Crystal and Molecular Structure of W(η²-HC≡COAlCl₃)(CO)(PMe₃)₃Cl, a Product of the Coupling of Methylidyne and Carbonyl Ligands on Tungsten

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A single-crystal X-ray diffraction analysis has been performed on the title complex, which was prepared by Holmes and Schrock through $AlCl_3$-promoted coupling of $W(CH)(PMe_3)_4Cl$ with carbon monoxide. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 10.420$ (2) Å, $b = 12.896$ (2) Å, $c = 19.319$ (4) Å, $\beta = 105.880$ (15)°, $V = 2497.1$ (9) Å³, ρ(calcd) = 1.73 g cm⁻³ for $Z = 4$, and mol wt = 650.0. Automated four-circle diffractometer intensity data (Syntex P2₁) were used to solve the structure; refinement led to $R_F = 3.2\%$ and $R_{wF} = 3.0\%$ for all 4423 unique reflections with $4.0° < 2\theta < 50.0°$ (Mo Kα radiation). The octahedral coordination environment about the central tungsten atom consists of three meridional PMe₃ ligands, a terminal carbonyl, a chloride, and an η²-HC≡COAlCl₃ ligand. The last is oriented parallel to the carbonyl ligand and is best described as a substituted acetylene with an acetylenic carbon–carbon linkage of 1.316 (6) Å and short tungsten–carbon distances of 2.034 (4) and 2.009 (5) Å. The aluminum–oxygen distance is 1.751 (3) Å; this value represents a significantly stronger Al–O interaction than has been observed in other structures containing Al–O (carbonyl; acyl) linkages.

Carbon–carbon bond formation via the reaction of surface-bound methylene or methylidyne groups with carbon monoxide might play a significant role in heterogeneous reductive oligomerization of carbon monoxide with molecular hydrogen,[1] even though the latest theory of the process suggests that the carbon–carbon bond is formed by migration of a surface alkyl to a surface alkylidene group.[2] Coupling of carbon monoxide with a methylidene or methylidyne ligand is also a possible step in homogeneous systems in which CO is reduced by molecular hydrogen. For instance, Masters has proposed the sequence of steps shown in Scheme I, whereby methylene attack at CO results in a coordinated acyl or alkyl species.[3a] Such a scheme is reasonable in light of the recent discovery that methylene or methylidyne ligands in complexes of early transition metals possess *nucleophilic* character.[3b,c]

The initial report of the preparation and structure of the terminal methylidyne complex W(CH)(Cl)(PMe₃)₄ along with the unusual aluminated derivatives W(CH·AlR₃)(Cl)-(PMe₃)₃[4,5] and W(CAl₂Me₄Cl)(CH₃)(PMe₃)₂(η²-C₂H₄)[6] prompted Schrock and co-workers to examine the reactions of such molecules with carbon monoxide. These workers found that W(CH)(Cl)(PMe₃)₄ does not react readily with carbon monoxide unless the reaction is carried out in the presence of aluminum reagents.[7] With AlMe₃ an orange-red crystalline product with the composition W(CH)(CO)(PMe₃)₃(Cl)-(AlMe₃) was isolated; an analogous AlCl₃ complex was also obtained. No unambiguous structure could be assigned to these molecules, and thus a single-crystal X-ray diffraction analysis was performed on the AlCl₃ derivative.

Discussion

The structure of the complex, which turns out to be W-

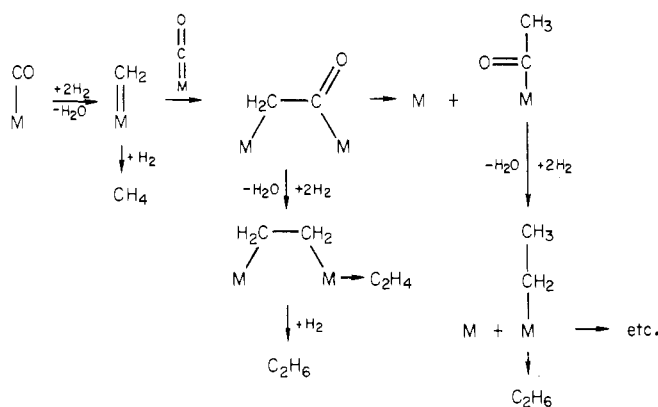(1) (a) Ford, P. C., Ed. "Catalytic Activation of Carbon Monoxide"; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 152. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (c) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (d) Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136. (e) Ponec, V. *Catal. Rev.—Sci. Eng.* **1978**, *18*, 151.
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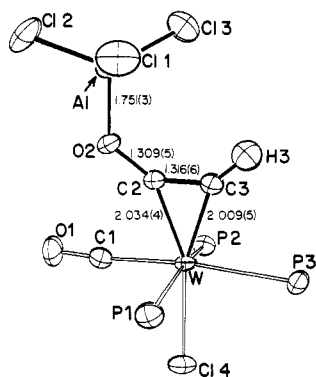(7) Churchill, M. R.; Wasserman, H. J.; Holmes, S. J.; Schrock, R. R. *Organometallics* **1982**, *1*, 766.

Scheme I

Table I. Interatomic Distances (Å) with Esd's for W(η²-HC≡COAlCl₃)(CO)(PMe₃)₃Cl[b]

(A) Distances from the Tungsten Atom			
W–P(1)	2.519 (1)	W–C(1)	1.984 (4)
W–P(2)	2.523 (1)	W···O(1)	3.132 (4)
W–P(3)	2.571 (1)	W–C(2)	2.034 (4)
W–Cl(4)	2.476 (1)	W–C(3)	2.009 (5)
W–Ac[a]	1.912		

(B) Distances within the HC≡COAlCl₃ and Carbonyl Ligands			
C(1)–O(1)	1.150 (6)	Al–Cl(1)	2.122 (2)
C(2)–O(2)	1.309 (5)	Al–Cl(2)	2.117 (2)
C(2)–C(3)	1.316 (6)	Al–Cl(3)	2.120 (2)
O(2)–Al	1.751 (3)	C(3)–H(3)	1.055 (52)

[a] Ac represents the midpoint of the C(2)–C(3) bond. [b] Distances within the PMe₃ ligands appear as supplementary data.

(η²-HC≡COAlCl₃)(CO)(PMe₃)₃Cl, is shown in Figure 1. Intramolecular distances and their associated estimated standard deviations (esd's) are listed in Table I; interatomic angles with esd's are given in Table II. A stereoscopic view of the molecule appears in Figure 2; a stereoview showing unit cell packing of the molecule is given in Figure 3.

The X-ray analysis shows that the complex results from coupling of the carbonyl and methylidyne moieties and suggests further that this process may be accelerated by coordination of the Lewis acid to a carbonyl oxygen atom. The molecule consists of an octahedral arrangement of three trimethylphosphines, a carbonyl, a chloride, and an anionic η²-HC≡COAlCl₃ ligand about a central tungsten(II) atom. The complex possesses approximate (i.e., *non*crystallographically imposed) $C_s(m)$ symmetry; the mirror plane contains all (except for two chlorine atoms) of the η²-HC≡COAlCl₃ lig-

Figure 1. Labeling of atoms in the W(η^2-HC≡COAlCl₃)(CO)-(PMe₃)₃Cl molecule. Methyl groups of the PMe₃ ligands have been omitted for clarity (ORTEP-II diagram; 30% ellipsoids). Selected bond lengths are given in Å.

and, the tungsten atom, and the chloride and carbonyl ligands and bisects one PMe₃ ligand.

The three PMe₃ ligands adopt a meridional arrangement in which the two mutually trans tungsten–phosphorus distances [W–P(1) = 2.519 (1) Å; W–P(2) = 2.523 (1) Å] are equivalent and significantly shorter than the trans-carbonyl W–P(3) distance of 2.571 (1) Å. This variation in metal–phosphorus distances is explicable in terms of the W–CO d$_\pi$–p$_\pi$ backbonding being substantially stronger than the W–P backbonding.

The η^2-HC≡COAlCl₃ ligand occupies a position almost directly trans to the chloride ligand, with Cl(4)–W–Ac = 176.3°. (Ac represents the midpoint of the C(2)–C(3) linkage.) Consequently, cis Ac–W–L angles are all obtuse, but more so for L = PMe₃ [Ac–W–P(1) = 98.9°; Ac–W–P(2) = 98.4°; Ac–W–P(4) = 96.7°] than for L = CO [Ac–W–C(1) = 90.2°]. The smaller spatial requirement of the carbonyl relative to those of the PMe₃ ligands is also evident from the deviation from linearity of the other "trans" angles about tungsten; viz., P(2)–W–C(1) = 173.01 (13)°, while P(1)–W–P(2) = 160.95 (4)°. Cis angles at tungsten subtended from Cl(4) are therefore all acute, with Cl(4)–W–P(1) = 81.19
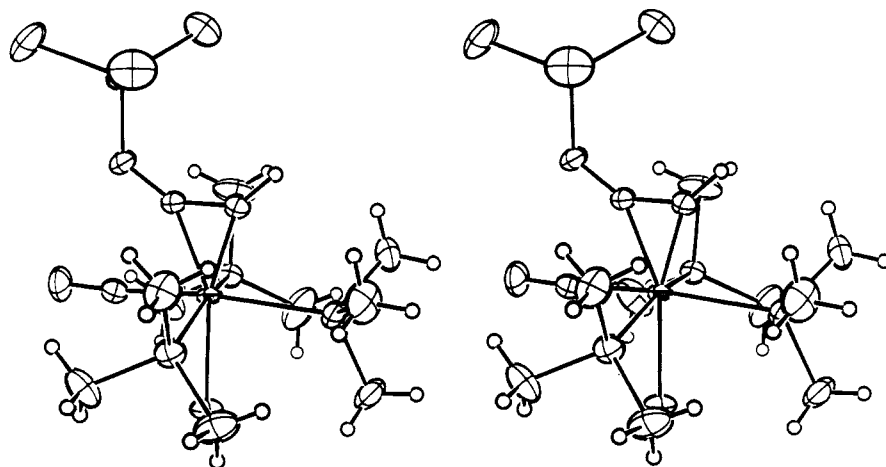
Figure 2. Stereoscopic view of the W(η^2-HC≡COAlCl₃)(CO)(PMe₃)₃Cl molecule. Hydrogen atoms are shown with artificially reduced thermal parameters for clarity.
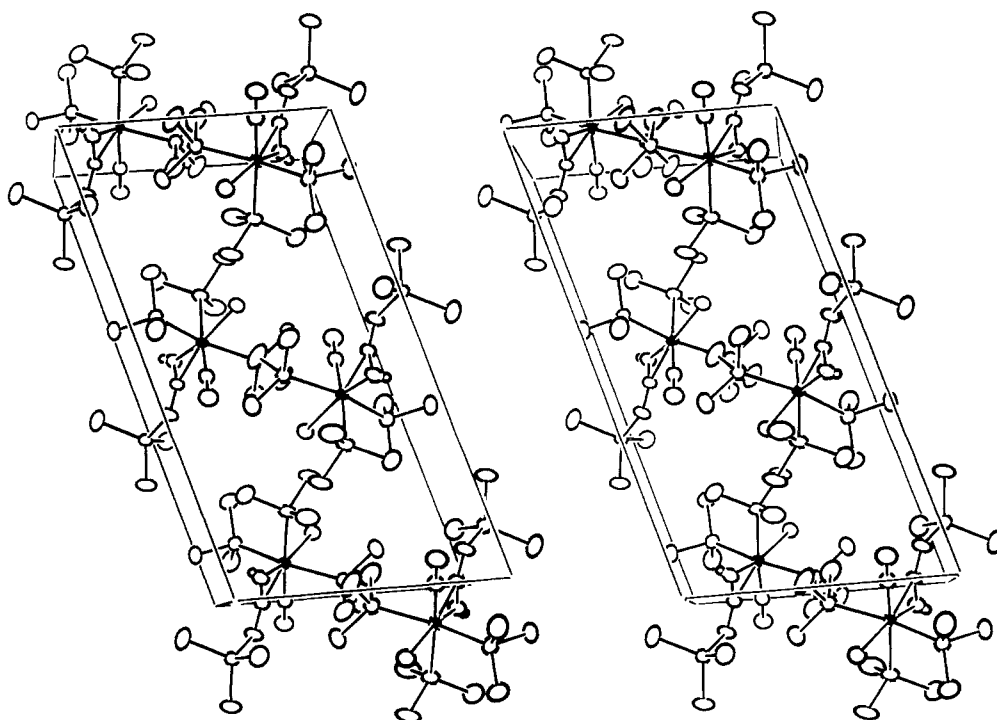
Figure 3. Stereoscopic view of the packing of W(η^2-HC≡COAlCl₃)(CO)(PMe₃)₃Cl molecules in the unit cell (*a* is horizontal and *c* is close to vertical).

Table II. Interatomic Angles (Deg) for
W(η^2-HC≡COAlCl$_3$)(CO)(PMe$_3$)$_3$Cl^a

	(A) Angles about Tungsten		
Ac-W-P(1)	98.9	Cl(4)-W-C(3)	164.61 (13)
Ac-W-P(2)	98.4	P(1)-W-P(2)	160.95 (4)
Ac-W-P(3)	96.7	P(3)-W-C(1)	173.01 (13)
Ac-W-C(1)	90.2	Cl(4)-W-Ac	176.3
Cl(4)-W-P(1)	81.19 (4)	C(2)-W-P(1)	97.94 (12)
Cl(4)-W-P(2)	81.06 (4)	C(2)-W-P(2)	95.79 (12)
Cl(4)-W-P(3)	86.98 (4)	C(2)-W-P(3)	115.59 (12)
Cl(4)-W-C(1)	86.01 (13)	C(2)-W-C(1)	71.35 (17)
P(1)-W-P(3)	92.39 (4)	C(3)-W-P(1)	98.88 (13)
P(2)-W-P(3)	93.52 (4)	C(3)-W-P(2)	100.07 (13)
P(2)-W-C(1)	84.73 (13)	C(3)-W-P(3)	77.63 (13)
P(1)-W-C(1)	87.21 (13)	C(3)-W-C(1)	109.32 (18)
Cl(4)-W-C(2)	157.41 (12)	C(2)-W-C(3)	37.99 (17)

	(B) Angles within the HC≡COAlCl$_3$ and Carbonyl Ligands		
H(3)-C(3)-C(2)	137.4 (28)	O(2)-Al-Cl(3)	108.72 (13)
H(3)-C(3)-W	150.6 (28)	O(2)-C(2)-W	146.6 (3)
C(3)-C(2)-O(2)	143.5 (4)	Cl(1)-Al-Cl(2)	111.34 (9)
C(2)-O(2)-Al	125.4 (3)	Cl(1)-Al-Cl(3)	110.62 (9)
O(2)-Al-Cl(1)	107.98 (13)	Cl(2)-Al-Cl(3)	112.70 (9)
O(2)-Al-Cl(2)	105.19 (13)	W-C(1)-O(1)	175.0 (4)

^{a} Angles within the PMe$_3$ ligands appear as supplementary data.

(4)°, Cl(4)-W-P(2) = 81.06 (4)°, Cl(4)-W-P(3) = 86.98 (4)°, and Cl(4)-W-C(1) = 86.01 (13)°. The tungsten atom is displaced 0.2631 (1) Å from the least-squares plane defined by atoms P(1)-P(3) and C(1) in a direction toward the acetylenic C(2)-C(3) system. (See Table III-S (supplementary material) for a list of selected least-squares planes.)

The W-CO bond length observed in W(η^2-HC≡COAlCl$_3$)(CO)(PMe$_3$)$_3$Cl, W-C(1) = 1.984 (4) Å, is only slightly longer than that found in the octahedral W(IV) complex W(=CHCMe$_3$)(CO)(PMe$_3$)$_2$Cl$_2$ [W-CO = 1.968 (4) Å],[8] in which the carbonyl is trans to a chloride ligand. A W-CO bond length of 1.957 (8) Å was observed for the single crystallographically ordered carbonyl in the [W-(CH$_2$PMe$_3$)(CO)$_2$Cl(PMe$_3$)$_3$$^+$][9] cation, in which the carbonyl is trans to the CH$_2$PMe$_3$ ligand and the central atom is (formally) W(II). The differences in these tungsten-carbon distances are too small to allow interpretation in terms of a significant trans effect.

The HC≡COAlCl$_3$ system, which binds to the complex through nearly equivalent distances of W-C(2) = 2.034 (4) Å and W-C(3) = 2.009 (5) Å, is best regarded as an acetylene derivative, rather than as a ketenoid derivative. The first significant point to be noted is that these tungsten-carbon distances are close to the average length of W=C *double* bonds found in tungsten alkylidene complexes [cf. W=C = 1.942 (9) Å[10a] in W(≡CCMe$_3$)(=CHCMe$_3$)(CH$_2$CMe$_3$)-dmpe; the W-C single bond length in this molecule is 2.258 (9) Å].

The "acetylenic" linkage, C(2)-C(3) = 1.316 (6) Å, is substantially greater than that in a free acetylene but is within the range expected for a coordinated acetylene.[10b] The HC≡COAlCl$_3$ ligand adopts the "cis-olefinic" geometry expected for coordinated acetylenes, with C(3)-C(2)-O(2) = 143.5 (4)° and C(2)-C(3)-H(3) = 137 (3)°. The X-ray-determined C(3)-H(3) distance of 1.05 (5) Å is reasonable.

The usual extreme valence-bond representations of acetylene coordination to a single transition metal are shown in structures **1** and **2**. In **1** the acetylene ligand acts as a 2-electron donor to an M^{n+} while in the "metallacyclopropene" description, **2**,
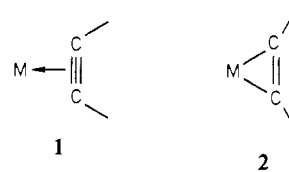
the acetylene is a 4-electron donor to an M$^{(n+2)+}$ ion.[11] The difference between **1** and **2** is merely formal, and a mixture of the two probably operates in all cases.

The present structural study of W(η^2-HC≡COAlCl$_3$)-(CO)(PMe$_3$)$_3$Cl indicates that an additional valence-bond description, **3**, must be invoked to adequately describe the
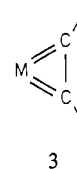
metal-acetylene bond. This "dicarbene" contribution was mentioned by Weiss et al.,[12] to account for average W-C distances of 2.03 ± 0.01 Å in W(CO)(C$_2$H$_2$)(S$_2$CNEt$_2$)$_2$, and was later used by Cotton and Hall[13] and by Churchill and Youngs,[14] to describe diphenylacetylene bonding in electron-deficient tantalum complexes. In each of these cases the acetylene ligand is assumed to donate 4 electrons, yielding a toal of 18 valence electrons in the tungsten-containing molecules and a 16-electron configuration in each tantalum species. Another very interesting example of 4-electron donation from an acetylene-like ligand occurs in the 16-electron species Ta(η^5-C$_5$Me$_5$)(η^2-C$_6$H$_4$)Me$_2$.[15]

It is interesting to note that the orientation of the η^2-HC≡COAlCl$_3$ ligand in the W(η^2-HC≡COAlCl$_3$)(CO)-(PMe$_3$)$_3$Cl molecule is such that it lies parallel with the bonding axis of the carbonyl ligand. This geometry was also found in the W(CO)(C$_2$H$_2$)(S$_2$CNEt$_2$) molecule[12] and was considered there as an important factor in the tungsten atom's ability to accept π-electron density from both of the mutually perpendicular acetylene π_g orbitals.

A theoretical "Frontier-orbital" treatment of metal-acetylene bonding has recently been completed[16] and shows the importance of $\pi(\perp)$ bonding in certain molecules.

The formulation of the HC≡COAlCl$_3$ ligand as determined in the X-ray analysis is in complete agreement with the spectroscopic data that have been reported for the W(η^2-HC≡COAlCl$_3$)(CO)(PMe$_3$)$_3$Cl molecule.[7] In particular, the C(2)-O(3) bond length of 1.309 (15) Å, significantly longer than that of a typical carbonyl, is consistent with a ν_{CO} stretch found at 1615 cm^{-1}. A distance of approximately 1.32 Å would be expected for a C(sp)-O(sp^3) bond;[17] the observed bond length does not differ significantly from this value. The HC≡COAl fragment is planar, with an rms deviation from planarity of only 0.008 Å.

The aluminum-oxygen bond length [Al-O(2) = 1.751 (3) Å; C(2)-O(2)-Al = 125.4 (3)°] is significantly shorter (and stronger) than the Al-O bond in molecules in which the AlX$_3$

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Table III. Experimental Data for the X-ray Diffraction Study of W(η^2-HC≡COAlCl$_3$)(CO)(PMe$_3$)$_3$Cl

(A) Crystal Parameters[a] at 24 °C

cryst system: monoclinic	$\beta = 105.880\ (15)°$
space group: $P2_1/c$	$V = 2497.1\ (9)$ Å^3
$a = 10.420\ (2)$ Å	$Z = 4$
$b = 12.896\ (2)$ Å	mol wt = 650.0
$c = 19.319\ (4)$ Å	ρ(calcd) = 1.73 g cm^{-3}

(B) Measurement of Data

radiation: Mo Kα ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite, equatorial
reflcns measd: $h,k,\pm l$
2θ range: 4.0–50.0°
scan type: coupled θ(cryst)–2θ(counter)
scan speed: 2.55° min^{-1}
scan range: $[2\theta(\text{Mo K}\alpha_1) - 0.9] - [2\theta(\text{Mo K}\alpha_2) + 0.9]°$
reflcns collected: 4684 total, yielding 4425 independent
stds: 3 every 97 reflcns; no significant changes in
    intensity observed
abs coeff: 55.5 cm^{-1}, reflcns corrected for absorption by an
    empirical method

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ component of 25 reflections, all with $2\theta = 27$–35°.

group acts as a bridge between the oxygen atom and the metal [e.g., Al–O = 1.81 (1) Å in $\overline{\text{Mn}(C(OAlBrBr_2)CH_3)(CO)_4}}$].[18] Comparison with molecules in which the oxygen atom is part of a carbonyl ligand shows the Al–O bond in the current structure to be shorter than that in R$_3$AlO≡CM systems, viz., Al–O = 2.00 (2) Å [C–O–Al = 155 (2)°] in Cp$_2$Fe$_2$(CO)$_2$-(μ-COAlEt$_3$)[19] and Al–O(average) = 1.827 ± 0.009 Å in Al[CpW(CO)$_3$]·3THF.[20] With respect to the former, Cp$_2$Fe$_2$(CO)$_2$(μ-COAlEt$_3$), with which comparison to the present structure is more appropriate, the longer Et$_3$Al–O bond is almost certainly due to the weaker acidity of AlEt$_3$ relative to that of AlCl$_3$.

Other features of the W(η^2-HC≡COAlCl$_3$)(CO)(PMe$_3$)$_3$Cl molecule are normal. Aluminum–chlorine distances range 2.117 (2)–2.122 (2) Å, O–Al–Cl angles range 105.19 (13)–108.72 (13)°, and Cl–Al–Cl angles range 110.62 (9)–112.70 (9)°. Finally, structural parameters associated with the PMe$_3$ ligands are unexceptional, with phosphorus–carbon distances in the range 1.806 (10)–1.828 (7) Å, W–P–Me angles ranging 111.6 (3)–121.1 (3)°, and Me–P–Me angles ranging 100.2 (4)–105.5 (4)°.

Experimental Section

Data Collection. A sample of the highly air- and moisture-sensitive material was kindly provided by Professor Richard R. Schrock and co-workers of MIT. Crystal mounting and examination with a binocular microscope was performed inside a specially modified inert-atmosphere drybox.[21] A crystal measuring approximately 0.28

Table IV. Final Positional and Isotropic Thermal Parameters for W(η^2-HC≡COAlCl$_3$)(CO)(PMe$_3$)$_3$Cl[a]

	x	y	z	B_{iso}, Å^2
W	0.30414 (1)	0.20553 (1)	0.07981 (1)	
P(1)	0.15678 (12)	0.09752 (10)	0.13531 (7)	
P(2)	0.49689 (11)	0.25934 (9)	0.03234 (6)	
P(3)	0.37737 (12)	0.32226 (10)	0.19160 (6)	
Cl(1)	−0.19063 (16)	0.34517 (15)	−0.06659 (10)	
Cl(2)	−0.10329 (17)	0.27413 (15)	−0.22259 (7)	
Cl(3)	0.05417 (16)	0.48602 (11)	−0.11781 (9)	
Cl(4)	0.47265 (11)	0.07933 (9)	0.14570 (6)	
Al	−0.03520 (13)	0.33827 (11)	−0.11808 (7)	
O(1)	0.23711 (36)	0.05047 (27)	−0.04988 (20)	
O(2)	0.08582 (30)	0.25151 (25)	−0.06991 (15)	
C(1)	0.26566 (40)	0.10404 (32)	−0.00043 (24)	
C(2)	0.15906 (40)	0.26475 (31)	−0.00374 (21)	
C(3)	0.18465 (44)	0.32951 (35)	0.05099 (24)	
C(11)	−0.01233 (56)	0.14996 (58)	0.11601 (39)	
C(12)	0.13228 (80)	−0.03322 (47)	0.09989 (44)	
C(13)	0.20464 (79)	0.07358 (71)	0.23208 (37)	
C(21)	0.44886 (86)	0.35965 (70)	−0.03523 (52)	
C(22)	0.65365 (68)	0.30251 (93)	0.09267 (44)	
C(23)	0.5541 (10)	0.15706 (61)	−0.01572 (60)	
C(31)	0.51512 (78)	0.28051 (65)	0.26608 (34)	
C(32)	0.43146 (90)	0.45118 (48)	0.17234 (39)	
C(33)	0.24942 (72)	0.35708 (67)	0.23559 (41)	
H(3)	0.1518 (47)	0.4032 (40)	0.0625 (27)	5.4 (12)

[a] The (refined) coordinates for the 27 hydrogen atoms of the PMe$_3$ groups appear in Table V-S (supplementary material).

× 0.30 × 0.45 mm was sealed into a glass capillary and was mounted on a Syntex P2$_1$ automated diffractometer; our use of this instrument has been described previously.[22] Crystal data and other parameters relevant to the data-collection process for the current analysis are listed in Table III.

Solution and Refinement. A Patterson synthesis allowed the determination of approximate coordinates for the tungsten atom. Several difference-Fourier calculations yielded the positions of all remaining atoms including all 28 hydrogen atoms. Full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$, led to final convergence, with $R_F = 3.2\%$, $R_{wF} = 3.0\%$, and GOF = 1.34. The final model, in which the positional and thermal (anisotropic for all non-hydrogen atoms) parameters for all 51 atoms were refined, consisted of 320 variables refined against all 4423 independent reflections (none rejected); NO:NV = 13.8:1. Final positional parameters are collected in Table IV. Final anisotropic thermal parameters for non-hydrogen atoms are listed in Table V-S (supplementary material).

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