

tion of ^{13}C O as the incoming ligand.

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Registry No. $\text{Co}_4(\text{CO})_9(\text{tripod})$, 75801-99-9; $\text{Co}_4(^{13}\text{C})_9(\text{tripod})$,

89958-44-1; $(\eta^6\text{-CH}_3\text{C}_6\text{H}_5)\text{Co}_4(\text{CO})_6(\text{tripod})$, 82264-80-0; ^{13}C O, 1641-69-6; CO, 630-08-0.

Supplementary Material Available: Tables of coordinates and isotropic thermal parameters for phenyl rings in $\text{Co}_4(\text{CO})_9(\text{tripod})$ and anisotropic thermal parameters, hydrogen coordinates, and structure factor amplitudes for $\text{Co}_4(\text{CO})_9(\text{tripod})$ (21 pages). Ordering information is given on any current masthead page.

Reactions of WCl_2L_4 (L = a Phosphine). 1.¹ A New Class of Tungsten(II) Ethylene Complexes

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WCl_2L_4 can be prepared by reducing WCl_4L_n with 2 equiv of sodium amalgam in the presence of L (L = PMe_3 , $n = 3$; L = PMe_2Ph and PMePh_2 , $n = 2$). Phosphine is displaced from WCl_2L_4 by ethylene to give first $\text{WCl}_2\text{L}_3(\text{C}_2\text{H}_4)$ (L = PMe_3) and then $\text{WCl}_2\text{L}_2(\text{C}_2\text{H}_4)_2$. $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ reacts with TIBF_4 , AlCl_3 , and AlMe_3 to give cationic complexes. The X-ray crystal structure of one of these, $[\text{WMe}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2][\text{ClAlMe}_2\text{Cl}_3]$, was determined. The crystals are monoclinic ($P2_1/n$) with $a = 9.922$ (2) Å, $b = 7.419$ (1) Å, $c = 29.241$ (4) Å, $\beta = 92.79$ (2)°, $V = 2150$ Å³, and $Z = 4$. The three-dimensional X-ray data were measured with the θ - 2θ scan technique with a scintillation detector. The structure was resolved by Patterson and Fourier methods and refined by full-matrix least-squares calculations to give $R(F_o) = 0.025$ and $R_w(F_o) = 0.032$ for 1362 observations above 2σ . The solid state structure consists of monomeric units with cis ethylenes, trans phosphines, and a weakly coordinated aluminate. NMR and conductivity data suggest the equilibrium in solution of this structure with an ionic complex formed by loss of the aluminate. The reaction of this complex with *t*meda (*N,N,N',N'*-tetramethylethylenediamine) or other Lewis bases gives neutral $\text{WMeCl}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ that loses Cl^- in polar, noncoordinating solvents.

Introduction

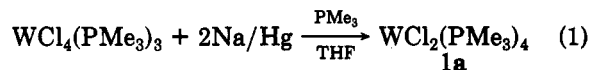
We recently communicated the preparation of $\text{WCl}_2(\text{PMe}_3)_4$ (**1a**) and its use to prepare tungsten methylidyne complexes² and a complex containing a W-W quadruple bond.³ We now wish to report the full details of the preparation of WCl_2L_4 (L = PMe_3 , PMe_2Ph , and PMePh_2) and reactions of these versatile starting materials with ethylene. The ethylene products and their derivatives comprise a new class of tungsten(II) ethylene complexes that, in a broader sense, are members of a group of W(II) and Mo(II) complexes which contain both π -acids and π -bases in their coordination sphere.

Such complexes have recently attracted attention from both a synthetic⁴ and a theoretical⁵ point of view. Many members of this group are considered unusual in that their formal electron count is only 16 yet they show low electrophilicity. This observation has been attributed to stabilization by π -donation from the π -base ligands.⁴ The new members reported here also follow this pattern but

in addition show a tendency to further decrease their electron count by the loss of ethylene, phosphine, or Cl^- . In one case the loss of Cl^- gives a stable, formally 14-electron complex with no π -base ligands in its coordination sphere.

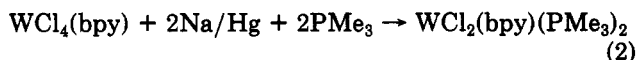
Results

Reduction of WCl_4L_n . Treating $\text{WCl}_4(\text{PMe}_3)_3$ with 2 equiv of sodium amalgam (0.4%) in the presence of PMe_3 gives high yields of $\text{WCl}_2(\text{PMe}_3)_4$ (**1a**, eq 1). Although **1a**



is paramagnetic ($\mu_{\text{eff}} = 2.3 \mu_B$), a single, broad resonance is observed in its ^1H NMR spectrum at 3.8 ppm, suggesting that the chlorides in **1a** are trans. Analogous complexes can be prepared with other phosphines by reducing WCl_4L_2 (L = PMe_2Ph and PMePh_2) in the presence of L, but the yields are lower and the products are harder to isolate.

A related complex, $\text{WCl}_2(\text{bpy})(\text{PMe}_3)_2$, results when $\text{WCl}_4(\text{bpy})$ is reduced in the presence of PMe_3 (eq 2). The



^1H NMR of this complex indicates that it too is paramagnetic. The ^1H NMR of this complex indicates that it too is paramagnetic. No signal for the bpy ligand could be detected, and the signal for the PMe_3 protons is found at -6 ppm. The fact that this signal is a virtual triplet

(1) Part 2 deals with hydride complexes derived from the addition of H_2 to $\text{WCl}_2(\text{PMe}_3)_4$. Frank, K. G.; Sharp, P. R., to be submitted for publication in *Inorg. Chem.*

(2) Sharp, P. R.; Holmes, S. J.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* 1981, 103, 965. Churchill, M. R.; Rheingold, A. L.; Wasserman, H. J. *Inorg. Chem.* 1981, 20, 3392.

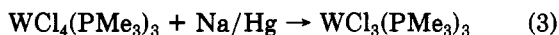
(3) (a) Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* 1980, 102, 1430. (b) Schrock, R. R.; Sturgeoff, L. G.; Sharp, P. R. *Inorg. Chem.* 1983, 22, 2801.

(4) Herrich, R. S.; Nieter-Burgmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* 1983, 105, 2599 and references cited therein.

(5) Kubacek, P.; Hoffmann, R. J. *J. Am. Chem. Soc.* 1981, 103, 4320.

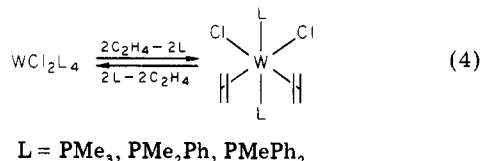
suggest that the PMe_3 ligands are *trans*⁶ in $\text{WCl}_2(\text{bpy})(\text{PMe}_3)_2$.

Finally, $\text{WCl}_3(\text{PMe}_3)_3$, a precursor to $\text{WCl}_2(\text{PMe}_3)_4$, can be isolated if only 1 equiv of sodium amalgam is used in the reduction of $\text{WCl}_4(\text{PMe}_3)_3$. No PMe_3 is required (eq 3). This complex is paramagnetic, as expected for its odd



electron count. While broad, its ^1H NMR spectrum indicates a *mer* geometry. (Two signals in a 2:1 ratio.)

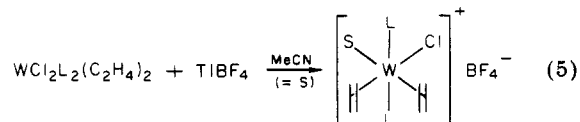
Ethylene Complexes. The phosphine ligands in WCl_2L_4 ($\text{L} = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2$) can be displaced by ethylene (but not by propylene) to give green, diamagnetic, $\text{WCl}_2\text{L}_2(\text{C}_2\text{H}_4)_2$ (2, eq 4). A brown, crys-



talline, paramagnetic complex can be isolated when $\text{L} = \text{PMe}_3$ by running the reaction at a lower temperature. It is believed to be $\text{WCl}_2(\text{PMe}_3)_3(\text{C}_2\text{H}_4)$ (3), but repeated attempts at elemental analysis gave variable results and only the PMe_3 could be found in its ^1H NMR spectra. Both reactions ($1 \rightarrow 3$ and $3 \rightarrow 2$) are reversible at 60°C when $\text{L} = \text{PMe}_3$. The second displacement does not occur as readily as the first and is suppressed as the concentrations of free PMe_3 increases during the course of the reaction. For this reason the reaction is best run in dilute solution so that the free PMe_3 concentration does not become large. Alternatively, the free PMe_3 can be removed as it forms by reaction with a Lewis acid (e.g., ZnCl_2). For larger and less basic phosphines the free phosphine concentration is not so critical and the displacement occurs more readily ($\text{PMePh}_2 > \text{PMe}_2\text{Ph} > \text{PMe}_3$). As a result, no monoethylene complexes were observed when $\text{L} = \text{PMe}_2\text{Ph}$ and PMePh_2 .

Two ^1H NMR signals are observed at 25°C for the ethylene ligands in 2. At higher temperatures the ethylene signals collapse and coalesce ($\Delta G^\ddagger = 17.9$ and 18.5 kcal mol^{-1} for $\text{L} = \text{PMe}_3$ and PMe_2Ph , respectively). A ^{13}C NMR spectrum of $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ indicates only one type of ethylene carbon atom and a ^{31}P NMR spectrum indicates only one type of PMe_3 . These data are consistent with a *cis* ethylene geometry as shown in eq 4. The "inside" and "outside" protons most likely interconvert at the higher temperatures by rotation of the ethylene ligands. Again, a virtual triplet signal for the phosphine protons suggests that the phosphines are *trans*.⁶

A solution of $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ in MeCN turns blue on addition of TIBF_4 . The blue solution turns red in a few minutes, and free ethylene can be detected by ^1H NMR. If ether is added to the blue solution, before it turns red, blue-green crystals of $[\text{WCl}(\text{MeCN})(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2]^+\text{BF}_4^-$, 4, can be isolated in moderate yield (eq 5, $\text{L} = \text{PMe}_3$). The

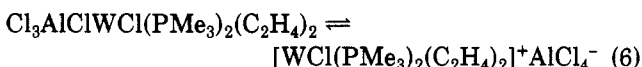


phosphine ligands in 4 are equivalent and most likely *trans*. The ^1H NMR spectrum of 4 at low temperatures shows four multiplet signals of area 2 each for four different sets

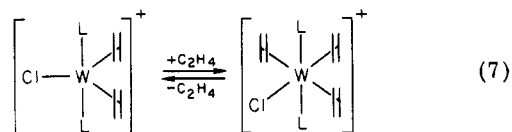
of ethylene protons. Two different, nonrotating ethylene ligands are therefore indicated. At higher temperatures two of the signals collapse and coalesce ($\Delta G^\ddagger = 11$ kcal mol^{-1}). One ethylene ligand must rotate more readily than the other. A structure consistent with these data is shown in eq 5.

$\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ does not react with TIBF_4 in non-coordinating solvents (e.g., dichloromethane). However, addition of 1 equiv of AlCl_3 to $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ in dichloromethane or chlorobenzene gives a royal blue solution from which red crystals of $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2(\text{AlCl}_3)$ (5) can be isolated. If *tmeda* is added to 5, $\text{AlCl}_3(\text{tmeda})$ forms and $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ is regenerated.

The ^1H NMR spectrum of 5 in CD_2Cl_2 shows one triplet for the phosphines and one triplet for the ethylenes, suggesting that the PMe_3 ligands are *trans* and that the ethylene protons are equivalent (due to rapid rotation of the ethylenes) and coupled to the phosphines. Upon cooling, the ethylene triplet collapses to two equal intensity multiplets ($\Delta G^\ddagger = 12$ kcal mol^{-1}), indicating that the ethylenes are probably *cis* as in the parent complex 2. By ^{31}P and ^{13}C NMR the phosphines and ethylenes are equivalent at all temperatures. In addition, solutions of 5 in CH_2Cl_2 are weakly conducting. These data suggest that the species in solution are trigonal-bipyramidal $[\text{WCl}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2]^+$ and AlCl_4^- . However, since solutions of 5 are only weakly conducting, an equilibrium process (rapid on the NMR time scale) involving association of the cation and anion is probably occurring (eq 6).



Other evidence for an ionic species being present is that when free ethylene is added to solutions of 5, only one broad ethylene signal is observed and it is shifted toward the position where the signal for free ethylene is found. In other words, free ethylene exchanges with coordinated ethylene in 5 (eq 7). (At low temperatures the equilibrium



in eq 7 must lie to the left since only 5 and free ethylene could be observed by NMR at -50°C .) Since free ethylene does not exchange with coordinated ethylene in the neutral parent at 25°C , the addition of AlCl_3 must open a coordination site by abstraction of a chloride. Finally, we note that the ethylene ligands rotate more readily in 5 than in the neutral parent ($\Delta G^\ddagger = 12$ vs. 17.6 kcal mol^{-1}) consistent with the reduced metal electron density of a cationic complex. (In this case the exchange process must be rotation since ^{31}P coupling to the ethylene is retained in the high-temperature limit.)

If $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ in CH_2Cl_2 is treated with AlMe_3 instead of AlCl_3 , a red solution results from which red crystals of 6 can be isolated in high yield. The ^1H NMR spectrum of 6 in CDCl_3 shows nonrotating, equivalent ethylene ligands, a phosphine triplet, and one methyl group that is strongly coupled to the phosphine ligands. Two other methyl groups are equivalent and are not coupled to the phosphines. Their broad signal suggests they are bound to the aluminum. Since solutions of this complex, like those of 5, are weakly conducting, a similar equilibrium between an ionic and a neutral form must exist and the species in solution on the NMR time scale must be trigonal bipyramidal $[\text{WMe}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2]^+$. When $\text{AlMe}_2\text{Cl}_2^-$

(6) Verkade, J. G. *Coord. Chem. Rev.* 1972, 9, 1.

Table I. Crystallographic and Data Collection Parameters^a

space group	$P2_1/c$	diffractometer	Enraf-Nonius CAD-4
a, Å	9.922 (2)	cryst size, mm	0.1 × 0.1 × 0.4
b, Å	7.419 (1)	λ , Å (Mo K α)	0.710 73
c, Å	29.241 (4)	μ , cm ⁻¹	61.4, transmission range 68.3–99%
β , deg	92.79 (2)	scan speed	variable to maintain 3% counting stats to a max time of 120 s/scan
V, Å ³	2149 (1)	θ -2 θ scan	96 steps/scan
p(calcd)	1.67	background	16 steps on each side of peak
Z	4	peak takeoff angle, deg	64 steps
f_w	535.11	scan width in θ (0.70 + 0.35 tan θ)	2.8
$R(F_o)$	0.025	2 θ max, deg	37.0
$R_w(F_o)$	0.032	hkl range	$\pm h, \pm k, \pm l$
no. of refl measd	1811	decay	1.00–1.42
unique data	1591	correctn range	
data/above 2 σ	1362		
no. of parameters refined	170		

^a Here and in following tables the numbers in parentheses are the estimated deviation in the least significant digit(s).

Table II. Positional Parameters for Non-Hydrogen Atoms

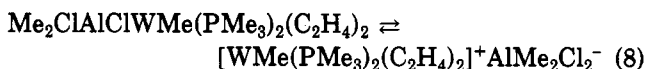
atom	x	y	z	B_{eqv} , Å ²
W	0.25571 (3)	0.20308 (6)	0.13277 (1)	2.736 (9)
Cl1	0.4731 (2)	-0.0287 (4)	0.11020 (8)	4.04 (6)
Cl*	0.7435 (3)	0.0687 (5)	0.1899 (1)	5.94 (8)
P1	0.2611 (3)	0.2994 (4)	0.05089 (9)	3.81 (7)
P2	0.2454 (3)	0.0018 (4)	0.20156 (3)	3.46 (6)
Al	0.6996 (3)	-0.0247 (5)	0.1202 (1)	3.82 (7)
CW	0.1716 (9)	-0.033 (1)	0.1011 (3)	3.9 (3)
C*	0.7691 (7)	0.158 (1)	0.0744 (3)	7.9 (2)
C2Al	0.759 (1)	-0.279 (1)	0.1138 (4)	5.8 (3)
C1P1	0.284 (1)	0.536 (2)	0.0378 (4)	7.3 (4)
C1E1	0.427 (1)	0.388 (1)	0.1349 (3)	4.4 (3)
C1P2	0.092 (1)	-0.128 (2)	0.2067 (3)	5.0 (3)
C1E2	0.0992 (9)	0.328 (1)	0.1713 (3)	3.9 (3)
C2P1	0.389 (1)	0.199 (2)	0.0168 (3)	5.4 (3)
C2E1	0.421 (1)	0.306 (1)	0.1785 (3)	3.9 (2)
C2E2	0.106 (1)	0.417 (1)	0.1281 (3)	4.5 (3)
C2P2	0.370 (1)	-0.174 (1)	0.2069 (4)	4.6 (3)
C3P1	0.108 (1)	0.254 (2)	0.0155 (4)	5.7 (3)
C3P2	0.263 (1)	0.104 (2)	0.2580 (3)	5.8 (3)

(actually $ClAlMe_xCl_{3-x}$, see structural results) coordinates, it must do so in such a way that the methyl group on

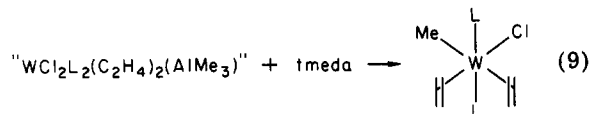
Table III. Selected Interatomic Distances (Å) and Angles (deg)

Bond Distances					
W-Cl1	2.861 (3)	W-CT1	2.075	P2-C2P2	1.799 (10)
W-P1	2.501 (3)	W-CT2	2.051	P2-C3P2	1.817 (11)
W-P2	2.511 (3)	Cl1-Al	2.252 (4)	Al-C*	2.047 (8)
W-CW	2.131 (10)	Cl*-Al	2.177 (4)	Al-C2Al	1.989 (11)
W-C1E1	2.183 (10)	P1-C1P1	1.814 (13)	C1E1-C2E1	1.417 (14)
W-C1E2	2.169 (9)	P1-C2P1	1.814 (10)	C1E2-C2E2	1.428 (14)
W-C2E1	2.202 (10)	P1-C3P1	1.826 (11)		
W-C2E2	2.174 (10)	P2-C1P2	1.818 (11)		
Bond Angles					
Cl1-W-P1	84.23 (8)	P1-W-CW	81.1 (3)	CT1-W-CT2	101.37
Cl1-W-P2	83.57 (8)	P1-W-CT1	96.94	C1E1-W-C2E1	37.7 (4)
Cl1-W-CW	71.9 (3)	P1-W-CT2	96.10	C1E2-W-C2E2	38.4 (4)
Cl1-W-CT1	77.53	P2-W-CW	80.2 (3)	CW-W-CT1	149.4
Cl1-W-CT2	178.88	P2-W-CT1	95.74	CW-W-CT2	109.2
P1-W-P2	160.1 (1)	P2-W-CT2	96.40	W-Cl1-Al	136.2 (1)

tungsten does not exchange with those on Al (eq 8).



Unlike the $AlCl_3$ complex 5, where adding tmeda regenerates the parent starting material, adding tmeda to 6 gives a new, dark green, pentane-soluble product that we have identified as $WMeCl(PMe_3)_2(C_2H_4)_2$ (7, eq 9, $L = PMe_3$). As expected for the structure shown in eq 9 two



different ethylene signals are observed in the ¹H and ¹³C NMR spectra of 7 in toluene at 30 °C. However, in $CDCl_3$ the sample must be cooled to -50 °C before two separate signals are observed. Corroborative ³¹P NMR data suggests that the different results in toluene and $CDCl_3$ arise from the rapid loss of Cl^- from 7 in $CDCl_3$ to give $[WMe(PMe_3)_2(C_2H_4)_2]^+ Cl^-$.

A final result, which confirms that $[WMe(PMe_3)_2(C_2H_4)_2]^+$ can form from 7, is that 7 reacts rapidly with $TiBF_4$ in CH_2Cl_2 to give red $[WMe(PMe_3)_2(C_2H_4)_2]^+ BF_4^-$ (8, eq 10, $L = PMe_3$) in an 80% yield. The NMR data



suggest that 8 has the structure shown in eq 10 and that the ethylene ligands do not rotate on the NMR time scale at 34 °C.

Solid-State Structure of $WMe(PMe_3)_2(C_2H_4)_2(ClAlMe_xCl_{3-x})$. In order to unambiguously establish the geometry of the bis(ethylene) complexes and to investigate the nature of the aluminates in the solid state, a single-crystal X-ray structure determination of 6 was performed. The experimental parameters and the crystal data are given in Table I. Table II gives the non-hydrogen atom fractional coordinates. The structure is shown in Figure 1, and the important bond distances and angles are noted in Table III. The overall geometry of the complex is that of a distorted octahedron with cis ethylenes and trans phosphines. The most notable feature is the Cl coordinated aluminate. The extremely long and presumably weak W-Cl bond involved in the bridge is consistent with the proposed loss of the aluminate in solution to generate $[WMe(PMe_3)_2(C_2H_4)_2]^+$. This bond distance of 2.861 (3) Å should be compared to that of typical terminal $W(II)-Cl$ bond distances which range from ca. 2.4 to 2.5 Å.⁷ Con-

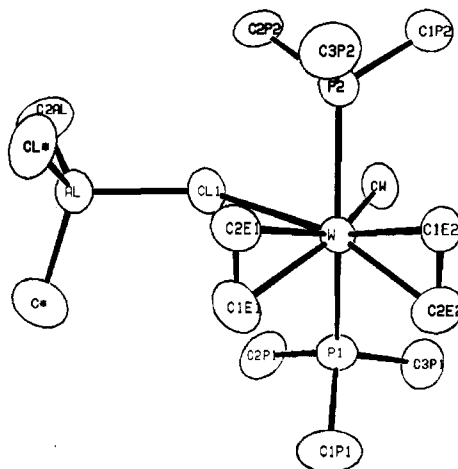


Figure 1. Perspective view of $\text{WMe}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2[\text{ClAlMe}_2\text{Cl}_{x-3}]_6$ (50% probability ellipsoids; C^* and Cl^* are composite images of carbon and chlorine).

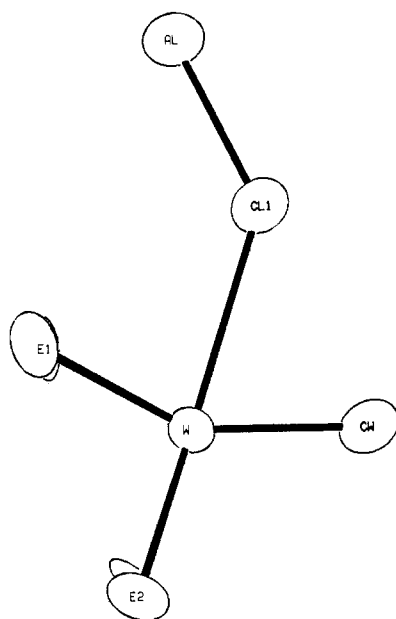


Figure 2. Perspective view down the P-W-P axis showing the long W-Cl bond and the distortion toward a trigonal-bipyramidal geometry. (The phosphine ligands and the other groups bound to Al have been omitted for clarity.)

sistent with a weak interaction of the aluminate with the W there is a strong distortion of the complex toward a trigonal-bipyramidal (TBPY) geometry as reflected in the angles in the plane perpendicular to the P-W-P axis (see Figure 2 and Table III). Despite this distortion, the atoms (W, CW, and Cl1) and the ethylene centroids (CT1 and CT2) do not deviate from the least-squares plane by more than 0.008 Å.

The P-W-P angle of 160° also shows deviation from the ideal octahedral (and TBPY) value. The phosphine ligands can be viewed as bending away from the ethylene ligands. This is apparent from the P1-W-Cl1, P2-W-Cl1 and P1-W-CW, P2-W-CW angles of 84.23 (8), 83.57 (8), 81.1 (3), and 80.3 (3)°, respectively; all less than 90°.

A complicating feature of the structure is a disorder at two of the terminal aluminate Me/Cl positions. Occu-

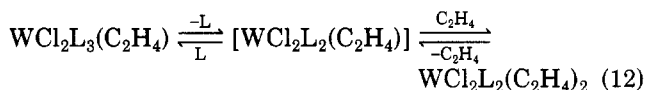
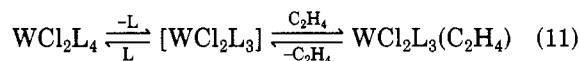
pancy refinement indicated that Cl^* is a composite image of 92% Cl and 8% C whereas C^* is a composite image of 75% C and 25% Cl. Since the C to Cl ratio is different at each site, a simple positional disorder model is inadequate. Instead the crystals can be considered to be composed of an isomorphous mixture of 67% $[\text{WMe}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2][\text{ClAlClMe}_2]$, 25% $[\text{WMe}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2][\text{ClAlCl}_2\text{Me}]$, and 8% $[\text{WMe}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2][\text{ClAlMe}_3]$.⁸ The presence of such a mixture in solution would not be detected since in all complexes loss of the aluminate gives the same cation. The solid-state composition might be expected to vary based on the crystallization conditions and the results of an elemental analysis on a different sample indicated a relative composition of ca. 25%, 75%, and 0% (see Experimental Section).

Discussion

Sodium reduction of molybdenum and tungsten halides has often been used for the preparation of low oxidation state complexes of these metals. In general, however, the metals have been reduced all the way to the zero oxidation level to give dinitrogen, ethylene, or CO complexes.⁹ Some exceptions are $\text{MoCl}_2(\text{dppe})_2$ (dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$)^{9a} and the molybdenum and tungsten hydrides MH_xL_y (L = a phosphine, $x = 2-6$, $y = 5-3$).¹⁰ However, the intermediates in the preparation of the hydrides may well be at the zero oxidation level.¹¹

The proposed trans structure for WCl_2L_4 is now well supported by the structural determination of a number of MX_2L_4 species¹² including the Ta analogue of 1, $\text{TaCl}_2(\text{PMe}_3)_4$.^{12a} One structural exception is $\text{Wl}_2(\text{PMe}_3)_4$ that is believed (by NMR) to have a cis geometry.¹³ The proposed *mer* structure of $\text{WCl}_3(\text{PMe}_3)_3$ is also supported by the structural determination of an isoelectronic complex, *mer*- $\text{MoCl}_3(\text{Py})_3$.¹⁴ This complex has been prepared by several routes including the reaction of $\text{Mo}_2\text{Cl}_4(\text{py})_4$ with pyridine.¹⁵ A similar complex, $\text{MoCl}_3(\text{THF})_3$, was prepared by reducing $\text{MoCl}_4(\text{THF})_2$ with Zn in $\text{CH}_2\text{Cl}_2/\text{THF}$. It reacts with phosphines (L) to give $\text{MoCl}_3(\text{THF})_x\text{L}_{3-x}$ ($x = 1, 2, \text{ or } 3$).^{9a,d}

The formation of the ethylene complexes is best explained by postulating five-coordinate, 14-electron intermediates (eq 11 and 12). Five-coordinate intermediates



should form most easily with the bulkier, less basic phosphines. This is consistent with our experimental

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observations on the ease of formation of the ethylene complexes ($L = PMePh_2 > PMe_2Ph > PMe_3$). Indeed, trimethylphosphine competes so strongly with ethylene that it is best to remove the PMe_3 as it is evolved in order to drive the reaction all the way to $WCl_2(PMe_3)_2(C_2H_4)_2$. We cannot, however, exclude the possibility of seven-coordinate intermediates. Both seven-coordinate and five-coordinate intermediates have been implicated in exchange reactions of formally isoelectronic $Mo(CO)(RC_2R')(S_2CNMe_2)_2$.¹⁶ (The acetylene is believed to stabilize the five-coordinate intermediate through π -donation, an option not present in the complexes studied here.)

Many structural analogues exist for the ethylene complexes reported here. For the five-coordinate, cationic, bis(ethylene) complexes the isoelectronic and isostructural Ta analogues $TaR(PMe_3)_2(C_2H_4)_2$ have been reported.¹⁷ In addition, since there seems to be some analogy between an ethylene ligand and an alkylidene or oxo or imido ligand, the Ta complexes $TaR(PMe_3)_2(CHCMe_3)_2$ ¹⁸ and the cationic W complexes $[WR(PR'_3)_2(O)(CHCMe_3)]^+^{19a}$ and $[WR(PR'_3)_2(NPh)(CHCMe_3)]^+^{20}$ can also be considered analogues of the five-coordinate bis(ethylene) complexes. Similarly, the six-coordinate complexes can be considered members of a large class of complexes that include $MoBr_2(CO)_2(PPh_3)_2$,²¹ $Mo(OBu)_2(py)_2(CO)_2$,²² $MoBr_2(PEt_3)_2(CO)(RC_2R')$,²³ $WCl_2(PR_3)_2(O)(CHCMe_3)$,¹⁹ $WCl_2(PR_3)(NPh)(CHCMe_3)$,²⁰ $WCl_2(PMe_3)_2(CHCMe_3)(CO)$,²⁴ $W(S_2CNMe_2)_2(O)(CHCMe_3)$,^{19a} and a variety of Mo and W cis dioxo, diimido, imido oxo, dicarbonyl, diacetylene, and acetylene carbonyl dithiocarbamate complexes^{4,25} (assuming a dithiocarbamate is analogous to a combination of a phosphine and a halide and that CO and acetylene are analogous to ethylene).

Experimental Section

General Procedures. All experiments were performed under a dinitrogen atmosphere in a VAC drybox or by Schlenk techniques. Solvents were dried and purified by standard techniques under dinitrogen. PMe_3 was prepared by the method of Wolfsberger and Schmidbaur²⁶ using dibutyl ether instead of diethyl ether, thus allowing the separation of the PMe_3 from the solvent by distillation. WCl_4L_2 were prepared by adding L to WCl_4 .²⁷ WCl_4 was prepared by McCarley's method as reported in ref 3b. Reagent grade tmeda was flushed with dinitrogen and passed down a column of grade I alumina. $AlMe_3$ and fresh, white free-flowing $AlCl_3$ were used as received.

NMR shifts are reported in parts per million referenced to Me_4Si for 1H and ^{13}C , to external H_3PO_4 for ^{31}P , and to CCl_3F

for ^{19}F (high field = positive ppm). The ^{13}C spectra were obtained in the gated decoupled mode except where noted. Only when the NMR spectra were run at relatively high fields or at temperatures different from 35 ± 5 °C are the particulars noted. Mass spectra were recorded on a Varian Matt 44 (direct inlet). All fragments displayed the correct isotope patterns. Magnetic susceptibilities were determined by the Evans method²⁸ in toluene at 60 MHz and 32 °C. Conductivity measurements were made with a Yellow Springs Model 3403 conductivity cell and a Serfass conductivity bridge.

Microanalyses were performed by using drybox techniques by Bernhardt or Schwartzkopf microanalytical labs.

Preparations. (1) $WCl_4(PMe_3)_3$. PMe_3 (18.8 mL, 198 mmol) was added to a stirred suspension of WCl_4 (19.54 g, 60 mmol) in 250 mL of CH_2Cl_2 at 0 °C. The stirred mixture was allowed to warm to 25 °C overnight. An aliquot was removed to check by 1H NMR for the presence of $WCl_4(PMe_3)_2$, and more PMe_3 was added as needed. The solution was filtered and reduced in vacuo to 20 mL, and 23.24 g of red crystals was removed by filtration. The filtrate was reduced to 5 mL in vacuo, and a second crop of 0.92 g was removed by filtration; total yield 24.16 g (73%). Traces of $W_2Cl_6(PMe_3)_4$ ³ were found in residues.

Anal. Calcd for $WC_9H_{27}Cl_4P_3$: C, 19.52; H, 4.91. Found: C, 19.71; H, 4.96. 1H NMR (CD_2Cl_2): δ -7.9 (br s, $\Delta\nu_{1/2} \approx 4$ Hz). The 1H NMR signal for $WCl_4(PMe_3)_2$ is a singlet at δ -24.5 ($\Delta\nu_{1/2} \approx 4$ Hz).

(2) WCl_2L_4 (1). (a) $L = PMe_3$. Sodium amalgam (0.4%, 112 g, 20 mmol of Na) was added to a stirred suspension of $WCl_4(PMe_3)_3$ (5.90 g, 10 mmol) in a mixture of THF (60 mL) and PMe_3 (1.1 mL, 11 mmol). After 2 h of stirring, the solution was decanted from the mercury pool and filtered through Celite. The pale brown filtrate was reduced to 5 mL in vacuo and filtered to give 350 g of orange crystals. All volatiles were removed from the filtrate in vacuo. The resulting residue was taken up in a minimum volume of toluene, and one volume of pentane was added. Cooling to -30 °C gave a second crop (0.43 g). A third crop (0.92 g) was obtained in a similar manner; total yield 4.85 g (87%). In THF the reaction sometimes gives poor yields. More consistent results are obtained in toluene or mixtures of toluene and ether. The progress of the reaction in toluene is easily monitored by 1H NMR.

Anal. Calcd for $WC_{12}H_{36}Cl_2P_4$: C, 25.78, H, 6.49. Found: C, 26.20; H, 6.48. 1H NMR (C_6D_6): δ 3.8 (br s, $\Delta\nu_{1/2} \approx 40$ Hz). Magnetic susceptibility: $\mu_{eff} = 2.3 \mu_B$. Mass spectrum: m/e 482 (parent - PMe_3), 406 (parent - $2PMe_3$). Also observed were fragments at m/e 443 ($WCl_3(PMe_3)_2$) and 367 ($WCl_3(PMe_3)$).

(b) $L = PMe_2Ph$. The procedure was the same as in 2a using $WCl_4(PMe_2Ph)_2$ and two equivalents of PMe_2Ph ; yield 44%.

(c) $L = PMePh_2$. The procedure was the same as in 2a using $WCl_4(PMePh_2)_2$ and two equivalents of $PMePh_2$; yield 32%.

(3) $WCl_2(bpy)(PMe_3)_2$. $WCl_4(bpy)$ (0.48 g, 1 mmol) was stirred with sodium amalgam (0.4%, 11.22 g, 2 mmol of Na) and PMe_3 (0.2 g, 2.2 mmol) in 5 mL of THF. After 1 h the dark red mixture was filtered through Celite and the solvent was removed from the filtrate in vacuo leaving 0.35 g (63%) of black crystals. Analytical quality crystals were grown from a mixture of dichloromethane and ether.

Anal. Calcd for $WC_{16}H_{26}Cl_2N_2P_2$: C, 34.13; H, 4.65. Found: C, 34.33; H, 5.10. 1H NMR (CH_2Cl_2): δ -6 (br t, $J = 7$ Hz, PMe_3).

(4) $WCl_3(PMe_3)_3$. $WCl_4(PMe_3)_3$ (1.11 g, 2 mmol) was added to THF (5 mL) and sodium amalgam (11.22 g, 0.4%, 2 mmol of Na) at -30 °C with stirring. The mixture was warmed to 25 °C while being shaken over a period of 10 min. The red-brown solution was decanted from the mercury and filtered through Celite. The solvent was removed from the filtrate in vacuo, and the resulting solid was taken up in a minimum volume of dichloromethane. Pentane was added to precipitate a small amount of $WCl_4(PMe_3)_3$. The solvent was removed from the filtrate in vacuo to give 0.6 g (68%) of $WCl_3(PMe_3)_3$ as brown needles. An analytical sample was obtained by addition of one volume of pentane to a saturated toluene solution and cooling to -30 °C.

Anal. Calcd for $WC_9H_{27}Cl_3P_3$: C, 20.85; H, 5.25. Found: C, 20.51; H, 5.91. 1H NMR (C_6D_6): δ -11 (very br s, $\Delta\nu_{1/2} \approx 80$ Hz, 9), -15 (very br s, $\Delta\nu_{1/2} \approx 80$ Hz). Magnetic susceptibility: μ_{eff}

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= 2.2 μ_B . Mass spectrum: m/e 519 (Parent), 443 (parent - PMe_3), 367 (parent - 2PMe_3).

(5) $\text{WCl}_2(\text{PMe}_3)_3(\text{C}_2\text{H}_4)$ (3). A solution of $\text{WCl}_2(\text{PMe}_3)_3$ (2.0 g, 3.58 mmol) in 5 mL of toluene was stirred under 30 psi of ethylene at 50 °C for 16 h. One volume of pentane was added, and 0.65 g of brown crystals was collected by filtration. A second crop of 0.41 g was obtained by cooling the filtrate to -30 °C. The solvent was removed from the filtrate in vacuo, and the residue was crystallized from toluene/pentane to give an additional 0.38 g; total yield 1.44 g (79%). This complex can be converted into $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ in the presence of ethylene or $\text{WCl}_2(\text{PMe}_3)_4$ in the presence of PMe_3 .

^1H NMR (C_6D_6): δ 2.32 (s, $\Delta\nu_{1/2} \approx 5$ Hz, 18, 2PMe_3), -13.1 (s, $\Delta\nu_{1/2} \approx 5$ Hz, 9, PMe_3). The ethylene signal was not located. Magnetic susceptibility: $\mu_{\text{eff}} = 1.6 \mu_B$. Mass spectrum: m/e 406 (parent - $\text{PMe}_3 - \text{C}_2\text{H}_4$). Also observed were fragments at m/e 443 ($\text{WCl}_3(\text{PMe}_3)_2$) and 367 ($\text{WCl}_3(\text{PMe}_3)$).

(6) $\text{WCl}_2\text{L}_2(\text{C}_2\text{H}_4)_2$ (2). (a) $\text{L} = \text{PMe}_3$. $\text{WCl}_2(\text{PMe}_3)_4$ (2.0 g, 3.58 mmol) was dissolved in 150 mL of toluene, and the solution was heated to 70 °C and stirred for 48 h under 30 psi of ethylene. The pressure was released, and the solvent was removed in vacuo. The residue was dissolved in a minimum volume of THF and cooled to -30 °C overnight. Large green needles (1.2 g) were removed by filtration. The filtrate was reduced in vacuo and cooled to give a second crop (0.22 g); total yield 1.42 g (75% based on $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2 \cdot \text{THF}$). Crystals free of THF were obtained from toluene/pentane. The reaction is accelerated by the addition of solid ZnCl_2 (dioxane).

Anal. Calcd for $\text{WC}_{10}\text{H}_{26}\text{Cl}_2\text{P}_2$: C, 25.94; H, 5.66. Found: C, 25.71; H, 5.58. ^1H NMR (C_6D_6 , 270 MHz): δ 2.67 (m, 4, C_2H_4), 1.29 (t, 18, $J_{\text{HP}} = 3.9$ Hz, PMe_3), 0.69 (m, 4, C_2H_4). The C_2H_4 signals coalesce at 95 °C; $\Delta G^\ddagger = 17.9$ kcal mol $^{-1}$. ^{13}C NMR (C_6D_6): δ 60 (t, $J_{\text{CH}} = 155$ Hz, C_2H_4), 14 (q of t, $J_{\text{CH}} = 130$ Hz, $J_{\text{CP}} = 15$ Hz, PMe_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 36.43 MHz, 30 °C): δ -24 (s with satellites, $J_{\text{PW}} = 177$ Hz). Mass spectrum: m/e 434 (parent - C_2H_4), 406 (parent - $2\text{C}_2\text{H}_4$), 358 (parent - $\text{PMe}_3 - \text{C}_2\text{H}_4$).

(b) $\text{L} = \text{PMe}_2\text{Ph}$. The procedure was identical with that in a except the reaction was done in benzene (2 equiv of PMe_2Ph was evolved), and the product was crystallized from toluene/pentane.

^1H NMR (C_6D_6): δ 2.70 (m, 4, C_2H_4), 1.72 (t, 12, $J_{\text{HP}} = 4$ Hz, PMe_2Ph), 0.58 (m, 4, C_2H_4). The C_2H_4 signals coalesce at 105 °C; $\Delta G^\ddagger = 18.5$ kcal mol $^{-1}$.

(c) $\text{L} = \text{PMePh}_2$. The procedure was the same in a except the reaction was done in benzene. The product was only observed by ^1H NMR. Two equivalents of PMePh_2 was evolved.

^1H NMR (C_6H_6): δ 3.10 (m, 4, C_2H_4), 2.08 (t, 6, $J_{\text{HP}} = 4$ Hz), 1.05 (m, 4, C_2H_4).

(7) $[\text{WCl}(\text{MeCN})(\text{PMe}_3)_2(\text{C}_2\text{H}_4)]^+\text{BF}_4^-$ (4). Solid TIBF_4 (0.32 g, 1.1 mmol) was rapidly added to a vigorously stirred solution of $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ (0.46 g, 1 mmol) in 5 mL of acetonitrile. After 30 s, 50 mL of ether were added and the mixture was quickly filtered. The solid was extracted with 10 mL of dichloromethane, and the volume of the resulting blue solution was reduced to 4 mL in vacuo. Ether (12 mL) was added, and the solution was cooled to -30 °C for 16 h and then filtered to give 0.33 g (59%) of blue-green crystals.

Anal. Calcd for $\text{WC}_{12}\text{H}_{26}\text{BCl}_4\text{NP}_2$: C, 25.95, H, 5.26. Found: C, 25.88; H, 5.36. ^1H NMR (CD_2Cl_2 , 270 MHz, -50 °C): δ 3.17 (m, 2, C_2H_4), 2.49 (t, 3, $J_{\text{HP}} = 1.6$ Hz, MeCN), 2.14 (m, 2, C_2H_4), 1.65 (t, 18, $J_{\text{HP}} = 4$ Hz, PMe_3), 1.24 (m, 2, C_2H_4), 1.02 (m, 2, C_2H_4). Upon warming, the two C_2H_4 signals coalesce and overlap with the C_2H_4 signal at 2.14 ppm; $T_c = -20$ °C, $\Delta G^\ddagger \approx 11$ kcal mol $^{-1}$. $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 132 (s, MeCN), 61 (s, C_2H_4), 14 (t, $J_{\text{CP}} = 16$ Hz, PMe_3), 4 (s, MeCN). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ -19 (s, with satellites, $J_{\text{PW}} = 168$ Hz).

(8) $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2(\text{AlCl}_3)$ (5). Pure, THF-free $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ (0.46 g, 1 mmol) was dissolved in 2 mL of dichloromethane and the solution was cooled to -30 °C. AlCl_3 (0.15 g, 1.1 mmol) was added with stirring. The resulting blue solution was warmed to 25 °C. Pentane (1 mL) was added, and the solution was rapidly filtered. The filtrate was cooled to -30 °C to give 0.1 g of cubic, dark red crystals. More pentane was added to the filtrate, and it was cooled to give a second crop (0.23 g); total yield 0.33 g (55%). The preparation is quantitative by NMR and can be reversed by the addition of tmeda or other Lewis bases.

^1H NMR (CD_2Cl_2 , 270 MHz, -60 °C): 2.10 (br m, 4, C_2H_4), 1.76 (t, 18, $J_{\text{HP}} = 4$ Hz, PMe_3), 0.77 (br m, 4, C_2H_4). The C_2H_4 signals coalesce to a triplet at 1.35 ppm ($J_{\text{HP}} = 4$ Hz) at ca. -10 °C; $\Delta G = 12$ kcal mol $^{-1}$. ^{13}C NMR (CD_2Cl_2 , 22.5 MHz, 0 °C): 55 (t, of t, $J_{\text{CH}} = 160$ Hz, $J_{\text{CP}} = 4.4$ Hz, C_2H_4), 14 (q of t, $J_{\text{CH}} = 129$ Hz, $J_{\text{CP}} = 16$ Hz, PMe_3). The spectrum was unchanged at -50 °C. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 36.43 MHz, 30 °C): δ 14 (s with satellites, $J_{\text{PW}} = 142$ Hz). Equivalent conductivity (10^{-3} M CH_2Cl_2): 22.

(9) $\text{WMe}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2(\text{ClAlMe}_x\text{Cl}_{3-x})$ (6). AlMe_3 (80 mg, 1.1 mmol) was added dropwise to a stirred solution of $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ (0.46 g, 1 mmol) in 1 mL of CH_2Cl_2 . The red solution was filtered, and 5 mL of pentane was added. An oil formed that crystallized upon scratching the glass. Filtration gave 0.43 g of red crystals. The filtrate was cooled to -30 °C to obtain a second crop of 0.05 g; total yield 0.48 g (89%).

Anal. Calcd for $\text{WC}_{12.3}\text{H}_{32.8}\text{AlCl}_{1.7}\text{P}_2$ (see Results): C, 26.80 H, 5.97. Found: C, 26.76; H, 6.16. ^1H NMR (CDCl_3 , 270 MHz, 10 °C): δ 1.73 (t, 18, $J_{\text{HP}} = 3.7$ Hz, PMe_3), 1.20 (m, 4, C_2H_4), 1.15 (t, 3, $J_{\text{HP}} = 15.9$ Hz, WMe), -0.03 (m, 4, C_2H_4), -0.81 (br s, AlMe_x). ^{13}C NMR (CDCl_3 , 22.5 MHz, 0 °C): δ 45 (t, $J_{\text{CH}} = 154$ Hz, C_2H_4), 14 (q of t, $J_{\text{CH}} = 127$ Hz, $J_{\text{CP}} = 15$ Hz, PMe_3). The methyl groups bound to aluminum and tungsten were not found. The tungsten methyl group was found in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at 58 ppm (br s). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ 11 (s with satellites, $J_{\text{PW}} = 132$ Hz). Equivalent conductivity (10^{-3} M CH_2Cl_2): 20.

(10) $\text{WClMe}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ (7). $\text{WCl}_2(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ (0.93 g, 2.0 mmol) was dissolved in 5 mL of dichloromethane. The solution was cooled to -30 °C, and AlMe_3 (0.14 g, 2 mmol) was added with stirring followed by tmeda (0.23 g, 2 mmol) in 1 mL of dichloromethane. The mixture was filtered, the volatiles were removed in vacuo, and the residue was extracted three times with 25 mL of pentane. The pentane was removed in vacuo and the residue dissolved in a minimum volume of toluene. One volume of pentane was added, and the mixture was cooled to -30 °C. Black crystals formed and were filtered off (0.32 g). The solvent was removed from the filtrate, and the residue was dissolved in a minimum of ether. This solution was cooled to -30 °C to give a second crop (0.28 g). A further 0.1 g was obtained by sublimation of the residues at 60-70 °C (1 μm); total yield 0.70 g (79%). $\text{WClMe}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ also can be prepared by adding tmeda to 6.

Anal. Calcd for $\text{WC}_{11}\text{H}_{26}\text{ClP}_2$: C, 29.85; H, 6.60. Found: C, 29.72; H, 6.43. ^1H NMR (CDCl_3 , 270 MHz, 10 °C): δ 1.69 (t, 18 $J_{\text{HP}} = 3.6$ Hz, PMe_3), 0.86 (t, 3, $J_{\text{HP}} = 13.4$ Hz, WMe), 0.10 (m, 4, C_2H_4). The other C_2H_4 signal could not be found. ^1H NMR (tol- d_8 , 250 MHz, 22 °C): 2.4 (br s, 2, C_2H_4), 1.34 (t, 18, $J_{\text{HP}} = 3.7$ Hz, PMe_3), 1.30 (br s, 2, C_2H_4), 0.62 (t, 3, $J_{\text{HP}} = 11.6$ Hz, WMe), 0.32 (br s, 2, C_2H_4), 0.01 (br m, 2, C_2H_4). Cooling the sample to -30 °C changes the C_2H_4 broad singlets into broad multiplets. ^{13}C NMR (tol- d_8 , 22.5 MHz, 0 °C): δ 53 (t, $J_{\text{CH}} = 156$ Hz, C_2H_4), 51 (t, $J_{\text{CH}} = 156$ Hz, C_2H_4), 41 (q of t, $J_{\text{CH}} = 120$ Hz, $J_{\text{CP}} = 10$ Hz, WMe), 14 (q of t, $J_{\text{CH}} = 129$ Hz, $J_{\text{CP}} = 14$ Hz, PMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_2 , 22.5 MHz, 0 °C): δ 49 (t, $J_{\text{CP}} = 4$ Hz, C_2H_4 and C_2H_4), 46 (t, $J_{\text{CP}} = 10$ Hz, WMe), 14 (t, $J_{\text{CP}} = 14$ Hz, PMe_3). At -40 °C two C_2H_4 signals are present, one at 49 and the other at 47 ppm. Both are broad singlets. $^{31}\text{P}\{^1\text{H}\}$ NMR (tol- d_8 , 36.2 MHz, 0 °C): δ -20 (s with satellites, $J_{\text{PW}} = 171$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 36.2 MHz, -20 °C): δ -13 (s with satellites, $J_{\text{PW}} = 164$ Hz).

(11) $[\text{WMe}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2]^+\text{BF}_4^-$ (8). TIBF_4 (0.29 g, 1 mmol) was added to a stirred solution of $\text{WClMe}(\text{PMe}_3)_2(\text{C}_2\text{H}_4)_2$ (0.44 g, 1 mmol) in 2 mL of dichloromethane. The red mixture was filtered and the volume was reduced to 1 mL. Ether (3 mL) was added and the solution was cooled to -30 °C for 16 h. The red crystals were isolated and dried in vacuo; yield 0.39 g (80%).

Anal. Calcd for $\text{WC}_{11}\text{H}_{26}\text{BF}_4\text{P}_2$: C, 26.76; H, 5.92. Found: C, 26.75; H, 5.91. ^1H NMR (CDCl_3 , 250 MHz, 22 °C): δ 1.70 (t, 18, $J_{\text{HP}} = 3$ Hz, PMe_3), 1.19 (t, 3, $J_{\text{HP}} = 15$ Hz, WMe), 1.09 (m, 4, C_2H_4), -0.14 (m, 4, C_2H_4). ^{13}C NMR (CDCl_3 , 62.83 MHz, 22 °C): 56 (q, $J_{\text{CH}} = 11$ Hz, WMe), 45 (t of t, $J_{\text{CH}} = 155$ Hz, $J_{\text{CP}} = 5$ Hz, C_2H_4), 14 (qt, $J_{\text{CH}} = 128$ Hz, $J_{\text{CP}} = 15$ Hz, PMe_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): δ -7 (s with satellites, $J_{\text{PW}} = 154$ Hz). ^{19}F NMR (CDCl_3): δ 159 (s, BF_4^-).

Structure Analysis. An outline of crystallographic and data collection parameters is given in Table I. Crystals were grown by adding toluene to a solution of the complex in $\text{CH}_2\text{ClCH}_2\text{Cl}$.

After examining upwards of 20 crystals from several different samples, only one was found to be of sufficiently high quality for data collection; all others showed evidence of twinning. Crystals from CH_2Cl_2 did not diffract at all. The crystal was mounted in a glass capillary under dinitrogen with the b axis nearly coincident with the diffractometer ϕ axis. Cell dimensions were based upon a Delaunay reduction of a cell obtained from the centering of 25 reflections on the diffractometer.

Intensity data (294 K) were measured by the θ - 2θ step scan technique with Mo $K\alpha$ radiation from a graphite monochromator. A total of 1811 Bragg reflections were measured before excessive decomposition of the crystal in the X-ray beam halted data collection. The intensities of three standard reflections were measured after each 7200 s exposure to the X-rays and were used to correct for the approximately 40% intensity decay which occurred during the experiment. The correction ranged from 1 to 1.42. Empirical absorption corrections were made with the ω scan technique ($\mu = 61.4$). Averaging of equivalent reflection gave 1591 data points of which 1325 had $F_o > \sigma(F_o^2/2F_o)$; these were used to refine the structure ($\sigma^2(F_o^2) = \sigma^2$ counting + $(0.05F_o^2)^2$ and $\sigma(F_o) = \sigma(F_o^2)/2F_o$).

The structure was resolved by Patterson and Fourier methods. Least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$, converged with $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.025$ and $R_w = [\sum (|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.032$. Hydrogen atoms were placed in "ideal" X-ray positions²⁹ based on the location of at least one peak in a reasonable hydrogen atom position for each hydrogen bearing group. No extinction correction was applied. The

occupancy refinement and calculations followed the procedure reported in ref 2.

The maximum parameter shift on the last cycle was less than 0.01 times its esd, and the error in an observation of unit weight was 1.06. Atomic scattering factors were taken from ref 30. Final atomic positional parameters are included in Table II. Selected interatomic bond distances and angles are given in Table III.

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Registry No. 1a, 85798-76-1; 1b, 39049-86-0; 1c, 90245-62-8; 2a, 90245-65-1; 2b, 90245-66-2; 2c, 90245-67-3; 3, 90245-64-0; 4, 90245-69-5; 5, 90245-70-8; 7, 90245-72-0; 8, 90319-41-8; WCl_4 -(Peme)₃, 73133-10-5; $\text{WCl}_2(\text{bpy})(\text{PMe}_3)_2$, 90245-63-9; $\text{WCl}_4(\text{bpy})$, 12116-41-5; $\text{WCl}_3(\text{PMe}_3)_3$, 73133-11-6.

Supplementary Material Available: A listing of structure factor amplitudes, a table of calculated hydrogen atom positional parameters, and a table of thermal parameters (10 pages). Ordering information is given on any current masthead page.

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Conversion of a (Methoxymethyl)iridium(I) Acetylene Complex to a Metallacyclobutene Iridium(III) Complex. Crystal and Molecular Structures of $\text{Ir}(\text{CH}_2\text{OCH}_3)(p\text{-tol-C}\equiv\text{C-}p\text{-tol})(\text{PMe}_3)_3$ and $\text{fac-Ir}[\text{CH}_2\text{C}(p\text{-tol})=\text{C}(p\text{-tol})]\text{Br}(\text{PMe}_3)_3$ [†]

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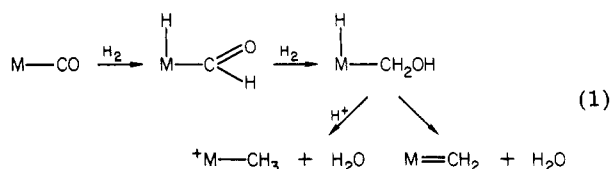
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The (methoxymethyl)iridium(I) acetylene complex $\text{Ir}(\text{CH}_2\text{OCH}_3)(p\text{-tol-C}\equiv\text{C-}p\text{-tol})(\text{PMe}_3)_3$ (1) reacts with bromotrimethylsilane to form the iridium(III) metallacyclobutene complex $\text{fac-Ir}[\text{CH}_2\text{C}(p\text{-tol})=\text{C}(p\text{-tol})]\text{Br}(\text{PMe}_3)_3$ (2). A methyleneiridium(I) complex is believed to be involved in the reaction. The kinetic product 2 thermally isomerizes to the *mer*-metallacyclobutene 3. Crystal structures of compounds 1 and 2 have been completed. Compound 1 (-100 °C): orthorhombic, space group $Pbca$, $a = 18.310$ (2) Å, $b = 17.696$ (3) Å, $c = 18.408$ (2) Å, $V = 5964$ (2) Å³, $Z = 8$. Compound 2 (-100 °C): monoclinic, space group $P2_1/n$, $a = 23.279$ (5) Å, $b = 8.579$ (3) Å, $c = 16.273$ (4) Å, $\beta = 103.97$ (2)°, $V = 3154$ (2) Å³, $Z = 4$. Final conventional and weighted agreement indices on F_o are 0.034 and 0.030 for compound 1 (3283 reflections with $F_o > 3\sigma(F_o)$) and 0.031 and 0.038 for compound 2 (4827 reflections with $F_o > 2\sigma(F_o)$). The important structural features of compound 1 are the $\text{IrCH}_2\text{-O}$ distance (1.449 (9) Å) and the $\text{C}\equiv\text{C}$ distance (1.30 (1) Å). The metallacyclobutene ring of compound 2 is planar with Ir-C distances of 2.134 (5) and 2.166 (6) Å and C-C distances of 1.344 (8) and 1.525 (7) Å.

Introduction

Transition-metal-bound carbene or alkylidene groups may participate in a number of important organometallic reactions, particularly olefin metathesis¹ and olefin polymerization.² Furthermore, methylene may play a key role in the Fischer-Tropsch process, both in CO reduction and the formation of multicarbon species (possibly by the reactions of eq 1 and 2).³ To understand how the carbene



or alkylidene group may be involved in the formation of new carbon-hydrogen or carbon-carbon bonds, we have been studying electrophilic methylene complexes of iridium. Our interest in such compounds arises from our

[†]Contribution No. 3339.