effects. For the latter, an empirical method similar to that of Churchill was employed.[32]

Calculations were carried out with the SHELX system of computer programs.[33] Neutral-atom scattering factors for Er and C were taken from Cromer and Waber,[34] and the scattering for erbium was corrected for the real and imaginary components of anomalous dispersion by using the table of Cromer and Liberman.[35] Scattering factors for H were from ref 36.

The position of the erbium atom was revealed by the inspection of a Patterson map. A difference Fourier map phased on the erbium atom readily revealed the positions of the nonhydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.095$. The hydrogen atoms of the cyclopentadienyl rings were placed at calculated positions 1.00 Å from the bonded carbon atoms and were not refined. The methyl hydrogen atoms could not be located. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.065$ and $R_w = 0.069$. A final difference Fourier showed no feature greater than 0.6 e/Å$^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs. $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table III.[37]

**Acknowledgment.** For support of this research we thank the Division of Basic Energy Sciences of the Department of Energy (W.J.E., A.L.W.) and the National Science Foundation (J.L.A., W.E.H.). We also thank Bell Laboratories for a fellowship (to A.L.W.) under the Bell Laboratories Graduate Research Program for Women and the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant (to W.J.E.).

**Registry No.** I, 76747-86-9; $[(C_5H_4CH_3)_2YbC{\equiv}CC(CH_3)_3]_2$, 76565-31-6; $[(C_5H_5)_2ErCH_3]_2$, 61127-35-3; $[(C_5H_4CH_3)_2YbCH_3]_2$, 76158-22-0.

**Supplementary Material Available:** Listings of structure factor amplitudes and anisotropic thermal parameters (9 pages). Ordering information is given on any current masthead page.

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[32] Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957.

[33] SHELX, a system of computer programs for X-ray structure determination by G. M. Sheldrick, 1976.

[34] Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.

[35] Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

[36] "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 72.

[37] See paragraph at the end of paper regarding supplementary material.

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Contribution from the Department of Chemistry,
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# Aluminated Metal Alkylidyne Complexes. 2.[1] Crystal and Molecular Structure of $W(CAl_2Me_4Cl)(CH_3)(PMe_3)_2(\eta^2\text{-}C_2H_4)$

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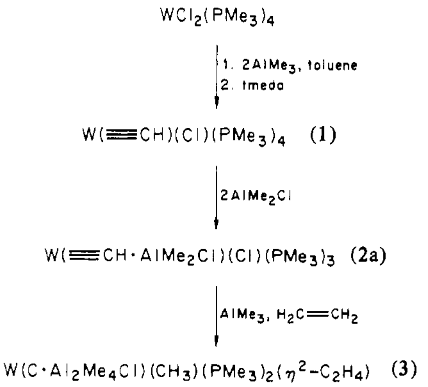
*Received March 10, 1981*

The dialumina–methylidyne complex $W(CAl_2Me_4Cl)(CH_3)(PMe_3)_2(\eta^2\text{-}C_2H_4)$ has been investigated by a single-crystal X-ray diffraction study. This complex crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ (No. 2) with $a = 10.385$ (2) Å, $b = 14.554$ (5) Å, $c = 8.717$ (2) Å, $\alpha = 78.40$ (2)°, $\beta = 68.55$ (2)°, $\gamma = 78.53$ (2)°, and $Z = 2$. Diffraction data were collected with a Syntex P2$_1$ automated diffractometer using Mo K$\alpha$ radiation, and the structure was refined to $R_F = 2.7\%$ and $R_{wF} = 2.9\%$ for all 3111 data with $3.5° < 2\theta < 45°$ ($R_F = 2.4\%$ and $R_{wF} = 2.8\%$ for those 2923 reflections with $|F_o| > 3.0\sigma(|F_o|)$). The trimethylphosphine ligands occupy axial sites about a (distorted) trigonal-bipyramidal W(IV) atom, with W–P(1) = 2.496 (2) Å and W–P(2) = 2.502 (2) Å. The equatorial sites are occupied by a methyl group (W–C(4) = 2.211 (6) Å), an $\eta^2$-ethylene ligand, which lies perpendicular to the equatorial coordination plane (W–C(1) = 2.181 (7) Å, W–C(2) = 2.187 (7) Å), and a $CAl_2Me_4Cl$ ligand (W–C(3) = 1.813 (5) Å). The W–($CAl_2Me_4Cl$) fragment is discussed, and it is concluded that the best simple description of the bonding involves a $W{\equiv}C{:}^-$ system linked by a three-center, two-electron bond to the two aluminum atoms of a $[Me_2Al(\mu\text{-}Cl)AlMe_2^+]$ moiety. The molecule is thus closely related to a mononuclear "bare" carbide (i.e., $M{\equiv}C{:}^-$).

## Introduction

We have previously reported the results of X-ray structural analyses of the simple tungsten methylidyne complex $W({\equiv}CH)(Cl)(PMe_3)_4$ (**1**) and of a mixture of the aluminated derivatives $W({\equiv}CH{\cdot}AlMe_2Cl)(Cl)(PMe_3)_3$ (**2a**) and $W({\equiv}CH{\cdot}AlMeCl_2)(Cl)(PMe_3)_3$ (**2b**).[1-3] These species were prepared by Schrock and co-workers,[2] who have extended this work to prepare a dialuminated complex of stoichiometry $W(CAl_2Me_4Cl)(CH_3)(PMe_3)_2(\eta^2\text{-}C_2H_4)$ (**3**), as indicated in Scheme I. We now report the results of a single-crystal X-ray diffraction study of the unusual dialuminated tungsten alkylidyne complex **3**.

Scheme I



## Experimental Section

**A. Data Collection.** The compound was supplied by Professor R. R. Schrock of MIT. The sample consisted of large aggregates of pale yellow crystals, individually ranging in size from about 0.2 to 0.5 mm.

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[1] The following paper should be considered as Part 1 of this series: Churchill, M. R.; Rheingold, A. L.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 3392.

[2] Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1981**, *103*, 965.

[3] The crystal studied contained ~82% of $W({\equiv}CH{\cdot}AlMe_2Cl)(Cl)(PMe_3)_3$ and ~18% of $W({\equiv}CH{\cdot}AlMeCl_2)(Cl)(PMe_3)_3$ (see ref 1 and 2).

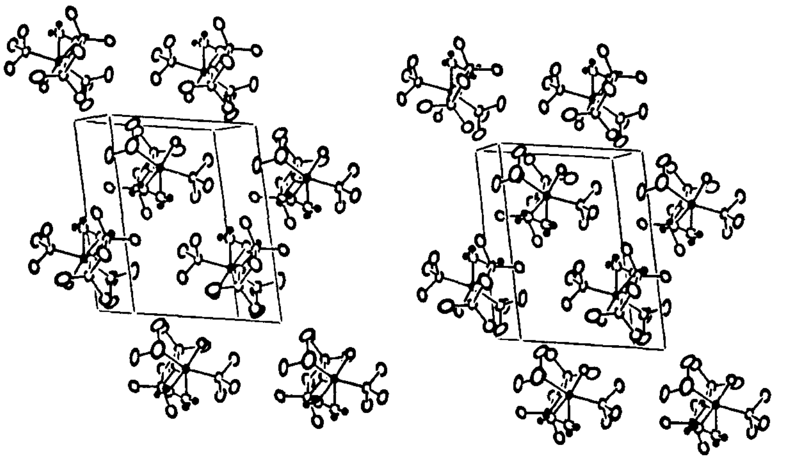

**Figure 1.** Stereoscopic view of the packing of molecules in the crystal, viewed approximately down *c*. The *a* axis is horizontal, while *b* is close to vertical (ORTEP-II diagram).

Table I. Experimental Data for the X-ray Diffraction Study

(A) Crystal Parameters at 25 (1) °C

cryst system: triclinic
space group: $P\bar{1}$
$a = 10.3852\ (17)$ Å
$\alpha = 78.401\ (22)°$
$b = 14.5543\ (49)$ Å
$\beta = 68.546\ (16)°$
$c = 8.7172\ (21)$ Å
$\gamma = 78.534\ (21)°$
$V = 1189.9\ (5)$ Å
$Z = 2$
$\rho$(calcd) = 1.51 g cm$^{-3}$
mol wt = 540.3

(B) Data Collection

diffractometer: Syntex $P2_1$
radiation: graphite-monochromatized Mo K$\bar{\alpha}$ ($\lambda = 0.710\,730$ Å)
cryst dimens: 0.27 × 0.33 × 0.33 mm
$2\theta$ limits: 3.5–45.0°
scan width: $[1.8 + \Delta(\alpha_2-\alpha_1)]°$
scan speed: 2.5° min$^{-1}$ in $2\theta$
scan type: coupled $2\theta$-$\theta$
reflctns measd: $\pm h, \pm k, +l$
reflctns collected: 3357 total yielding 3111 unique data
abs coefficient: 54.5 cm$^{-1}$

The material was found to be fairly air and moixture sensitive (decomposition led to a brown amorphous powder in approximately $^1/_2$ h); hence visual examination and mounting operations were carried out in an inert-atmosphere (Ar) drybox.

A large single crystal, cleaved from a group and further trimmed to give an approximately cube-shaped specimen, was jammed into a capillary, which was flame-sealed and transferred directly to the Syntex $P2_1$ diffractometer for which operational procedures used in this laboratory have been previously described. Details may be found in Table I.[4] Final lattice parameters are based upon a least-squares analysis of the setting angles of 15 reflections with $2\theta$ values for Mo K$\alpha$ radiation between 28 and 32.5°.

The absence of any diffraction symmetry other than the Friedel condition ($\bar{1}$) and the lack of systematically absent reflections limited the space group to either $P1$ or $P\bar{1}$. Successful refinement was achieved in the centrosymmetric space group $P\bar{1}$ ($C_i^1$; No. 2).

An absorption correction based on the $\psi$-scan method was employed. Twelve sets consisting of six Friedel-related pairs were collected at 10° intervals of $\phi$ from $\phi = 0°$ to $\phi = 350°$ (having $2\theta$ values of 14.47, 20.87, 26.36, 30.17, 34.31, and 41.45°) and were then averaged to give six unique absorption curves. The treatment of these data in the correction of X-ray intensities has been described previously.[5] Data reduction routines as well as structure solution and refinement programs were all from the SUNYAB-modified Syntex XTL structure-solving package.

**B. Solution and Refinement of Structure.** A Patterson map revealed the coordinates of the tungsten atom. All other nonhydrogen atoms were then located by using difference-Fourier syntheses phased on an increasing number of atoms. Following refinement using anisotropic thermal parameters, a difference synthesis yielded the positions of the four hydrogen atoms associated with the ethylene ligand. These hydrogen atoms were included and refined, while those of the PMe$_3$ ligands were fixed in idealized positions (assuming $d$(C–H) = 0.95 Å[6] and a perfectly staggered conformation) with $B_{\text{iso}} = 6.0$ Å$^2$. Refinement proceeded to convergence, yielding $R_F = 2.7\%$, $R_{wF} = 2.9\%$, and GOF = 1.36 for all 3111 data (none rejected). The residuals for those 2923 reflections for which $|F_o| > 3.0\sigma(|F_o|)$ were $R_F = 2.4\%$, $R_{wF} = 2.8\%$, and GOF = 1.36. The final cycle of refinement consisted of 197 variables refined against the 3111 observations; the overdetermination ratio is thus 15.8:1.0. The usual tests of the weighting scheme indicated its validity. No correction was necessary for secondary extinction. Final positional and thermal parameters are listed in Tables II and III.

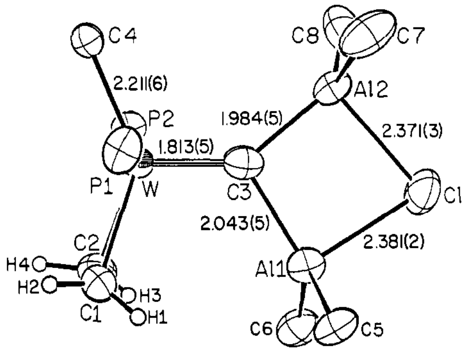

**Figure 2.** Labeling of important atoms in the W(CAl$_2$Me$_4$Cl)(CH$_3$)(PMe$_3$)$_2$($\eta^2$-C$_2$H$_4$) molecule. The molecule is projected onto its equatorial coordination plane (defined by C(3), the methyl group (C(4)), and the midpoint of the C(1)–C(2) bond). The methyl groups on P(1) and P(2) and all hydrogen atoms other than those of the $\eta^2$-ethylene ligand have been omitted for the sake of clarity (ORTEP-II diagram; 30% probability ellipsoids).

## Discussion

The crystal consists of discrete monomeric units of W(CAl$_2$Me$_4$Cl)(CH$_3$)(PMe$_3$)$_2$($\eta^2$-C$_2$H$_4$), which are separated by normal van der Waals distances (see Figure 1). There are no abnormally short intermolecular contacts.

Interatomic distances and angles (with esd's) are collected in Tables IV and V. Figure 2 shows the scheme used to label atoms within the molecule, while Figure 3 provides a stereoscopic view of the molecule.

The tungsten atom has a rather irregular five-coordinate geometry, which is (to a first approximation) on the reaction coordinate between an idealized trigonal bipyramid and a square pyramid (i.e., "pseudorotation" with the W–C(3) bond as the pivot). We will use the parlance of the trigonal-bipy-

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

(5) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

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

**Table II.** Final Positional Parameters and Isotropic Thermal Parameters (Å$^2$)

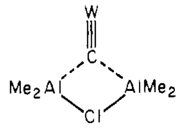
| atom | $x$ | $y$ | $z$ | $B_{iso}$ |
|---|---|---|---|---|
| W | 0.284 13 (2) | 0.258 76 (1) | 0.061 14 (2) | |
| Cl | 0.287 25 (19) | 0.281 23 (15) | −0.515 26 (19) | |
| P(1) | 0.077 37 (16) | 0.173 34 (12) | 0.213 42 (18) | |
| P(2) | 0.530 77 (15) | 0.292 64 (11) | −0.038 28 (19) | |
| Al (1) | 0.193 29 (17) | 0.360 61 (12) | −0.275 97 (20) | |
| Al(2) | 0.360 45 (19) | 0.166 79 (13) | −0.317 63 (21) | |
| C(1) | 0.123 13 (71) | 0.374 49 (48) | 0.157 3 (10) | |
| C(2) | 0.253 94 (70) | 0.407 57 (46) | 0.093 6 (10) | |
| C(3) | 0.286 53 (50) | 0.252 80 (36) | −0.145 61 (58) | |
| C(4) | 0.384 02 (60) | 0.126 79 (42) | 0.171 78 (71) | |
| C(5) | −0.005 76 (66) | 0.365 74 (50) | −0.233 28 (83) | |
| C(6) | 0.262 83 (79) | 0.482 25 (53) | −0.353 5 (10) | |
| C(7) | 0.254 9 (10) | 0.062 64 (56) | −0.276 74 (92) | |
| C(8) | 0.561 87 (77) | 0.144 53 (58) | −0.432 30 (86) | |
| C(11) | 0.012 41 (83) | 0.170 48 (68) | 0.437 24 (81) | |
| C(12) | 0.099 5 (10) | 0.050 10 (61) | 0.190 5 (11) | |
| C(13) | −0.078 48 (72) | 0.216 00 (67) | 0.164 2 (10) | |
| C(21) | 0.583 07 (69) | 0.332 26 (54) | 0.110 75 (88) | |
| C(22) | 0.579 47 (68) | 0.382 49 (55) | −0.217 63 (88) | |
| C(23) | 0.670 17 (62) | 0.196 63 (51) | −0.102 79 (87) | |
| H1 | 0.063 0 (52) | 0.394 6 (33) | 0.098 1 (55) | 3.2 (11) |
| H2 | 0.076 5 (69) | 0.360 2 (46) | 0.275 7 (82) | 7.3 (18) |
| H3 | 0.267 5 (58) | 0.448 2 (41) | 0.009 2 (66) | 4.5 (14) |
| H4 | 0.283 9 (89) | 0.413 1 (58) | 0.196 (10) | 11.2 (25) |
| H5A | −0.058 0 | 0.396 4 | −0.138 4 | 6.0 |
| H5B | −0.028 0 | 0.303 2 | −0.213 4 | 6.0 |
| H5C | −0.028 1 | 0.400 0 | −0.327 2 | 6.0 |
| H6A | 0.207 1 | 0.523 4 | −0.411 3 | 6.0 |
| H6B | 0.356 9 | 0.473 4 | −0.426 2 | 6.0 |
| H6C | 0.258 4 | 0.509 2 | −0.260 8 | 6.0 |
| H7A | 0.279 4 | 0.013 8 | −0.197 8 | 6.0 |
| H7B | 0.275 8 | 0.038 5 | −0.377 9 | 6.0 |
| H7C | 0.157 7 | 0.084 6 | −0.234 4 | 6.0 |
| H8A | 0.581 9 | 0.102 2 | −0.510 6 | 6.0 |
| H8B | 0.607 1 | 0.117 6 | −0.353 3 | 6.0 |
| H8C | 0.594 5 | 0.202 8 | −0.488 6 | 6.0 |
| H11A | −0.065 8 | 0.136 8 | 0.484 9 | 6.0 |
| H11B | −0.014 8 | 0.233 3 | 0.463 1 | 6.0 |
| H11C | 0.083 8 | 0.139 7 | 0.481 0 | 6.0 |
| H12A | 0.014 9 | 0.024 8 | 0.253 2 | 6.0 |
| H12B | 0.172 1 | 0.016 1 | 0.229 7 | 6.0 |
| H12C | 0.123 2 | 0.044 4 | 0.076 3 | 6.0 |
| H13A | −0.148 6 | 0.177 5 | 0.230 5 | 6.0 |
| H13B | −0.059 7 | 0.213 7 | 0.049 8 | 6.0 |
| H13C | −0.109 9 | 0.279 4 | 0.186 2 | 6.0 |
| H21A | 0.677 7 | 0.343 1 | 0.061 5 | 6.0 |
| H21B | 0.573 4 | 0.285 1 | 0.205 5 | 6.0 |
| H21C | 0.525 5 | 0.389 3 | 0.143 5 | 6.0 |
| H22A | 0.674 5 | 0.389 8 | −0.244 9 | 6.0 |
| H22B | 0.522 1 | 0.440 8 | −0.192 7 | 6.0 |
| H22C | 0.567 3 | 0.363 9 | −0.309 3 | 6.0 |
| H23A | 0.757 8 | 0.218 9 | −0.137 3 | 6.0 |
| H23B | 0.661 8 | 0.173 5 | −0.192 7 | 6.0 |
| H23C | 0.664 0 | 0.147 0 | −0.012 0 | 6.0 |

ramidal case during further discussions.

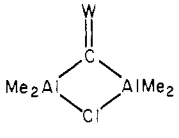
The two trimethylphosphine ligands occupy axial sites with W–P(1) = 2.496 (2) Å, W–P(2) = 2.502 (2) Å, and P(1)–W–P(2) = 159.08 (5)°. Angles between the equatorial ligands are C(3)–W–C(4) = 113.04 (23)°, C(3)–W–Et[7] = 109.03°, and C(4)–W–Et[7] = 137.92°.

The $\eta^2$-ethylene ligand lies with its C(1)–C(2) vector essentially *perpendicular* to the equatorial coordination plane (see Table VI), the W–Et[7] distance being 2.086 Å, with W–C(1) = 2.181 (7) Å and W–C(2) = 2.187 (7) Å. This contrasts with the observation that an olefin generally lies *in* the equatorial plane both for trigonal and for trigonal-bipyramidal complexes.[8a,9] The C(1)–C(2) bond length of 1.409 (11) Å is significantly longer than that of 1.337 (2) Å in free ethylene but is in the range expected for a coordinated olefin.[8b] The four ethylenic hydrogen atoms were all located and refined in the course of the structural analysis, albeit with limited precision. The resulting C–H distances are C(1)–H(1) = 0.92 (5) Å, C(1)–H(2) = 0.96 (7) Å, C(2)–H(3) = 0.83 (6) Å, and C(2)–H(4) = 1.07 (9) Å (average = 0.95 ± 0.10 Å). Despite the limitations inherent in the positioning of the hydrogen atoms, it is clear that all four hydrogen atoms are displaced from coplanarity with the C–C bond, in a direction *away from* the tungsten atom. This is in agreement with all other such studies.[8c] In particular, a neutron diffraction study of Zeise's salt, K[PtCl$_3$($\eta^2$-C$_2$H$_4$)]·H$_2$O, shows the ethylenic carbon atoms to lie 0.164 Å (average) from the plane defined by the four ethylenic hydrogen atoms.[10]

We now come to the truly unique features of the present structure, i.e., those involving the W–C(3)–[Al$_2$Me$_4$Cl] system. The two features which require detailed consideration are (1) the nature of the W–C(3) linkage and (2) the nature of the bonding between the Al$_2$Me$_4$Cl fragment and C(3). These problems are interrelated and basically depend upon whether the complex is viewed as a tungsten–methylidyne derivative with electron deficient (two-electron, three-center) bonding between the Al$_2$Me$_4$Cl moiety and C(3) (see **4**) or as a dialumina–methylidene complex with discrete Al–C(3) $\sigma$-bonds (see **5**).



**4**



**5**

We prefer to view the molecule in terms of structure **4** for the following reasons.

(1) The W–C(3) bond length of 1.813 (5) Å is close to the tungsten–carbon triple-bond lengths observed in other structural studies. Accurate measurements reported previously include 1.785 (8) Å in W(≡CCMe$_3$)(=CHCMe$_3$)(CH$_2$CMe$_3$)(dmpe),[11] 1.82 (2) Å in W[≡C($p$-tolyl)]($\eta^5$-C$_5$H$_5$)(CO)$_2$,[12] and 1.807 (6) Å in W(≡CH·AlMe$_{2-x}$Cl$_{1+x}$)(Cl)(PMe$_3$)$_3$.[1,2] In contrast to this, known tungsten–carbon double bonds have the following values: 1.942 (9) Å in square-pyramidal W(≡CCMe$_3$)(=CHCMe$_3$)(CH$_2$CMe$_3$)(dpme),[11] 1.882 (14) Å in trigonal-bipyramidal W(=O)(=CHCMe$_3$)(PEt$_3$)Cl$_2$,[13,14] and 2.006 (15) Å in octahedral W(=O)(=CHCMe$_3$)(PMe$_3$)$_2$Cl$_2$.[15] [W=C distances in the two crystallographically independent molecules of W(=CPh$_2$)(CO)$_5$ are 2.13 (2) Å and 2.15 (2) Å;[16] the chemical nature of this *secondary* alkylidene species is, however, substantially different from that of the other alkylidene species.] Note that the tungsten–methyl $\sigma$-bond length in the present molecule is W–C(4) = 2.211 (6) Å.

(2) Structure **4** is more reasonable than **5** from the viewpoint of the tungsten atom. The molecule can be recognized as a

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[7] "Et" here is the midpoint of the ethylenic C(1)–C(2) bond.

[8] Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33–61: (a) see Figure 1 p 34; (b) see Table I on pp 40–43; (c) see section III.A.3. on pp 48–51.

(9) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

(10) Love, R. A.; Koetzle, T. F.; Williams, G. J. B.; Andrews, L. C.; Bau, R. *Inorg. Chem.* **1975**, *14*, 2653.

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

(12) Huttner, G.; Frank, A.; Fischer, E. O. *Isr. J. Chem.* **1976–1977**, *15*, 133–142.

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

(14) Churchill, M. R.; Missert, J. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 3388.

(15) Churchill, M. R.; Rheingold, A. L.; Youngs, W. J.; Schrock, R. R.; Wengrovius, J. H. *J. Organomet. Chem.* **1981**, *204*, C17.

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

**Table III.** Final Anisotropic Thermal Parameters[a]

| atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| W | 2.602 (10) | 3.315 (10) | 3.596 (11) | −0.5009 (65) | −0.8368 (68) | −0.4299 (66) |
| Cl | 6.99 (10) | 9.98 (12) | 3.992 (67) | 0.882 (86) | −2.084 (65) | −0.687 (71) |
| P(1) | 3.913 (70) | 6.339 (87) | 4.202 (68) | −2.076 (63) | −1.085 (55) | 0.535 (60) |
| P(2) | 3.166 (63) | 4.663 (73) | 5.409 (73) | −1.033 (53) | −1.355 (55) | −0.273 (57) |
| Al(1) | 3.628 (76) | 4.510 (82) | 4.832 (80) | −0.525 (62) | −1.350 (63) | 0.459 (63) |
| Al(2) | 4.978 (89) | 5.362 (93) | 4.561 (81) | −0.032 (71) | −1.526 (68) | −1.325 (68) |
| C(1) | 4.47 (33) | 5.66 (35) | 6.10 (38) | 0.37 (27) | −1.57 (31) | −1.56 (28) |
| C(2) | 5.39 (36) | 3.83 (30) | 6.39 (38) | −0.28 (25) | −2.03 (30) | −0.86 (28) |
| C(3) | 3.06 (23) | 4.20 (25) | 3.67 (23) | −0.57 (19) | −0.77 (19) | −0.88 (19) |
| C(4) | 4.42 (29) | 4.94 (30) | 5.46 (30) | −0.39 (23) | −1.94 (24) | 1.11 (23) |
| C(5) | 4.50 (32) | 7.16 (40) | 6.88 (36) | 0.05 (27) | −1.98 (27) | −0.09 (29) |
| C(6) | 7.09 (43) | 6.72 (42) | 9.73 (48) | −2.51 (34) | −4.06 (38) | 3.13 (35) |
| C(7) | 11.12 (59) | 7.14 (44) | 7.29 (41) | −2.64 (41) | −2.79 (40) | −2.31 (34) |
| C(8) | 6.43 (40) | 9.12 (49) | 6.56 (38) | 2.09 (34) | −1.66 (31) | −2.81 (34) |
| C(11) | 7.15 (44) | 13.32 (66) | 4.58 (32) | −4.46 945) | −0.68 (29) | 0.29 (35) |
| C(12) | 9.11 (54) | 7.47 (48) | 11.78 (59) | −5.02 (43) | −2.56 (45) | −0.02 (41) |
| C(13) | 4.24 (34) | 12.68 (64) | 9.39 (48) | −3.82 (38) | −3.12 (33) | 3.23 (44) |
| C(21) | 4.96 (34) | 8.48 (45) | 8.13 (41) | −1.88 (31) | −2.57 (30) | −2.17 (34) |
| C(22) | 4.58 (33) | 8.28 (45) | 7.75 (40) | −2.71 (31) | −1.79 (29) | 1.39 (33) |
| C(23) | 3.23 (28) | 7.33 (40) | 8.38 (41) | −0.02 (26) | −1.02 (26) | −1.89 (32) |

[a] The anisotropic thermal parameters are in the form $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

**Table IV.** Interatomic Distances, Å, with Esd's

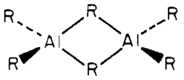
| | | | |
|---|---|---|---|
| (A) Distances from the Tungsten Atom | | | |
| W–P(1) | 2.496 (2) | W–C(2) | 2.187 (7) |
| W–P(2) | 2.502 (2) | W–C(3) | 1.813 (5) |
| W–C(1) | 2.181 (7) | W–C(4) | 2.211 (6) |
| (B) Distances from the Aluminum Atoms | | | |
| Al(1)–C(3) | 2.043 (5) | Al(2)–C(3) | 1.984 (5) |
| Al(1)–C(5) | 1.951 (8) | Al(2)–C(7) | 1.945 (9) |
| Al(1)–C(6) | 1.945 (8) | Al(2)–C(8) | 1.952 (9) |
| Al(1)–Cl | 2.381 (2) | Al(2)–Cl | 2.371 (3) |
| (C) Phosphorus–Carbon Distances | | | |
| P(1)–C(11) | 1.811 (7) | P(2)–C(21) | 1.805 (8) |
| P(1)–C(12) | 1.805 (9) | P(2)–C(22) | 1.809 (8) |
| P(1)–C(13) | 1.786 (9) | P(2)–C(23) | 1.811 (7) |
| (D) Distances within the Ethylene Ligand | | | |
| C(1)–H(1) | 0.92 (5) | C(2)–H(3) | 0.83 (6) |
| C(1)–H(2) | 0.96 (7) | C(2)–H(4) | 1.07 (9) |
| C(1)–C(2) | 1.409 (11) | | |

**Table V.** Interatomic Angles (Deg) with Esd's

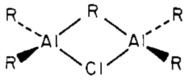
| | | | |
|---|---|---|---|
| (A) Equatorial–Equatorial Angles about Tungsten | | | |
| C(3)–W–C(4) | 113.04 (23) | C(1)–W–C(3) | 107.31 (26) |
| C(4)–W–C(1) | 135.57 (26) | C(2)–W–C(3) | 108.70 (26) |
| C(4)–W–C(2) | 133.66 (25) | Et–W–C(3) | 109.03 |
| | | Et–W–C(4) | 137.92 |
| (B) Axial–Axial Angle about Tungsten | | | |
| P(1)–W–P(2) | 159.08 (5) | | |
| (C) Axial–Equatorial Angles about Tungsten | | | |
| P(1)–W–C(1) | 78.64 (20) | P(2)–W–C(1) | 115.85 (20) |
| P(1)–W–C(2) | 115.59 (20) | P(2)–W–C(2) | 78.33 (20) |
| P(1)–W–Et | 97.42 | P(2)–W–Et | 96.80 |
| P(1)–W–C(3) | 95.74 (17) | P(2)–W–C(3) | 94.03 (17) |
| P(1)–W–C(4) | 79.60 (16) | P(2)–W–C(4) | 79.56 (16) |
| (D) Interior Angles about the Aluminum Atoms | | | |
| C(3)–Al(1)–Cl | 90.92 (17) | C(3)–Al(2)–Cl | 92.71 (17) |
| (E) Exterior Angles about the Aluminum Atoms | | | |
| C(3)–Al(1)–C(5) | 117.89 (27) | C(3)–Al(2)–C(7) | 115.01 (31) |
| C(3)–Al(1)–C(6) | 121.10 (29) | C(3)–Al(2)–C(8) | 118.73 (29) |
| Cl–Al(1)–C(5) | 99.90 (23) | Cl–Al(2)–C(7) | 105.12 (28) |
| Cl–Al(1)–C(6) | 104.14 (26) | Cl–Al(2)–C(8) | 101.58 (25) |
| C(5)–Al(1)–C(6) | 114.90 (33) | C(7)–Al(2)–C(8) | 117.67 (36) |
| (F) Angles about the Methylidyne Carbon Atom | | | |
| W–C(3)–Al(1) | 122.53 (27) | Al(1)–C(3)–Al(2) | 97.06 (23) |
| W–C(3)–Al(2) | 140.40 (30) | | |
| (G) Angles Involving the Ethylene Ligand | | | |
| W–C(1)–C(2) | 71.4 (4) | W–C(2)–C(1) | 71.0 (4) |
| W–C(1)–H(1) | 113.4 (32) | W–C(2)–H(3) | 118.4 (41) |
| W–C(1)–H(2) | 111.4 (42) | W–C(2)–H(4) | 109.6 (47) |
| H(1)–C(1)–C(2) | 118.3 (32) | H(3)–C(2)–C(1) | 116.7 (41) |
| H(2)–C(1)–C(2) | 120.9 (42) | H(4)–C(2)–C(1) | 108.4 (47) |
| H(1)–C(1)–H(2) | 114 (5) | H(3)–C(2)–H(4) | 122 (6) |
| (H) Aluminum–Chlorine–Aluminum Angle | | | |
| Al(1)–Cl–Al(2) | 78.85 (9) | | |

tungsten(IV) complex in which a deprotonated methylidyne ligand interacts with an ($Al_2Me_4Cl^+$) moiety. This indicates that the complex under consideration is closely related to a mononuclear carbide complex, viz., ($W{\equiv}C^-$)($Al_2Me_4Cl^+$).

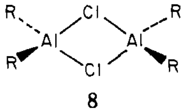
(3) Structure **4** is very reasonable from the viewpoint of aluminum chemistry.[17] It represents an example of the intermediate form **7** in the sequence **6**, **7**, and **8** (R = some organic radical). To the best of our knowledge, it is one of the very few dialuminum complexes to be examined in which there is one "electron-precise" and one "electron-deficient" bridging system.[18] It is interesting to note that the species $Ph_2Al(\mu\text{-}C{\equiv}CPh)_2AlPh_2$ has been shown to have an unsymmetrical structure[19] (see **9**); the centrosymmetric species



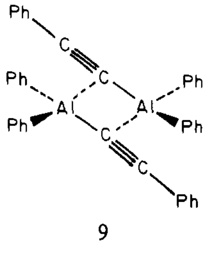
**6**



**7**



**8**



**9**

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[17] Oliver, J. P. *Adv. Organomet. Chem.* **1977**, *15*, pp 235–271.

[18] The species $Me_2Al(\mu\text{-}CH_3)(\mu\text{-}NPh_2)AlMe_2$ has been examined crystallographically. See: (a) Magnuson, V. R.; Stucky, G. D. *J. Am. Chem. Soc.* **1968**, *90*, 3269. (b) Magnuson, V. R.; Stucky, G. D. *Ibid.* **1969**, *91*, 2544.

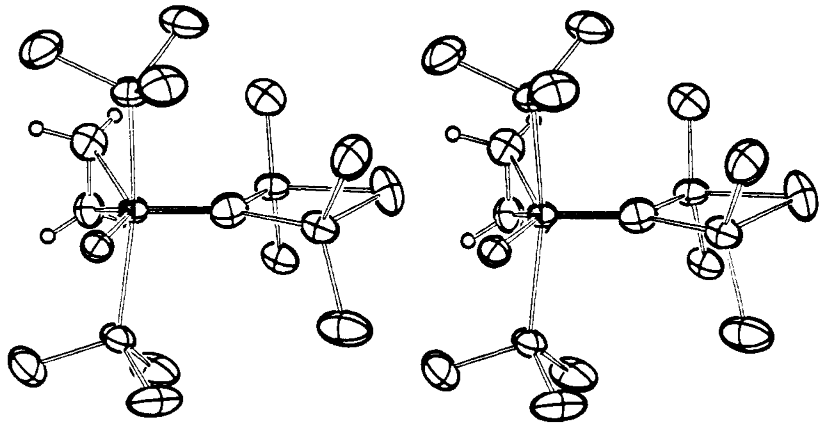


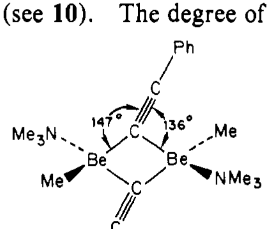
**Figure 3.** Stereoscopic view of the $W(CAl_2Me_4Cl)(CH_3)(PMe_3)_2(\eta^2\text{-}C_2H_4)$ molecule. All hydrogen atoms except the ethylenic hydrogen atoms are omitted for clarity. The view in this figure is related to that in Figure 2 by a rotation of approximately 95° about the W–C(3) axis (ORTEP-II diagram; 30% ellipsoids).

**Table VI.** Important Least-Squares Planes[a] and Deviations Therefrom

| atom | dev | atom | dev |
|---|---|---|---|
| I. Equatorial Coordination Plane<br>$0.7888X + 0.4557Y - 0.4124Z = 4.2578$ | | | |
| W*[b] | −0.0070 (2) | C(4)* | −0.012 (6) |
| C(1)* | −0.705 (8) | P(1) | −2.463 (2) |
| C(2)* | 0.702 (8) | P(2) | 2.453 (2) |
| C(3)* | 0.022 (5) | | |
| II. Axial Coordination Plane<br>$0.0483X + 0.6232Y + 0.7806Z = 3.3109$ | | | |
| W* | 0.0000 | C(2) | 1.540 (8) |
| P(1)* | 0.0000 | C(3) | −1.601 (5) |
| P(2)* | 0.0000 | C(4) | −0.189 (6) |
| C(1) | 1.485 (8) | | |
| III. C(3)-Al(1)-Cl-Al(2) Plane<br>$0.7861X + 0.5299Y - 0.3181Z = 4.4059$ | | | |
| C(3)* | 0.055 (5) | C(5) | −1.790 (7) |
| Al(1)* | −0.047 (2) | C(6) | 1.473 (8) |
| Al(2)* | −0.048 (2) | C(7) | −1.785 (9) |
| Cl* | 0.040 (2) | C(8) | 1.537 (8) |
| W | 0.2138 (2) | | |

[a] Equations defining planes are in orthonormal (Å) coordinates. [b] Only those atoms marked with an asterisk (*) were used in calculating the plane.

$(Me_3N)MeBe(\mu\text{-}C{\equiv}CPh)_2BeMe(NMe_3)$ has slightly asymmetric bridges[20] (see **10**). The degree of asymmetry in **10**



10

is slight and rather similar to that observed in our present complex (viz., W–C(3)–Al(1) = 122.53 (27)° and W–C(3)–Al(2) = 140.40 (30)°).

(4) Within the $W{\equiv}C{\cdot}Al_2Me_4Cl$ system, the angle Al(1)–C(3)–Al(2) is obtuse (97.06 (23)°), while the angle Al(1)–Cl–Al(2) is acute (78.85 (9)°). As shown in Figure 2, the C(3)–Al distances are slightly asymmetric, with the C(3)–Al(2) distance of 1.984 (5) Å being 0.059 (7) Å shorter than the C(3)–Al(1) distance of 2.043 (5) Å. Each of these aluminum–(bridging methylidyne) distances is longer than the terminal aluminum–methyl distances (i.e., Al(1)–C(5) = 1.951 (8) Å, Al(1)–C(6) = 1.945 (8) Å, Al(2)–C(7) = 1.945 (9) Å, Al(2)–C(8) = 1.952 (9) Å; Al–Me (average) = 1.948 [3] Å[21]). This would be expected if the Al(1)–C(3)–Al(2) system is electron deficient, i.e., consistent with structure **4**.[22]

Other geometric features of the molecule are normal.

## Conclusions

The reaction of Lewis acids such as trialkylaluminum with metal methylidynes has been shown (Both in this paper and in ref 1) to give rise to most unusual species, which result principally from the need of both the metal atom and the aluminum atom to be surrounded by a greater number of valence electrons than are readily available. The chemistry of these species has only just begun to emerge,[2] and we prefer to await further developments before making any general comments. Suffice it to say that trialkylaluminum molecules and alkylaluminum halides are used as cocatalysts in a variety of transition-metal-catalyzed reactions[23] (e.g., $WCl_6/R_nAlCl_{3-n}$ or $MoCl_5/R_3Al$ for olefin metathesis). The nature of certain reaction initiators may well be far more unusual than originally believed.[24] Thus, we have observed $W{\equiv}CH{\cdot}AlR_3$[1,2] and $W{\equiv}C{\cdot}Al_2R_4Cl$ (this work) systems. Presumably, even bare mononuclear carbides ($W{\equiv}C{:}^-$) might be attainable during these reactions.

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**Registry No.** 3, 79255-12-2.

**Supplementary Material Available:** A listing of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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(19) Stucky, G. D.; McPherson, A. M.; Rhine, W. E.; Eisch, J. J.; Considine, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1941.

(20) Morosin, B.; Howatson, J. *J. Organomet. Chem.* **1971**, *29*, 7.

(21) Esd's of average distances, shown in square brackets, are calculated via the "scatter" formula $[\sigma] = [\sum(d_i - \bar{d})^2/(N-1)]^{1/2}$.

(22) A similar $Me_2Al(\mu\text{-}Cl)AlMe$ system participates in an electron-deficient bridge across a cyclopentadienyl carbon atom in $(\eta^5\text{-}C_5H_5)Fe[\eta^5\text{-}C_5H_4Al_2(CH_3)_4Cl]$: Rogers, R. D.; Cook, W. J.; Atwood, J. L. *Inorg. Chem.* **1979**, *18*, 279–282.

(23) Calderon, N.; Lawrence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449–492. (See, especially, section II.B on pp 453–455.)

(24) Muetterties, E. L. *Inorg. Chem.* **1975**, *14*, 951 (and references contained therein).