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Facile Conversion of Tungsten(VI) Neopentylidyne Complexes into Oxo and Imido Neopentylidene Complexes and the Crystal Structure of $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$[1]

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Tungsten(VI) neopentylidyne complexes react with water to give six-coordinate oxo neopentylidene complexes of the type $W(O)(CHCMe_3)L_2Cl_2$ ($L = PMe_3$ or PEt_3). If an amine is used, amido neopentylidyne complexes, $W(CCMe_3)(NHR)L_2Cl_2$ (R = Ph or H) can be isolated. At 70 °C in toluene these can be converted into the imido neopentylidene complexes, $W(CHCMe_3)(NR)L_2Cl_2$ ($\Delta G^{\ddagger} = 22 \pm 4$ kcal mol^{-1} for R = Ph and $L = PEt_3$). The reaction follows first-order kinetics and is unaffected by addition of PEt_3 or changing the solvent to chloroform or bromobenzene. The analogous phosphido complex, $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$, has also been prepared. It cannot be transformed readily into hypothetical $W(CHCMe_3)(PPh)(PEt_3)_2Cl_2$, in spite of the fact that the planar phosphido ligand is cis to the neopentylidyne ligand and its α-proton is pointed toward the neopentylidyne α-carbon atom as determined by an X-ray diffraction study. Crystals of $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$ belong to the centrosymmetric orthorhombic space group *Pnam* (D_{2h}^{16}; No. 62) with $a = 22.693$ (13) Å, $b = 8.545$ (1) Å, $c = 15.082$ (4) Å, $V = 2924.6$ (20) Å^3, and ρ(calcd) = 1.52 g cm^{-3} for $Z = 4$ and mol wt = 669.4. The structure was refined by full-matrix least-squares methods to $R_F = 2.8\%$ and $R_{wF} = 2.9\%$ for all 2007 absorption-corrected point-group independent reflections having $2\theta_{MoK\alpha} < 50°$ (none rejected). The molecule possesses precise (crystallographically imposed) mirror symmetry. The central tungsten atom is in a distorted octahedral coordination environment, which consists of mutually trans PEt_3 ligands (W–P(2) = W–P(2′) = 2.556 (1) Å), two mutually cis chloride ligands, a neopentylidyne ligand (W≡C = 1.808 (6) Å, and a phenylphosphido ligand (W–P = 2.291 (1) Å). Space group symmetry requires the entire W(PHPh) system to be precisely planar.

Introduction

There has been considerable progress in the last 2 years in understanding the mechanism of the olefin metathesis reaction.[3] An example is the discovery of well-defined oxo alkylidene complexes of W(VI) which will metathesize olefins.[4] Other workers have shown that oxo alkyl complexes are important metathesis catalyst precursors (presumably precursors to oxo alkylidene complexes) and that Lewis acids that bind to the oxo ligand can rapidly increase the rate of formation of an alkylidene ligand and probably also increase the rate of olefin metathesis.[5a] Theoretical studies also support the theory that oxo alkylidene complexes are likely to be an important type of tungsten-based olefin metathesis catalsyt.[6] Recently it has been shown that two alkoxide ligands can take the place of the oxo ligand.[5b]

One question which still has not been answered satisfactorily (in part because there may be no single answer) is what is the origin of the initial alkylidene ligand? Some version of α-hydrogen abstraction[7] is one of the most attractive routes to the initial alkylidene complex, especially since it now seems possible that α-hydrogen processes can compete with, or even be favored over, β-hydrogen processes.[8,9] But an *alkylidyne* complex, $W(CCMe_3)(CH_2CMe_3)_3$, is the product of the reaction between $LiCH_2CMe_3$ and WCl_6,[10] and other alkylidyne complexes (with the metal often in a lower oxidation state) appear to form under a variety of conditions.[11] Therefore it would be interesting if alkylidyne complexes could be precursors to oxo (or imido[12]) alkylidene complexes. In this paper we show that this is the case. We also show that phosphinidene alkylidene complexes *cannot* be prepared by analogous methods.

Results

Oxo neopentylidene complexes so far have only been prepared indirectly by transferring a neopentylidene ligand from tantalum to tungsten.[4c] With the discovery of neopentylidyne complexes such as $[NEt_4][W(CCMe_3)Cl_4]$[13,14]

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[1] Multiple Metal Carbon Bonds. 29. For part 28 see ref 12.

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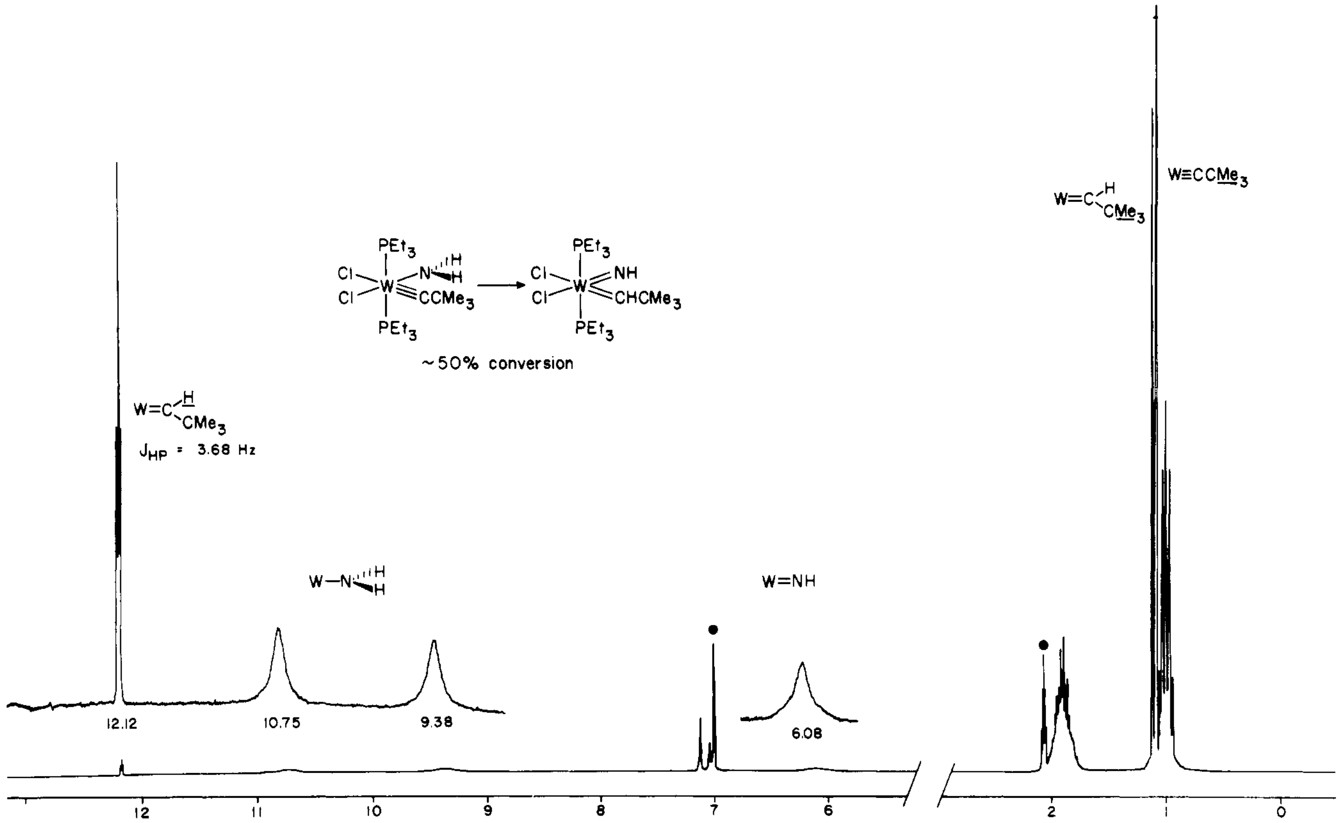
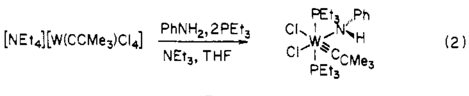


Figure 1. The 250-MHz ^{1}H NMR spectrum of a mixture (~1:1) of $W(CCMe_3)(NH_2)(PEt_3)_2Cl_2$ and $W(CHCMe_3)(NH)(PEt_3)_2Cl_2$ at 350 K in toluene-d_8 (●).

came the opportunity of forming a neopentylidene ligand by protonating a neopentylidyne ligand. Indeed, oxo neopentylidene complexes can be formed quantitatively from $[NEt_4][W(CCMe_3)Cl_4]$ in the presence of PR_3, water, and triethylamine, as shown in eq 1.[15] Alternatively, oxo neopentylidene complexes can be prepared by using lithium hydroxide instead of NEt_3/H_2O. In no case have we been able to observe the logical intermediate, a hydroxo neopentylidyne complex.

$$[NEt_4][W(CCMe_3)Cl_4] \xrightarrow[NEt_3,\ THF]{2PEt_3,\ H_2O} W(O)(CHCMe_3)(PEt_3)_2Cl_2 + NEt_3HCl + NEt_4Cl \quad (1)$$

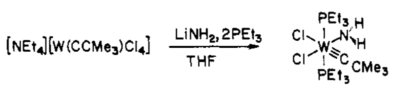
Imido neopentylidene complexes[12] appear to be similar to oxo neopentylidene complexes, even to the point of metathesizing olefins.[16] However, when $[NEt_4][W(CCMe_3)Cl_4]$ is treated with aniline and triethylamine the product is a red-orange amido neopentylidyne complex rather than the known[12] yellow imido neopentylidene complex (eq 2). The fact that the amido ligand is an excellent π-electron donor[17] would suggest that it is planar and, in order not to compete with the formation of the W≡C bond, that it is cis to the neopentylidyne ligand. This argument was also used to rationalize the fact that the oxo ligand (also a good π-electron donor ligand which is essentially triply bound to the metal[18]) and the neopentylidene ligand in $W(O)(CHCMe_3)(PMe_3)_2Cl_2$ are also cis to one another.[4] The triplet signal for the neopentylidyne α-carbon atom is found at 300.5 ppm (J_{CP} = 12 Hz) in the ^{13}C NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum consists of a sharp singlet at 16 ppm (J_{PW} = 276 Hz) which is unaffected by addition of free PEt_3. The amido proton is found as a broad singlet at 13.2 ppm in the ^{1}H NMR spectrum. If rotation of the amido ligand about the W≐N bond is slow on the NMR time scale (a fact which is true for the analogous WNH_2 complex; see later), then two isomers (phenyl group pointing in and phenyl group pointing out) are possible. So far we have seen only one isomer.



A PMe_2Ph complex analogous to that shown in eq 2 can be prepared straightforwardly by a similar method. Its ^{1}H NMR spectrum shows that the phosphine's methyl groups are inequivalent, as expected.

Five-coordinate $W(CCMe_3)(NHPh)(PEt_3)Cl_2$ can be prepared from $W(CCMe_3)(PEt_3)Cl_3$ and LiN(H)Ph (or $PhNH_2$ in the presence of NEt_3). Unfortunately, $W(CCMe_3)(NHPh)(PEt_3)Cl_2$ is a non-sublimable oil and therefore is not readily purified. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance at 40 ppm (J_{PW} = 308 Hz) and a signal ascribable to a small amount of the bis(phosphine) complex, $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$, at 16 ppm. The $^{13}C\{^1H\}$ NMR spectrum of $W(CCMe_3)(NHPh)(PEt_3)Cl_2$ shows a doublet signal for the alkylidyne α-carbon atom at 304.6 ppm (J_{CP} = 12 Hz).

The unsubstituted amido complex, $W(CCMe_3)(NH_2)(PEt_3)_2Cl_2$, can be prepared as shown in eq 3. Since $LiNH_2$ is not very soluble in THF, the reaction is slow (~8 h).



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(15) J. Wengrovius prepared the first oxo neopentylidene complex from a neopentylidyne complex by treating $W(CCMe_3)(PMe_3)_3Cl_3$[14] with 1 equiv of water in dichloromethane. The products are $W(O)(CHCMe_3)(PMe_3)_2Cl_2$ and PMe_3HCl in quantitative yield.

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Table I. Kinetic and Thermodynamic Parameters for Decomposition of $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$ to $W(CHCMe_3)(NPh)(PEt_3)_2Cl_2$ in Toluene-d_8[a]

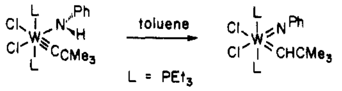
T, K	$10^3(1/T)$	10^3k, min^{-1}	$-\log k$	$t_{1/2}$, min
350	2.857	55.5	1.26	12
347	2.882	33.7	1.47	21
346	2.890	30.2	1.52	23
343	2.915	25.6	1.59	27
338	2.959	9.9	2.00	70
334	2.994	6.0	2.22	116
329	3.039	2.3	2.64	301

$\log A = 20 \pm 2$
$E_a = 34 \pm 3$ kcal mol^{-1}
$\Delta G^{\ddagger} = 22 \pm 4$ kcal mol^{-1}
$\Delta H^{\ddagger}$ (343 K) $= 33 \pm 3$ kcal mol^{-1}
$\Delta S^{\ddagger}$ (343 K) $= 31 \pm 9$ eu

[a] The difference between the largest and smallest possible slopes in the Arrhenius plot were used to estimate the error in k (±10%). Temperatures are accurate to ±0.5 degrees.

Signals for the amido protons are found at 9.4 and 10.8 ppm in the 250-MHz ^{1}H NMR spectrum (Figure 1). Therefore the amido ligand is not freely rotating about the W$\overset{\cdots}{=}$N bond on the ^{1}H NMR time scale. The amido protons probably lie in the plane which includes the neopentylidyne α-carbon atom, the amido nitrogen atom, and the chloride ligands.

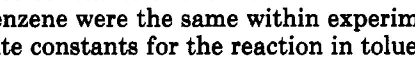
When $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$ is heated to 70 °C in toluene, the known yellow imido neopentylidene complex forms quantitatively (eq 4). This reaction can be monitored by ^{1}H NMR and the rate of conversion measured by integrating the ortho proton signals in the spectrum of a mixture of the two compounds (see Experimental Section). The reaction is first order in metal through 3 half-lives. In toluene-d_8 the measured rate constants were 2.8×10^{-2} and 3.0×10^{-2} min^{-1} for solutions 0.03 and 0.30 M in tungsten, respectively. These rate constants are the same within experimental error (±10%). Rate constants determined at various temperatures along with thermodynamic parameters derived from an Arrhenius plot are given in Table I.



(4)

The conversion of $W(CCMe_3)(NHPh)L_2Cl_2$ to $W(CHCMe_3)(NPh)L_2Cl_2$ is a well-behaved reaction. At 343 K the rate constants of the reaction in chloroform-d or bromobenzene were the same within experimental error as the rate constants for the reaction in toluene. At 338 K in toluene-d_8 (0.15 M in W) k was independent of PEt_3 concentration (0.77 M = 5 equiv; 1.54 M = 10 equiv). Therefore, we cannot propose that loss of either PEt_3 or Cl^- is an important part of this process. However, if 10 equiv of NEt_3 are added to a solution of $W(CCMe_3)(NHPh)L_2Cl_2$, the rate of its conversion to $W(CHCMe_3)(NPh)L_2Cl_2$ increases tenfold.

The above finding suggested that a strong base might deprotonate or dehydrohalogenate $W(CCMe_3)(NHPh)L_2Cl_2$. We have found this to be the case using $Ph_3P{=}CH_2$ (eq 5). Red $W(CCMe_3)(NPh)(PEt_3)_2Cl$ is a potentially interesting species since the imido ligand should not be able to fully donate its π-electron pair to tungsten in competition with the neopentylidyne ligand. Therefore, the imido ligand should be bent and relatively basic compared to a linear imido ligand.[17] Nevertheless, the neopentylidyne ligand in $W(CCMe_3)(NPh)(PEt_3)_2Cl$ is protonated more readily, perhaps because the imido ligand in $W(CHCMe_3)(NPh)(PEt_3)_2Cl_2$ thereby *can* donate its π-electron pair to the metal. $W(CCMe_3)(NPh)(PEt_3)_2Cl$ reacts in less than 1 min with HCl to give $W(CHCMe_3)(NPh)(PEt_3)_2Cl_2$. $W(CCMe_3)(NPh)(PEt_3)_2Cl$ can also be converted to $W(CHCMe_3)(NPh)(PEt_3)_2Cl_2$ in benzene by using NEt_3HCl, but presumably because NEt_3HCl is not very soluble in benzene, the reaction requires 3 h at 55 °C to go to completion.



(5)

The monophosphine amido complex, $W(CCMe_3)(NHPh)(PEt_3)Cl_2$, *cannot* be readily converted into $W(CHCMe_3)(NPh)(PEt_3)Cl_2$. When a sample of W-

Table II. Experimental Data for the X-ray Diffraction Study of $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$

(a) Crystal Data[a] at 24 °C

crystal system: orthorhombic
space group: *Pnam*
$a = 22.693$ (13) Å
$b = 8.545$ (1) Å
$c = 15.082$ (4) Å
$V = 2924.6$ (20) Å^3
$Z = 4$
mol wt = 669.4
ρ(calcd) = 1.52 g cm^{-3}

(b) Measurement of Intensity Data

radiation: Mo Kα ($\bar{\lambda} = 0.710730$ Å)
reflections measd: $+h,+k,\pm l$
scan type: coupled θ(crystal)-2θ(counter)
2θ range: 4.0-50.0°
scan speed: 2.55° min^{-1}
scan width: $[C + (K\alpha_1 - K\alpha_2)]°$ ($C = 2.0°$)
reflections collected: 3845 total yielding 2007 point group unique data
data averaging: $R_I = 1.91\%$ for 1827 reflections having two or more contributors
absorption coeff: 45.3 cm^{-1}

[a] Unit cell parameters were obtained from least-squares fit to the setting angles of the unresolved Mo Kα components of 25 reflections with $20° < 2\theta \leqslant 30°$.

Table III. Final Positional Parameters for Non-Hydrogen Atoms in $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$[a]

atom	x	y	z
W	0.11323 (1)	0.22042 (3)	0.25000 (0)
Cl(1)	0.01591 (8)	0.0648 (2)	0.25000 (0)
Cl(2)	0.16332 (10)	−0.0343 (2)	0.25000 (0)
P(1)	0.05782 (7)	0.4446 (2)	0.25000 (0)
P(2)	0.11490 (5)	0.16782 (15)	0.08341 (8)
C(1)	0.1740 (3)	0.3573 (6)	0.25000 (0)
C(2)	0.2195 (3)	0.4842 (8)	0.25000 (0)
C(3)	0.2115 (2)	0.5858 (6)	0.1680 (3)
C(4)	0.2805 (3)	0.4136 (10)	0.25000 (0)
C(5)	−0.0188 (3)	0.5058 (7)	0.25000 (0)
C(6)	−0.0662 (3)	0.4040 (8)	0.25000 (0)
C(7)	−0.1225 (3)	0.4617 (10)	0.25000 (0)
C(8)	−0.1336 (4)	0.6172 (11)	0.25000 (0)
C(9)	−0.0871 (4)	0.7203 (8)	0.25000 (0)
C(10)	−0.0307 (3)	0.6654 (7)	0.25000 (0)
C(11)	0.1861 (2)	0.1980 (6)	0.0288 (4)
C(12)	0.2361 (3)	0.0997 (8)	0.0644 (4)
C(13)	0.0922 (3)	−0.0325 (6)	0.0537 (4)
C(14)	0.0998 (3)	−0.0814 (8)	−0.0428 (4)
C(15)	0.0644 (3)	0.2860 (6)	0.0157 (4)
C(16)	0.0820 (3)	0.4556 (7)	0.0043 (4)
H	0.095	0.579	0.250

[a] The atom labeled "H" represents the P-bonded hydrogen atom, whose *calculated* coordinates were used in preparing the figures only; they were not included in any structure factor calculations.

Table IV. Interatomic Distances (Å) with Esd's for W(CCMe$_3$)(PHPh)(PEt$_3$)$_2$Cl$_2$

(A) Distances about the Tungsten Atom			
W-Cl(1)	2.578 (2)	W-P(1)	2.291 (1)
W-Cl(2)	2.456 (2)	W-P(2)	2.553 (1)
W-C(1)	1.808 (6)		
(B) Distances within the Neopentylidyne Ligand			
C(1)-C(2)	1.498 (9)	C(2)-C(4)	1.509 (10)
C(2)-C(3)	1.523 (6)		
(C) Distances within the Phenylphosphido Ligand			
P(1)-C(5)	1.815 (6)	C(8)-C(9)	1.373 (12)
C(5)-C(6)	1.385 (9)	C(9)-C(10)	1.365 (11)
C(6)-C(7)	1.369 (11)	C(10)-C(5)	1.390 (9)
C(7)-C(8)	1.352 (13)		
(D) Distances within the Triethylphosphine Ligands			
P(2)-C(11)	1.833 (6)	C(11)-C(12)	1.510 (8)
P(2)-C(13)	1.843 (6)	C(13)-C(14)	1.523 (9)
P(2)-C(15)	1.837 (6)	C(15)-C(16)	1.512 (8)

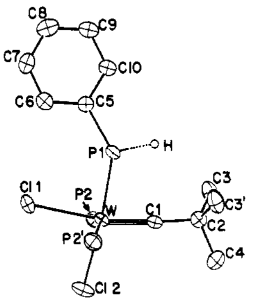
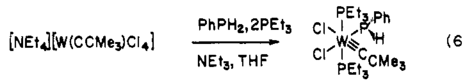


Figure 2. ORTEP-II drawing (30% ellipsoids) of W(CCMe$_3$)(PHPh)(PEt$_3$)$_2$Cl$_2$ with hydrogen atoms and carbon atoms of the PEt$_3$ ligands omitted. H(1) is shown in a calculated position based upon the external bisectrix of W-P-C(5) and d(P-H) = 1.44 Å.

(CCMe$_3$)(NHPh)(PEt$_3$)Cl$_2$ is heated to 50 °C in benzene, no imido alkylidene complex is observed after 24 h. Higher temperatures could not be used since W(CHCMe$_3$)(NPh)(PEt$_3$)Cl$_2$ is not stable above ~50 °C.

W(CCMe$_3$)(NH$_2$)(PEt$_3$)$_2$Cl$_2$ is cleanly transformed into W(CHCMe$_3$)(NH)(PEt$_3$)$_2$Cl$_2$ (Figure 1) at about half the rate at which W(CCMe$_3$)(NHPh)(PEt$_3$)$_2$Cl$_2$ is converted into W(CHCMe$_3$)(NPh)(PEt$_3$)$_2$Cl$_2$ ($t_{1/2} \approx 25$ min at 350 K vs. 12 min, respectively). The slower rate could be ascribed to a decrease in acidity on going from WN(H)Ph to WNH$_2$. (The pK_a for PhNH$_2$ is ~27 while the pK_a of NH$_3$ is ~36.)

Our observations concerning the conversion of amido neopentylidyne and (hypothetical) hydroxo neopentylidyne complexes into neopentylidene complexes raised the question as to whether phosphido neopentylidyne complexes could be prepared and, if they could, whether they could be converted into phenylphosphinidene neopentylidene complexes. The reaction between [NEt$_4$][W(CCMe$_3$)Cl$_4$] and PPhH$_2$ in the presence of PEt$_3$ and NEt$_3$ does yield an orange-red, crystalline phenylphosphido neopentylidyne complex (eq 6). NMR studies suggest that



(6)

its structure is analogous to the amido neopentylidyne complexes, i.e., that the phosphido ligand is cis to the neopentylidyne ligand and planar. The size of the phosphido PW coupling constant (410 Hz) vs. the phosphine PW coupling constant (242 Hz) is consistent with donation of the phosphido ligand's lone pair of electrons to the metal in order to form a bond to the metal of order greater than one. However, unlike the amido ligands, the phosphido ligand will not release its proton to the neopentylidyne ligand; W(CCMe$_3$)(PHPh)(PEt$_3$)$_2$Cl$_2$ is unchanged after heating it in benzene at 75 °C for 24 h. Since we wanted to be absolutely certain of the identity of this species and, in particular, of which way the phosphido ligand was oriented, we undertook a single-crystal X-ray structural study.

The atomic-labeling scheme for W(CCMe$_3$)(PHPh)(PEt$_3$)$_2$Cl$_2$ is shown in Figure 2, and the molecular geometry is presented as a stereoview in Figure 3. Interatomic distances and angles are collected in Tables IV and V, respectively.

The W(CCMe$_3$)(PHPh)(PEt$_3$)$_2$Cl$_2$ molecule possesses precise (i.e., crystallographically-imposed) C_s (m) symmetry with the crystallographic mirror plane containing all atoms save those of the PEt$_3$ ligands, two Me groups, and two hydrogen atoms of the third methyl group in the neopentylidyne ligand. The central tungsten(VI) atom is in a distorted octahedral coordination environment, which consists of mutually trans PEt$_3$ ligands [P(2)-W-P(2′) = 159.65 (4)°], two mutually cis chloride ligands, a neopentylidyne ligand, and the phenylphosphido ligand. The tungsten-neopentylidyne bond length (W-C(1) = 1.808 (6) Å) is comparable to values found previously for the W≡C bond,[19] and the W-C(1)-C(2) angle is 174.0 (4)°. It is

Table V. Interatomic Angles (Deg) with Esd's for W(CCMe$_3$)(PHPh)(PEt$_3$)$_2$Cl$_2$

(A) Angles about Tungsten			
Cl(1)-W-Cl(2)	86.53 (5)	Cl(2)-W-P(2)	80.62 (5)
Cl(1)-W-P(1)	87.77 (4)	Cl(2)-W-C(1)	102.75 (15)
Cl(1)-W-P(2)	85.52 (4)	P(1)-W-P(2)	98.94 (4)
Cl(1)-W-C(1)	170.72 (15)	P(1)-W-C(1)	82.96 (15)
Cl(2)-W-P(1)	174.30 (5)	P(2)-W-C(1)	95.89 (15)
P(2)-W-P(2′)	159.65 (4)		
(B) Angles Involving the Neopentylidyne Ligand			
W-C(1)-C(2)	174.0 (4)	C(1)-C(2)-C(4)	110.1 (5)
C(1)-C(2)-C(3)	109.3 (4)	C(4)-C(2)-C(3)	109.7 (5)
(C) Angles Involving the Phenylphosphido Ligand			
W-P(1)-C(5)	140.02 (17)	C(7)-C(8)-C(9)	119.2 (7)
P(1)-C(5)-C(6)	124.4 (4)	C(8)-C(9)-C(10)	120.0 (6)
P(1)-C(5)-C(10)	118.0 (4)	C(9)-C(10)-C(5)	121.3 (5)
C(5)-C(6)-C(7)	120.0 (5)	C(10)-C(5)-C(6)	117.7 (5)
C(6)-C(7)-C(8)	121.8 (6)		
(D) Angles Involving the Triethylphosphine Ligands			
W-P(2)-C(11)	115.5 (2)	P(2)-C(11)-C(12)	115.1 (4)
W-P(2)-C(13)	113.5 (2)	P(2)-C(13)-C(14)	117.1 (4)
W-P(2)-C(15)	116.2 (2)	P(2)-C(15)-C(16)	115.2 (4)

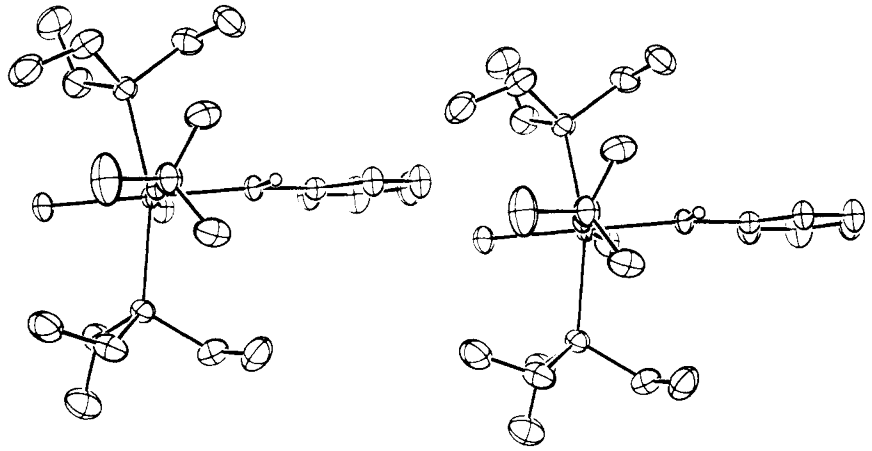


Figure 3. Stereoscopic view of the $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$ molecule.

notable that there is a substantial difference in the two tungsten–chlorine distances; that trans to the neopentylidyne ligand (W–Cl(1) = 2.578 (2) Å) is approximately 0.12 Å longer than that trans to the phosphido ligand (W–Cl(2) = 2.456 (2) Å). The trans angles for the chloride ligands are Cl(1)–W–C(1) = 170.72 (15)° and Cl(2)–W–P(1) = 174.30 (5) Å. The various cis angles range from Cl(2)–W–P(2) = Cl(2)–W–P(2′) = 80.62 (5)° through Cl(2)–W–C(1) = 102.75 (15)°.

The tungsten–phosph*ide* bond (W–P(1) = 2.291 (1) Å; cf. the Mo–phosphide bond length of 2.29 (4) Å in $Mo[P(OMe)_3]_5[P(OMe)_2]^+$ [23]) is substantially shorter than the tungsten-phosph*ine* distances (W–P(2) = W–P(2′) = 2.553 (1) Å). The P–Ph linkage is normal (P(1)–C(5) = 1.815 (6) Å), but the W–P(1)–C(5) angle (140.02 (17)°) seems large. It is important to note that the space group symmetry requires the entire W(PHPh) system to be precisely planar and to lie in the same plane as that which contains W, Cl(1), Cl(2), and C(1). (This finding is consistent with formation of a π bond between P(1) and W which does not compete with formation of the triple bond between W and C(1).) Consequently, the phosphido hydrogen atom (which was not located directly in the analysis) points toward the neopentylidyne ligand's α-carbon atom. The calculated position of this hydrogen atom (on the basis of P–H = 1.44 Å and an external bisecting geometry relative to the W–P–C(5) angle) places this atom approximately 2.6 Å from the α-carbon atom of the neopentylidyne ligand (Figure 2).

Discussion

The kinetics of the transfer of an amido proton to the neopentylidyne ligand suggests that the process is intramolecular. An intermolecular process cannot be ruled out, but it seems unlikely, at least for octahedral amido complexes. The simplest intramolecular process would be essentially direct transfer of the proton from nitrogen to carbon, analogous to the α-hydrogen atom abstraction reaction in which an alkylidene ligand is formed by migration of an α-proton from one alkyl group to the α-carbon atom of another alkyl group. Postulating an intramolecular hydrogen transfer should not be inconsistent with dehydrohalogenation of the amido complex by a strong base ($Ph_3P{=}CH_2$) or acceleration of the proton transfer by triethylamine, since, among other reasons, alkylidene ligands can also be formed by dehydrohalogenation of an alkyl halide complex.[7] Perhaps the most interesting similarity with the α-hydrogen atom abstraction reaction is the fact that the proton transfers more slowly in $W(CCMe_3)(NHPh)(PEt_3)Cl_2$ (if at all) than it does in $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$. α-Hydrogen atom abstraction is also slow in complexes of low coordination number and also is promoted by addition of donor ligands.[24] The structure of $W(CCMe_3)(NHPh)(PEt_3)Cl_2$ is likely to be a trigonal bipyramid with the neopentylidyne and amido ligands in the trigonal plane (cf. the structure of $W(O)(CHCMe_3)(PEt_3)Cl_2$[4d]); i.e., the neopentylidyne and amido ligands should be ~110° apart.

One of the most interesting features of the structure of $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$ is that the W–P–Ph angle is rather large. Certain alkylidene complexes are similarly distorted.[25] In fact, some $M–C_\alpha–H_\alpha$ angles can be as small as 70°.[26] It is now clear that the alkylidene complexes are distorted for largely electronic reasons;[27] the metal is acquiring π-electron density from the $C_\alpha–H_\alpha$ bond. It is probably for similar reasons that the W–PHPh system is distorted to the extent it is. Furthermore, although the overall structure of $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$ is likely to be analogous to that of $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$, the shorter W–N bond (~2.0 Å[17]) would probably lead to an even greater distortion of the NHPh ligand.[28] The shorter W–N bond alone would place the amido proton ~2.3 Å from the neopentylidyne α-carbon atom. We conclude that the phenyl*amido* proton would probably be close enough to the neopentylidyne α-carbon atom to transfer directly to it and that the reason why the phenyl*phosphido* proton does not transfer to the neopentylidyne α-carbon atom is simply that it is too far away.

The slower rate of transfer of the amido proton in $W(CCMe_3)(NH_2)(PEt_3)_2Cl_2$ to the neopentylidyne α-car-

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(19) For example, the W≡C bond length is 1.785 (8) Å in $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$,[20] 1.807 (6) Å in $W(CHAlMe_{2-x}Cl_{1+x})(Cl)(PMe_3)_3$,[21] and 1.82 (2) Å in $W(C(p\text{-tolyl}))(\eta^5\text{-}C_5H_5)(CO)_2$.[22]

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(28) The W-N-adamantyl angle in *trans*-$Mo[NH(adamantyl)]_2(OSiMe_3)_4$ is 151°; Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1980**, *19*, 777.

bon atom is probably best ascribed to the likely higher acidity of the proton in the phenylamido complex. Since methylene ligands distort as much as neopentylidene ligands,[27] the $\mathrm{NH_2}$ ligand should be as distorted as the NHPh ligand.

Although we cannot prove that intermediate hydroxo complexes analogous to the amido complexes are formed initially in the process of generating oxo alkylidene complexes from water and the alkylidyne complex, that proposal is a reasonable one. A hydroxo ligand should lose a proton to the neopentylidyne α-carbon atom more easily than an amido ligand does on the basis of the greater acidity of an alcohol relative to the analogous amine.

Viewing the conversion of an alkylidyne into an alkylidene ligand as proton transfer constrasts sharply with prevailing nucleophilic attack on Fischer-type carbyne complexes (e.g., $\mathrm{[MCp(CO)_2(CPh)][BF_4]}$ (M = Mn, Re)[29]) which all contain metals with at least two more d electrons. Yet it should be noted that $\mathrm{[W(CCMe_3)Cl_4]^-}$ cannot be protonated readily by HCl in dichloromethane.[14] Therefore we can postulate that W(VI) alkylidyne complexes will not be protonated readily unless good π-donor ligands are present or can be formed as a result of the protonation process. If this is so, then we should be able to form the recently discovered[5b] oxo ligand free complexes of the type $\mathrm{W(CHCMe_3)(OR)_2Cl_2}$ from $\mathrm{[W(CCMe_3)Cl_4]^-}$, 2ROH, and $\mathrm{Et_3N}$. Preliminary results suggest that this is a quantitative reaction for R = $\mathrm{CMe_3}$.[16]

Alkylidyne complexes should now be added to the list of possible precursors to alkylidene complexes responsible for the metathesis of olefins.[3-5] Alkylidyne complexes can form under a variety of conditions[10-14] and even small amounts reacting with (e.g.) traces of water would be sufficient to generate one of the extremely active metathesis catalysts.

Experimental Section

General experimental procedures may be found elsewhere.[24] $\mathrm{[NEt_4][W(CCMe_3)Cl_4]}$ was prepared by treating $\mathrm{W(CCMe_3)(CH_2CMe_3)_3}$[10] with 3 equiv of HCl in the presence of $\mathrm{NEt_4Cl}$.[14] NMR data are listed in parts per million relative to $\mathrm{Me_4Si}$ (^{1}H and ^{13}C NMR) or external 85% $\mathrm{H_3PO_4}$ (^{31}P NMR). ^{13}C NMR spectra were run in both the ^{1}H decoupled and gated ^{1}H decoupled modes in order to extract all coupling constants.

Preparation of $\mathbf{W(O)(CHCMe_3)(PEt_3)_2Cl_2}$ from $\mathbf{[NEt_4][W(CCMe_3)Cl_4]}$. $\mathrm{[NEt_4][W(CCMe_3)Cl_4]}$ (0.26 g, 0.5 mmol) was dissolved in THF (10 mL), and $\mathrm{PEt_3}$ (0.12 g, 1.0 mmol) and LiOH (0.012 g, 0.5 mmol) were added. After the solution was stirred overnight, the volatiles were removed in vacuo and the residue was extracted with diethyl ether. The extract was filtered, and the volatiles were removed in vacuo to give a greenish yellow solid which by ^{31}P and ^{1}H NMR is identical with authentic $\mathrm{W(O)(CHCMe_3)(PEt_3)_2Cl_2}$.[4c]

Preparation of $\mathbf{W(CCMe_3)(NHPh)(PEt_3)_2Cl_2}$. $\mathrm{PEt_3}$ (0.95 g, 8.0 mmol) and $\mathrm{NEt_3}$ (560 μL, 4.0 mmol) were added to $\mathrm{[NEt_4][W(CCMe_3)Cl_4]}$ (2.10 g, 4.0 mmol) in THF (25 mL). The green slurry was cooled to −30 °C, and $\mathrm{PhNH_2}$ (365 μL, 4.0 mmol) was added to the stirred slurry. The solution turned orange-red as it warmed to room temperature. After 2 h the volatiles were removed in vacuo. The residue was extracted with ether, the mixture was filtered, and the filtrate was concentrated in vacuo to ~10 mL. Cooling the filtrate to −30 °C for several hours gave orange crystals (75%): ^{1}H NMR ($\mathrm{C_6D_6}$) δ 13.20 (br s, 1, NHPh), 7.53 (d, 2, J_{HH} = 8.5 Hz, $\mathrm{H_o}$), 7.07 (t, 2, J_{HH} = 7.9 Hz, $\mathrm{H_m}$), 6.91 (t, 1, J_{HH} = 7.3 Hz, $\mathrm{H_p}$), 1.96 (m, 12, $\mathrm{PC\mathit{H}_2CH_3}$), 1.32 (s, 9, $\mathrm{CCMe_3}$), 0.90 (m, 18, $\mathrm{PCH_2C\mathit{H}_3}$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 300.5 (t, $^2J_{\mathrm{CP}}$ = 10.7 Hz, $\mathrm{\mathit{C}CMe_3}$), 153.5 (s, $\mathrm{C_{ipso}}$), 128.9, 125.7, 121.3 (d, J_{CH} = 153–165 Hz, $\mathrm{C_{phenyl}}$), 49.6 (s, $\mathrm{C\mathit{C}Me_3}$), 32.4 (q, J_{CH} = 125 Hz, $\mathrm{CC\mathit{Me}_3}$), 17.4 (tt, J_{CH} = 130 Hz, J_{CP} = 12 Hz, $\mathrm{P\mathit{C}H_2CH_3}$), 7.7 (q, J_{CH} = 127 Hz, $\mathrm{PCH_2\mathit{C}H_3}$); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$) δ 15.6 (s, J_{PW} = 276 Hz). Anal. Calcd for $\mathrm{WC_{23}H_{45}NP_2Cl_2}$: C, 42.35; H, 6.95. Found: C, 42.19; H, 7.08.

Preparation of $\mathbf{W(CCMe_3)(NHPh)(PMe_2Ph)_2Cl_2}$. $\mathrm{PMe_2Ph}$ (0.28 g, 2.0 mmol) was added to $\mathrm{[NEt_4][W(CCMe_3)Cl_4]}$ (0.52 g, 1.0 mmol) in THF (10 mL). LiNHPh (0.10 g, 1.0 mmol) was added, and the red-orange solution was stirred for 2 h. The mixture was filtered, and the filtrate was evaporated to dryness. A filtered dichloromethane (5 mL) extract of the residue was cooled to −30 °C to give 0.4 g of red-orange crystals (60%): ^{1}H NMR ($\mathrm{C_6D_6}$) δ 13.07 (br s, 1, NHPh), 7.41–6.88 (m, 15, phenyl), 1.91 (t, 6, $^2J_{\mathrm{HP}}$ = 4.4 Hz, $\mathrm{PCH_3(A)}$), 1.83 (t, 6, $^2J_{\mathrm{HP}}$ = 4.4 Hz, $\mathrm{PCH_3(B)}$), 0.93 (s, 9, $\mathrm{CCMe_3}$).

Observation of $\mathbf{W(CCMe_3)(NHPh)(PEt_3)Cl_2}$. LiNHPh (0.05 g, 0.50 mmol) was added to $\mathrm{W(CCMe_3)(PEt_3)Cl_3}$[14] (0.24 g, 0.5 mmol) at −30 °C in ether (10 mL). The reaction immediately turned orange. After the solution was stirred for 4 h, the LiCl was removed by filtration and the orange solution evaporated to an orange oil which could not be crystallized. The ^{31}P{^{1}H} NMR spectrum shows mostly $\mathrm{W(CCMe_3)(NHPh)(PEt_3)Cl_2}$ at 40.3 ppm (J_{PW} = 308 Hz), but ~20% of the reaction mixture is the bis(phosphine) complex, $\mathrm{W(CCMe_3)(NHPh)(PEt_3)_2Cl_2}$. The ^{13}C{^{1}H} NMR spectrum shows a doublet signal for the alkylidyne α-carbon atom ($^2J_{\mathrm{CP}}$ = 12 Hz) at 304.5 ppm. The amido N–H proton is found at 10.5 ppm in the ^{1}H NMR spectrum.

Preparation of $\mathbf{W(CCMe_3)(NPh)(PEt_3)_2Cl}$. $\mathrm{Ph_3P{=}CH_2}$ (0.11 g, 0.38 mmol) was added to a solution of $\mathrm{W(CCMe_3)(NHPh)(PEt_3)_2Cl_2}$ in toluene (~7 mL) which had been cooled to −30 °C. The orange solution immediately turned cherry red. After 45 min $\mathrm{[Ph_3PCH_3]Cl}$ was filtered off, and the purple solution was evaporated to dryness, yielding pure product: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.6–7.0 (m, 5, phenyl), 2.05 (m, 12, $\mathrm{PC\mathit{H}_2CH_3}$), 1.65 (s, 9, $\mathrm{CC\mathit{Me}_3}$), 1.24 (m, 18, $\mathrm{PCH_2C\mathit{H}_3}$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$) δ 322.7 (t, $^2J_{\mathrm{CP}}$ = 9.9 Hz, $\mathrm{\mathit{C}CMe_3}$), 161.0 (s, $\mathrm{C_{ipso}}$), 128.5–124.0 (d, $J_{\mathrm{CH}} \approx$ 160 Hz, $\mathrm{C_{phenyl}}$), 52.4 (s, $\mathrm{C\mathit{C}Me_3}$), 34.2 (q, J_{CH} = 125 Hz, $\mathrm{CC\mathit{Me}_3}$), 17.9 (tt, J_{CH} = 128 Hz, J_{CP} = 13 Hz, $\mathrm{P\mathit{C}H_2CH_3}$), 8.8 (t, J_{CH} = 125 Hz, $\mathrm{PCH_2\mathit{C}H_3}$); ^{31}P{^{1}H} NMR ($\mathrm{C_6D_6}$) δ 32 (s, J_{PW} = 295 Hz). Anal. Calcd for $\mathrm{WC_{23}H_{44}NP_2Cl}$: C, 44.91; H, 7.20. Found: C, 45.19; H, 7.17.

Preparation of $\mathbf{W(CCMe_3)(NH_2)(PEt_3)_2Cl_2}$. $\mathrm{LiNH_2}$ (0.09 g, 3.8 mmol) was added to a THF (40 mL) solution containing $\mathrm{PEt_3}$ (0.90 g, 7.6 mmol) and $\mathrm{[NEt_4][W(CCMe_3)Cl_4]}$ (2.0 g, 3.8 mmol). After 2 h the reaction began turning orange. After being stirred overnight, the reaction mixture was filtered through a Celite pad, the solvent was removed from the filtrate to give a sticky orange solid which was recrystallized from a mixture of ether and THF (10:1) by cooling a concentrated solution to −30 °C for several hours. Orange crystals (1.0 g) were isolated by filtration. The filtrate was concentrated in vacuo and cooled to −30 °C for a second crop: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 10.84 (br s, 2, $\mathrm{NH_A}$), 9.37 (br s, 1, $\mathrm{NH_B}$), 1.95 (m, 12, $\mathrm{PC\mathit{H}_2CH_3}$), 1.09 (s, 9, $\mathrm{CCMe_3}$), 1.02 (m, 18, $\mathrm{PCH_2C\mathit{H}_3}$); ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$) δ 299 (t, J_{CP} = 11 Hz, $\mathrm{CCMe_3}$), 48.2 (s, $\mathrm{C\mathit{C}Me_3}$), 31.3 (q, J_{CH} = 126 Hz, $\mathrm{CC\mathit{Me}_3}$), 16.4 (tt, J_{CH} = 127 Hz, $^2J_{\mathrm{CP}}$ = 13 Hz, $\mathrm{P\mathit{C}H_2CH_3}$), 6.9 (q, J_{CH} = 126 Hz, $\mathrm{PCH_2\mathit{C}H_3}$). Anal. Calcd for $\mathrm{WC_{17}H_{41}NP_2Cl_2}$: C, 35.44; H, 7.17. Found: C, 35.34; H, 7.25.

Preparation of $\mathbf{W(CCMe_3)(PHPh)(PEt_3)_2Cl_2}$. $\mathrm{PEt_3}$ (0.24 g, 2.0 mmol) and $\mathrm{NEt_3}$ (0.10 g, 1.0 mmol) were added to a solution of $\mathrm{[NEt_4][W(CCMe_3)Cl_4]}$ (0.52 g, 1.0 mmol) in 10 mL of THF. $\mathrm{PhPH_2}$ (0.11 g, 1.0 mmol) was added after the solution was cooled to −30 °C. The solution immediately turned red. After 2 h the reaction mixture was filtered and the filtrate was evaporated to dryness. An ether/THF (10:1) extract of the residue was cooled to −30 °C to give 0.44 g of red-orange $\mathrm{W(CCMe_3)(PHPh)(PEt_3)_2Cl_2}$ (65%): ^{1}H NMR ($\mathrm{C_6D_6}$) δ 10.00 (d, 1, J_{HP} = 362 Hz, $^2J_{\mathrm{HW}}$ = 65 Hz, PHPh), 8.56–7.04 (m, 5, $\mathrm{H_{phenyl}}$), 2.01 (m, 12, $\mathrm{PC\mathit{H}_2CH_3}$), 1.30 (s, 9, $\mathrm{CCMe_3}$), 0.98 (m, 18, $\mathrm{PCH_2C\mathit{H}_3}$); ^{13}C{^{1}H} NMR ($\mathrm{C_6D_6}$) δ 289 (br s, $\mathrm{\mathit{C}CMe_3}$), 149 (d, J_{CP} = 10 Hz, $\mathrm{C_{ipso}}$), 133–128 (d, $J_{\mathrm{CH}} \approx$ 160 Hz, $\mathrm{C_{phenyl}}$), 50.5 (s, $\mathrm{C\mathit{C}Me_3}$), 32.2 (q, J_{CH} = 126 Hz, $\mathrm{CC\mathit{Me}_3}$), 19.1 (tt, J_{CH} = 129 Hz, $^2J_{\mathrm{CP}}$ = 12 Hz, $\mathrm{P\mathit{C}H_2CH_3}$), 8.1 (q, J_{CH} = 126 Hz, $\mathrm{PCH_2\mathit{C}H_3}$); ^{31}P{^{1}H} NMR ($\mathrm{C_6H_6}$) δ 233 (t, $J_{\mathrm{PP'}}$ = 59 Hz, J_{PW} = 410 Hz, $\mathrm{\mathit{P}HPh}$), 15.2 (d, $J_{\mathrm{PP'}}$ = 59 Hz, J_{PW} = 242 Hz, $\mathrm{PEt_3}$);

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^{31}P (proton-coupled) NMR δ 232.3 (dt, J_{PH} = 362 Hz, $J_{PP'}$ = 59 Hz, *P*HPh), 15.2 (d, $J_{PP'}$ = 59 Hz). Anal. Calcd for $WC_{23}H_{45}P_3Cl_2$: C, 41.28; H, 6.78. Found: C, 41.71; H, 6.82.

Crystal Structure Determination. A. Data Collection. Deep red plate-like crystals of $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$ were grown from toluene. A crystal measuring approximately 0.24 × 0.24 × 0.32 mm was sealed into a glass capillary under inert-atmospheric conditions. Description of our use of the Syntex P2$_1$ diffractometer has been published;[30] details pertaining to the present analysis are in Table II. Systematic absences observed were *h*0*l* for $h = 2n + 1$ and 0*kl* for $k + l = 2n + 1$; possible space groups are the noncentrosymmetric orthorhombic space group *Pna*2$_1$ (C_{2v}^{9} No. 33) or the centrosymmetric space group *Pnam* (a nonstandard setting of *Pnma*—D_{2h}^{16}; No. 62).

In view of the possibility of the noncentrosymmetric space group *Pna*2$_1$ (with polar *c* axis), intensity data were collected for the two forms *hkl* and $hk\bar{l}$. The intensity data were corrected for absorption by using the empirical ψ-scan method with seven reflections covering the 2θ range 19–45°.

B. Solution and Refinement. The structure was initially solved in the acentric space group *Pna*2$_1$ by Patterson and difference-Fourier techniques, which determined the coordinates of all non-hydrogen atoms. Full-matrix least-squares refinement led to R_F = 4.8%. However, unreasonably large C–C distances within the PEt_3 ligands, coupled with the appearance of mirror symmetry within the molecule, led us to attempt further refinement in the higher symmetry centric space group *Pnam*; this choice proved to be correct as verified by successful refinement and chemically reasonable features throughout the molecule. Difference-Fourier calculations failed to locate the unique P-bonded hydrogen atom; all other hydrogen atoms were included in calculated positions.[31] The final agreement factors were R_F = 2.8%, R_{wF} = 2.9%, and GOF = 1.01 for all 2007 point-group independent data with $4.0 \le 2\theta \le 50.0°$ (none rejected). The ratio of observations to variables was 2007:151 = 13.3:1. Structure factor calculations excluding data with $|F_o| < 3\sigma(|F_o|)$ gave R_F = 2.4%, R_{wF} = 2.8%, and GOF = 0.99.

Final positional parameters are listed in Table III.

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Registry No. $W(O)(CHCMe_3)(PEt_3)_2Cl_2$, 74666-77-6; $[NEt_4][W(CCMe_3)Cl_4]$, 78251-20-4; $W(CCMe_3)(NHPh)(PEt_3)_2Cl_2$, 82661-13-0; $W(CCMe_3)(NHPh)(PMe_2Ph)_2Cl_2$, 82661-14-1; $W(CCMe_3)(NHPh)(PEt_3)Cl_2$, 82661-15-2; $W(CCMe_3)(PEt_3)Cl_3$, 82661-16-3; $W(CCMe_3)(NPh)(PEt_3)_2Cl$, 82661-17-4; $Ph_3P{=}CH_2$, 3487-44-3; $W(CCMe_3)(NH_2)(PEt_3)_2Cl_2$, 82661-18-5; $W(CCMe_3)(PHPh)(PEt_3)_2Cl_2$, 82661-19-6.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, positional parameters for hydrogen atoms (Table I-S), and anisotropic thermal parameters (Table II-S) (14 pages). Ordering information is given on any current masthead page.

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Photochemistry of Solution and Surface-Confined Alkyl- and Benzyltricarbonylcyclopentadienyltungsten Complexes

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A variety of surface-confined species $(\eta^5\text{-}C_5H_5)W(CO)_3R$ (R = Cl, CH_3, C_2H_5, $CH_2C_6H_5$) has been synthesized and characterized and their photochemistry examined and compared to solution analogues. High surface area (400 m^2/g) SiO_2, $[SiO_2]$–, has been functionalized first with $-SiMe_2C_5H_5$ by reaction of surface OH groups with $ClSiMe_2C_5H_5$ or $EtOSiMe_2C_5H_5$. The resulting $[SiO_2]\text{–}SiMe_2C_5H_5$ can then be treated in a series of conventional synthetic steps to yield $[SiO_2]\text{–}SiMe_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_3R$ (R = Cl, CH_3, C_2H_5). Elemental analyses and infrared spectroscopy has been used to establish that the average coverage is generally submonolayer, with an average separation between W centers of 10–20 Å. Chloromethylated polystyrene reacts with $[(\eta^5\text{-}C_5H_5)W(CO)_3]^-$ to yield $(\eta^5\text{-}C_5H_5)W(CO)_3(\eta^1\text{-}CH_2C_6H_4\text{–}[P])$ or with C_5H_5Na followed by conventional synthetic procedures to yield $[P]\text{–}C_6H_4CH_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_3R$ (R = CH_3, C_2H_5). In all cases near-UV (355 nm) irradiation yields chemistry consistent with efficient, dissociative loss of CO as the primary reaction following photoexcitation as has been found for the analogous solution species ($\Phi_{366} \approx 0.35 \pm 0.05$). Direct spectroscopic evidence for the photogeneration of surface-confined, 16-valence-electron intermediates comes from the infrared analysis of Nujol suspensions of $[SiO_2]\text{–}SiMe_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_3R$ (R = CH_3, C_2H_5) irradiated at 77 K. For R = CH_3 warm-up of the irradiated sample yields nearly complete regeneration of the starting complex by back-reaction with the photoejected CO, whereas for R = C_2H_5 warm-up yields some regeneration of the starting complex and some conversion to $[SiO_2]\text{–}SiMe_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_2(H)(C_2H_4)$. Unlike the analogous complex in solution, prolonged irradiation of the $[SiO_2]\text{–}SiMe_2\text{–}(\eta^5\text{-}C_5H_4)W(CO)_3R$ does not yield W–W bonded products, consistent with the immobilized centers remaining anchored sufficiently far apart that W–W bonds cannot form. Irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3(\eta^1\text{-}CH_2C_6H_4\text{–}[P])$ at 77 K does not allow the observation of a 16-valence-electron intermediate rather $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}CH_2C_6H_4\text{-}[P])$ is formed. These and similar results for the solution species R = $CH_2C_6H_5$ and $CH(CH_3)C_6H_5$ allow an upper limit for the activation energy for the conversion of an η^1-benzyl to η^3-benzyl to be set at ~6 kcal/mol. Irradiation of $(\eta^5\text{-}C_5H_5)W(CO)_3CH_2CH_2C_6H_5$ leads to a blue 16-valence-electron species at 77 K which gives *trans*-$(\eta^5\text{-}C_5H_5)W(CO)_2(H)$(styrene) upon warming. This styrene–hydride rearranges slowly at 300 K ($t_{1/2}$ = ~400 s) to form $(\eta^5\text{-}C_5H_5)W(CO)_2(\eta^3\text{-}CH(CH_3)C_6H_5)$.

Surface-confined organometallic species have recently received widespread attention[1–7] and have been the subject of two recent reviews.[1,2] The interest in these materials is due to their potential ability to effect catalysis of nu-