Å; for the carbonyls trans to the bridging hydride, the bond lengths are Os(1)–C(13) = 1.911 (15) Å and Os(3)–C(32) = 1.897 (13) Å. The carbonyl ligands on Os(2) may be grouped as equatorial or axial. The equatorial distances are Os(2)–C(22) = 1.930 (13) Å and Os(2)–C(24) = 1.908 (13) Å (average 1.919 [16] Å), while the axial distances are Os(2)–C(21) = 1.979 (14) Å and Os(2)–C(23) = 1.936 (13) Å (average 1.958 [30] Å). This pattern, while on the borderline of statistical significance in the present complex, is expected as a result of competition for π-electron density between the axial pair of carbonyl groups. A structural study of $Os_3(CO)_{12}$[2] showed the following average bond distances: Os–CO(equatorial) = 1.912 [7] Å and Os–CO(axial) = 1.946 [6] Å.

Finally, we note that carbon–oxygen distances range from 1.102 (19) to 1.151 (16) Å (average 1.130 [17] Å) and that Os–C–O systems are close to linear (range 174.2 (14)–179.6 (12)°).

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE77-04981, to M.R.C.).

Registry No. $(\mu\text{-H})(\mu\text{-Cl})Os_3(CO)_{10}$, 12557-93-6.

Supplementary Material Available: A table of data-processing formulas and a listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 11: Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1979**, *18*, 848.
(2) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 878.
(3) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 2397.
(4) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 3546.
(5) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1979**, *18*, 161.
(6) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.*, **1979**, *18*, 843.
(7) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J. *Inorg. Chem.* **1976**, *15*, 1843.
(8) Churchill, M. R. *Adv. Chem. Ser.* **1978**, *No. 167*, 36.
(9) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2697.
(10) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* **1977**, *16*, 1141.
(11) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* **1977**, *140*, 297.
(12) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.
(13) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol IV: (a) pp 99–101; (b) pp 149–50.
(14) Esd's on average values are given in square brackets. They are calculated via the expression $\sigma = [\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$ where d_i is the ith and $\bar{d}$ is the average of N equivalent values.
(15) Pauling, L. "Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; Table 7-2, p 224
(16) Churchill, M. R.; Ni, S. W. Y. *J. Am. Chem. Soc.* **1973**, *95*, 2150.
(17) Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1977**, *16*, 1488.

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

Crystal Structure and Molecular Geometry of $Ta(=CHCMe_3)_2(mesityl)(PMe_3)_2$, a Bis(alkylidene) Complex of Tantalum with Remarkably Obtuse Ta=C(α)—C(β) Angles of 154.0 (6) and 168.9 (6)°

MELVYN ROWEN CHURCHILL* and WILEY J. YOUNGS

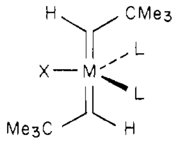
Received January 19, 1979

Mesitylbis(neopentylidene)bis(trimethylphosphine)tantalum(V), $Ta(=CHCMe_3)_2(mesityl)(PMe_3)_2$, previously prepared by Schrock and co-workers, has been subjected to a single-crystal X-ray structural analysis. The complex crystallizes in the centrosymmetric monoclinic space group $C2/c$ (C_{2h}^6; No. 15) with a = 17.966 (3) Å, b = 18.217 (4) Å, c = 18.531 (3) Å, β = 97.99 (2)°, V = 6006 (2) Å^3, and Z = 8. Diffraction data were collected with a Syntex $P2_1$ four-circle automated diffractometer by using a coupled θ(crystal)–2θ(counter) scan. The structure was solved by means of Patterson, Fourier, and least-squares refinement techniques. All nonhydrogen atoms were located and refined, the final discrepancy indices being R_F = 5.3% and R_{wF} = 3.7% for all 3946 reflections with $4.5 < 2\theta < 45°$ (Mo Kα radiation). The central tantalum atom is a distorted trigonal-bipyramidal coordination environment, with the phosphine ligands in axial sites (Ta–P(1) = 2.565 (2) Å, Ta–P(2) = 2.569 (2) Å, $\angle$ P(1)–Ta–P(2) = 166.34 (7)°). The three equatorial sites are occupied by an η^1-mesityl ligand (Ta–C(11) = 2.303 (6) Å and two η^1-neopentylidene ligands (Ta–C(1) = 1.932 (7) Å, Ta–C(6) = 1.955 (7) Å). The Ta=C(α)—C(β) angles in the two neopentylidene ligands are extraordinarily obtuse for angles at formally sp^2-hybridized carbon atoms and have values of 154.0 (6) and 168.9 (6)°, respectively.

Introduction

Alkylidene,[1] alkylidyne,[1] and benzyne[2] complexes of tantalum have been synthesized by Schrock and co-workers. We have previously reported the results of X-ray structural studies on a tantalum–alkylidene complex $[Ta(\eta^5\text{-}C_5H_5)_2(=CHCMe_3)Cl]$,[3,4] a tantalum–benzylidyne complex $[Ta(\eta^5\text{-}C_5Me_5)(\equiv CPh)(PMe_3)_2Cl]$,[5,6] and a tantalum–benzyne complex $[Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_6H_4)Me_2]$.[7]

A series of bis(alkylidene) complexes of tantalum and niobium, of formula $M(=CHCMe_3)_2(X)L_2$, have recently been reported by Schrock and co-workers.[8] These complexes, as well as certain mono(alkylidene) complexes, have some anomalous physical properties[9] which require explanation, viz., (1) the $^1J_{CH\alpha}$ values are unusually low (ca. 75–100 Hz), and (2) the C–Hα stretches are observed at very low frequencies (ca. 2400–2600 cm^{-1}). In addition to these curiosities, NMR studies did not lead to any umambiguous assignment of the geometry of these molecules; **1** was favored, however. As a result of these problems, we decided to examine one of these species. An attempt to solve the structure of $Nb(=CHCMe_3)_2(CH_2CMe_3)(PMe_3)_2$ was unsuccessful, due to severe disorder problems.[10] Prolonged attempts to find a suitable crystal of $Ta(=CHCMe_3)_2Cl(PMe_3)_2$ were also unsuccessful, due again (we believe) to disorder and also, possibly, decomposition of the material in the X-ray beam. Finally we investigated the crystal structure of the species $Ta(=CHCMe_3)_2(mesityl)(PMe_3)_2$ and found it to be suffi-



1

Table I. Experimental Data for the X-ray Diffraction Study of Ta(=CHCMe$_3$)$_2$(mesityl)(PMe$_3$)$_2$

(A) Crystal Parameters^a at 25 °C

cryst system: monoclinic	$a = 17.966$ (3) Å
space group: $C2/c$	$b = 18.217$ (4) Å
$Z = 8$	$c = 18.531$ (3) Å
mol wt 592.56	$\beta = 97.99$ (2)°
ρ(calcd) = 1.311 g cm^{-3}	$V = 6006$ (2) Å^3

(B) Measurement of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo Kα ($\bar{\lambda} = 0.710730$ Å)
monochromator: highly oriented graphite, equatorial, $2\theta_{\text{mono}} = 12.2°$
rflctns measd: $+h, +k, \pm l$
2θ range: 4.5–45.0°
scan type: coupled θ(cryst)–2θ(counter)
scan speed: 2.0°/min (in 2θ)
scan range: [2θ(Mo Kα_1) − 0.8]°–[2θ(Mo Kα_2) + 0.8]°
bkgd: stationary cryst and counter at beginning and end of the scan; each measd for one-fourth of the scan time
stds: 3 every 97 rflctns
rflctns collected: 4249 total, yielding 3946 symmetry-independent data
abs coeff: $\mu = 39.7$ cm^{-1}
abs cor: empirical (see text)

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of the 24 reflections of the forms $\{11,1,2\}$, $\{1,11,1\}$, $\{1,1,10\}$, $\{\overline{11},1,6\}$, $\{\bar{6},10,1\}$ and $\{\bar{7},3,11\}$ all with $2\theta = 20$–$30°$.

ciently ordered to provide atomic positions. Our results appear below. A preliminary account has appeared previously.[11]

Experimental Section

A. Collection and Processing of the X-ray Diffraction Data. A crystalline sample of Ta(CHCMe$_3$)$_2$(mesityl)(PMe$_3$)$_2$ was provided by Professor R. R. Schrock of the Massachusetts Institute of Technology. The complex forms clear yellow columnar crystals, which are elongated along [101]. The material may be handled in the air but decomposes to an amorphous white powder after some 5–10 h exposure to the atmosphere.

A well-formed crystal of approximate dimensions 0.15 × 0.19 × 0.35 mm was carefully wedged into a 0.2-mm diameter thin-walled glass capillary, which was then purged with argon, flame-sealed, fixed into an aluminum pin with beeswax and mounted into a eucentric goniometer. Preliminary precession and cone-axis photographs indicated that the crystal was of excellent quality and possessed C_{2h} ($2/m$) Laue symmetry. The crystal was transferred to our Syntex $P2_1$ automated diffractometer. Crystal alignment, determination of orientation matrix and accurate cell dimensions, and data collection were all carried out as described previously.[12] Details specific to the present analysis appear in Table I. A survey of the data set revealed the systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$. Possible space groups are the noncentrosymmetric monoclinic space group Cc [C_s^4, No. 9] and the centrosymmetric monoclinic space group $C2/c$ [C_{2h}^6; No. 15]. The latter was indicated as the correct space group by an analysis of intensity statistics; the correctness of this choice is confirmed by the successful solution of the structure.

All crystallographic computations were carried out with our in-house Syntex XTL system, including the XTL interactive crystallographic program package[13] as modified by our research group at S.U.N.Y. at Buffalo.

Data were corrected for absorption ($\mu = 39.7$ cm^{-1}) by an empirical method, based on a series of ψ scans.[14] The reflections used to obtain the normalized absorption curves, their 2θ values and their maximum:minimum intensity ratios, were as follows: 404 [$2\theta = 14.22$, (max)/(min) = 1.330:1], 606 [$2\theta = 20.48$, (max)/(min) = 1.270:1], and 806 [$2\theta = 24.22$, (max)/(min) = 1.285:1].

Redundant and equivalent data were averaged ($R(I) = 1.82\%$) and 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 approximate absolute scale via a Wilson plot, which also provided the overall isotropic thermal parameter, $\bar{B} = 3.57$ Å^2. Interpretation of a three-dimensional Patterson map led to the location of the tantalum atom. Full-matrix least-squares refinement of the scale factor and positional and isotropic thermal parameters for the tantalum atom led to $R_F = 20.6\%$ and $R_{wF} = 26.4\%$ after three cycles. A difference Fourier synthesis yielded the positions of the two phosphorus atoms and 19 carbon atoms. The methyl groups on the two neopentylidene ligands were not located from this map. One cycle of least-squares refinement led to $R_F = 9.5\%$ and $R_{wF} = 10.6\%$.

A second difference Fourier synthesis, phased now by 22 atoms, indicated the approximate locations of the missing methyl groups; there was also evidence of disorder. Attempted refinement of positional and thermal parameters for the carbon atoms of these methyl groups (by using an ordered model) was only partially successful. The set of carbon atoms defining the methyl groups attached to that neopentylidene ligand based on C(6) and C(7) behaved satisfactorily. The other set of methyl groups (i.e., those arranged about C(2) of the other neopentylidene ligand) behaved erratically. Careful surveys of subsequent difference Fourier maps (based on structure factor calculations from which this neopentylidene ligand had been removed) suggested a model with ordered positions for C(1) and C(2), but with two alternate rotational possibilities (separated by ca. 60°) for the methyl groups attached to C(2). This model behaved satisfactorily. A further difference Fourier synthesis revealed the positions of all hydrogen atoms associated with the mesityl group and the hydrogen atom associated with C(6) (i.e., H(6)). Attempts to refine the positional parameters for these atoms were unsuccessful. All hydrogen atoms of the PMe$_3$ ligands, the mesityl ligand, and the ordered neopentylidene ligand were now included in idealized positions (based upon d(C–H) = 0.95 Å[15] and the appropriate idealized geometry, assuming a staggered conformation where appropriate). A survey of the data set indicated that secondary extinction could safely be ignored.

Six cycles of full-matrix least-squares refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms led to final convergence [$(\Delta/\sigma)_{\max} = 0.02$] with $R_F = 5.3\%$, $R_{wF} = 3.7\%$, and GOF = 1.23 for all 3946 independent reflections (*none* rejected).

The largest peak on a final difference Fourier synthesis was of height 0.7 e Å^{-3} and was close to a methyl group of the mesityl system. The structure is thus complete. The function $\sum w(|F_o| - |F_c|)^2$ showed no significant dependence on $|F_o|$, $(\sin\theta)/\lambda$, sequence number, or identity or parity of the Miller indices; the weighting scheme is thus satisfactory.

Final positional and thermal parameters are collected in Tables II and III.

Results and Discussion

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. Important least-squares planes (and deviations of atoms therefrom) are collected in Table VI. The scheme used for numbering nonhydrogen atoms is shown in Figure 1, and a stereoview of the molecule can be seen in Figure 2.

The molecule consists of a central tantalum(V) atom surrounded by two trimethylphosphine ligands, two η^1-neopentylidene ligands, and an η^1-mesityl ligand. As shown clearly in Figure 3, the tantalum atom is in a (distorted) trigonal-bipyramidal coordination environment. The trimethylphosphine ligands occupy the two axial sites [Ta–P(1) = 2.565 (2) Å, Ta–P(2) = 2.569 (2) Å, P(1)–Ta–P(2) = 166.34 (7)°], while the two neopentylidene ligands and the mesityl ligand occupy the three equatorial sites. Angles between the axial and equatorial ligands are all close to the idealized value of 90°, viz., P(1)–Ta–C(1) = 94.20 (21)°, P(1)–Ta–C(6) = 92.78 (23)°, P(1)–Ta–C(11) = 82.95 (17)°, P(2)–Ta–C(1) = 94.22 (21)°, P(2)–Ta–C(6) = 94.62 (23)°, P(2)–Ta–C(11) = 83.43 (17)°. In contrast to this, angles *between* the equatorial ligands show significant deviations from the ideal angle of 120°, viz., C(1)–Ta–C(6) = 109.03 (31)°, C(6)–Ta–C(11) = 118.62 (28)°, C(1)–Ta–C(11) = 132.35 (26)°.

The dihedral angle between the equatorial plane (defined by Ta, C(1), C(6), C(11)) and the axial plane (defined by Ta, P(1), P(2)) is 90.58°. The phosphine ligands are displaced from truly vertical positions above the tantalum atom in such a way as to lie above and below the Ta–C(11) bond. The

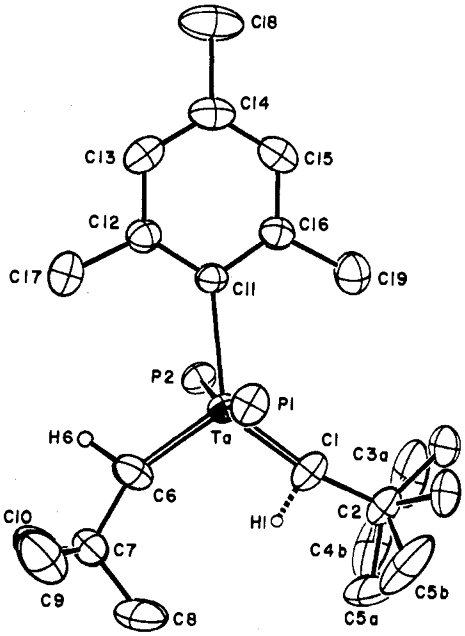
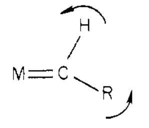


Figure 1. Labeling of nonhydrogen atoms in the $Ta(=CHCMe_3)_2(mesityl)(PMe_3)_2$ molecule. The position of H(6) is that determined from a difference Fourier synthesis; H(1) is shown in its predicted position. The methyl groups on C(2) are subject to a twofold disorder, the two conformers being designated as "a" and "b" (ORTEP-II diagram). Methyl groups on P(1) and P(2) are omitted for clarity.

mesityl ligand (as defined by atoms C(11)–C(16)) lies essentially in the equatorial plane, defining an angle of only 1.86° with the C(1)–Ta–C(6) plane; in addition to this, both C(2) and C(7) also lie essentially in the equatorial coordination plane (cf., Table VI). H(6) (which *was* located by difference Fourier methods) and H(1) (which was not located directly) each must also lie in the equatorial coordination plane so as to conserve a *planar* trigonal geometry about C(1) and C(6).

We now turn our attention to the two neopentylidene ligands. The Ta–C(α) distances are Ta–C(1) = 1.932 (7) Å and Ta–C(6) = 1.955 (7) Å; these bond lengths are shorter than any other tantalum–alkylidene linkages. [Previously determined values are 2.026 (10) Å for the $Ta{=}CH_2$ bond in $Ta(\eta^5\text{-}C_5H_5)_2(=CH_2)(CH_3)$,[16] 2.030 (6) Å for the $Ta{=}CHCMe_3$ linkage in $Ta(\eta^5\text{-}C_5H_5)_2(=CHCMe_3)Cl$,[3,4] and 2.07 (1) Å for the $Ta{=}CHPh$ linkage in $Ta(\eta^5\text{-}C_5H_5)_2(=CHPh)(CH_2Ph)$.[17]] The tantalum–neopentylidene bond lengths found in the present complex are almost midway between previous tantalum–alkylidene linkages (vide supra) and tantalum–alkylidyne bond lengths (viz., $Ta{\equiv}CPh$ = 1.849 (8) Å in $Ta(\eta^5\text{-}C_5Me_5)(\equiv CPh)(PMe_3)_2Cl$[5,6] and $Ta{\equiv}CCMe_3$ = 1.76 (2) Å in $[(Me_3CCH_2)_3Ta(\equiv CCMe_3)][Li(dmp)]$[18]). The anomalously short tantalum–neopentylidene bond lengths may be associated with the fact that the present molecule is electron poor (i.e., only 14 outer valence electrons associated with the tantalum atom), or it may result directly from the peculiar hybridization of atoms C(1) and C(6) (see below).

The most remarkable features of the present structure are, however, the extraordinarily obtuse Ta–C(α)–C(β) angles. These have the values Ta–C(1)–C(2) = 168.90 (56)° and Ta–C(6)–C(7) = 154.02 (59)° and are increased by ~49 and ~34°, respectively, from the normal angle of 120° found at an sp^2-hybridized carbon atom. We may note that large Ta–C(α)–C(β) angles appear to be general for a certain class of tantalum–alkylidene linkages. Previously determined values are 150.4 (5)° in $Ta(\eta^5\text{-}C_5H_5)_2(=CHCMe_3)Cl$[3,4] and 135.4 (5)° in $Ta(\eta^5\text{-}C_5H_5)_2(=CHPh)(CH_2Ph)$.[17] The Ta–C(α)–H(α) angles in the methylene complex $Ta(\eta^5\text{-}C_5H_5)_2(=CH_2)(CH_3)$[16] appear "normal", having a value of 126 (5)°; the esd on this angle is, however, sufficiently large to preclude any detailed analysis. In $(OC)_5W(=CPh_2)$,[19] a secondary alkylidene complex of tungsten, the W–C(α)–C(β) angles again appear to be normal, ranging from 120.7 (11) to 126.1 (11)° and averaging 124.0°. Anomalously large M–C(α)–C(β) angles appear, so far, to be specific to primary alkylidenes, i.e., species containing the system shown in **2**. The effect has only been demonstrated for complexes of tantalum



2 (R ≠ H)

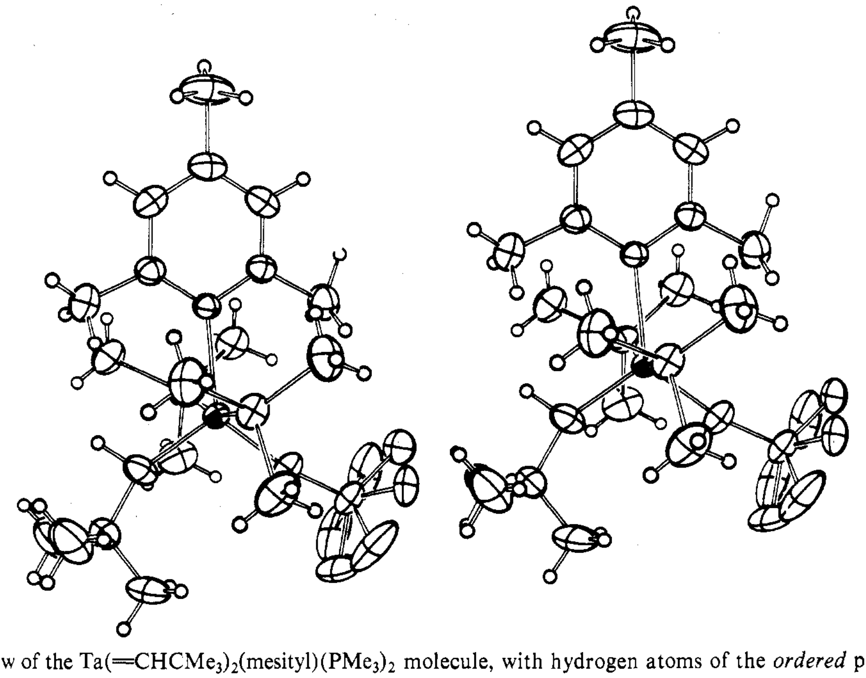


Figure 2. Stereoscopic view of the $Ta(=CHCMe_3)_2(mesityl)(PMe_3)_2$ molecule, with hydrogen atoms of the *ordered* portion included in idealized positions.

Table II. Final Positional Parameters for Ta(=CHCMe$_3$)$_2$(mesityl)(PMe$_3$)$_2$

atom[a]	*x*	*y*	*z*
Ta	0.23755 (2)	0.06977 (2)	0.17551 (1)
P(1)	0.33788 (11)	−0.00486 (11)	0.25611 (11)
P(2)	0.16316 (11)	0.15157 (11)	0.07801 (11)
C(1)	0.1673 (4)	−0.0109 (4)	0.1603 (4)
C(2)	0.1199 (5)	−0.0783 (4)	0.1359 (5)
C(3A)	0.0847 (27)	−0.0710 (16)	0.0573 (15)
C(4A)	0.1680 (13)	−0.1478 (10)	0.1443 (17)
C(5A)	0.0645 (20)	−0.0856 (17)	0.1897 (24)
C(3B)	0.1511 (24)	−0.1161 (22)	0.0731 (26)
C(4B)	0.0364 (13)	−0.0531 (13)	0.1134 (27)
C(5B)	0.1222 (24)	−0.1299 (18)	0.1983 (17)
C(6)	0.2142 (4)	0.1289 (4)	0.2575 (4)
C(7)	0.1699 (5)	0.1475 (5)	0.3187 (5)
C(8)	0.1149 (7)	0.0900 (7)	0.3316 (7)
C(9)	0.2238 (7)	0.1557 (7)	0.3875 (6)
C(10)	0.1266 (7)	0.2179 (6)	0.3041 (6)
C(11)	0.3381 (3)	0.1035 (4)	0.1181 (4)
C(12)	0.3867 (4)	0.1641 (4)	0.1351 (4)
C(13)	0.4467 (4)	0.1783 (4)	0.0961 (4)
C(14)	0.4614 (4)	0.1328 (5)	0.0395 (4)
C(15)	0.4150 (5)	0.0733 (5)	0.0232 (4)
C(16)	0.3558 (4)	0.0598 (4)	0.0610 (4)
C(17)	0.3778 (5)	0.2174 (5)	0.1956 (5)
C(18)	0.5289 (5)	0.1496 (6)	−0.0025 (5)
C(19)	0.3067 (5)	−0.0074 (5)	0.0385 (4)
C(21)	0.3013 (6)	−0.0607 (5)	0.3252 (5)
C(22)	0.4119 (5)	0.0468 (5)	0.3101 (5)
C(23)	0.3918 (5)	−0.0711 (5)	0.2114 (5)
C(24)	0.1919 (5)	0.2466 (4)	0.0795 (5)
C(25)	0.1632 (5)	0.1269 (5)	−0.0169 (4)
C(26)	0.0638 (5)	0.1585 (5)	0.0843 (5)
H(8A)	0.0888	0.1047	0.3704
H(8B)	0.1405	0.0452	0.3439
H(8C)	0.0799	0.0833	0.2887
H(9A)	0.1968	0.1674	0.4265
H(9B)	0.2584	0.1939	0.3816
H(9C)	0.2503	0.1110	0.3978
H(10A)	0.0994	0.2278	0.3434
H(10B)	0.1605	0.2569	0.2992
H(10C)	0.0924	0.2131	0.2603
H(13)	0.4782	0.2203	0.1092
H(15)	0.4241	0.0391	−0.0160
H(17A)	0.4203	0.2443	0.2177
H(17B)	0.3394	0.2503	0.1795
H(17C)	0.3619	0.1882	0.2352
H(18A)	0.5597	0.1608	0.0554
H(18B)	0.5215	0.1707	−0.0461
H(18C)	0.5417	0.0972	0.0139
H(19A)	0.3337	−0.0077	−0.0128
H(19B)	0.2548	0.0179	0.0069
H(19C)	0.3121	−0.0478	0.0799
H(21A)	0.3414	−0.0866	0.3528
H(21B)	0.2778	−0.0297	0.3566
H(21C)	0.2655	−0.0946	0.3021
H(22A)	0.4456	0.0139	0.3376
H(22B)	0.3904	0.0786	0.3422
H(22C)	0.4382	0.0750	0.2787
H(23A)	0.4268	−0.0950	0.2468
H(23B)	0.4179	−0.0464	0.1773
H(23C)	0.3586	−0.1064	0.1866
H(24A)	0.1616	0.2726	0.0418
H(24B)	0.1861	0.2676	0.1253
H(24C)	0.2431	0.2496	0.0721
H(25A)	0.1338	0.1613	−0.0471
H(25B)	0.2133	0.1273	−0.0278
H(25C)	0.1425	0.0791	−0.0254
H(26A)	0.0404	0.1895	0.0466
H(26B)	0.0571	0.1785	0.1303
H(26C)	0.0417	0.1110	0.0794

[a] *B* values for all hydrogen atoms were taken to be 7.0 Å^2.

and tungsten[20] but almost certainly occurs in niobium complexes; it will presumably be found to be general as further studies on metal alkylidene complexes are completed.

In the present complex, the neopentylidene ligand containing C(6) and C(7) is ordered, and H(6) was located from a difference Fourier map. The Ta–C(6)–C(7) angle of 154.02 (59)° is undoubtedly correctly determined. The other neopentylidene ligand contains disordered methyl groups, which leads to concern over whether the Ta–C(1)–C(2) angle of 168.90 (56)° is correct or whether it might be an erroneous result due to disorder of the entire neopentylidene system. Several pieces of evidence point strongly toward the reported angle being correct.

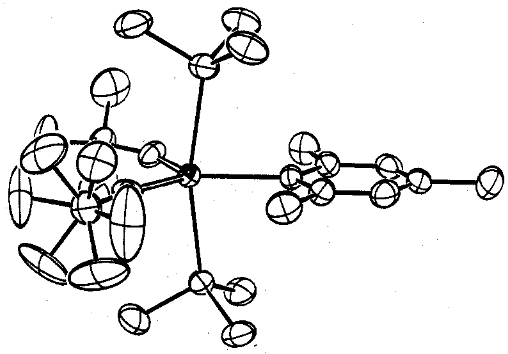


Figure 3. Trigonal-bipyramidal coordination environment about the tantalum atom.

(1) The fact that the Ta–C(1)–C(2) angle is substantially greater than the Ta–C(6)–C(7) angle may be explained as a direct result of the steric interaction of the mesityl ligand (specifically, the methyl group centered on C(19)) with the methyl groups associated with atom C(2) (i.e., C(3a), C(3b), and their associated hydrogen atoms).

(2) The thermal ellipsoid for C(1) is of essentially the same shape and size as that for C(6), and the thermal ellipsoid for C(2) is of essentially the same shape and size as that for C(7). This can be deduced from the anisotropic thermal parameters (Table III) and from the root-mean-square amplitudes of vibration of these atoms about the principal axes of their vibration ellipsoids (see Table VII). It is more readily demonstrated by Figures 1 and 2. *There is no evidence favoring disorder of atoms C(1) and C(2).*

(3) A recent neutron-diffraction study of [Ta(=CHCMe$_3$)Cl$_3$(PMe$_3$)]$_2$[21] yielded a Ta=C(α)—C(β) angle of 161.2 (1)°. Our value of 168.90 (56)°, although the largest Ta=C(α)—C(β) angle to be measured, is supported as reasonable by this independent study.

Other distances and angles in the neopentylidene ligands are as expected. The C(α)–C(β) distances are C(1)–C(2) = 1.527 (11) Å and C(6)–C(7) = 1.511 (11) Å, in agreement with the accepted C(sp^2)–C(sp^3) single bond length of 1.510 ± 0.005 Å.[22] The C–Me distances range from 1.482 (15) to 1.504 (15) Å in the ordered neopentylidene ligand and from 1.487 (33) to 1.569 (28) Å within the disordered neopentylidene ligand. The ring of disordered methyl groups in this latter system makes an angle of 90.02° with the equatorial coordination plane about the tantalum atom. The C(6)–C(7)–Me angles range from 108.37 (76) to 113.32 (79)° and Me–C(7)–Me angles range from 106.91 (85) to 108.92 (84)°. Within the disordered neopentylidene system, the C(1)–C(2)–Me angles are 105.5 (16)–110.9 (15)° and the Me–C(2)–Me angles (within a given –CMe$_3$ system) are 105.9 (18)–114.8 (21)°. All the evidence is consistent with the –CMe$_3$ group of the disordered neopentylidene ligand being subject only to a twofold rotational disorder (rather than full rotational disorder).

The mesityl ligand is bonded to tantalum with Ta–C(11) = 2.303 (6) Å. This distance is comparable to various tantalum–alkyl bond lengths that have been reported, e.g., Ta–CH$_3$ = 2.246 (12) Å in Ta(η^5-C$_5$H$_5$)$_2$Ta(=CH$_2$)(CH$_3$)[16] and Ta–CH$_2$Ph = 2.30 (1) Å in Ta(η^5-C$_5$H$_5$)$_2$Ta-

Table III. Anisotropic Thermal Parameters[a] (Å^2) for Ta(=CHCMe$_3$)$_2$(mesityl)(PMe$_3$)$_2$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ta	3.448 (13)	3.441 (13)	3.541 (14)	−0.104 (13)	0.570 (9)	0.372 (13)
P(1)	4.59 (10)	4.63 (10)	5.18 (11)	0.06 (8)	−0.45 (8)	0.49 (8)
P(2)	4.34 (10)	4.41 (10)	4.90 (10)	−0.02 (8)	0.43 (8)	1.11 (8)
C(1)	4.3 (4)	4.0 (4)	5.5 (4)	−0.63 (29)	−1.0 (3)	1.3 (3)
C(2)	5.8 (4)	4.5 (4)	6.7 (5)	−1.9 (4)	0.1 (4)	0.0 (4)
C(3A)	18.6 (32)	7.4 (16)	6.6 (14)	−3.0 (19)	−6.3 (18)	−0.6 (13)
C(4A)	9.1 (13)	3.2 (8)	8.9 (14)	0.4 (8)	1.8 (12)	−0.8 (10)
C(5A)	10.2 (20)	9.9 (21)	20.2 (36)	−2.5 (15)	10.7 (24)	0.2 (19)
C(3B)	18.0 (30)	12.2 (25)	16.6 (30)	−11.6 (22)	11.2 (26)	−11.8 (24)
C(4B)	5.2 (12)	7.0 (15)	20.0 (30)	−1.9 (10)	−6.1 (16)	−2.2 (18)
C(5B)	16.0 (28)	8.9 (19)	10.0 (20)	−7.6 (18)	−2.9 (20)	4.1 (16)
C(6)	6.5 (4)	5.6 (4)	4.2 (4)	1.6 (4)	1.8 (3)	0.7 (3)
C(7)	7.1 (5)	5.3 (4)	5.4 (5)	0.0 (4)	2.2 (4)	−0.5 (4)
C(8)	12.3 (9)	10.6 (8)	14.9 (10)	−1.1 (7)	10.7 (8)	−1.2 (7)
C(9)	13.5 (9)	12.0 (9)	7.1 (6)	0.9 (7)	2.8 (6)	−2.3 (6)
C(10)	14.7 (9)	9.2 (7)	9.6 (7)	4.8 (7)	5.2 (7)	0.5 (6)
C(11)	3.4 (3)	3.6 (3)	3.9 (3)	0.21 (26)	0.91 (26)	0.34 (27)
C(12)	3.9 (3)	4.4 (4)	4.7 (4)	0.21 (29)	0.76 (29)	0.21 (30)
C(13)	3.9 (4)	4.6 (4)	6.3 (5)	−0.2 (3)	−0.0 (3)	1.5 (3)
C(14)	3.8 (4)	6.2 (5)	5.9 (5)	1.7 (4)	1.2 (3)	2.4 (4)
C(15)	5.6 (4)	6.1 (5)	4.3 (4)	1.6 (4)	1.3 (3)	0.4 (4)
C(16)	4.3 (3)	4.6 (4)	4.1 (3)	0.2 (3)	0.82 (29)	0.3 (3)
C(17)	7.0 (5)	5.7 (5)	7.2 (5)	−1.4 (4)	0.7 (4)	−1.3 (4)
C(18)	7.3 (6)	11.7 (8)	9.0 (6)	2.8 (5)	3.9 (5)	5.9 (6)
C(19)	7.2 (5)	5.9 (5)	5.5 (5)	−0.1 (4)	0.5 (4)	−0.7 (4)
C(21)	8.7 (6)	7.1 (5)	6.9 (5)	−1.0 (5)	−1.3 (4)	3.0 (4)
C(22)	6.7 (5)	7.0 (5)	7.1 (5)	−0.1 (4)	−2.1 (4)	−0.9 (4)
C(23)	6.5 (5)	6.3 (5)	9.0 (6)	2.1 (4)	−0.7 (4)	−0.7 (5)
C(24)	7.4 (5)	4.9 (4)	7.5 (5)	0.0 (4)	0.1 (4)	1.8 (4)
C(25)	7.3 (5)	6.1 (5)	4.9 (4)	−0.0 (4)	−0.5 (4)	1.5 (4)
C(26)	4.8 (4)	8.5 (6)	10.2 (7)	1.5 (4)	0.5 (4)	2.6 (5)

[a] These enter the equation for the calculated structure factor in the form $\exp[-0.25(h^2a^{*2}B_{11} + \ldots + 2hka^*b^*B_{12} + \ldots)]$.

Table IV. Intramolecular Distances (Å), with Esd's, for Ta(=CHCMe$_3$)$_2$(mesityl)(PMe$_3$)$_2$

(A) Distances from the Tantalum Atom			
Ta–C(1)	1.932 (7)	Ta–P(1)	2.565 (2)
Ta–C(6)	1.955 (7)	Ta–P(2)	2.569 (2)
Ta–C(11)	2.303 (6)		
(B) Distances within the Ordered Neopentylidene Ligand			
C(6)–C(7)	1.511 (11)	C(7)–C(9)	1.498 (14)
C(7)–C(8)	1.482 (15)	C(7)–C(10)	1.504 (15)
(C) Distances within the Disordered Neopentylidene Ligand			
C(1)–C(2)	1.527 (11)		
C(2)–C(3A)	1.511 (32)	C(2)–C(3B)	1.523 (46)
C(2)–C(4A)	1.529 (22)	C(2)–C(4B)	1.569 (28)
C(2)–C(5A)	1.508 (41)	C(2)–C(5B)	1.487 (33)
(D) Phosphorus–Carbon Distances			
P(1)–C(21)	1.828 (9)	P(2)–C(24)	1.806 (8)
P(1)–C(22)	1.813 (9)	P(2)–C(25)	1.816 (8)
P(1)–C(23)	1.818 (9)	P(2)–C(26)	1.809 (9)
(E) Distances within the Mesityl Ligand			
C(11)–C(12)	1.415 (10)	C(12)–C(17)	1.508 (11)
C(12)–C(13)	1.404 (10)	C(14)–C(18)	1.560 (12)
C(13)–C(14)	1.391 (12)	C(16)–C(19)	1.534 (11)
C(14)–C(15)	1.373 (12)	C–Me(av)	1.534 [26]
C(15)–C(16)	1.375 (11)		
C(16)–C(11)	1.395 (10)		
C–C(av)	1.392 [16]		

Table V. Interatomic Angles (deg), with Esd's, for Ta(=CHCMe$_3$)$_2$(mesityl)(PMe$_3$)$_2$

(A) Angles around the Tantalum Atom			
C(1)–Ta–C(6)	109.03 (31)	P(2)–Ta–C(1)	94.22 (21)
C(1)–Ta–C(11)	132.35 (26)	P(1)–Ta–C(6)	92.78 (23)
C(6)–Ta–C(11)	118.62 (28)	P(2)–Ta–C(6)	94.62 (23)
P(1)–Ta–P(2)	166.34 (7)	P(1)–Ta–C(11)	82.95 (17)
P(1)–Ta–C(1)	94.20 (21)	P(2)–Ta–C(11)	83.43 (17)
(B) Angles within the Ordered Neopentylidene Ligand			
Ta–C(6)–C(7)	154.02 (59)	C(8)–C(7)–C(9)	107.45 (86)
C(6)–C(7)–C(8)	113.32 (79)	C(8)–C(7)–C(10)	106.91 (85)
C(6)–C(7)–C(9)	108.37 (76)	C(9)–C(7)–C(10)	108.92 (84)
C(6)–C(7)–C(10)	111.71 (76)		
(C) Angles within the Disordered Neopentylidene Ligand			
Ta–C(1)–C(2)	168.90 (56)		
C(1)–C(2)–C(3A)	110.9 (15)	C(1)–C(2)–C(3B)	109.9 (17)
C(1)–C(2)–C(4A)	110.6 (11)	C(1)–C(2)–C(4B)	108.5 (14)
C(1)–C(2)–C(5A)	105.5 (16)	C(1)–C(2)–C(5B)	108.9 (15)
C(3A)–C(2)–C(4A)	109.0 (18)	C(3B)–C(2)–C(4B)	111.6 (21)
C(4A)–C(2)–C(5A)	105.9 (18)	C(4B)–C(2)–C(5B)	108.3 (20)
C(5A)–C(2)–C(3A)	114.8 (21)	C(5B)–C(2)–C(3B)	109.6 (22)
C(3A)–C(2)–C(3B)	56.8 (22)	C(5B)–C(2)–C(5A)	51.6 (20)
C(3B)–C(2)–C(4A)	56.0 (19)	C(5A)–C(2)–C(4B)	60.5 (20)
C(4A)–C(2)–C(5B)	56.2 (17)	C(4B)–C(2)–C(3A)	57.4 (19)
(D) Angles within the PMe$_3$ Ligands			
Ta–P(1)–C(21)	114.26 (31)	C(21)–P(1)–C(22)	102.10 (42)
Ta–P(1)–C(22)	116.62 (30)	C(21)–P(1)–C(23)	102.49 (42)
Ta–P(1)–C(23)	117.53 (30)	C(22)–P(1)–C(23)	101.57 (42)
Ta–P(2)–C(24)	115.17 (29)	C(24)–P(2)–C(25)	102.33 (39)
Ta–P(2)–C(25)	117.88 (28)	C(24)–P(2)–C(26)	102.40 (41)
Ta–P(2)–C(26)	114.60 (31)	C(25)–P(2)–C(26)	102.34 (41)
(E) Angles within the Mesityl Ligand			
Ta–C(11)–C(12)	127.2 (5)	C(13)–C(14)–C(15)	117.6 (7)
Ta–C(11)–C(16)	118.3 (5)	C(13)–C(14)–C(18)	120.0 (7)
C(16)–C(11)–C(12)	114.5 (6)	C(15)–C(14)–C(18)	122.4 (8)
C(11)–C(12)–C(13)	121.6 (7)	C(14)–C(15)–C(16)	121.2 (7)
C(11)–C(12)–C(17)	122.8 (6)	C(15)–C(16)–C(11)	123.9 (7)
C(13)–C(12)–C(17)	115.5 (7)	C(15)–C(16)–C(19)	117.4 (7)
C(12)–C(13)–C(14)	121.1 (7)	C(11)–C(16)–C(19)	118.6 (6)

(=CHPh)(CH$_2$Ph).[17] While a metal–aryl linkage is normally expected to be shorter than an analogous metal–alkyl linkage,[23,24] the expected shortening (other than that due to a difference of 0.03 Å in the radii of sp^3 and sp^2 hybridized carbon atoms) will not occur unless the metal atom has π-electron density available for back donation to the σ-aryl system. The metal atom in the present complex is a tantalum(V) atom (d^0 configuration), with no available d$_\pi$ electrons.

Carbon–carbon distances within the aromatic ring range from 1.373 (12) to 1.415 (10) Å, averaging 1.392 [16] Å. Angles within the six-membered ring show substantial deviations from D_{6h} (down to C_{2v}) symmetry. The internal angle at C(11), C(16)–C(11)–C(12), is reduced to 114.5 (6)°, and

Table VI. Least-Squares Planes and Atomic Deviations (Å) Therefrom for Ta(=CHCMe$_3$)$_2$(mesityl)(PMe$_3$)$_2$[a,b]

(A) Equatorial Coordination Plane

$-0.5255X + 0.5668Y - 0.6346Z + 3.3284 = 0$

C(1)*	−0.014 (7)	C(2)	−0.011 (8)
C(6)*	−0.014 (8)	C(7)	−0.032 (9)
Ta*	0.0001 (3)	C(15)	−0.070 (8)
C(11)*	−0.011 (7)	C(16)	−0.041 (7)
C(12)	−0.018 (7)	C(17)	−0.007 (9)
C(13)	−0.037 (8)	C(18)	−0.094 (10)
C(14)	−0.063 (8)	C(19)	−0.040 (8)

(B) C(1)–Ta–C(6) Plane

$-0.5357X + 0.5644Y - 0.6281Z + 3.3495 = 0$

C(1)*	0.000	C(2)	0.012 (8)
C(6)*	0.000	C(7)	−0.003 (8)
Ta*	0.000	C(11)	−0.039 (7)

(C) Plane of Aromatic Ring

$-0.5122X + 0.5611Y - 0.6502Z + 3.3103 = 0$

C(11)*	0.003 (7)	C(17)	−0.020 (9)
C(12)*	−0.005 (7)	C(18)	−0.001 (10)
C(13)*	0.002 (8)	C(19)	0.003 (8)
C(14)*	0.003 (8)	C(1)	−0.043 (7)
C(15)*	−0.004 (8)	C(2)	−0.036 (8)
C(16)*	0.000 (7)	C(6)	−0.077 (8)
Ta	−0.0251 (3)	C(7)	−0.128 (9)

(D) Axial Coordination Plane

$-0.1471X - 0.8021Y - 0.5788Z + 3.4449 = 0$

Ta*	0.000	C(1)	1.521 (7)
P(1)*	0.000	C(6)	−1.642 (8)
P(2)*	0.000	C(11)	−0.171 (7)

(E) Plane of Disordered Methyl Groups

$-0.5429X - 0.7978Y - 0.2623Z - 0.0062 = 0$

C(3A)*	0.005 (36)	C(3B)*	−0.042 (42)
C(4A)*	0.011 (21)	C(4B)*	0.023 (27)
C(5A)*	−0.039 (35)	C(5B)*	0.012 (36)

Dihedral Angles (deg)

A–D	90.58	A–E	90.02
B–C	1.86		

[a] Atoms marked with an asterisk were used in calculating the planes (weight = σ^{-2}). All other atoms were given zero weight. [b] Equations are in Cartesian (Å) coordinates.

Table VII. Root-Mean-Square Amplitudes of Vibration (Å) along Principal Axes of Vibration Ellipsoids for Selected Atoms

atom	$\langle U\rangle_{\text{min}}$	$\langle U\rangle_{\text{med}}$	$\langle U\rangle_{\text{max}}$
Ta	0.196	0.210	0.221
P(1)	0.217	0.243	0.282
P(2)	0.211	0.234	0.272
C(1)	0.202	0.211	0.310
C(6)	0.212	0.238	0.318
C(2)	0.200	0.282	0.314
C(7)	0.230	0.265	0.313

the internal angle at the para carbon, C(13)–C(14)–C(15), is reduced to 117.6 (7)°; the ortho angles are each increased from 120° (C(11)–C(12)–C(13) = 121.6 (7)° and C(15)–C(16)–C(11) = 123.9 (7)°) as are the meta angles (C(12)–C(13)–C(14) = 121.1 (7)° and C(14)–C(15)–C(16) = 121.2 (7)°). Perturbations of σ-aryl ligands from D_{6h} symmetry have been discussed previously by Churchill and Veidis[25] and by Domenicano et al.[26]

Three final points should be noted.

(1) The strange stereochemistry of C(1) (and, to a lesser extent, C(6)) explains the anomalous spectroscopic results detailed in the Introduction.

(2) The flexibility of M=C(α)—C(β) systems is almost certainly relevant to a detailed topological treatment of the olefin metathesis reaction.

(3) The unusual stereochemistry about the α carbon atoms is probably related to the ease of α-hydride abstraction in these species (i.e., conversion of η^1-alkylidene to η^1-alkylidyne complex). Similar arguments probably apply to those η^1-alkyl systems that are subject to α-hydride abstraction to form η^1-alkylidene complexes. (We have noted previously[27] that the M–C(α)–C(β) angles in alkyl and fluoroalkyls are frequently far greater than the ideal tetrahedral angle of 109.47°. In [(Me$_3$CCH$_2$)$_3$Ta(≡CCMe$_3$)][Li(dmp)][18], the *alkyl* Ta–C(α)–C(β) angles are 128 (4)°; in Ta(η^5-C$_5$H$_5$)$_2$(=CHPh)(CH$_2$Ph),[17] the Ta–C(α)–C(β) (*benzyl*) angle is 123.1 (10)°; in W(≡CCMe$_3$)(=CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe),[20] the W–C(α)–C(β) (*alkyl*) angle is 125.1 (10)°.)

Acknowledgment. We thank Professor R. R. Schrock for providing the crystals and for his continued interest in this work. Financial support was provided by the National Science Foundation through Grant CHE77-04981 to M.R.C.

Registry No. Ta(CHCMe$_3$)$_2$(mesityl)(PMe$_3$)$_2$, 69552-43-8.

Supplementary Material Available: A table of data-processing formulas and a listing of observed and calculated structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774. See also previous parts of this series on "Multiple Metal-Carbon Bonds" (by Schrock and co-workers) referenced therein.

(2) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263.

(3) Churchill, M. R.; Hollander, F. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 647.

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

(5) McLain, S. J.; Wood, C. D.; Messerle, L. W.; Schrock, R. R.; Hollander, F. J.; Youngs, W. J.; Churchill, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5962.

(6) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 171.

(7) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1697.

(8) Fellman, J. D.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 5964.

(9) Schrock, R. R., personal communication to M.R.C.

(10) Churchill, M. R.; Hollander, F. J.; Youngs, W. J., unpublished work.

(11) Churchill, M. R.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.* **1978**, 1048.

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

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

(14) Churchill, M. R.; Lashewycz, R. A. *Inorg. Chem.* **1978**, *17*, 1291.

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

(16) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6578.

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

(18) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 2935.

(19) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C., *J. Am. Chem. Soc.* **1977**, *99*, 2127.

(20) A W=C(α)—C(β) angle of 149.7 (11)° is observed in the mixed "alkyl–alkylidene–alkylidyne" complex W(≡CCMe$_3$)(=CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe): Churchill, M. R.; Youngs, W. J. *J. Chem. Soc., Chem. Commun.*, in press.

(21) Schultz, A. J.; Williams, J. M.; Schrock, R. R.; Rupprecht, G. A.; Fellman, J. D. *J. Am. Chem. Soc.*, **1979**, *101*, 1593. We thank Professor R. R. Schrock for providing a preprint of this work.

(22) *Chem. Soc., Spec. Publ.* **1965**, *No. 18*, S-15s.

(23) Churchill, M. R.; Kalra, K. L.; Veidis, M. V. *Inorg. Chem.* **1973**, *12*, 1656.

(24) Churchill, M. R. *Perspect. Struct. Chem.* **1970**, *3*, 91. See Table II on p 155.

(25) Churchill, M. R.; Veidis, M. V. *J. Chem. Soc. A* **1971**, 3463. See Table 6 on p 3468.

(26) Domenicano, A.; Vaciago, A.; Coulson, C. A. *Acta Crystallogr., Sect. B* **1975**, *31*, 1630.

(27) Churchill, M. R.; Fennessey, J. P. *Inorg. Chem.* **1967**, *6*, 1213.