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Structural Studies on Tungsten-Methylidyne Complexes. Molecular Geometry of $W(\equiv CH)(Cl)(PMe_3)_4$ and $W(\equiv CH{\cdot}AlMe_{2-x}Cl_{1+x})(Cl)(PMe_3)_3$ ($x \simeq 0.18$), a Lewis Acid Adduct of the Tungsten-Methylidyne Triple Bond

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Two tungsten-methylidyne complexes have been investigated by single-crystal X-ray diffraction studies. $W(\equiv CH)(Cl)(PMe_3)_4$ crystallizes in space group $P2/c$ (No. 13) with $a = 16.4641$ (17) Å, $b = 9.6626$ (13) Å, $c = 15.8992$ (31) Å, $\beta = 116.979$ (13)°, and $Z = 4$. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer, and the structure was refined to $R_F = 3.3\%$ and $R_{wF} = 3.5\%$ for 2577 reflections with $I > 3\sigma(I)$ and $2\theta = 3$–$45°$ (Mo Kα radiation). There are two different sites for molecules, both of which are of C_2 symmetry. The $W(PMe_3)_4$ portion of the molecule is ordered, but there is disorder of the methylidyne and chloride ligands. The species $W(\equiv CH{\cdot}AlMe_{2-x}Cl_{1+x})(Cl)(PMe_3)_3$ ($x \simeq 0.18$) crystallizes in space group $P2_1/c$ (No. 14) with $a = 9.669$ (2) Å, $b = 11.987$ (3) Å, $c = 19.971$ (5) Å, $\beta = 103.06$ (2)°, and $Z = 4$. This structure was refined to $R_F = 3.1\%$ and $R_{wF} = 3.7\%$ for 3719 reflections with $I > \sigma(I)$ and $2\theta = 4$–$50°$ (Mo Kα). The phosphine atoms occupy meridional sites about an octahedral W(IV) atom. The other sites are occupied by a chloride ligand, a methylidyne ligand (W–C(1) = 1.807 (6) Å, W–C(1)–H(1) = 163.8 (44)°), and a weak interaction with C* which is a disordered CH_3/Cl site (82%:18% abundance) with W–C* = 2.526 (5) Å. The unique feature of the structure is the $AlMe_2Cl/AlMeCl_2$ fragment which interacts with the methylidyne carbon (Al–C(1) = 2.113 (6) Å) to give aluminum a tetrahedral arrangement; the Me/Cl group of this system defines C* in a coordination site about the tungsten atom.

Introduction

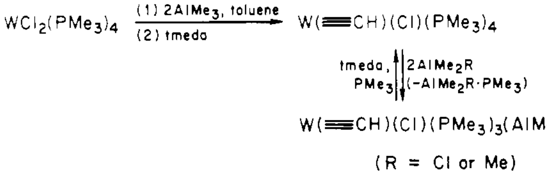
While Fischer and co-workers have synthesized a number of tungsten carbyne complexes of general formula *trans*-$W(\equiv CR)(X)(CO)_4$,[2] there are very few other reports of tungsten carbyne or "alkylidyne" complexes. (The species $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$ has been synthesized and studied crystallographically;[3,4] some related bis(monophosphine) derivatives are also known.[3])

In addition, it should be noted that, to our knowledge, there had been no reports of the isolation of terminal methylidyne complexes (i.e., containing the M≡C—H system) *for any metal* prior to the discovery of Scheme I by Schrock and co-workers.[5]

We have undertaken a single-crystal X-ray diffraction study of the simple chloromethylidyne complex of tungsten(IV), $W(\equiv CH)(Cl)(PMe_3)_4$; unfortunately, as outlined below, a disorder of the chloride and methylidyne ligands causes a lack of definition in this crucial portion of the complex despite a precise structural analysis ($R_F = 3.3\%$ for those 2577 reflections with $I > 3\sigma(I)$; here $R_F = [\sum||F_o| - |F_c||/\sum|F_o|] \times 100$).

We therefore have also carried out an X-ray diffraction study of the chlorodimethylaluminum adduct "$W(\equiv CH)(Cl)(PMe_3)_3(AlMe_2Cl)$"; despite a subtle compositional disorder (the complex is found to have the approximate composition $W(\equiv CH)(Cl)(PMe_3)_3(AlMe_{2-x}Cl_{1+x})$ with $x \simeq 0.18$), this species has been fully characterized ($R_F = 3.1\%$ for 3719 reflections with $I > \sigma(I)$), the geometry of the W≡C—H system has been ascertained, and an unusual interaction of an $AlMe_2Cl$ fragment with both the alkylidyne linkage and the tungsten atom has been discovered. A preliminary account of this second structural study has appeared previously.[5]

Scheme I



Experimental Section

Samples of the materials under study were provided by Professor R. R. Schrock of the Massachusetts Institute of Technology. All samples were handled in a KSE inert atmosphere (argon) "drybox" with a recirculating system and purification chain which had been modified (at SUNY—Buffalo) by adding a transparent port between the glove mounts, thus enabling crystals in the box to be viewed through an externally mounted binoccular polarizing microscope. For each sample several (~10) crystals were mounted into thin glass capillaries. Each was flame sealed, fixed into an aluminum pin with beeswax, and mounted in a eucentric goniometer. Each crystal was examined optically and its diffraction pattern checked both by photographic techniques and via a series of 2θ and ω scans of axial reflections. The "best" crystal was then used for collection of intensity data with the use of a Syntex $P2_1$ automated four-circle diffractometer and Mo Kα radiation. Determination of cell dimensions and orientation matrix was as described previously.[6]

All crystallographic calculations were performed with the use of our in-house Syntex XTL system (NOVA 1200 computer; Diablo disk; Versatec printer/plotter; our SUNY—Buffalo modified XTL interactive crystallographic program package). Analytical scattering factors for neutral atoms[7a] corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion[7b] were used in calculating structure factors. The function minimized during the least-squares refinement process was $\sum w(|F_o| - |F_c|)^2$.

Since unusual problems were encountered in each of the structural analyses, they are described separately below.

Data Collection and Structural Determination

(A) $W(\equiv CH)(Cl)(PMe_3)_4$. Although optical inspection suggested that a sample recrystallized from THF ("globular" crystals of rather indefinite shape) was different from a sample recrystallized from CH_3CN (well-formed thin columnar platelets), the unit cell parameters of the two samples were found to be identical within the tolerances of the reported esd's. The crystal selected for the diffraction study was from THF and approximated to a yellow ellipsoid of dimensions 0.13 × 0.14 × 0.27 mm. Details of the data collection appear in Table

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(1) On sabbatical leave from SUNY College at Plattsburgh, Jan-June, 1980.

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(3) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774-6776.

(4) (a) Churchill, M. R.: Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454-2458; (b) *J. Chem. Soc., Chem. Commun.* **1979**, 321-322.

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Table I. Details of Data Collection for the Two Complexes

	$W(\equiv CH)(Cl)(PMe_3)_4$	$W(\equiv CH \cdot AlMe_{2-x}Cl_{1+x})(Cl)(PMe_3)_3$
(A) Crystal Parameters		
crystal system	monoclinic	monoclinic
space group	$P2/c$ [C_{2h}^4 (No. 13)]	$P2_1/c$ [C_{2h}^5 (No. 14)]
a, Å	16.4641 (17)	9.6689 (24)
b, Å	9.6626 (13)	11.9868 (30)
c, Å	15.8992 (31)	19.9714 (51)
β, deg	116.979 (13)	103.059 (20)
V, Å^3	2254.1 (6)	2254.8 (10)
Z	4	4
mol wt	536.33	555.24
ρ(calcd), g cm^{-3}	1.58	1.64
temp, °C	23	23
(B) Measurement of Intensity Data		
diffractometer	Syntex $P\overline{2}_1$	
radiation	Mo Kα ($\overline{\lambda}$ = 0.710 73 Å)	
monochromator	highly oriented graphite, equatorial, 2θ(mono) = 12.2°	
reflctns measd	$\pm h,+k,\pm l$ (two forms)	$+h,+k,\pm l$ (one form)
2θ range, deg	3.0–45.0	4.0–50.0
scan type	coupled θ(crystal)–2θ(counter)	
scan width, deg	$1.6 + \Delta(\alpha_1 - \alpha_2)$	$1.9 + \Delta(\alpha_1 - \alpha_2)$
scan speed, deg/min	2.5	2.5
bkgd measurement	at beginning and end of scan; each for one-fourth total time	
abs coeff, cm^{-1}	59.1	~58.9
std reflctns	3 (118, 161, 731); intensities were corrected for observed 5% decay	3 (600, 081, 0,0,12); no decay

Table II. Intensity Distribution for Diffraction Data from $W(\equiv CH)(Cl)(PMe_3)_4$

	obsd	theoretical	
		centric	acentric
$\langle \lvert E \rvert \rangle$	0.824	0.798	0.886
$\langle \lvert E^2 \rvert \rangle$	0.995	1.000	1.000
$\langle \lvert E^2 - 1 \rvert \rangle$	0.891	0.968	0.736
$\lvert E \rvert > 1.0$	37.42%	31.73%	36.79%
$\lvert E \rvert > 2.0$	2.04%	4.55%	1.89%
$\lvert E \rvert > 3.0$	0.00%	0.27%	0.01%

I. The observed diffraction symmetry (C_{2h} or $2/m$) and the systematic absences $h0l$ for $l = 2n + 1$ (only) are consistent with the noncentrosymmetric monoclinic space group Pc (No. 7) or the centrosymmetric monoclinic space group $P2/c$ (No. 13). One hemisphere of data was collected ($\pm h,+k,\pm l$). In the presence of an anomalous scatterer, this provides a single asymmetric data set for the noncentrosymmetric space group Pc or two equivalent forms for the centrosymmetric space group $P2/c$ [$I(hkl) = I(\bar{h}k\bar{l}) \neq I(\bar{h}kl) = I(hk\bar{l})$].

A survey of the intensity statistics (see Table II) generally favored an acentric crystal; the structure was, nevertheless, solved and refined satisfactorily with use of the centrosymmetric space group $P2/c$.

Data were corrected for Lorentz and polarization factors, absorption (with use of a series of Ψ scans), and for the 5% decay observed in the intensities of the check reflections. The two forms of data were averaged ($R(I)$ = 2.79% for 2948 pairs of averaged reflections) and placed on an approximate absolute scale by means of a Wilson plot ($\bar{B}$ = 3.20 Å^2).

The structure was solved by direct methods (via the program MULTAN[8]) with the use of the 156 reflections with $\lvert E \rvert > 1.8$. This showed the four molecules in the unit cell to be in special positions of C_2 symmetry with the tungsten atoms lying at $^1/_2$, –0.06, $^1/_4$ and $^1/_2$, 0.06, $^3/_4$ (set 1, Wyckoff notation f) and 0, 0.35, $^1/_4$ and 0, –0.35, $^3/_4$ (set 2, Wyckoff notation e). Subsequent difference-Fourier syntheses and full-matrix least-squares refinement led to the location and satisfactory refinement of all atoms (including all hydrogen atoms) in the $W(PMe_3)_4$ portion of each of the two half molecules which define the crystalline asymmetric unit. Unfortunately, both in molecule 1 and molecule 2, the chloride and methylidyne ligand are necessarily disordered about the crystallographic twofold axis. Attempts to refine the chlorine and methylidyne carbon atom simultaneously were unsuccessful, i.e., the resolution of these two atoms was insufficient for independent determination of their positional parameters (see Figure 1). This problem was solved by using the following procedure (which is, we confess, only semilegitimate!) The position of the methylidyne carbons were fixed in the most chemically reasonable geometry, such that C–W–Cl = 180° and d(W≡C) = 1.84 Å. Full-matrix least-squares refinement of the scale factor, anisotropic thermal parameters for the $WCl(PC_3)_4$ portions of the molecules, positional parameters for all atoms (including hydrogens) in the $WCl(PMe_3)_4$ portion of the molecule, and isotropic thermal parameters for the methylidyne ligands (58 atoms, 283 parameters) led to convergence with R_F = 3.3%, R_{wF} = 3.5%, and GOF = 1.28 for those 2577 reflections with $I > 3\sigma(I)$ (R_F = 4.0%, R_{wF} = 3.6% for all 2948 reflections).

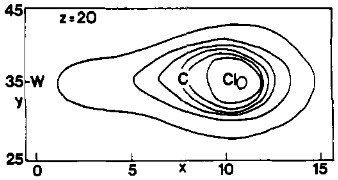

Figure 1. Electron density map showing the sites occupied by the disordered carbon and chlorine atoms in molecule 2. Contours are at 0.5, 1, 2, 4, 6, 8, and 10 e Å^{-3}. Fractional cell coordinates are ×100.

Tests of refinement to convergence as before, but with different values for the W≡C(methylidyne) distance, led to higher residuals—with d(W≡C) = 1.80 Å, R_F = 3.4%, and R_{wF} = 3.6% and with d(W≡C) = 1.88 Å, R_F = 3.5%, and R_{wF} = 3.7%. It seems that a W≡C distance of ~1.84 Å gives the best refinement.

No corrections for secondary extinction were necessary (as judged by comparison between $\lvert F_o \rvert$ and $\lvert F_c \rvert$ values for the strongest reflections). The largest peak on a final difference-Fourier map was of height 0.47 e Å^{-3} and was close to a tungsten atom. Final positional and thermal parameters are collected in Table III. (It should be noted that attempts to refine this structure in the noncentrosymmetric space group Pc were not successful. Those parameters related by a C_2 axis in the higher space group showed very strong correlations, and the refinement process did not converge. We assume therefore that the true space group is $P2/c$.)

(B) $W(\equiv CH \cdot AlMe_{2-x}Cl_{1+x})(Cl)(PMe_3)_3$. A deep-red well-formed platelike crystal of dimensions 0.40 × 0.29 × 0.13 mm was mounted on the Syntex $P2_1$ diffractometer with [100] close to coincident with the instrumental ϕ axis. The observed diffraction symmetry (C_{2h}) and the systematic absences ($h0l$ for $l = 2n + 1$, $0k0$ for $k = 2n + 1$) uniquely indicate the centrosymmetric monoclinic space group $P2_1/c$. Details of data collection etc. appear in Table I.

The position of the tungsten atom was determined from a three-dimensional Patterson synthesis; a series of difference-Fourier syntheses led to the location of all nonhydrogen atoms and of the hydrogen atom of the methylidyne ligand.

Full-matrix least-squares refinement using weights as given in eq 1 was now commenced. Only reflections with $I > \sigma(I)$ were included in the refinement.

$$w = [\sigma(\lvert F_o \rvert)^2 + (0.025 \lvert F_o \rvert)^2]^{-1} \qquad (1)$$

The structural analysis was begun under the assumption that coordination about the aluminum atom consisted of two methyl groups and one chlorine atom, on the basis of the starting materials used in the preparation. With atoms C(2) and Cl(2) unambiguously identified, the atom labeled as C* was therefore treated as a carbon atom; at convergence, this model had refined to R_F = 3.6%. Anisotropic thermal parameters were used for all nonhydrogen atoms except C* for which B_{iso} = 2.64 (11) Å^2. However, the fact that atom C* occupied a position within the coordination sphere of the tungsten atom, but with a W···C* distance of ~2.5 Å, prompted us to search for a less esoteric and more conventional chemical solution.

The possibility that the aluminate group actually consisted entirely of $AlMeCl_2$ rather than $AlMe_2Cl$ was next considered. Refinement was continued with use of the form factors of neutral chlorine for atom C*.

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Table III. Final Parameters for $W(\equiv CH)(Cl)(PMe_3)_4$

atom	x	y	z	atom	x	y	z
W(1)	0.50000 (0)	−0.06323 (4)	0.25000 (0)	H1132	0.3295 (64)	−0.1273 (88)	0.3577 (58)
W(2)	0.00000 (0)	0.35024 (4)	0.25000 (0)	H1133	0.4267 (63)	−0.1432 (86)	0.4383 (63)
Cl(1)	0.39931 (26)	−0.06428 (38)	0.08221 (28)	H1211	0.3543 (62)	0.2697 (91)	0.3340 (55)
Cl(2)	0.11095 (28)	0.35275 (35)	0.18762 (25)	H1212	0.4529 (65)	0.250 (10)	0.3772 (60)
P(11)	0.42283 (13)	−0.24168 (20)	0.29902 (12)	H1213	0.3950 (66)	0.1465 (91)	0.3857 (65)
P(12)	0.39002 (14)	0.11442 (20)	0.24456 (12)	H1221	0.3265 (66)	0.3158 (90)	0.1678 (60)
P(21)	−0.10558 (14)	0.52716 (20)	0.14539 (13)	H1222	0.4283 (63)	0.3033 (92)	0.1962 (62)
P(22)	0.07225 (13)	0.17131 (18)	0.37184 (12)	H1223	0.3538 (59)	0.2213 (84)	0.0965 (58)
C111	0.49252 (72)	−0.3894 (10)	0.36565 (70)	H1231	0.2337 (63)	0.1337 (89)	0.1912 (61)
C112	0.32122 (66)	−0.3302 (10)	0.21129 (69)	H1232	0.2518 (61)	−0.0136 (91)	0.2209 (57)
C113	0.38303 (71)	−0.1897 (10)	0.38551 (64)	H1233	0.2553 (62)	0.0222 (93)	0.1398 (60)
C121	0.40311 (76)	0.1997 (10)	0.35168 (68)	H2111	−0.2506 (63)	0.5621 (90)	0.0463 (57)
C122	0.37542 (73)	0.2650 (10)	0.16711 (68)	H2112	−0.2475 (63)	0.4546 (85)	0.1182 (62)
C123	0.27054 (61)	0.0636 (10)	0.19174 (69)	H2113	−0.2407 (59)	0.3844 (94)	0.0385 (59)
C211	−0.22571 (65)	0.4775 (11)	0.07636 (69)	H2121	−0.0871 (63)	0.5439 (92)	0.0142 (61)
C212	−0.08119 (91)	0.6113 (13)	0.05722 (78)	H2122	−0.1277 (64)	0.6673 (91)	0.0257 (60)
C213	−0.12517 (71)	0.67760 (87)	0.20303 (78)	H2123	−0.0270 (68)	0.642 (10)	0.0865 (66)
C221	0.10405 (76)	0.2223 (11)	0.49397 (56)	H2131	−0.0772 (61)	0.7333 (92)	0.2358 (59)
C222	0.17700 (73)	0.0864 (12)	0.38663 (72)	H2132	−0.1405 (62)	0.6546 (82)	0.2558 (60)
C223	0.00261 (69)	0.0200 (10)	0.36772 (68)	H2133	−0.1665 (65)	0.7300 (93)	0.1525 (58)
C(11)[a]	0.42344 (0)	−0.06406 (0)	0.12238 (0)	H2211	0.1275 (60)	0.1431 (86)	0.5327 (60)
C(21)[b]	0.08349 (0)	0.35212 (0)	0.20288 (0)	H2212	0.0573 (63)	0.251 (10)	0.4955 (60)
H1111[c]	0.5004 (61)	−0.4349 (89)	0.3149 (59)	H2213	0.1647 (61)	0.2892 (86)	0.5244 (55)
H1112	0.5420 (69)	−0.3519 (88)	0.4206 (63)	H2221	0.1722 (71)	0.049 (10)	0.3431 (65)
H1113	0.4475 (61)	−0.4502 (83)	0.3823 (57)	H2222	0.2192 (62)	0.1575 (88)	0.3976 (62)
H1121	0.3065 (59)	−0.4181 (92)	0.2403 (57)	H2223	0.1893 (59)	0.0119 (92)	0.4337 (57)
H1122	0.2751 (60)	−0.2511 (92)	0.1899 (55)	H2231	−0.0139 (61)	−0.0243 (90)	0.3054 (60)
H1123	0.3380 (65)	−0.3575 (84)	0.1680 (63)	H2232	0.0446 (61)	−0.0426 (85)	0.4254 (59)
H1131	0.3641 (61)	−0.2779 (92)	0.4030 (56)	H2233	−0.0433 (66)	0.0585 (89)	0.3735 (64)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W(1)	2.968 (23)	2.948 (19)	4.656 (22)	0.0000 (0)	1.981 (17)	0.0000 (0)
W(2)	3.009 (22)	2.637 (18)	2.721 (17)	0.0000 (0)	0.410 (14)	0.0000 (0)
Cl(1)	3.60 (18)	5.78 (22)	2.52 (17)	0.97 (15)	0.71 (14)	−0.21 (12)
Cl(2)	4.40 (20)	4.69 (19)	3.81 (15)	0.29 (15)	2.69 (17)	−0.07 (13)
P(11)	3.235 (90)	3.733 (82)	3.980 (78)	−0.412 (76)	1.492 (71)	0.114 (70)
P(12)	3.48 (10)	3.468 (79)	3.590 (78)	0.514 (75)	1.367 (72)	−0.102 (65)
P(21)	4.08 (10)	3.718 (81)	4.182 (85)	0.921 (81)	1.949 (80)	0.987 (70)
P(22)	3.231 (94)	3.767 (80)	2.831 (71)	0.228 (71)	0.970 (67)	0.613 (62)
C111	5.62 (57)	4.80 (43)	6.04 (47)	0.34 (42)	2.18 (43)	1.74 (39)
C112	4.18 (48)	5.18 (44)	6.42 (47)	−1.92 (36)	2.34 (39)	−1.34 (38)
C113	5.47 (54)	6.22 (50)	5.06 (41)	−0.78 (41)	3.05 (39)	−0.00 (38)
C121	5.62 (54)	5.31 (49)	5.98 (50)	−0.18 (41)	2.83 (45)	−1.62 (38)
C122	5.89 (54)	4.70 (45)	5.94 (46)	1.49 (42)	2.21 (43)	1.47 (38)
C123	2.79 (42)	6.14 (53)	5.94 (47)	1.06 (36)	1.10 (37)	−0.22 (39)
C211	4.50 (49)	5.87 (48)	6.21 (50)	1.54 (44)	1.50 (40)	0.31 (39)
C212	8.31 (77)	7.67 (69)	6.32 (60)	2.17 (62)	4.04 (61)	3.33 (50)
C213	4.62 (54)	3.80 (39)	7.61 (56)	0.17 (35)	2.65 (45)	−0.43 (37)
C221	7.20 (63)	6.64 (54)	2.78 (32)	0.10 (49)	1.59 (38)	0.72 (33)
C222	4.48 (52)	6.67 (57)	6.19 (52)	1.38 (43)	2.10 (46)	1.35 (44)
C223	5.86 (56)	4.67 (42)	5.48 (42)	−0.14 (41)	2.44 (43)	0.78 (36)

[a] B_{iso} for C(11) = 4.80 (53) Å². [b] B_{iso} for C(21) = 5.28 (57) Å². [c] B_{iso} for all H atoms listed = 7.0 Å².

Four cycles of least-squares refinement led to $R_F = 4.3\%$ and B_{iso}("C*") = 16.7 Å². In the last cycle, Δ/σ for the isotropic thermal parameter for C* was still approximately 18 times larger than the Δ/σ value for the next most unsettled parameter. Thus, as a result of the substantially higher residual obtained for this model and the clearly divergent behavior of the thermal parameter with C* treated as chlorine, we decided to try a model in which C* was treated as mixture of carbon and chlorine. This was accomplished by using the form factor for carbon and refining its population factor or "occupancy". At convergence, the residuals had been lowered to $R_F = 3.1\%$, $R_{wF} = 3.7\%$, and GOF = 1.14 for the 3719 reflections with $|F_o| > \sigma(|F_o|)$. The resulting occupancy factor for C* (treated as a carbon atom with anisotropic thermal motion) was 1.33 (2). The aluminate thus consists of more $AlMe_2Cl$ than $AlMeCl_2$. The relative stoichiometric quantities of each were calculated in the following manner. It was assumed that the scattering factor curves for carbon and chlorine remain as the ratio of their atomic numbers throughout the range 4° < 2θ < 50°, and eq 2 was solved to give a value of x,

$$x[Z(\text{Cl})] + (1 - x)[Z(\text{C})] = 1.33[Z(\text{C})] \qquad (2)$$

the fraction of chlorine at the disordered site, equal to 0.180. The formula of the material studied is thus found to be $W(CH)(Cl)(PMe_3)_3(AlMe_{1.82}Cl_{1.18})$.[9]

In the final model, hydrogen atoms for all methyl groups (other than for C*) were included in fixed idealized positions. Thus 176 variables were refined against the 3719 observations, yielding NO/NV = 21.1. The usual tests of the residuals revealed no unusual trends. A final difference-Fourier synthesis showed a peak of height 1.03 e Å⁻³ located within 1.0 Å of the tungsten atom. No correction for secondary extinction was necessary.

Final positional and thermal parameters are listed in Table IV.

Discussion

Structure of $W(\equiv CH)(Cl)(PMe_3)_4$. Intramolecular distances and angles with estimated standard deviations (esd's)

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(9) Refinement of the "occupancy" of atom C* using the scattering curve for chlorine gave essentially equivalent results. The occupancy of 0.47 yields 8.0 electrons at the position C*—identical with that calculated from an occupancy of 1.33 for carbon. We emphasize that the site is not occupied by an oxygen atom (Z = 8). NMR studies[5] suggest the presence of two complexes in the reaction mixture and are consistent in all ways with our derived crystallographic model.

Table IV. Final Parameters for $W(\equiv CH\cdot AlMe_{2-x}Cl_{1+x})(Cl)(PMe_3)_3$

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
W	0.19206 (2)	0.21223 (2)	0.12566 (1)	H11C	0.26952 (0)	−0.07083 (0)	0.21067 (0)
P(1)	0.37883 (14)	0.07231 (12)	0.16265 (8)	H12A	0.57757 (0)	0.04307 (0)	0.25161 (0)
P(2)	0.04698 (15)	0.12960 (13)	0.20190 (8)	H12B	0.46455 (0)	0.10955 (0)	0.27916 (0)
P(3)	0.35026 (16)	0.32794 (13)	0.07059 (9)	H12C	0.55860 (0)	0.16992 (0)	0.23700 (0)
Cl(1)	0.29786 (16)	0.32447 (13)	0.23153 (8)	H13A	0.56032 (0)	−0.01641 (0)	0.12494 (0)
Cl(2)	−0.23266 (17)	0.16548 (18)	0.01969 (10)	H13B	0.54163 (0)	0.10378 (0)	0.09547 (0)
Al	−0.02796 (17)	0.23639 (14)	0.02021 (9)	H13C	0.43700 (0)	0.01042 (0)	0.06255 (0)
C(1)	0.13496 (56)	0.11814 (48)	0.05405 (31)	H21A	−0.14215 (0)	0.17783 (0)	0.24988 (0)
C(2)	−0.02816 (55)	0.29104 (43)	−0.07531 (24)	H21B	−0.15920 (0)	0.23563 (0)	0.17899 (0)
C*	0.00667 (49)	0.36326 (40)	0.09350 (27)	H21C	−0.05389 (0)	0.28351 (0)	0.24288 (0)
C(11)	0.32308 (67)	−0.07044 (51)	0.17627 (37)	H22A	0.07538 (0)	0.06348 (0)	0.31398 (0)
C(12)	0.51054 (65)	0.10227 (58)	0.24224 (36)	H22B	0.18239 (0)	0.15946 (0)	0.31275 (0)
C(13)	0.49292 (68)	0.03852 (57)	0.10457 (40)	H22C	0.21280 (0)	0.04089 (0)	0.28841 (0)
C(21)	−0.09373 (78)	0.21715 (63)	0.22081 (40)	H23A	−0.10030 (0)	−0.02315 (0)	0.20354 (0)
C(22)	0.14028 (74)	0.09384 (65)	0.28967 (34)	H23B	0.01716 (0)	−0.05468 (0)	0.16534 (0)
C(23)	−0.04884 (70)	0.00162 (58)	0.17154 (36)	H23C	−0.11270 (0)	0.01523 (0)	0.12824 (0)
C(31)	0.37748 (78)	0.27943 (73)	−0.01171 (38)	H31A	0.43910 (0)	0.32900 (0)	−0.02781 (0)
C(32)	0.53319 (68)	0.35120 (64)	0.11977 (40)	H31B	0.28898 (0)	0.27579 (0)	−0.04393 (0)
C(33)	0.29803 (80)	0.47228 (65)	0.05134 (56)	H31C	0.41915 (0)	0.20685 (0)	−0.00613 (0)
H1[a]	0.1290 (64)	0.0645 (54)	0.0264 (33)	H32A	0.58213 (0)	0.39597 (0)	0.09316 (0)
H2A[b]	−0.10226 (0)	0.34403 (0)	−0.08926 (0)	H32B	0.57998 (0)	0.28132 (0)	0.12894 (0)
H2B	−0.04293 (0)	0.22987 (0)	−0.10634 (0)	H32C	0.53139 (0)	0.38785 (0)	0.16135 (0)
H2C	0.06046 (0)	0.32521 (0)	−0.07543 (0)	H33A	0.36561 (0)	0.50750 (0)	0.03040 (0)
H11A	0.40429 (0)	−0.11676 (0)	0.19029 (0)	H33B	0.29354 (0)	0.50979 (0)	0.09234 (0)
H11B	0.26594 (0)	−0.09877 (0)	0.13443 (0)	H33C	0.20732 (0)	0.47385 (0)	0.02032 (0)

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
W	2.260 (10)	2.203 (10)	2.751 (10)	0.0171 (63)	0.7526 (66)	−0.0754 (69)
P(1)	2.628 (54)	2.907 (59)	3.868 (67)	0.237 (45)	0.716 (48)	0.135 (50)
P(2)	3.298 (59)	3.821 (66)	3.258 (64)	−0.078 (51)	1.412 (51)	0.126 (54)
P(3)	3.101 (61)	3.663 (66)	4.805 (79)	−0.373 (52)	1.283 (57)	0.953 (59)
Cl(1)	4.044 (65)	3.962 (64)	4.344 (73)	−0.504 (52)	0.506 (55)	−1.348 (55)
Cl(2)	3.647 (68)	7.23 (10)	5.934 (95)	−0.712 (68)	1.052 (64)	−0.874 (81)
Al	2.750 (65)	3.238 (71)	3.271 (73)	0.285 (54)	0.673 (54)	0.099 (58)
C(1)	3.11 (23)	2.87 (24)	3.79 (27)	0.07 (18)	1.15 (20)	−0.48 (21)
C(2)	3.13 (22)	3.81 (24)	1.50 (18)	0.46 (18)	0.41 (16)	0.93 (17)
C*	4.11 (23)	3.52 (23)	5.59 (29)	0.49 (17)	0.90 (19)	−0.63 (19)
C(11)	4.70 (30)	3.30 (27)	5.82 (36)	0.61 (23)	1.72 (26)	0.65 (25)
C(12)	3.58 (26)	4.85 (32)	4.97 (33)	0.70 (23)	−0.82 (23)	0.00 (26)
C(13)	4.35 (30)	4.42 (32)	6.96 (41)	0.66 (25)	2.66 (29)	0.02 (29)
C(21)	5.01 (35)	6.56 (43)	5.72 (39)	0.59 (29)	3.16 (31)	−0.63 (31)
C(22)	5.45 (34)	7.06 (41)	3.35 (28)	0.34 (31)	1.76 (25)	0.59 (28)
C(23)	4.91 (31)	4.71 (32)	4.97 (34)	−1.35 (26)	1.35 (26)	0.67 (27)
C(31)	4.63 (34)	9.10 (56)	4.25 (33)	−0.98 (32)	1.73 (27)	0.51 (34)
C(32)	3.74 (28)	5.66 (37)	6.05 (39)	−0.85 (27)	0.99 (26)	0.29 (31)
C(33)	5.28 (38)	4.53 (37)	12.64 (73)	−0.19 (29)	2.53 (42)	3.30 (43)

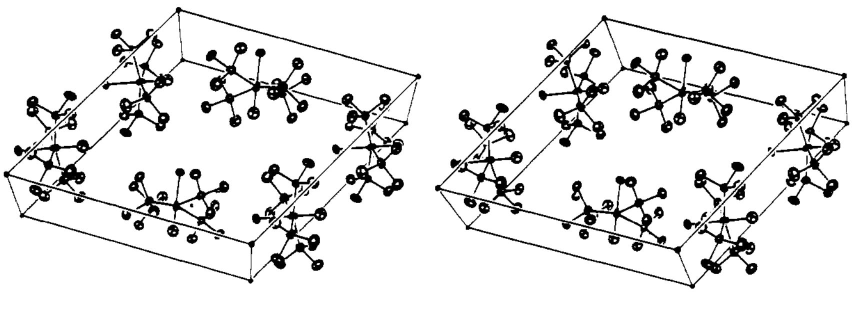

Figure 2. Packing of $W(\equiv CH)(Cl)(PMe_3)_4$ molecules in the unit cell. The Cl–W–C systems are simplified by showing one ordered arrangement per molecule. The unit cell is viewed down *b*. Axis *a* is the closest to horizontal. Molecules of type 1 lie at $x = {}^1/_2$; those of type 2 lie at $x = 0$ and 1.

are listed in Table V. There are two crystallographically unrelated sites for molecules (each having crystallographically imposed C_2 symmetry). The geometry of the two independent molecules ("molecule 1" and "molecule 2") is equivalent in all ways. Figure 2 shows the packing of the molecules within the unit cell, while Figure 3 shows a deconvoluted view of "molecule 2".

The $W(\equiv CH)(Cl)(PMe_3)_4$ molecule has an equatorial belt of four PMe_3 ligands and has mutually trans chloride and methylidyne ligands (disordered; vide supra). The assigned $W\equiv C$ bond length of 1.84 Å is close to the mean of the three tungsten–carbon triple bond distances appearing in the literature, viz., 1.785 (8) Å in $W(\equiv CCMe_3)(=CHCMe_3)(CH_2CMe_3)(dmpe)$,[4] 1.82 (2) Å in $W[\equiv C(p\text{-tolyl})](\eta^5\text{-}C_5H_5)(CO)_2$,[10] and 1.88 (10) Å in *trans*-$W(\equiv CPh)(I)(CO)_4$.[10]

The tungsten atom in the present molecule is in a rather distorted octahedral environment. As far as we can tell in the

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(10) Huttner, G.; Frank, A.; Fischer, E. O. *Isr. J. Chem.* **1976**, *77*, 133.

(11) Equations of planes are in orthonormalized (Å) coordinates.

Table V. Selected Intramolecular Distances (Å) and Angles (Deg) for $W(\equiv CH)(Cl)(PMe_3)_4$

molecule 1		molecule 2	
atoms	dist	atoms	dist
W(1)-P(11)	2.468 (2)	W(2)-P(21)	2.467 (2)
W(1)-P(12)	2.468 (2)	W(2)-P(22)	2.463 (2)
W(1)-Cl(1)	2.419 (2)	W(2)-Cl(2)	2.442 (5)
W(1)-C(11)	1.84	W(2)-C(21)	1.84
P(11)-C(111)	1.836 (10)	P(21)-C(211)	1.838 (11)
P(11)-C(112)	1.833 (10)	P(21)-C(212)	1.816 (13)
P(11)-C(113)	1.841 (11)	P(21)-C(213)	1.824 (10)
P(12)-C(121)	1.815 (10)	P(22)-C(221)	1.834 (9)
P(12)-C(122)	1.850 (10)	P(22)-C(222)	1.826 (13)
P(12)-C(123)	1.821 (11)	P(22)-C(223)	1.844 (11)
C-H(min)	0.80 (10)	C-H(min)	0.76 (10)
C-H(max)	1.10 (8)	C-H(max)	1.10 (10)
C-H(av)	0.96 [8]	C-H(av)	0.94 [8]

molecule 1		molecule 2	
atoms	angle	atoms	angle
Cl(1)-W(1)-P(11)	98.73 (11)	Cl(2)-W(2)-P(21)	98.47 (11)
Cl(1)-W(1)-P(11′)	80.93 (11)	Cl(2)-W(2)-P(21′)	80.73 (11)
Cl(1)-W(1)-P(12)	80.76 (11)	Cl(2)-W(2)-P(22)	98.22 (11)
Cl(1)-W(1)-P(12′)	99.58 (11)	Cl(2)-W(2)-P(22′)	82.58 (11)
P(11)-W(1)-P(11′)	91.38 (7)	P(21)-W(2)-P(21′)	92.27 (7)
P(11)-W(1)-P(12)	91.28 (7)	P(21)-W(2)-P(22)	163.30 (7)
P(11)-W(1)-P(12′)	161.69 (7)	P(21)-W(2)-P(22′)	90.86 (7)
P(12)-W(1)-P(12′)	91.85 (7)	P(22)-W(2)-P(22′)	90.83 (6)
P(12)-W(1)-P(11′)	161.69 (7)	P(21′)-W(2)-P(22′)	163.30 (7)
W(1)-P(11)-C(111)	116.65 (35)	W(2)-P(21)-C(211)	117.38 (35)
W(1)-P(11)-C(112)	120.58 (34)	W(2)-P(21)-C(212)	119.71 (44)
W(1)-P(11)-C(113)	117.00 (34)	W(2)-P(21)-C(213)	116.40 (36)
W(1)-P(12)-C(121)	120.66 (36)	W(2)-P(22)-C(221)	116.61 (35)
W(1)-P(12)-C(122)	116.24 (35)	W(2)-P(22)-C(222)	120.49 (38)
W(1)-P(12)-C(123)	116.77 (34)	W(2)-P(22)-C(223)	117.30 (34)
C(111)-P(11)-C(112)	101.06 (48)	C(211)-P(21)-C(212)	102.17 (55)
C(111)-P(11)-C(113)	97.00 (48)	C(211)-P(21)-C(213)	96.92 (49)
C(112)-P(11)-C(113)	100.63 (47)	C(212)-P(21)-C(213)	100.52 (56)
C(121)-P(12)-C(122)	101.07 (49)	C(221)-P(22)-C(222)	100.67 (50)
C(121)-P(12)-C(123)	101.46 (49)	C(221)-P(22)-C(223)	97.19 (48)
C(122)-P(12)-C(123)	96.78 (47)	C(222)-P(22)-C(223)	100.65 (50)

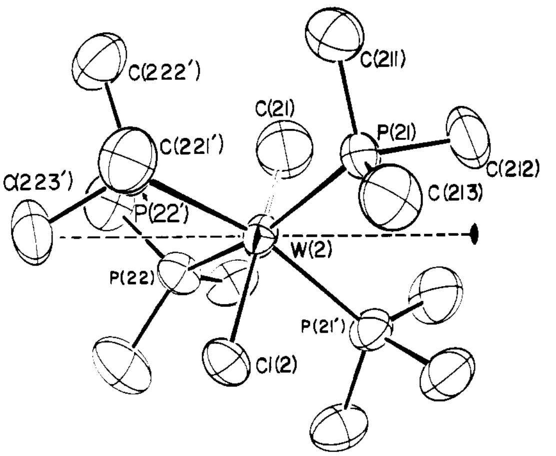

Figure 3. Geometry of "molecule 2" in the $W(\equiv CH)(Cl)(PMe_3)_4$ structure. The isolated molecule is shown. In the crystal, the sites of C(21) and Cl(2) are disordered about the crystallographic C_2 axis.

presence of disorder, the Cl—W≡CH moiety is linear. The four equatorial PMe_3 groups are not strictly perpendicular to the W–Cl vector. Rather, the arrangement of the PMe_3 ligands has approximate $\bar{4}$ symmetry, with the phosphorus atoms displaced alternately above and below the idealized equatorial plane. The Cl–W–P angles in molecule 1 are (cyclically) Cl(1)–W(1)–P(11) = 98.73 (11)°, Cl(1)–W(1)–P(11′) = 80.93 (11)°, Cl(1)–W(1)–P(12′) = 99.58 (11)°, and Cl(1)–W(1)–P(12) = 80.76 (11)°. The corresponding angles in molecule 2 are (cyclically) Cl(2)–W(2)–P(21) = 98.47 (11)°, Cl(2)–W(2)–P(21′) = 80.73 (11)°, Cl(2)–W(2)–P(22) = 98.22 (11)°, and Cl(2)–W(2)–P(22′) = 82.58 (11)°. The distortion of phosphine ligands from truly equatorial sites is also illustrated by the trans angles P(11)–W(1)–P(12′) = P(12)–W(1)–P(11′) = 161.69 (7)° and P(21)–W(2)–P(22) = P(21′)–W(2)–P(22′) = 163.30 (7)°. The phosphorus atoms in molecule 1 are displaced by 0.392–0.394 Å from the least-squares plane through the WP_4 system; molecule 2 is slightly less distorted, with phosphorus atoms lying 0.355–0.360 Å from the least-squares plane through the $W(2)P_4$ core.

A number of molecules containing $M(PMe_3)_4$ systems have recently been studied by Wilkinson and co-workers. In $W(PMe_3)_4(CH_3)_2$,[12] $Rh(PMe_3)_4Cl$,[13] and *trans*-$Mo(H)(BH_4)(PMe_3)_4$,[14] the $M(PMe_3)_4$ moieties have an arrangement distorted from planarity in a similar fashion to that observed in the present $W(\equiv CH)(Cl)(PMe_3)_4$ molecule.

The $W(PMe_3)_4$ portions of $W(PMe_3)_4(CH_3)_2$[12] and the present $W(\equiv CH)(Cl)(PMe_3)_4$ system show close similarities. The WP_4 cores each have $\bar{4}$ symmetry (i.e., are distorted toward a tetrahedral arrangement) and the average W–P distances are, respectively, 2.457 (4) and 2.467 [2] Å. The similarities are surprizing when it is realized that W-

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(12) Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1979**, 926–927.

(13) Jones, R. A.; Real, F. M.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 511–518.

(14) Atwood, J. L.; Hunter, W. E.; Carmona-Guzman, G.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1980**, 467–470.

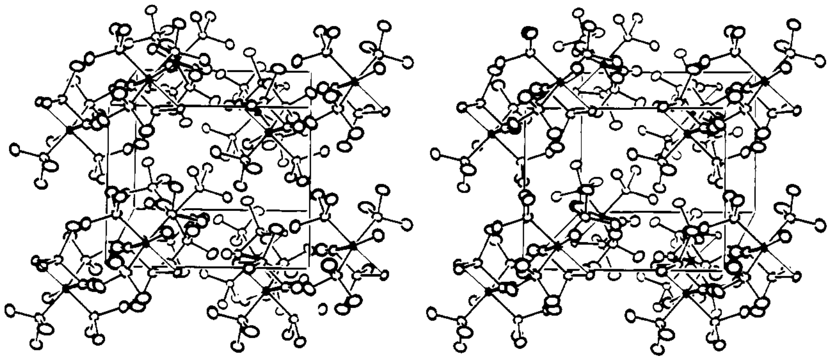


Figure 4. Packing of W(≡CH·AlMe$_{2-x}$Cl$_{1+x}$)(Cl)(PMe$_3$)$_3$ molecules within the unit cell, viewed approximately down *c*. The *a* axis is horizontal (+*x* to the right), and the *b* axis is vertical (+*y* to the top).

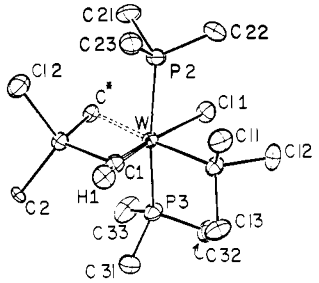
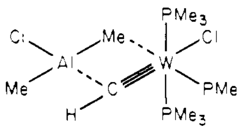


Figure 5. Labeling of atoms within the W(≡CH·AlMe$_{2-x}$Cl$_{1+x}$)(Cl)(PMe$_3$)$_3$ system.

(PMe$_3$)$_4$(CH$_3$)$_2$ is nominally a tungsten(II) derivative, whereas W(≡CH)(Cl)(PMe$_3$)$_4$ is a tungsten(IV) complex.

It is most unfortunate that the C_2-enforced disorder obviates any detailed discussion of the tunsten-methylidyne linkage in this system. Fortunately, this feature is clearly visible in the structural study of the chlorodimethylaluminum derivative (vide infra).

Structure of W(≡CH·AlMe$_{2-x}$Cl$_{1+x}$)(Cl)(PMe$_3$)$_3$. Intramolecular distances and angles (with esd's) are collected in Table VI. The packing of molecules within the unit cell is shown in Figure 4, while the labeling of atoms is given in Figure 5, and a stereoview appears as Figure 6. The composition determined for the crystalline material is W(≡CH·AlMe$_{2-x}$Cl$_{1+x}$)(Cl)(PMe$_3$)$_3$ with $x \simeq 0.18$. We regard this as indicating that the crystals contain a mixture of ~82% of W(≡CH·AlMe$_2$Cl)(Cl)(PMe$_3$)$_3$ (I) and ~18% of W(≡CH·AlMeCl$_2$)(Cl)(PMe$_3$)$_3$ (II). (It was noted in the original synthesis of this material[5] that NMR studies indicated two species in solution.) The images of the two species overlap cleanly at all atomic sites, and C* is regarded as the composite image of ~82% methyl group and ~18% chloride ligand.



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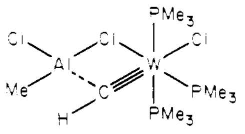


II

The three PMe$_3$ ligands take up meridional sites around the tungsten atom, with P(1)-W-P(2) = 91.25 (5)°, P(1)-W-P(3) = 91.75 (5)°, and P(2)-W-P(3) = 166.83 (5)°. The mutually trans PMe$_3$ ligands are associated with closely similar tungsten-phosphorus bond lengths of W-P(2) = 2.496 (2) Å and W-P(3) = 2.497 (2) Å; the third PMe$_3$ ligand, which is trans to C*, has a shorter metal-phosphorus bond length, with W-P(1) = 2.453 (1) Å.

The tungsten-chlorine bond length, W-Cl(1) = 2.520 (2) Å (which is *trans* to the methylidyne ligand), is substantially longer than those found in W(≡CH)(Cl)(PMe$_3$)$_4$ (2.419 (4) and 2.442 (5) Å; vide supra).

Table VI. Intramolecular Distances (Å) and Angles (Deg) for the W(≡CH·AlMe$_{2-x}$Cl$_{1+x}$)(Cl)(PMe$_3$)$_3$ System

(A) Distances around the Tungsten Atom			
W-C(1)	1.807 (6)	W-P(1)	2.453 (1)
W-Cl(1)	2.520 (2)	W-P(2)	2.496 (2)
W-C*	2.526 (5)	W-P(3)	2.497 (2)
(B) Distances around the Aluminum Atom			
Al-C(1)	2.113 (6)	Al-Cl(2)	2.152 (2)
Al-C(2)	2.017 (5)	Al-C*	2.085 (5)
(C) Phosphorus-Carbon Distances			
P(1)-C(11)	1.833 (6)	P(2)-C(23)	1.824 (7)
P(1)-C(12)	1.834 (7)	P(3)-C(31)	1.818 (8)
P(1)-C(13)	1.818 (7)	P(3)-C(32)	1.840 (7)
P(2)-C(21)	1.824 (8)	P(3)-C(33)	1.819 (8)
P(2)-C(22)	1.832 (7)		
(D) Carbon-Hydrogen Distance			
C(1)-H(1)	0.84 (6)		
(E) "Cis" Angles about Tungsten			
C(1)-W-P(1)	83.34 (19)	Cl(1)-W-P(2)	82.97 (5)
P(1)-W-Cl(1)	88.89 (5)	P(1)-W-P(2)	91.25 (5)
Cl(1)-W-C*	87.76 (12)	C(1)-W-P(3)	96.10 (19)
C*-W-C(1)	100.01 (22)	C*-W-P(3)	87.71 (12)
C(1)-W-P(2)	96.99 (19)	Cl(1)-W-P(3)	84.26 (5)
C*-W-P(2)	88.58 (12)	P(1)-W-P(3)	91.71 (5)
(F) "Trans" Angles about Tungsten			
C(1)-W-Cl(1)	172.23 (19)	P(2)-W-P(3)	166.83 (5)
C*-W-P(1)	176.64 (12)		
(G) Angles about the Methylidyne Carbon Atom			
W-C(1)-H(1)	163.8 (44)	W-C(1)-Al	84.65 (23)
Al-C(1)-H(1)	111.5 (44)		
(H) Angles about Aluminum			
C(1)-Al-C(2)	111.21 (23)	C(2)-Al-Cl(2)	108.63 (17)
C(1)-Al-Cl(2)	110.79 (18)	C(2)-Al-C*	113.14 (21)
C(1)-Al-C*	105.95 (22)	Cl(2)-Al-C*	107.04 (16)
(I) Angle at "C*"			
Al-C*-W	69.38 (15)		
(J) Tungsten-Phosphorus-Carbon Angles			
W-P(1)-C(11)	117.51 (22)	W-P(2)-C(23)	116.37 (23)
W-P(1)-C(12)	116.56 (22)	W-P(3)-C(31)	116.67 (26)
W-P(1)-C(13)	118.15 (24)	W-P(3)-C(32)	117.38 (24)
W-P(2)-C(21)	116.50 (25)	W-P(3)-C(33)	116.94 (30)
W-P(2)-C(22)	116.96 (24)		
(K) Carbon-Phosphorus-Carbon Angles			
C(11)-P(1)-C(12)	102.95 (31)	C(22)-P(2)-C(23)	102.99 (32)
C(11)-P(1)-C(13)	97.35 (22)	C(31)-P(3)-C(32)	102.30 (35)
C(12)-P(1)-C(13)	101.18 (32)	C(31)-P(3)-C(33)	101.72 (39)
C(21)-P(2)-C(22)	99.53 (34)	C(32)-P(3)-C(33)	98.98 (38)
C(21)-P(2)-C(23)	101.90 (34)		

We now turn our attention to the tungsten-methylidyne system. The tungsten-carbon distance is W-C(1) = 1.807 (6) Å, the C-H distance is 0.84 (6) Å (in reasonable compliance with the expected "X-ray determined" value of ≃0.95

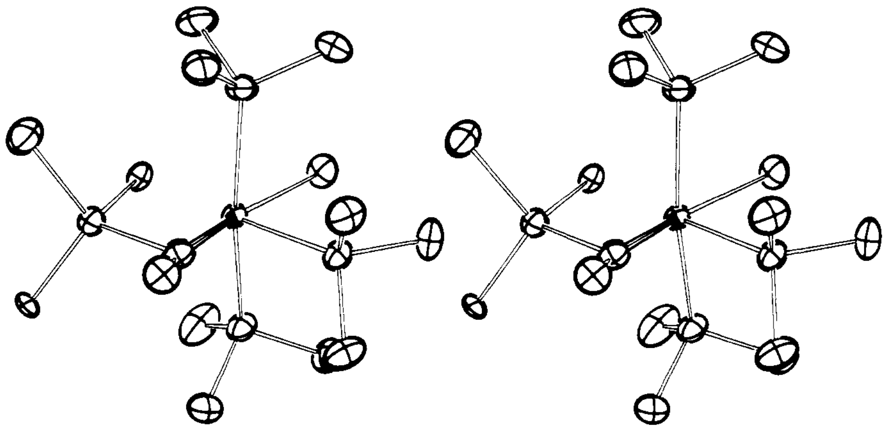
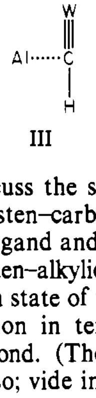


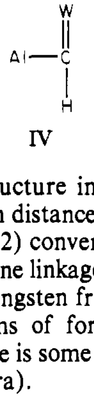
Figure 6. Stereoscopic view of the $W(\equiv CH\cdot AlMe_{2-x}Cl_{1+x})(Cl)(PMe_3)_3$ system.

Å),[15] and the W-C(1)-H(1) angle is 163.8 (44)°. The nonlinearity of this system (which is significant at the 3.7σ level) is clearly caused by the interaction of the methylidyne system with the aluminum atom (Al-C(1) = 2.113 (6) Å, ∠W-C(1)-Al = 84.65 (23)°, ∠H(1)-C(1)-Al = 111.5 (44)°; note that the Al⋯W distance is 2.649 (2) Å, so the aluminum atom interacts principally with C(1) rather than with the W≡C triple bond).

The *degree* of the interaction of C(1) with the aluminum atom is difficult to assess. The Al–C(1) distance of 2.113 (6) Å is significantly longer than the Al-C(2) distance of 2.017 (5) Å but is clearly still strong. Obvious extreme structures are III and IV.



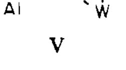
III



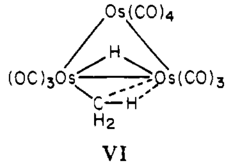
IV

We prefer to discuss the structure in terms of form III because (1) the tungsten–carbon distance is more compatible with an alkylidyne ligand and (2) conversion of a tungsten–alkylidyne to a tungsten–alkylidene linkage will cause a formal decrease in oxidation state of tungsten from +4 to +3 unless there is compensation in terms of formation of another tungsten–(ligand$^-$) bond. (There is some such compensation, but not completely so; vide infra).

The most unusual feature of the structure, however, is associated with the composite atom C*. It is situated so as to take up the sixth octahedral site around the tungsten(IV) center. The W-C* distance is 2.526 (5) Å, i.e., almost identical with the W-Cl(1) distance of 2.520 (2) Å; yet detailed refinement indicates that C* is mainly a methyl group (82%) with a small chloride component (18%). There is thus a *weak* tungsten-methyl linkage, since one would expect a normal W-Me distance to be about 2.30 Å (on the basis of W-Cl(1) = 2.520 (2) Å, r(Cl) = 0.99 Å, r(C) = 0.77 Å).[16] Possibly the interaction could be of the type shown in V (the Al-C*-W angle is 69.38 (15)°). Such a bonding scheme is indicated in $(\mu\text{-H})(\mu\text{-Me})Os_3(CO)_{10}$ (VI).[17]



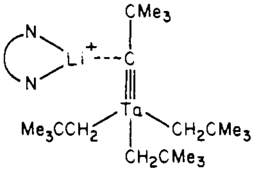
V



VI

Angles around the aluminum atom are all close to the ideal tetrahedral value of 109.47°, the smallest being the chelate "bite angle", C(1)-Al-C* = 105.95 (22)° and the largest being C(2)-Al-C* = 113.14 (21)°.

Relationship to Other Structural Studies. There have been previous reports of interactions of the α-carbon atom of alkylidyne moieties with various other Lewis acids or electrophiles. Thus, in $[Ta(\equiv CCMe_3)(CH_2CMe_3)_3^-][Li(dmp)^+]$,[18] a N,N'-dimethylpiperazine-complexed Li^+ ion is associated with the α-carbon atom of the neopentylidyne ligand (see VII).



VII

Here the tantalum–carbon multiple bond has a length of 1.76 (2) Å, i.e., it is far more consistent with an alkylidyne (Ta≡C) linkage than with a lithiacarbene (Ta=C) system;[19-27] the Ta≡C—C angle is 165 (1)° and the Ta≡C⋯Li angle is ≃90°.

Roper and co-workers have recently shown that the species $Os(\equiv CR)(Cl)(CO)(PPh_3)_2$ (R = p-tolyl) reacts with HCl, forming the carbene complex $Os(=CHR)(Cl)_2(CO)(PPh_3)_2$.[28] The same initial carbyne complex also reacts with a variety of Cu(I), Ag(I), and Au(I) complexes, forming species of the

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(19) The Ta≡C distance in $Ta(\equiv CPh)(\eta^5\text{-}C_5H_5)(PMe_3)_2Cl$ is 1.849 (8) Å.[20] Ta=C distances are 2.026 (10) Å in $Ta(=CH_2)(CH_3)(\eta^5\text{-}C_5H_5)_2$,[21] 2.030 (6) Å in $Ta(=CHCMe_3)(Cl)(\eta^5\text{-}C_5H_5)_2$,[22] 2.07 (1) Å in $Ta(=CHPh)(CH_2Ph)(\eta^5\text{-}C_5H_5)_2$,[23] 1.932 (7) and 1.955 (7) Å in $Ta(=CHCMe_3)_2(\eta^1\text{-mesityl})(PMe_3)_2$,[24] 1.898 (2) Å in $[Ta(=CHCMe_3)(PMe_3)Cl_3]_2$,[25] and 1.932 (9) and 1.937 (9) Å in $[Ta(=CHCMe_3)(CH_2CMe_3)(PMe_3)_2]_2(\mu\text{-}N_2)$.[26,27]

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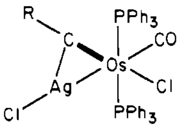
type Os(AgCl)(CR)(Cl)(CO)(PPh$_3$)$_2$ for which structure VIII has been determined from an X-ray diffraction study.[29]



VIII

Here the Os–CR linkage is now 1.839 (5) Å as compared to 1.77 (2) Å found in the parent carbyne complex.[28] While Roper et al.[29] consider species VIII to be a dimetalacyclopropene complex,[29] we would prefer it to be considered as a carbyne complex.

Stone and co-workers[30] have found that platinum(0) complexes will also interact with tungsten carbynes, and a structural study of the derived species W[(CR)Pt(PMe$_2$Ph)$_2$](η^5-C$_5$H$_5$)(CO)$_2$ has been carried out. The W≡C linkage increases from 1.82 (2) Å in the parent carbyne complex[10] to 1.96 Å in the platinated derivative. Here, the tungsten–platinum interaction appears sufficiently strong as to suggest consideration of the product as the dimetalacyclopropene derivative.

Clearly, the chemistry of transition-metal alkylidynes (or, more generally, carbyne complexes) is only beginning. We are in the process of studying a wide variety of aluminated metal–alkylidyne complexes, and our results will be reported in subsequent publications.

Acknowledgment. We thank Professor R. R. Schrock for providing the samples and the National Science Foundation for their financial support (Grants CHE79-24560 and CHE80-23448 to M.R.C.).

Registry No. W(≡CH)(Cl)(PMe$_3$)$_4$, 76642-46-1; W(≡CH·AlMe$_2$Cl)(Cl)(PMe$_3$)$_3$, 76642-47-2; W(≡CH·AlMeCl$_2$)(Cl)(PMe$_3$)$_3$, 78420-99-2.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes for the two complexes (39 pages). Ordering information is given in any current masthead page.

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2:1 Lewis Base Adducts of Palladium Bis(hexafluoroacetylacetonate). Structure and β-Diketonate Exchange in (bpy)Pd(C$_5$HF$_6$O$_2$)$_2$

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Palladium bis(hexafluoroacetylacetonate), Pd(F$_6$acac)$_2$, forms 2:1 complexes of the type Pd(F$_6$acac)$_2$·2L with molecular Lewis bases where L = Ph$_3$As, $^1/_2$ (Ph$_2$As)$_2$CH$_2$, (CH$_3$)$_3$N, (CH$_3$)$_2$NH, t-C$_4$H$_9$NC, phenothiazine, phenoselenazine, $^1/_2$ bipyridyl, and $^1/_2$ tetrathianaphthacene. These compounds are ionic and may be represented as [L$_2$Pd(F$_6$acac)]$^+$F$_6$acac$^-$. Variable-temperature ^{19}F NMR spectra of [(bpy)Pd(F$_6$acac)]F$_6$acac demonstrated a rapid interconversion between the ionic and coordinated F$_6$acac groups with ΔH = 10.4 ± 1 kcal/mol and ΔS = −11 ± 4 eu. The bipyridyl complex crystallizes in space group $P2_1/c$ with a = 11.991 (5) Å, b = 9.295 (4) Å, c = 21.008 (9) Å, β = 101.32 (2)°, and V = 2305 Å^3. A structure solution based on 1526 observed reflections converged at R = 0.057 and R_w = 0.063. The (bpy)Pd(F$_6$acac)$^+$ units are essentially planar and pack in a slipped-stack arrangement; d(Pd–N)$_{av}$ is 1.987 (8) Å and d(Pd–O)$_{av}$ is 2.005 (7) Å.

Introduction

The acid–base chemistry of palladium bis(hexafluoroacetylacetonate), Pd(F$_6$acac)$_2$, is extensive in scope. This fluorinated metalloorganic forms adducts with molecular Lewis bases, which may be grouped into four broad classes, Pd(F$_6$acac)$_2$·nL (L = base, n = 1, 2, 3, 4), according to their stoichiometry. Previously,[1] we described the members of the n = 1 class. This work reports the synthesis and properties of the 2:1 adducts, Pd(F$_6$acac)$_2$·2L, and describes the crystal structure of a representative member, Pd(F$_6$acac)$_2$(bpy). In addition, we find that in solution, this compound undergoes an unusual exchange process involving the hexafluoroacetylacetonate (F$_6$acac) ligand. Detailed characterization of the n = 2 class is especially important since this type of material is formed as a surface compound when Pd(F$_6$acac)$_2$ reacts with condensed-phase donors such as alumina.[2]

Synthetic Chemistry and Physical Properties

When Pd(F$_6$acac)$_2$ in nonpolar solvents is treated with a Lewis base, the limiting composition, i.e., the highest value for n in Pd(F$_6$acac)$_2$·nL, appears to be thermodynamically determined by a combination of the steric and electronic properties of the base. Thus, triphenylarsine, bis(diphenylarsino)methane, phenothiazine (PTZ), and phenoselenazine (PSZ) generate in isolable amounts only adducts of the n = 2 class, regardless of the amount of base employed. The effect of the electronic nature of the base is seen in a comparison of the products formed from triphenylphosphine and triphenylarsine in solvents of low dielectric constant such as chloroform or toluene. The former yields only the 1:1 adduct Pd(F$_6$acac)$_2$·Ph$_3$P[3] whereas the latter produces Pd(F$_6$acac)$_2$(PH$_3$As)$_2$ (**1**). The effect of the steric properties of the donor is shown in a comparison of the chemistry of ammonia and the methylamines (CH$_3$)$_x$NH$_{3-x}$. Treatment of Pd(F$_6$acac)$_2$ in pentane with excess trimethylamine affords Pd(F$_6$acac)$_2$[(CH$_3$)$_3$N]$_2$ (**3**). Under the same conditions, the less sterically hindered donors ammonia and methylamine yield Pd(F$_6$acac)$_2$(NH$_3$)$_4$ and Pd(F$_6$acac)$_2$(CH$_3$NH$_2$)$_4$. The behavior of dimethylamine, with intermediate steric bulk, is different in that the equilibrium constants for the formation of the n = 1, 2, 4 adducts, eq 1–3, are sufficiently different that either

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