12B)	0.4631 (54)	0.2863 (79)	0.3356 (65)	11.0 (24)
H(12C)	0.4447 (43)	0.1361 (70)	0.3231 (59)	7.9 (23)
H(13A)	0.4459 (47)	0.0337 (67)	0.1044 (50)	10.0 (19)
H(13B)	0.3758 (33)	0.0069 (52)	0.1891 (42)	6.3 (14)
H(13C)	0.3489 (71)	0.047 (11)	0.0562 (80)	18.4 (42)
H(21A)	−0.0024 (39)	0.2883 (58)	0.4146 (43)	6.5 (14)
H(21B)	0.1016 (51)	0.2657 (80)	0.4626 (61)	8.6 (23)
H(21C)	0.0610 (43)	0.1836 (62)	0.3578 (55)	7.5 (19)
H(22A)	0.1394 (49)	0.5257 (75)	0.4472 (59)	11.0 (24)
H(22B)	0.1137 (37)	0.6119 (65)	0.3441 (45)	7.1 (16)
H(22C)	0.0429 (35)	0.5539 (53)	0.4029 (39)	6.2 (13)
H(23A)	0.0325 (39)	0.4768 (64)	0.1662 (48)	8.7 (18)
H(23B)	−0.0325 (33)	0.4271 (50)	0.2414 (35)	5.7 (12)
H(23C)	0.0240 (43)	0.3174 (65)	0.1728 (50)	9.8 (18)

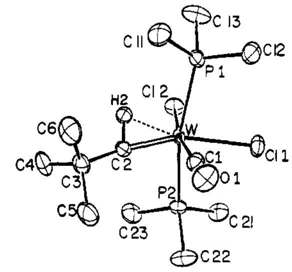


Figure 2. Labeling of non-hydrogen atoms in the $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$ molecule (ORTEP II diagram.)

Table IV. Selected Interatomic Distances (Å) with Esd's for $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$

A. Distances from the Tungsten Atom			
W-P(1)	2.522 (1)	W-C(1)	1.968 (4)
W-P(2)	2.506 (1)	W-C(2)	1.859 (4)
W-Cl(1)	2.458 (1)	W- - -H(2)	1.835 (36)
W-Cl(2)	2.478 (1)		
B. Distances within the Neopentylidene Ligand			
C(2)-H(2)	1.053 (36)	C(3)-C(5)	1.543 (7)
C(2)-C(3)	1.502 (5)	C(3)-C(6)	1.529 (7)
C(3)-C(4)	1.528 (8)		
C. Carbon-Oxygen Distance			
C(1)-O(1)	1.154 (5)		
D. Distances within the PMe_3 Ligands			
P(1)-C(11)	1.806 (7)	P(2)-C(21)	1.823 (6)
P(1)-C(12)	1.810 (7)	P(2)-C(22)	1.811 (6)
P(1)-C(13)	1.821 (7)	P(2)-C(23)	1.811 (6)

as an empirical absorption correction, were applied, and after merging, data were converted to unscaled $|F_o|$ values, subject to the condition that $|F_o| = 0$ for any reflection having $I < 0$.

Solution and Refinement. The location of the tungsten atom was determined from a Patterson synthesis. All other atoms, including all hydrogen atoms, were easily located from difference-Fourier maps; the positional parameters for all were refined. The function $\sum w(|F_o| - |F_c|)^2$ was minimized by full-matrix least-squares refinement, leading to convergence with $R_F = 2.6\%$, $R_{wF} = 2.3\%$, and GOF = 1.02 for 275 variables and all 3471 independent reflections having $4.0° \leq 2\theta \leq 50.0°$ (Mo Kα radiation; *none* rejected). The "overdetermination" ratio, NO:NV, was 12.6. The corresponding agreement indices for those 3085 data having $F_o > 3\sigma(F_o)$ were $R_F = 2.0\%$, $R_{wF} = 2.2\%$, and GOF = 1.04. A correction for the effects of secondary extinction was applied; the correction is of the form $F(\text{cor}) = F(\text{uncor})[1 + KI_0]$. The value of K was determined[16] by using 15 reflections with $I_0 > 4.5 \times 10^5$ and had a value of 6.3×10^{-8}. Final positional and isotropic thermal parameters are listed in Table II; anisotropic thermal parameters for non-hydrogen atoms are given in Table III (supplementary material).

Description of the Structure

The crystal consists of discrete molecules of $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$ that are separated by normal van der Waals distances. A stereoview illustrating the packing of molecules in the unit cell is shown in Figure 1. The scheme used for numbering the non-hydrogen atoms is shown in Figure 2; a stereoview of the molecule is presented in Figure 3. Interatomic distances and their estimated standard deviations (esd's) are listed in Table IV while interatomic angles and their esd's are given in Table V.

The molecule consists of a central W(IV) atom coordinated to a pair of mutually trans trimethylphosphine ligands, two

---

(15) "Syntex XTL Operations Manual", 2nd ed.; Syntex Analytical Instruments: Cupertino, CA, 1976.

(16) Fortran program EXTINC, written by Dr. Frederick J. Hollander.

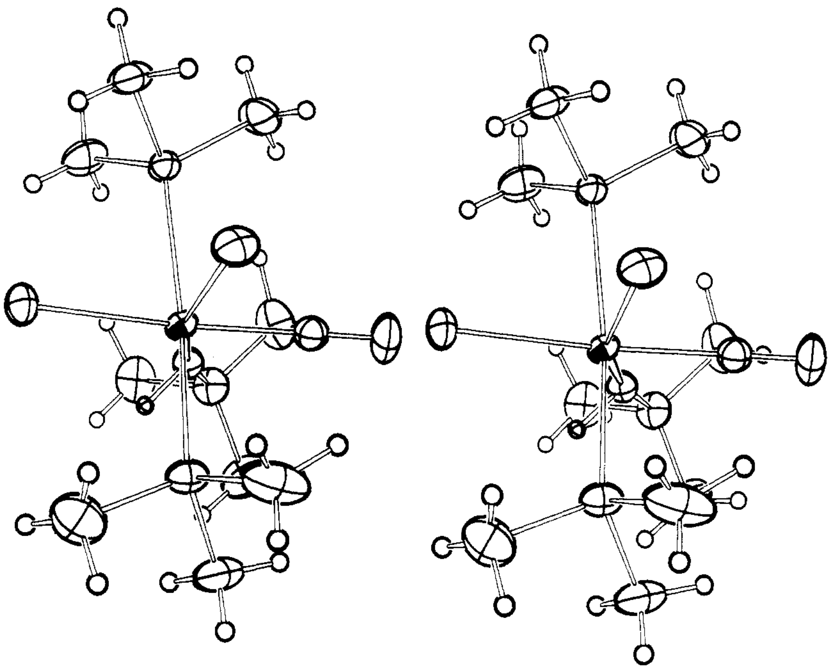


Figure 3. Stereoscopic view of the W(=CHCMe$_3$)(CO)(PMe$_3$)$_2$Cl$_2$ molecule with all hydrogen atoms included. Note the close approach of the alkylidene α-hydrogen to the tungsten atom.

Table V. Selected Interatomic Angles (deg) for W(=CHCMe$_3$)(CO)(PMe$_3$)$_2$Cl$_2$

A. "Cis" Angles about Tungsten			
Cl(1)-W-Cl(2)	90.76 (3)	Cl(2)-W-C(2)	110.67 (11)
Cl(1)-W-P(1)	85.78 (3)	P(1)-W-C(1)	88.36 (11)
Cl(1)-W-P(2)	82.25 (3)	P(1)-W-C(2)	103.69 (11)
Cl(1)-W-C(1)	78.36 (11)	P(2)-W-C(1)	97.25 (11)
Cl(2)-W-P(1)	89.38 (3)	P(2)-W-C(2)	90.52 (11)
Cl(2)-W-P(2)	82.58 (3)	C(1)-W-C(2)	80.30 (16)
B. "Trans" Angles about Tungsten			
Cl(1)-W-C(2)	156.37 (11)	P(1)-W-P(2)	165.46 (3)
Cl(2)-W-C(1)	169.02 (11)		
C. Angles Involving the Neopentylidene Ligand			
W-C(2)-H(2)	72.2 (20)	C(2)-C(3)-C(4)	109.3 (4)
W-H(2)-C(2)	74.7 (20)	C(2)-C(3)-C(5)	108.8 (4)
H(2)-W-C(2)	33.1 (11)	C(2)-C(3)-C(6)	109.7 (4)
W-C(2)-C(3)	168.7 (3)	H(2)-C(2)-C(3)	116.6 (20)
D. Tungsten-Carbonyl Angle			
W-C(1)-O(1)	179.2 (3)		

mutually cis chloride ligands, a carbonyl ligand, and a neopentylidene ligand. The geometry about tungsten is that of a highly distorted octahedron, closely approaching, in fact, a (seven-coordinate) capped octahedron. The basic reasons for the distortion are the large deformation of the alkylidene ligand, such that W-C(2)-C(3) = 168.7 (3°), coupled with a substantial interaction between tungsten and H(2), with W- - -H(2) = 1.835 (36) Å. Most significantly, H(2) is situated as a "capping" ligand on the C(2)- - -P(1)- - -Cl(2) octahedral face; see Figure 4. As such, the "capped" face is the largest of the eight possible octahedral faces and is defined by the angles Cl(2)-W-C(2) = 110.67 (11)°, P(1)-W-C(2) = 103.69 (11)°, and Cl(2)-W-P(1) = 89.38 (3)°. The octahedral face opposite the "capped" face, which comprises the same type of ligand atoms (Cl, P, C), is associated with substantially smaller interligand angles, viz., Cl(1)-W-C(1) = 78.36 (11)°, Cl(1)-W-P(2) = 82.25 (3)°, and P(2)-W-C(1) = 97.25 (11)°. Within the "distorted octahedral" description of the coordination geometry, other "cis" angles about tungsten include C(1)-W-C(2) = 80.30 (16)°, Cl(2)-W-P(2) = 82.58 (3)°, Cl(1)-W-P(1) = 85.78 (3)°, P(1)-W-C(1) = 88.36 (11)°, P(2)-W-C(2) = 90.52 (11)°, and Cl(1)-W-Cl(2) = 90.76 (3)°.

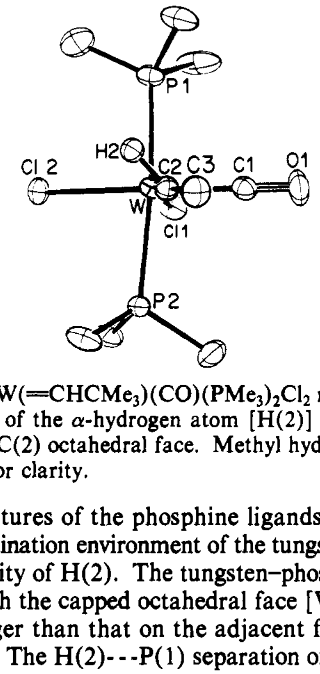


Figure 4. The W(=CHCMe$_3$)(CO)(PMe$_3$)$_2$Cl$_2$ molecule, showing the orientation of the α-hydrogen atom [H(2)] relative to the P(1)- - -Cl(2)- - -C(2) octahedral face. Methyl hydrogen atoms have been omitted for clarity.

Certain features of the phosphine ligands also reflect the crowded coordination environment of the tungsten atom caused by the proximity of H(2). The tungsten-phosphorus distance associated with the capped octahedral face [W-P(1) = 2.522 (1) Å] is longer than that on the adjacent face [W-P(2) = 2.506 (1) Å]. The H(2)- - -P(1) separation of 2.82 (4) Å, the shortest intramolecular contact involving the neopentylidene ligand, is smaller than the sum of van der Waals (vdW) radii for these atoms (3.05-3.30 Å[17]). The next shortest contact involving H(2) is the H(2)- - -Cl(2) distance of 3.04 (4) Å (vdW distance ≅ 2.90 Å).

The tungsten-neopentylidene bond length, W-C(2), is 1.859 (4) Å. This value is actually slightly smaller than any other tantalum- or tunsten-neopentylidene distance.[1] In the square-pyramidal W(VI) species W(≡CCMe$_3$)(=CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe)[4] the corresponding W=C distance is 1.942 (9) Å [the W≡C triple-bond distance in this molecule is 1.785 (8) Å], while in the oxo complexes W(=O)(=CHCMe$_3$)(PEt$_3$)Cl$_2$[2] and W(=O)(=CHCMe$_3$)(PMe$_3$)$_2$Cl$_2$,[3] the W=C distances are 1.882 (1) and 1.986 (21) Å, respectively. The W-C$_\alpha$ distances determined for the two independent molecules of the secondary alkylidene derivative

---

(17) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Table VI. M–C_α–C_β Angles and M–C_α Distances in Neopentylidene Complexes

complex	M–C_α–C_β, deg	M–C_α, Å	ref
$Ta(=CHCMe_3)(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_2H_4)(PMe_3)$	170.0 (2)	1.946 (3)	18
$W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$	168.7 (3)	1.859 (4)	this work
$Ta(=CHCMe_3)_2(\eta^1\text{-mesityl})(PMe_3)_2$	168.9 (6) 154.0 (6)	1.932 (7) 1.955 (7)	26
$[Ta(=CHCMe_3)(PMe_3)Cl_3]_2$	161.2 (1)	1.898 (2)	18
$[Ta(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$	160.3 (7) 158.5 (5)	1.937 (9) 1.932 (9)	27
$Ta(=CHCMe_3)(\eta^5\text{-}C_5H_5)_2Cl$	150.4 (5)	2.030 (6)	28
$W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$	150.4 (8)	1.942 (9)	4
$W(=O)(=CHCMe_3)(PMe_3)_2Cl_2$	142.4 (19)	1.986 (21)	3
$W(=O)(=CHCMe_3)(PEt_3)Cl_2$	140.6 (11)	1.882 (14)	2

$W(=CPh_2)(CO)_5$ are 2.13 (2) and 2.15 (2) Å.[5] Metal–alkylidene bond distances (and M–C_α–C_β angles) for these, as well as for selected neopentylidene complexes of tantalum, are listed in Table VI. It may be seen that there is little correlation between M–C_α distances and M–C_α–C_β angles. For example, the species $Ta(\eta^5\text{-}C_5Me_5)(=CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$[18] has the largest M–$C_\alpha$–$C_\beta$ angle characterized to date; yet the Ta=C linkage in this molecule is one of the longest. Metal–carbon distances appear to be more a function of coordination environment, i.e. geometry and ligand set. Such is clearly the case in the tungsten oxo–neopentylidene complexes. In these complexes the M–C_α–C_β angles are essentially the same; the difference of 0.10 Å in W–C_α bond lengths has been ascribed principally to the change in coordination number about the central tungsten(VI) atom. Thus, while the short W–C_α distance in the present structure may, in fact, be due to its being far along the reaction coordinate from alkylidene toward an alkylidyne–hydride complex (see below), other factors are also of importance.

Within the neopentylidene ligand the H_α–C_α–C_β angle is only slightly reduced from its ideal trigonal-planar value of 120°, with H(2)–C(2)–C(3) = 116.6 (20)°. In alkylidenes for which H_α has been located, this angle customarily lies between 110 and 120°.[1] Further evidence for the activation of the C_α–H_α system is the extremely acute W–C(2)–H(2) angle of 72.2 (20)°. Note that in an X-ray diffraction experiment the centroid of electron density associated with a hydrogen atom is normally displaced from its "true" nuclear position toward the atom to which it is attached.[19] In a highly distorted alkylidene ligand, the "X-ray determined" position of H_α may be displaced significantly toward the metal or M–C_α bond, since this type of interaction is actually responsible for the alkylidene distortion.[18] Therefore, the derived W–C(2)–H(2) angle could be somewhat smaller than the true internuclear angle. In $Ta(\eta^5\text{-}C_5Me_5)(=CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$, the *neutron*-determined Ta–C_α–H_α angle is 78.1 (3)°.[18] (The C(2)–H(2) distance of 1.053 (38) Å appears to be longer than the normal "X-ray determined" C–H distance of 0.95 Å;[19] however, the esd associated with this measurement is such that we are unable to claim that the lengthening is significant at the 3σ level.)

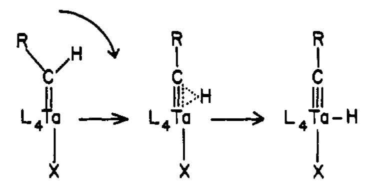
Other distances involving the neopentylidene ligand are normal. The C_α–C_β distance [C(2)–C(3) = 1.502 (5) Å] is in good agreement with the accepted C(sp^2)–C(sp^3) single-bond distance of 1.510 ± 0.005 Å.[20] Carbon–hydrogen distances within the neopentylidene ligand range 0.89 (5)–1.09 (7) Å [average 0.97 [7] Å], in good agreement with the expected X-ray determined distance of 0.95 Å.[19]

The carbonyl ligand is bonded to tungsten with W–C(1) = 1.968 (4) Å, a value that is some 0.11 Å longer than the tungsten–alkylidene distance in $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$. The carbonyl ligand is linear with C(1)–O(1) = 1.154 (5) Å and W–C(1)–O(1) = 179.2 (3)°. It is interesting to note that the tungsten–carbene bond lengths in $W(=CPh_2)(CO)_5$ are approximately 0.13 Å *longer* than the average tungsten–carbonyl bond length in this molecule. The diphenylcarbene ligand is an effective π-acceptor and competes for π-electron density with the CO ligands (albeit not as effectively as CO). The neopentylidene ligand in $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$ should be viewed as an excellent *π-donor* ligand,[21] the tungsten–carbon bond of which is *strengthened* through removal of electron density by the carbon monoxide. The tungsten–carbonyl bond is also strengthened as a result. (The average W–CO distance in $W(CO)_6$ is 2.058 ± 0.003 Å.[22])

Other features of the molecule are unexceptional. The average P–Me distance is 1.814 [7] Å, and the average W–P–Me angle is 115.4 [15]°.[23]

Discussion

The structural analysis of $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$ is the first to be performed on a primary alkylidene complex in which tungsten is present in the formal oxidation state of +IV. We have been using the term "reduced complexes" to denote those in which the metal is formally in a lower oxidation state (by two electrons) than the characteristic group valency. (N.B. Most tungsten alkylidenes formally contain tungsten(VI): cf. $W(=O)(=CHCMe_3)(PR_3)_2Cl_2$, $W(=O)(=CHCMe_3)(PR_3)Cl_2$, and $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$.) Evidence available for reduced oxidation state alkylidene complexes of tantalum indicate that these species are among the most unusual yet encountered. For example, the 16-electron tantalum(III) complex $Ta(\eta^5\text{-}C_5Me_5)(=CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$[18] displays J_{CH_α} = 74 Hz and ν_{CH_α} = 2480 cm^{-1} and $\delta(H_\alpha)$ is actually found 2.86 ppm *upfield* from Me_4Si. Neutron diffraction results for this complex have been mentioned above. Similar spectroscopic data have been obtained for $Ta(=CHCMe_3)(dmpe)_2X$ (X = Cl, I, $CF_3SO_3^-$).[12] Although no crystallographic data are yet available for any of these species, the structures are expected to be such that Ta–C_α–C_β ≈ 180° with H_α occupying a bridging position between Ta and C_α (see **4**). Thus, while alkylidene ligand deformation occurs in all known electron-deficient complexes of tantalum, it appears to be maximized in the reduced complexes (i.e., Ta(III) vis à vis Ta(V)). Such species may be regarded as "incipient alkylidyne–hydride" complexes; the driving force for the severe distortion of the alkylidene is the ultimate production of an 18-electron species **5**, as shown (schematically) below.



3 4 5

It is likely that the "reduced" nature of the present molecule $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$ accounts for the large distortion of the neopentylidene ligand [W–C_α–C_β = 168.7 (3)°]

---

[18] Schultz, A. J.; Brown, R. K.; Williams, J. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 169–176.

[19] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

[20] *Spec. Publ.-Chem. Soc.* **1965**, *No. 18*, S14s–S15s.

[21] Churchill, M. R.; Hollander, F. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 647.

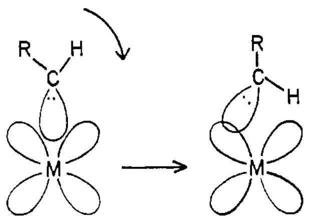
[22] Arnesen, S. P.; Seip, H. M. *Acta Chem. Scand.* **1966**, *20*, 2711 and references therein.

[23] The esd of an average distance is shown in brackets and is calculated by the expression $[\sigma] = [\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$.

and, therefore, the strong W–H_α interaction. However, a significant question is why the conversion to alkylidyne–hydride is incomplete in $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$. This problem has also been considered by Schrock et al.,[24] who provide evidence that the answer cannot be based on steric factors alone.

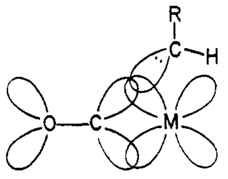
The carbonyl ligand may be important in stabilizing the highly distorted alkylidene relative to the alkylidyne–hydride. Two important structural features concerning the neopentylidene–carbonyl relationship in $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$ are (i) the C(1)–W–C(2) angle is only 80.30 (16)° and (ii) the neopentylidene ligand is oriented in such a way that H_α points *away* from the cis-carbonyl ligand.

According to Hoffmann et al.,[25] the deformation of an alkylidene ligand from a "Y-shaped" to a "T-shaped" geometry at C_α is accompanied by a pivoting of the methylene (sp^2-derived) σ orbital from its position along the M–C axis (**6** → **7**). As this pivoting increases (as $M-C_\alpha-C_\beta \rightarrow 180°$), the extent of the carbene σ–metal interaction increases, reaching a maximum at $M-C_\alpha-C_\beta = 180°$.



6 7

In an octahedral molecule the metal acceptor orbital is one of the t_{2g} set and is one of the two such orbitals involved in π-back-bonding to the carbonyl (see **8**).



8

This three-way interaction results in electron density being donated to the carbonyl π^* orbital from the alkylidene σ orbital. Upon conversion to an alkylidyne, such an interaction would no longer be possible. It is interesting to note that the opposite effect occurs in oxo– (and, to a lesser extent) imido–alkylidenes. In these, donation of electron density from C_α *competes* with donation of π-electron density from the oxo ligand, and the alkylidene ligand is *less* distorted than usual.[6]

In the present structural study, the atom H_α occupies a face-bridging rather than an edge-bridging position on the octahedron (i.e., it lies precisely between two of the possible edge-bridging positions).[29] We assume, therefore, that (with the $W=C_\alpha$ linkage defining the *z* direction) the alkylidene carbon atom is interacting with a linear combination of the metal d_{xz} and d_{yz} orbitals. It is of interest to note that the cationic species $[W(CH_2)(PMe_3)_4Cl^+]$[30] shows a temperature-dependent ^1H NMR spectrum that has been interpreted in terms of a T-shaped methylene complex in which a methylene hydrogen atom is orientated over one face of the octahedron and migrates around the four faces of the octahedron which are adjacent to the methylene carbon atom.

There have only been two previous structural studies of primary alkylidene complexes with octahedral coordination. In each of these, $[Ta(=CHCMe_3)(PMe_3)Cl_3]_2$[18] and $W(=O)(=CHCMe_3)(PMe_3)_2Cl_2$,[3] H_α is found in a plane parallel to an edge of the octahedron. (In $W(=O)(=CHCMe_3)(PMe_3)_2Cl_2$, H_α was not located directly; however, the orientation of the *t*-Bu group with respect to a cis-chloride ligand defines the position of H_α as on an edge.)

The barrier to alkylidene rotation in octahedral complexes such as $W(=CHCMe_3)(CO)(PMe_3)_2Cl_2$ is not known; it is, however, expected to be smaller than in the $Cp_2Ta(=CHR)R'$ species (R = H, R′ = Me;[31] R = Ph, R′ = CH_2Ph;[32] R = *t*-Bu, R′ = Cl[21]), in which it ranges 20–17 kcal/mol.[21]

Acknowledgment. This work was supported in part by the National Science Foundation (Grant CHE80-23448, to M.R.C.). We thank Professor R. R. Schrock for providing the sample studied.

Registry No. **2**, 80679-43-2.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes and anisotropic thermal parameters for all non-hydrogen atoms (Table III) (20 pages). Ordering information is given on any current masthead page.

---

(24) Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R., submitted for publication. We thank Professor Schrock for supplying a preprint of this work.

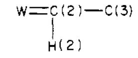
(25) Goddard, R. J.; Hoffmann, R.; Jemmis, E. D. *J. Am. Chem. Soc.* **1980**, *102*, 7667–7676.

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

(27) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 2899.

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

(29) The angle between the



$$\underset{\displaystyle H(2)}{W=C(2)}-C(3)$$

plane and equatorial W, Cl(1), Cl(2), C(1), C(2) plane is 45.3°. Equations (orthonormal coordinates) are respectively $0.8553X - 0.3509Y - 0.3813Z = 0.9219$ and $0.9699X + 0.1953Y + 0.1456Z = 4.7374$.

(30) Holmes, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 4599.

(31) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

(32) Schrock, R. R.; Guggenberger, L. J.; Messerle, L. W.; Wood, C. D. *J. Am. Chem. Soc.* **1978**, *100*, 3793–3799.