fall within the range 2.083 (3)–2.181 (7) Å found in ten related crystal structures containing Pd(II)–C(sp^3) bonds.[8,21,22] The Pd–Br distance of 2.404 (1) Å is not unusual.[24] The chelating N–Pd–N angles of 82.54 (13)° in 18 and 85.66 (15)° in 23 differ significantly from each other as well as from that of the corresponding dichloro complex 11, in which this angle is 87.1 (2)°.[15]

In both 18 and 23, the six-membered chelate ring assumes a *boat conformation* (see Table V). The coordination environment around palladium in both is tetrahedrally distorted square planar. Deviations (Å) from the coordination plane are as follows: N(1), 0.054 (5); N(2), –0.070 (5); Pd, 0.034 (1); C(14), 0.052 (6); C(17), –0.069 (6). In 23, similar deviations (Å) are as follows: N(1), 0.051 (6); N(2), 0.045 (6); Pd, 0.014 (1); Br, 0.040 (1); C(14), –0.048 (7). Each of the four pyridine rings is planar and produces intramolecular dihedral angles of 72.6° and 67.3° in 18 and 23, respectively. Thes angles are somewhat larger than the two independent values of 64.5° and 63.4° found in 11.[15]

The ethoxycarbonyl groups of both complexes are probably disordered, exhibiting large thermal parameters in the crystal (not illustrated in Figures 1 and 2), and leading to unrealistically short observed bond distances, particularly for C–C(ethyl) bonds.

The ketal rings of the two complexes differ in conformation (see Table V); both adopt a half-chair conformation, but C(13) lies on the local twofold axis in 18, whereas in 23, O(2) occupies that unique position. The Pd···O(1) distances [2.844 (3) and 2.865 (3) Å in 18 and 23, respectively] are close to the minimum expected van der Waals distance of 3.0 Å. This contact is also observed in dichloro(dihydroxydi-2-pyridylmethane)palladium(II), in which the Pd···O distance is 2.824 (6) Å,[25] and in dichloro[2,2-bis(2-pyridyl)1,3-dioxolane]palladium(II), in which it has two independent values of 2.987 (4) and 2.935 (3) Å.[15] No intermolecular contacts less than 3.5 Å exists between the non-hydrogen atoms.

Supplementary Material Available: Tables of the bond distances, bond angles, hydrogen atom coordinates, and anisotropic thermal parameters and a listing of observed and calculated structure factors for 18 and 23 (49 pages). Ordering information is given on any current masthead page.

(24) Giordano, T. J.; Butler, W. M.; Rasmussen, P. G. *Inorg. Chem.* 1978, *17*, 1917.

(25) Annibale, G.; Canovese, L.; Cattalini, L.; Natile, G.; Biagini-Cingi, M.; Manotti-Lanfredi, A.-M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* 1981, 2280.

Metathesis of Acetylenes by Triphenoxytungstenacyclobutadiene Complexes and the Crystal Structure of W(C₃Et₃)[O-2,6-C₆H₃(/-Pr)₂]₃

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The reaction between W(CCMe₃)(1,2-dimethoxyethane)Cl₃ and LiO-2,6-C₆H₃(i-Pr)₂ (LiOR) yields yellow, crystalline W(CCMe₃)(OR)₃ (1). 3-Hexyne reacts with 1 to give Me₃CC≡CEt and W(C₃Et₃)(OR)₃ (2) quantitatively. W(C₃Et₃)[O-2,6-C₆H₃(i-Pr)₂]₃ crystallizes in the monoclinic space group $P2_1/c$ with a = 19.271 (6) Å, b = 13.000 (3) Å, c = 17.195 (6) Å, β = 96.55 (2)°, and Z = 4. Diffraction data were collected with a Syntex P2₁ diffractometer, and the structure was refined to R_F = 4.67% for all 3873 data with 2θ = 4.5–40.0° (Mo Kα). This sterically crowded molecule is approximately a trigonal bipyramid in which the planar tungstenacyclobutadiene ring is located in the equatorial position with the two W–C$_\alpha$ bond lengths being 1.883 (10) and 1.949 (9) Å and the W···C$_\beta$ bond distance being 2.159 (10) Å. Both 2 and an analogous W(C₃Pr₃)[O-2,6-C₆H₃(i-Pr)₂]₃ complex (3) catalyze the metathesis of 3-heptyne or 4-nonyne. They each react with 3-hexyne-d_{10} at a rate that is independent of the concentration of 3-hexyne-d_{10}, characteristic of rate limiting loss of 3-hexyne from 2 or 4-octyne from 3: $\Delta H^\ddagger \simeq$ 26 kcal mol⁻¹ and $\Delta S^\ddagger \simeq$ 16 eu in each case. Related studies employing O-2,6-C₆H₃Me₂ suggested that this ligand is not bulky enough to yield metathesis catalysts, while use of O-2,6-C₆H₃(CMe₃)₂ led to a neopentylidene complex through addition of a *tert*-butyl CH bond to the W≡C bond.

Introduction

The metathesis of dialkylacetylenes by W(CCMe₃)(OCMe₃)₃[2] and analogous W(CR)(OCMe₃)₃ complexes (R = Me, Et, etc.[3]) is believed to proceed by formation and decomposition of tungstenacyclobutadiene complexes. This hypothesis is supported by kinetic studies of the rate at which W(CCMe₃)(OCMe₃)₃ reacts with diphenylacetylene at 0 °C in ether to give W(CPh)(OCMe₃)₃ and

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(2) (a) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* 1981, *103*, 3932. (b) Sancho, J.; Schrock, R. R. *J. Mol. Catal.* 1982, *15*, 75.

(3) (a) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* 1982, *1*, 1645. (b) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* 1982, *104*, 4291.
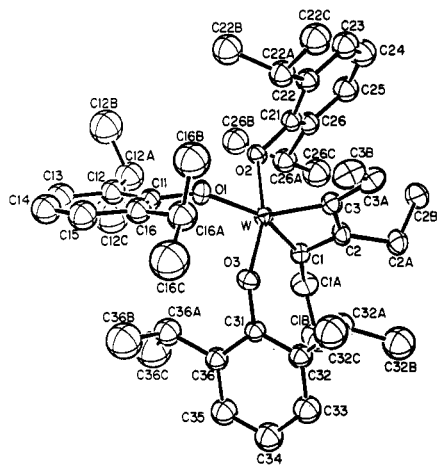
Figure 1. Labeling of atoms in the $W(C_3Et_3)[O-2,6-C_6H_3(i-Pr)_2]_3$ molecule (ORTEP-II diagram with 30% probability ellipsoids).

$Me_3CC{\equiv}CPh$[2b] and by the discovery of an isolable tungstenacyclobutadiene complex formed by the reaction between $W(CCMe_3)(1,2\text{-dimethoxyethane})Cl_3$ and 2-butyne.[4] The isolable metallacycle $W[C(CMe_3)C(Me)C(Me)]Cl_3$[5] is *not* a catalyst for acetylene metathesis; it reacts with alkynes to give cyclopentadienyl complexes.[6] Since an X-ray structure of trigonal-bipyramidal $W[C(CMe_3)C-(Me)C(Me)]Cl_3$ revealed some unusual features of the planar tungstenacyclobutadiene ring, in particular the short $W{\cdots}C_\beta$ interaction of 2.115 (8) Å, speculation arose as to whether this metallacyclic ring was significantly different from one presumably formed in a catalytically active system. We then discovered that some mono-, di-, and trialkoxytungstenacyclobutadiene complexes (e.g., $W[C(CMe_3)C(Et)C(Et)](OCMe_2CMe_2O)(OCMe_3))$ could be isolated but that they too would *not* metathesize acetylenes.[6] A careful search for isolable, catalytically *active* tungstenacyclobutadiene complexes led to the system reported here, and in the second paper in this series to metathesis catalysts that contain fluoroalkoxide ligands. In the third paper in this series we explore the formation of tungstenacyclobutadiene complexes and cyclopentadienyl complexes in some systems that will not metathesize acetylenes. Only some of the results in the third paper have been reported in preliminary form.[4]

Results

The Formation of $W(C_3Et_3)[O-2,6-C_6H_3(i-Pr)_2]_3$. Yellow, crystalline $W(CCMe_3)[O-2,6-C_6H_3(i-Pr)_2]_3$ (1) can be prepared by treating $W(CCMe_3)(1,2\text{-dimethoxy-}$
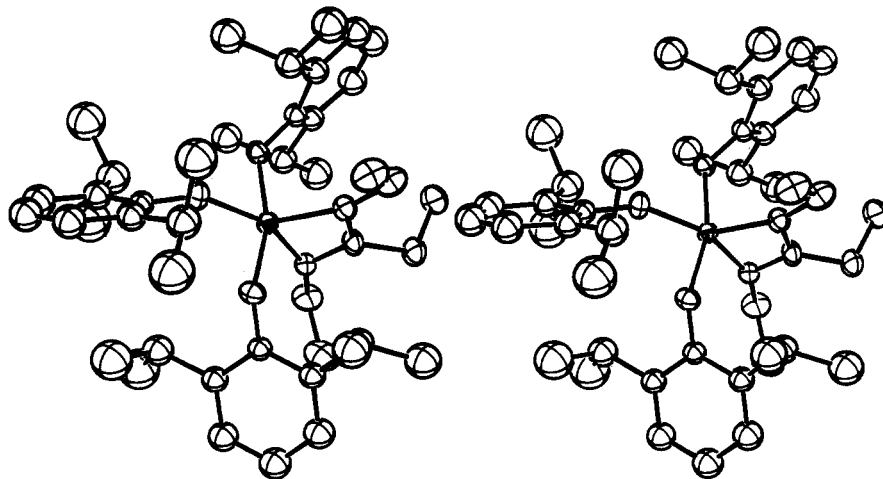
ethane)Cl_3[3a] with 3 equiv of $LiO-2,6-C_6H_3(i-Pr)_2$. It is likely to be a monomer or at most a weakly associated dimer (in the solid state) formed when one of the three alkoxides ligands bridges to another metal (cf. the structure of [W-$(CMe)(OCMe_3)_3]_2$[7]). In this class of compounds relatively nonbulky alkoxide ligands generally allow dimers (e.g., $[W(CCMe_3)(OCHMe_2)_3]_2$,[8] $[W(CCMe_3)(OMe)_3-(Me_2NH)]_2$,[3a] $[W(CCMe_3)(OPh)_3(Me_2NH)]_2$[8]) or oligomers (e.g., $[W(CCMe_3)(OEt)_3(py)_x]_y$[8]) to form. On the basis of the results we will present here, we estimate that the 2,6-diisopropylphenoxide ligand has steric properties that approach those of the *tert*-butoxide ligand.

The reaction of 1 with 2 equiv of 3-hexyne in toluene at 25 °C yields 1 equiv of $Me_3CC{\equiv}CEt$ and a red, crystalline complex of composition $W(C_3Et_3)[O-2,6-C_6H_3(i-Pr)_2]_3$ (2) virtually quantitatively by ^{1}H NMR. ^{13}C NMR studies suggest that 2 is a tungstenacyclobutadiene complex analogous to $W[C(CMe_3)C(Me)C(Me)]Cl_3$; i.e., the two signals found at 244.9 and 136.6 ppm can be ascribed to the α- and β-carbon atoms in the WC_3 ring. This molecule shows no evidence of any intramolecular rearrangement process whose rate is on the order of the NMR time scale, and the NMR spectra are unchanged in the presence of excess 3-hexyne.

If only 1 equiv of 3-hexyne is added to 1, 0.5 equiv of 2 is obtained and 0.5 equiv of 1 remains. This 1:1 mixture of 1 and 2 is unchanged after 24 h at 25 °C. These results suggest that (i) 1 reacts with 3-hexyne to give a tungstenacyclobutadiene complex from which $Me_3CC{\equiv}CEt$ is lost relatively rapidly to give $W(CEt)[O-2,6-C_6H_3(i-Pr)_2]_3$ (eq 1), (ii) the fastest step in the sequence is the reaction

$$1 \xrightarrow{\text{3-hexyne}} (RO)_3W \xrightarrow{-Me_3CC{\equiv}CEt} (RO)_3W{\equiv}CEt \qquad (1)$$
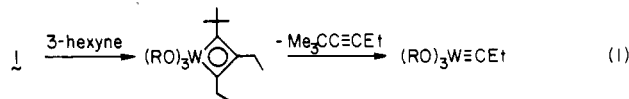
of $W(CEt)[O-2,6-C_6H_3(i-Pr)_2]_3$ with 3-hexyne to give the final product 2, and (iii) 2 does not readily lose 3-hexyne. At this point we cannot tell if the stability of a mixture of 1 and 2 results from thermodynamic or kinetic control.

The X-ray Structure of $W(C_3Et_3)[O-2,6-C_6H_3(i-Pr)_2]_3$. $W(C_3Et_3)[O-2,6-C_6H_3(i-Pr)_2]_3$ crystallizes as discrete molecular units separated by normal van der Waal's distances; there are no abnormally short intermolecular contacts (see Figures 1–3). Interatomic distances and angles are collected in Tables I and II, respectively.

The coordination geometry about tungsten is somewhere between trigonal bipyramidal and square pyramidal with C(3) at the apex. The TBP description is attractive since the atoms O(1), W, C(1), C(2), and C(3) all lie in a plane

Figure 2. Stereoscopic view of the $W(C_3Et_3)[O-2,6-C_6H_3(i-Pr)_2]_3$ molecule.
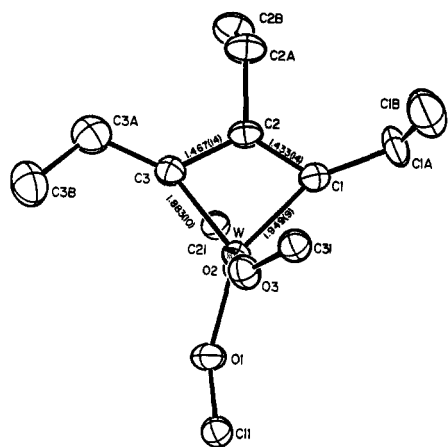
Figure 3. A portion of the molecule projected onto the WC_3 plane. Note the asymmetric location of O(1) relative to the WC_3 ring and the orthogonality of W-O(2)-C(21) and W-O(3)-C(31) planes.

Table I. Interatomic Distances (Å) for
$W(C_3Et_3)[O\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]_3$

(A) Distances about the Tungsten Atom

W-O(1)	1.885 (6)	W-C(1)	1.949 (9)
W-O(2)	2.008 (6)	W-C(2)	2.159 (10)
W-O(3)	1.979 (6)	W-C(3)	1.883 (10)

(B) Distances within C_3Et_3 Ligand

C(1)-C(2)	1.433 (14)	C(2)-C(2A)	1.533 (14)
C(2)-C(3)	1.467 (14)	C(2A)-C(2B)	1.547 (16)
C(1)-C(1A)	1.517 (14)	C(3)-C(3A)	1.517 (16)
C(1A)-C(1B)	1.500 (19)	C(3A)-C(3B)	1.537 (17)

(C) O-C Distances within Phenoxide Ligands

O(1)-C(11)	1.368 (12)	O(3)-C(31)	1.363 (12)
O(2)-C(21)	1.354 (12)		

(D) Distances within Six-Membered Rings

C(11)-C(12)	1.393 (15)	C(21)-C(22)	1.415 (15)
C(12)-C(13)	1.414 (18)	C(22)-C(23)	1.430 (17)
C(13)-C(14)	1.381 (19)	C(23)-C(24)	1.357 (17)
C(14)-C(15)	1.371 (20)	C(24)-C(25)	1.335 (19)
C(15)-C(16)	1.441 (17)	C(25)-C(26)	1.437 (17)
C(16)-C(11)	1.395 (15)	C(26)-C(21)	1.373 (14)
C(31)-C(32)	1.413 (15)	C(34)-C(35)	1.405 (19)
C(32)-C(33)	1.414 (17)	C(35)-C(36)	1.411 (17)
C(33)-C(34)	1.389 (19)	C(36)-C(31)	1.420 (15)

(E) Distances within Isopropyl Groups

C(12)-C(12A)	1.572 (18)	C(22)-C(22A)	1.551 (15)
C(12A)-C(12B)	1.515 (24)	C(22A)-C(22B)	1.565 (19)
C(12A)-C(12C)	1.515 (26)	C(22A)-C(22C)	1.560 (19)
C(16)-C(16A)	1.515 (18)	C(26)-C(26A)	1.526 (16)
C(16A)-C(16B)	1.559 (23)	C(26A)-C(26B)	1.538 (18)
C(16A)-C(16C)	1.583 (25)	C(26A)-C(26C)	1.555 (18)
C(32)-C(32A)	1.498 (16)	C(36)-C(36A)	1.540 (17)
C(32A)-C(32B)	1.567 (19)	C(36A)-C(36B)	1.538 (23)
C(32A)-C(32B)	1.523 (19)	C(36A)-C(36C)	1.551 (25)

(see Table III). But the SP description is suggested by the fact that the W-O(2) and W-O(3) bonds are tipped away from the WC_3 ring to a significant extent (O(2)-W-O(3) = 163.5 (3)°; see Table II), that the equatorial W-O(1) bond does *not* lie symmetrically in an exterior position

(4) Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808.

(5) In this, and all other metallacyclobutadiene complexes mentioned in this paper, the first and third monoaubatituted carbon atoms are the α-carbon atoms in the WC_3 ring.

(6) See the third paper in this series of three.

(7) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903.
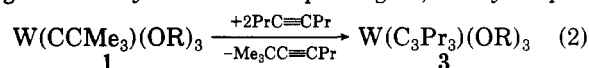
(8) Pedersen, S. F. Ph.D. Thesis, Massachusetts Institute of Technology, 1983.

between C(1) and C(3) (O(1)-W-C(1) = 150.0 (4)° and O(1)-W-C(3) = 127.7 (3)°; see Table II), and that the W-C(3) bond (1.883 (10) Å) is somewhat shorter than the W-C(1) bond (1.949 (9) Å; see below). However, in order to simplify discussion we will continue to refer to the molecule as a trigonal bipyramid.

There are several interesting structural features of the WC_3Et_3 system. Perhaps the most important potentially is the difference between the W-C(3) and W-C(1) bond lengths mentioned above. The difference (0.07 Å) is significant, since 3σ is ~0.03 Å. The difference between the C(2)-C(3) and C(1)-C(2) bond lengths is not statistically significant, but the relative lengths are at least consistent with a tendency toward a "long-short-long-short" alternation of bond lengths within the WC_3 ring, as if the acetylene containing C(1) and C(2) is beginning to be lost. It is also important to note that the W-C(2) distance of 2.159 (10) Å is of the order of a typical W-C single bond; it is only slightly longer than the $W\text{-}C_\beta$ distance (2.115 (8) Å) found in $W[C(CMe_3)C(Me)C(Me)]Cl_3$.[4] The substituent methylene carbon atoms [C(1A), C(2A), C(3A)] are close to coplanar with the cyclic WC_3 system; individual deviations from the plane are +0.007 (11), −0.083 (11), and +0.027 (11) Å, respectively. The terminal carbon atoms of the ethyl groups are oriented such that, relative to Figure 3, C(1B) points upward (deviation from WC_3 plane is +1.349 (13) Å), C(2B) points downward (deviation, −1.547 (11) Å), and C(3B) points slightly upward (deviation, +0.739 (12) Å). Other features of interest within the WC_3Et_3 system include the internal angle at the β-carbon atom (C(1)-C(2)-C(3) = 120.8 (9)°) and the large external angles at the α-carbon atoms (W-C(1)-C(1A) = 155.1 (8)° and W-C(3)-C(3A) = 152.7 (8)°).

The two axial phenoxide ligands differ substantially from the equatorial phenoxide ligand in how they are bound to the metal. The axial tungsten-oxygen distances are relatively long (W-O(2) = 2.008 (6) Å and W-O(3) = 1.979 (6) Å), and the W-O-C angles are relatively sharp (W-O(2)-C(21) = 131.4 (6)° and W-O(3)-C(31) = 135.1 (5)°). In contrast, the equatorial tungsten-oxygen distance is foreshortened (W-O(1) = 1.885 (6) Å) and the angle at oxygen much larger (W-O(1)-C(11) = 151.5 (6)°). We conclude that the equatorial phenoxide ligand donates its π electrons more efficiently to the metal. The fact that the angle between O(1) and C(1) is 150.0 (4)° while that between O(1) and C(3) is only 127.7 (3)° could account for the lengthening of W-C(1) by 0.066 (14) Å relative to the otherwise chemically equivalent W-C(3) bond and loss of the acetylene containing C(1) and C(2). But it is also possible that at least some of the W-C(1) bond lengthening can be ascribed to steric interaction between the substituent on C(1) and the isopropyl groups and that the metallacycle shown in eq 1 is relatively unstable compared to 2 for that reason. In order to explore this possibility we turned to an analogous metallacycle containing propyl substituents on C(1), C(2), and C(3).

The Preparation of $W(C_3Pr_3)[O\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]_3$ (3). $W(C_3Pr_3)[O\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]_3$ can be prepared straightforwardly as shown in eq 2. Again, if only 1 equiv

$$W(CCMe_3)(OR)_3 \xrightarrow[-Me_3CC{\equiv}CPr]{+2PrC{\equiv}CPr} W(C_3Pr_3)(OR)_3 \quad (2)$$
$$\mathbf{1} \qquad\qquad\qquad\qquad\qquad \mathbf{3}$$

of 4-octyne is added, the reaction proceeds only halfway and even after 2 days a 1:1 mixture of 1 and 3 in ether at 25 °C is virtually unchanged. Therefore the general features of the preparation and properties of 3 are similar to those of 2 we discussed above. However, one interesting difference between 2 and 3 is that the ^1H NMR spectrum of 3 is not completely normal. In particular the signal for
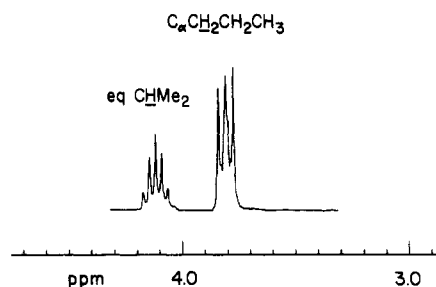
Table II. Interatomic Angles (deg) for W(C₃Et₃)[O-2,6-C₆H₃(*i*-Pr)₂]₃

(A) Angles about the Tungsten Atom

O(1)-W-O(2)	81.8 (3)	O(2)-W-O(3)	163.5 (3)	O(3)-W···C(2)	99.0 (3)
O(1)-W-O(3)	84.3 (3)	O(2)-W-C(3)	96.2 (4)	C(1)-W-C(3)	82.3 (4)
O(1)-W-C(1)	150.0 (4)	O(2)-W···C(2)	96.2 (3)	C(1)-W···C(2)	40.4 (4)
O(1)-W-C(3)	127.7 (3)	O(3)-W-C(1)	93.2 (3)	C(3)-W···C(2)	41.9 (4)
O(1)-W···C(2)	169.3 (3)	O(3)-W-C(3)	99.4 (4)		

(B) Angles Involving C₃Et₃ Ligand

C(1)-C(2)-C(3)	120.8 (9)	C(3)-C(3A)-C(3B)	111.7 (10)	C(1)-C(2)-C(2A)	121.9 (9)
W-C(1)-C(2)	77.7 (6)	W···C(2)-C(2A)	175.7 (8)	C(3)-C(2)-C(2A)	117.3 (9)
W-C(3)-C(2)	79.2 (6)	W-C(1)-C(1A)	155.1 (8)	C(2)-C(1)-C(1A)	127.2 (9)
C(1)-C(1A)-C(1B)	113.5 (10)	W-C(3)-C(3A)	152.7 (8)	C(2)-C(3)-C(3A)	128.1 (9)
C(2)-C(2A)-C(2B)	110.1 (9)				

(C) W-O-C Angles

W-O(1)-C(11)	151.5 (6)	W-O(2)-C(21)	131.4 (6)	W-O(3)-C(31)	135.1 (5)

(D) O-C-C Angles

O(1)-C(11)-C(12)	119.3 (9)	O(2)-C(21)-C(22)	119.6 (8)	O(3)-C(31)-C(32)	118.8 (9)
O(1)-C(11)-C(16)	116.9 (9)	O(2)-C(21)-C(26)	119.2 (9)	O(3)-C(31)-C(36)	119.9 (9)

(E) Angles within Six-Membered Rings

C(11)-C(12)-C(13)	118.3 (10)	C(21)-C(22)-C(23)	118.0 (9)	C(31)-C(32)-C(33)	117.7 (10)
C(12)-C(13)-C(14)	119.1 (12)	C(22)-C(23)-C(24)	118.5 (12)	C(32)-C(33)-C(34)	121.7 (12)
C(13)-C(14)-C(15)	122.5 (13)	C(23)-C(24)-C(25)	124.5 (13)	C(33)-C(34)-C(35)	120.1 (12)
C(14)-C(15)-C(16)	120.1 (12)	C(24)-C(25)-C(26)	118.8 (11)	C(34)-C(35)-C(36)	120.0 (12)
C(15)-C(16)-C(11)	116.3 (10)	C(25)-C(26)-C(21)	118.8 (10)	C(35)-C(36)-C(31)	119.1 (10)
C(16)-C(11)-C(12)	123.6 (10)	C(26)-C(21)-C(22)	121.1 (10)	C(36)-C(31)-C(32)	121.1 (9)

(F) External C(aromatic)-C(aromatic)-C(isopropyl) Angles

C(11)-C(12)-C(12A)	120.1 (10)	C(21)-C(22)-C(22A)	119.1 (9)	C(31)-C(32)-C(32A)	120.6 (10)
C(13)-C(12)-C(12A)	121.6 (11)	C(23)-C(22)-C(22A)	122.8 (10)	C(33)-C(32)-C(32A)	121.6 (10)
C(11)-C(16)-C(16A)	121.2 (10)	C(21)-C(26)-C(26A)	119.0 (10)	C(31)-C(36)-C(36A)	119.9 (10)
C(15)-C(16)-C(16A)	122.5 (10)	C(25)-C(26)-C(26A)	122.2 (9)	C(35)-C(36)-C(36A)	120.9 (10)

(G) Angles within Isopropyl Groups

C(12)-C(12A)-C(12B)	109.3 (11)	C(22)-C(22A)-C(22B)	108.4 (10)	C(32)-C(32A)-C(32B)	112.8 (10)
C(12)-C(12A)-C(12C)	108.3 (13)	C(22)-C(22A)-C(22C)	112.8 (10)	C(32)-C(32A)-C(32C)	110.6 (10)
C(12B)-C(12A)-C(12C)	109.4 (14)	C(22B)-C(22A)-C(22C)	110.8 (10)	C(32B)-C(32A)-C(32C)	110.2 (11)
C(16)-C(16A)-C(16B)	108.8 (12)	C(26)-C(26A)-C(26B)	108.7 (10)	C(36)-C(36A)-C(36B)	108.8 (11)
C(16)-C(16A)-C(16C)	112.7 (12)	C(26)-C(26A)-C(26C)	114.2 (10)	C(36)-C(36A)-C(36C)	111.2 (12)
C(16B)-C(16A)-C(16C)	111.0 (12)	C(26B)-C(26A)-C(26C)	110.0 (10)	C(36B)-C(36A)-C(36C)	113.0 (14)

### Table III. Least-Squares Planes within the W(C₃Et₃)[O-2,6-C₆H₃(*i*-Pr)₂]₃ Molecule

atoms	dev, Å	atoms	dev, Å
(A) WC₃ Plane			
0.8009X + 0.5500Y − 0.2367Z − 2.7858 = 0			
W*	−0.0066 (4)	C(1A)	0.007 (11)
C(1)*	0.010 (9)	C(1B)	1.349 (13)
C(2)*	−0.013 (9)	C(2A)	−0.083 (10)
C(3)*	0.010 (9)	C(2B)	−1.547 (11)
O(1)	−0.069 (6)	C(3A)	0.027 (11)
C(11)	0.338 (9)	C(3B)	0.739 (12)
(B) C(11)→C(16) Plane			
0.4240X + 0.2413Y − 0.8729Z + 8.8337 = 0			
C(11)*	0.019 (9)	C(14)*	0.011 (13)
C(12)*	−0.017 (10)	C(15)*	−0.009 (12)
C(13)*	0.001 (12)	C(16)*	−0.006 (10)
(C) C(21)→C(26) Plane			
0.0861X + 0.9421Y − 0.3239Z − 0.4101 = 0			
C(21)*	0.031 (9)	C(24)*	0.011 (13)
C(22)*	−0.003 (10)	C(25)*	0.017 (11)
C(23)*	−0.018 (11)	C(26)*	−0.038 (10)
(D) C(31)→C(36) Plane			
−0.8446X − 0.1685Y − 0.5082Z + 11.150 = 0			
C(31)*	0.023 (9)	C(34)*	0.011 (12)
C(32)*	−0.020 (9)	C(35)*	−0.008 (12)
C(33)*	0.003 (11)	C(36)*	−0.009 (10)

Figure 4. Partial ¹H NMR spectrum of W(C₃Pr₃)[O-2,6-C₆H₃-(*i*-Pr)₂]₃.

the methylene group next to the α-carbon atom is not the expected first-order 1:2:1 triplet (Figure 4). The pattern most likely results from restricted rotation within each

propyl group.[9a] In contrast, the $C_\alpha CH_2CH_3$ protons in **2** are coupled in a first-order manner to the much more freely rotating methyl groups. We also note that the signal for the $C_\beta CH_2CH_2CH_3$ protons in **3**, as far as we can tell, is normal. These data provide direct evidence that the α substituents in the WC₃ ring interact significantly with one or more of the alkoxide ligands in **3**. Presumably, the same is true to some extent in **2**.

Metathesis of Acetylenes by W(C₃R₃)[O-2,6-C₆H₃-(*i*-Pr)₂]₃ Complexes. W(CCMe₃)[O-2,6-C₆H₃(*i*-Pr)₂]₃ (**1**) catalyzes the metathesis of 3-heptyne in ether or pentane ($t_{1/2}$ to equilibrium for 20 equiv ≈ 4.5 h at 25 °C). The metathesis of 4-nonyne is substantially faster ($t_{1/2}$ to equilibrium for 20 equiv ≈ 25 min at 25 °C). In both cases *tert*-butyl-containing cleavage products are formed rapidly and quantitatively at the beginning of the reaction. We suspected that the slowest step of the metathesis mechanism in each case consists of loss of acetylene from the least
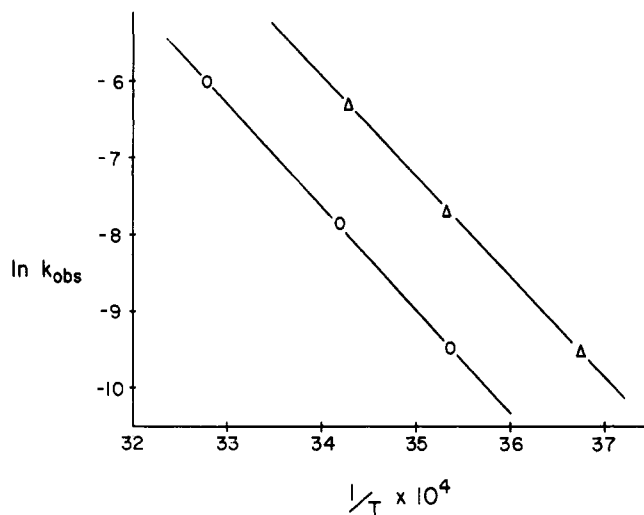
Figure 5. Arrhenius plot for the reaction of $W(C_3R_3)[O-2,6-C_6H_3(i-Pr)_2]_3$ with excess 3-hexyne-d_{10}: O, R = Et (2); △, R = Pr (3).

sterically crowded WC_3 complex possible in a given system (2 and 3, respectively) and that 3 loses 4-octyne more readily than 2 loses 3-hexyne.

In order to obtain more quantitative data and substantiate the proposed mechanism, we studied the rate of incorporation of 3-hexyne-d_{10} into 2 and 3. In each case the reaction was performed in the presence of a large excess of 3-hexyne-d_{10}, and the rate of disappearance of the methyl resonance in the β-alkyl group of the WC_3R_3 ring was monitored by ^1H NMR. The resonance for the methyl group in the β substituent was chosen for two reasons. First, it is located well away from all other resonances. Second, the rate of disappearance of the β-$(CH_2)_xCH_3$ signal *should* equal the rate of loss of 3-hexyne or 4-octyne from the ring. We will discuss this assumption after we present the kinetic results.

The rates of reaction of 2 and 3 with excess 3-hexyne-d_{10} were found to be nicely first order in 2 and 3 for 2–3 halflives and independent of 3-hexyne-d_{10} concentration (see Table VI). A variable-temperature study led to values of $\Delta H^{\ddagger}$ = +26.1 (4) kcal mol^{-1} and $\Delta S^{\ddagger}$ = +15.2 (15) eu for 2 and $\Delta H^{\ddagger}$ = +25.4 (5) kcal mol^{-1} and $\Delta S^{\ddagger}$ = +16.3 (16) eu for 3 (Figure 5). These data are consistent with a rate-limiting loss of 3-hexyne from 2 (or 4-octyne from 3) to give the putative alkylidyne complex, which then reacts rapidly with the excess 3-hexyne-d_{10} (eq 3). Near room

$$\text{(3)}$$
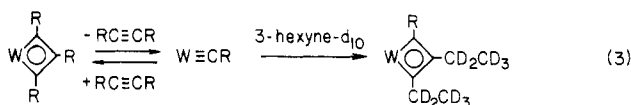
temperature 3 reacts with 3-hexyne-d_{10} at a rate that is approximately 5 times faster than the rate at which 2 reacts with 3-hexyne-d_{10}. Since we noted evidence for restricted rotation of the α-propyl group in 3 (see above), the difference in the rate of reaction of 2 and 3 with 3-hexyne-d_{10} is probably best ascribed largely to steric factors, rather than to what are likely to be relatively small electronic differences.

Now let us come back to our assumption that the rate of disappearance of the β-$(CH_2)_xCH_3$ signal in 2 or 3 in the presence of 3-hexyne-d_{10} equals the rate of loss of 3-hexyne or 4-octyne, respectively, from the ring (eq 3). This would *not* be true only if $W(OR)_3[C(Pr)C(CD_2CD_3)C(CD_2CD_3)]$ were to rearrange *intramolecularly* to $W(OR)_3[C-(CD_2CD_3)C(Pr)C(CD_2CD_3)]$ at a rate that is competitive with loss of $PrC\equiv CCD_2CD_3$ to give putative W-

$(CCD_2CD_3)(OR)_3$. After a sample of 3 had been allowed to *equilibrate* with 1.5 equiv of 3-hexyne-d_{10}, the ^1H NMR spectrum showed $C_\alpha CH_2CH_2CH_3$ signals for 3 plus $C_\alpha CH_2CH_2CH_3$ signals for at least one other α-propyl-substituted tungstenacyclobutadiene complex; four are possible—$W[C(Pr)C(CD_2CD_3)C(CD_2CD_3)]$, $W[C(Pr)C(C-D_2CD_3)C(Pr)]$, $W[C(Pr)C(Pr)C(CD_2CD_3)]$, and 3. Unfortunately, signals for all $C_\beta(CH_2)_2CH_3$ groups in the metallacycles in this mixture are coincident; however, the relatively high area of the $C_\beta(CH_2)_2CH_3$ peak relative to the total area of all $C_\alpha CH_2CH_2CH_3$ peaks reveals that $W[C(CD_2CD_3)C(Pr)C(CD_2CD_3)]$ and $W[C(Pr)C(Pr)C(C-D_2CD_3)]$ isomers must be present. This is important since in the reaction between 3 and excess 3-hexyne-d_{10} one other $C_\alpha CH_2CH_2CH_3$ signal grows in with time, but the ratio of the $C_\beta(CH_2)_2CH_3$ signal to the $C_\alpha CH_2CH_2CH_3$ peak in 3 remains 3:4 throughout the kinetic run, suggesting that only the $W[C(Pr)C(CD_2CD_3)C(CD_2CD_3)]$ isomer is present. Secondly, we note that kinetic runs at all temperatures and concentrations of reactants produce excellent first-order plots. These two pieces of evidence give us confidence that $W(OR)_3[C(CD_2CD_3)C(Pr)C(CD_2CD_3)]$ is, in fact, never present, as we initially assumed (eq 3), and that the rate of disappearance of the $C_\beta(CH_2)_xCH_3$ signal therefore equals the rate of loss of $RC\equiv CR$ from the WC_3 ring. We realize that a *small* amount of $W(OR)_3[C(CD_2CD_3)C-(Pr)C(CD_2CD_3)]$ could still be present under these conditions but that quantity would be of no consequence to us at this point.

Related Results. The reaction between $W(CCMe_3)-[O-2,6-C_6H_3(i-Pr)_2]_3$ and 1 equiv of 2-butyne produces two new metallacyclobutadiene complexes (by ^1H NMR) and an unidentified polymer;[9b] some starting material remains. One of the metallacycles is the expected trimethyl-substituted complex 4, while the other is the α-*tert*-butyl-substituted complex (5; eq 4), according to NMR spectra.

$$\text{(4)}$$
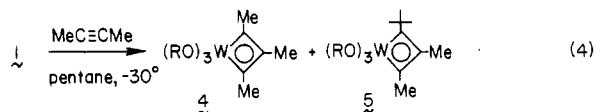
The fraction of 5 in mixtures of 4 and 5 decreases markedly in 1 day. We believe that 5 decomposes in this time period but have yet to identify the decomposition products. Note that the $W[C(CMe_3)C(Et)C(Et)]$ analogue of 5 is *not* observable (eq 1). The most straightforward explanation is that for steric reasons 5 loses $Me_3CC\equiv CMe$ significantly more slowly than $W[C(CMe_3)C(Et)C(Et)](OR)_3$ loses $Me_3CC\equiv CEt$.

So far we have not been able to isolate either 4 or 5 or prepare a solution containing exclusively one or the other. For example, an attempt to prepare pure 4 by adding a large excess of 2-butyne to 1 yielded a great deal more polymer but only some enrichment of the mixture in 4. Attempts to prepare pure 5 by treating $W[C(CMe_3)C-(Me)C(Me)](dme)Cl_3$ with 3 equiv of lithium 2,6-diisopropylphenoxide resulted in only partial substitution to give $W[C(CMe_3)C(Me)C(Me)][O-2,6-C_6H_3(i-Pr)_2]_2Cl$ (7). If only 1 equiv of lithium 2,6-diisopropylphenoxide is added to $W[C(CMe_3)C(Me)C(Me)](dme)Cl_3$, $W[C-(CMe_3)C(Me)C(Me)][O-2,6-C_6H_3(i-Pr)_2]Cl_2$ (6) is formed in high yield. NMR data are consistent with 6 and 7 being

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(9) (a) The observed pattern results from an AA'XX' spin system in which $J_{AX} \neq J_{AX'}$. In cases of unrestricted rotation an apparent A_2X_2 pattern (i.e., $J_{AX} \simeq J_{AX'}$) usually results. This is in fact the case for $W(C_3Pr_3)[OCH(CF_3)_2]_3$ (see second paper in this series) in which the $C_\alpha CH_2CH_2CH_3$ signal appears as a normal triplet. (b) We have assumed this is a 2-butyne polymer. We have not attempted to determine if it is metal-free.

trigonal bipyramids with one equatorial phenoxide (6) and one equatorial and one axial phenoxide ligand (7). Neither 6 nor 7 catalyzes the metathesis of 4-nonyne (25 °C, 48 h).

As we alluded to in the Introduction, the steric bulk of the alkoxides is of great import in this type of chemistry. This can be illustrated nicely by comparing the results we have been discussing for the diisopropoxide system with those obtained by using other 2,6-disubstituted phenoxide ligand systems. For example, the reaction between W-(CCMe$_3$)Cl$_3$(dme) and 3 equiv of lithium 2,6-dimethylphenoxide in tetrahydrofuran produces W(CCMe$_3$)[O-2,6-C$_6$H$_3$Me$_2$]$_3$(THF) (8) in good yield. We propose that 8 is a trigonal-bipyramidal molecule containing the three phenoxide ligands in equatorial positions. It reacts with 3-heptyne to produce a substantial amount of polymer, but it is a poor metathesis catalyst. We suspect that the *2,6-dimethylphenoxide* ligands in a tungstenacyclobutadiene complex are to small to force the loss of an acetylene and too small to prevent further reactions with an acetylene to yield larger and larger ring systems. Such a "ring expansion" would explain the polymerization of 3-heptyne by 8 and of 2-butyne even by O-2,6-C$_6$H$_3$(i-Pr)$_2$ catalysts. Analogous ring expansion reactions involving MC$_x$ rings (where x is *even*) have been observed recently in M(η^5-C$_5$H$_5$)$_2$ systems (M = Ti or Zr).[10]

Reactions involving 2,6-di-*tert*-butylphenoxide ligands illustrate that steric effects can easily become the problem rather than the solution. W(CCMe$_3$)(dme)Cl$_3$ will react with only 2 equiv of LiO-2,6-C$_6$H$_3$(CMe$_3$)$_2$. The product is an alkylidene complex in which $J_{CH_a} \simeq 130$ Hz. Two structures are likely (9a and 9b). The one which seems
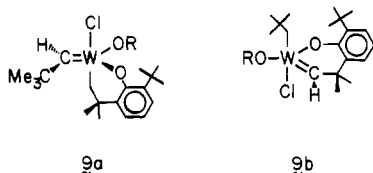
more likely is 9a by comparison with W(CHCMe$_3$)-(OCH$_2$CMe$_3$)$_2$Cl$_2$,[11] which is thought to be a trigonal-bipyramidal complex containing axial chloride ligands. We feel that 9b is less likely since (i) it would most likely form from 9a and there is no reason to expect 9a to rearrange to 9b under mild conditions and (ii) addition of a CH bond from a *tert*-butyl group in O-2,6-C$_6$H$_3$(CMe$_3$)$_2$ to a metal to form a bidentate ligand analogous to that in 9a has been observed in tantalum chemistry.[12]

Discussion

One of the most surprising results of this study is the similarity of the structure of W(C$_3$Et$_3$)[O-2,6-C$_6$H$_3$(i-Pr)$_2$]$_3$ to that of W[C(CMe$_3$)C(Me)C(Me)]Cl$_3$ (Figure 6). With the exception of the slight bond alternation in the WC$_3$ ring of the W(OR)$_3$ complex, the bond distances and angles within the WC$_3$R$_3$ systems are, within experimental error, virtually identical. In each complex the axial substituents are bent back from the WC$_3$ ring and the equatorial substituent is unsymmetrically placed relative to the α-carbon atoms of the WC$_3$ ring. In attempting to explain the latter it might be worth noting that the C$_\alpha$-W-C$_\alpha$ angle cannot possibly approach the 120° required in an ideal trigonal bipyramid. Perhaps that is why the molecule distorts
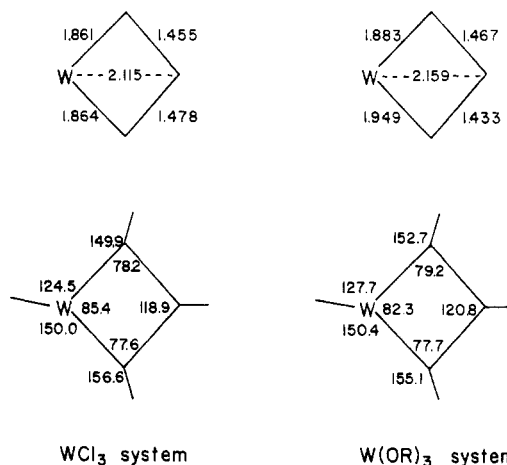

Figure 6. A comparison of some bond distances and angles in the equatorial plane in W[C(CMe$_3$)C(Me)C(Me)]Cl$_3$ and W-(C$_3$Et$_3$)[O-2,6-C$_6$H$_3$(i-Pr)$_2$]$_3$.

toward a tetragonal-pyramidal geometry with one of the α-carbon atoms of the WC$_3$ ring being approximately at the apex.

It is now clear that steric bulk of the alkoxide ligands is an extremely important factor in determining whether metathesis reactions will succeed or fail. Diisopropylphenoxide ligands are bulky enough to keep alkylidyne complexes from dimerizing through the phenoxide oxygen, to block further reaction of most acetylenes with a tungstenacyclobutadiene complex, and to encourage loss of an acetylene from a tungstenacyclobutadiene complex. The last of these also depends upon the size of the substituents on the WC$_3$ ring, as has been demonstrated here in several ways. In contrast, in the trichloride system, which we will describe and discuss in some detail in the third paper in this series, an acetylene is not lost from a WC$_3$ ring and another acetylene can attack the metal to give, ultimately, a cyclopentadienyl complex. We now feel that both results can be ascribed to a comparative lack of steric hindrance by chloride ligands. It should be noted that chloride ligands are not antithetical to metathesis, as the first observed metathesis activity by a characterized complex involved W(CCMe$_3$)Cl$_3$(PMe$_3$)$_3$ as the catalyst at ~80° with phenyltolylacetylene as the substrate.[13]

We suspect that there is no significant difference between the mechanism of acetylene metathesis that we have elucidated here and that presumed to operate in the *tert*-butoxide system, except that W(C$_3$R$_3$)(OCMe$_3$)$_3$ complexes have never been observed. From a steric point of view it is not clear why they have not been. But what we have not yet considered in this discussion are electronic differences. The much poorer basicity of the phenoxide ion (pK_a of phenol $\simeq$ 9) relative to the *tert*-butoxide ion (pK_a of *tert*-butyl alcohol $\simeq$ 16) would likely cause the metal in a phenoxide complex to be more electron poor in general and less likely to lose a reasonably good electron-donating acetylene from the WC$_3$R$_3$ ring system. Another way of looking at it is that the much better π-electron-donating *tert*-butoxide ligands in a W(C$_3$R$_3$)-(OCMe$_3$)$_3$ complex would more extensively labilize one RC≡CR in the WC$_3$R$_3$ ring system.

It is interesting to contemplate to what extent the rather finely tuned chemistry we have uncovered here can be duplicated in heterogeneous acetylene metathesis systems, the first to be discovered.[14] We might suspect that it

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Table IV. Experimental Data for X-ray Diffraction Study of $W(C_3Et_3)[O-2,6-C_6H_3(i-Pr)_2]_3$

(A) Crystal Parameters at 23 °C (296 K)

crystal system: monoclinic

space group: $P2_1/c$ [No. 14; C_{2h}^5] $V = 4279$ (2) Å^3
$a = 19.271$ (6) Å $Z = 4$
$b = 13.000$ (3) Å   mol wt = 838.95
$c = 17.195$ (6) Å ρ(calcd) = 1.30 g cm^{-3}
$\beta = 96.55$ (2)°

(B) Data Collection

diffractometer: Syntex P2$_1$

radiation: Mo Kα ($\bar{\lambda} = 0.710\ 730$ Å)

monochromator: pyrolytic graphite

scan type: coupled θ(crystal)-2θ(counter)

scan width: symmetrical, $[1.8 + \Delta(\alpha_2 - \alpha_1)]°$

scan speed: 2.50 deg/min

reflctns collected: $+h,+k,\pm l$ for $2\theta = 4.5-40.0°$;
 4181 total yielding 3873 uniqud data

abs coeff: $\mu = 28.9$ cm^{-1}; corrected by interpolation between experimental ψ scans of four close-to-axial reflections ($2\bar{2}6$, $14\bar{1}\bar{1}$, $2\bar{3}\bar{7}$, $3\bar{4}\bar{7}$)

cannot be or at least that the selectivity for metathesis (vs. polymerization, cyclotrimerization, etc.) will never be as high in the heterogeneous as in the homogeneous systems. Therein lies a likely fundamental difference between acetylene metathesis systems and olefin metathesis systems.

Experimental Section

General Data. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmosphere HE43-2 drybox or by using standard Schlenk techniques. Reagent grade ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. 3-Hexyne, 3-heptyne, 4-octyne, and 4-nonyne were degassed and passed down a column of activated alumina prior to use. 3-Hexyne-d_{10} was prepared from EtBr-d_5 by a method analogous to that of Brandsma for 5-decyne.[15] EtBr-d_5 was either purchased or prepared from CD_3CO_2H and LiAlD$_4$ by standard organic reactions.[16] Lithium phenoxides were prepared from the appropriate phenol and n-butyllithium in pentane. The precipitated salts were used without further purification. W(CCMe$_3$)(dme)Cl$_3$[3a] and W[C(CMe$_3$)C(Me)C(Me)]Cl$_3$[4,6] were prepared according to published methods.

Benzene-d_6 and toluene-d_8 were degassed and passed down a column of activated alumina prior to use. NMR data are listed in parts per million relative to the residual resonance of benzene-d_5 (7.15 ppm). NMR spectra were acquired at 250 or 270 MHz (^{1}H) or 67.9 MHz (^{13}C).

Collection of X-ray Diffraction Data and Solution of the Crystal Structure of $W(C_3Et_3)[O-2,6-C_6H_3(i-Pr)_2]_3$. A carefully selected dark red crystal of $W(C_3Et_3)[O-2,6-C_6H_3(i-Pr)_2]_3$ was mounted in a thin-walled glass capillary under an inert (Ar) atmosphere and was aligned on the Syntex P2$_1$ automated four-circle diffractometer at SUNY—Buffalo. Determination of the unit cell parameters, crystal orientation matrix, and Bravais lattice were carried out as described previously;[17] diffraction data were collected under the conditions described in Table IV.

The resulting data were corrected for the effects of absorption and for Lorentz and polarization factors and were reduced to

unscaled $|F_o|$ values. Any reflection with I(net) < 0 was assigned a value of $|F_o| = 0$. All data were placed on an approximately absolute scale by means of a Wilson plot.

The position of the tungsten atom was derived from a three-dimensional Patterson synthesis. All remaining non-hydrogen atoms were located from a series of difference Fourier syntheses. The structure was refined to convergence using the "block-cascade" method. Final discrepancy indices were $R_F = 4.67\%$ and $R_{wF} = 5.28\%$ for 262 parameters refined against all 3873 unique data and $R_F = 4.17\%$ and $R_{wF} = 5.02\%$ for those 3449 data with $|F_o| > 3\sigma(|F_o|)$.

Final positional parameters are listed in Table V; anisotropic thermal parameters (Table VS) and a table of observed and calculated structure factors appear as supplementary material.

Initial data processing was performed by using the Syntex XTL system on our in-house NOVA 1200 computer; structure solution and refinement were carried out on the SUNY—Buffalo CDC Cyber 173 computer using the SHELX76 program set of G. Sheldrick. The calculated structure factors were based upon the analytical form of the neutral atom form factor;[18] both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for all non-hydrogen atoms. Hydrogen atom contributions were not included in the calculation.

Preparations. W(CCMe$_3$)[O-2,6-C$_6$H$_3$(i-Pr)$_2$]$_3$ (1). W-(CCMe$_3$)(dme)Cl$_3$ (1.71 g, 3.80 mmol) was added as a solid to a solution of lithium 2,6-diisopropylphenoxide (2.10 g, 11.4 mmol) in ether (25 mL) at room temperature. After 10 min the orange solution was filtered through Celite and stripped to dryness. The resulting orange waxy crystals of essentially pure product (2.70 g, 91% yield) were extremely soluble in pentane. Therefore the product could not be recrystallized and was used without purification for subsequent reactions: ^{1}H NMR (C$_6$D$_6$) δ 7.14 (d, 6, $^3J_{HH} = 7.3$ Hz, H$_{meta}$), 6.98 (t, 3, $^3J_{HH} = 7.3$ Hz, H$_{para}$), 3.72 (sep, 6, $^3J_{HH} = 6.8$ Hz, CHMe$_2$), 1.27 (d, 36, $^3J_{HH} = 6.8$ Hz, CHMe_2), 0.65 (S, 9, CCMe$_3$); ^{13}C NMR (C$_6$D$_6$) δ 295.2 (s, $J_{CW} = 289$ Hz, $CCMe_3$), 161.1 (s, C$_{ipso}$), 137.3 (s, C$_{ortho}$), 123.6 (d, $J_{CH} = 160$ Hz, C$_{para}$), 123.4 (d, $J_{CH} = 157$ Hz, C$_{meta}$), 51.9 (s, CCMe$_3$), 32.7 (q, $J_{CH} = 125$ Hz, CCMe_3), 27.9 (d, $J_{CH} = 127$ Hz, CHMe$_2$), 23.5 (q, $J_{CH} = 126$ Hz, CHMe_2).

W(C$_3$Et$_3$)[O-2,6-C$_6$H$_3$(i-Pr)$_2$]$_3$ (2). 3-hexyne (160 μL, 1.4 mmol) was added to a pentane solution (~10 mL) of 1 (0.50 g, 0.64 mmol) at room temperature. The solution turned dark red immediately. After 5 min the solvent was removed in vacuo leaving a red solid. The red solid was dissolved in a minimum of pentane, and the solution was cooled to −30 °C to give large, dark red prisms (2 crops, 0.38 g, 72% yield): ^{1}H NMR (C$_6$D$_6$) δ 7.20 (d, 2, $^3J_{HH} = 8.0$ Hz, eq H$_m$), 7.00 (t, 1, $^3J_{HH} = 8.0$ Hz, eq H$_p$), 6.91 (d, 4, $^3J_{HH} = 7.3$ Hz, ax H$_m$), 6.72 (t, 2, $^3J_{HH} = 7.3$ Hz, ax H$_p$), 4.15 (sep, 2, $^3J_{HH} = 7.4$ Hz, eq CHMe$_2$), 3.72 (q, 4, $^3J_{HH} = 7.6$ Hz, C$_\alpha$CH_2CH$_3$), 3.06 (sep, 4, $^3J_{HH} = 6.7$ Hz, ax CHMe$_2$), 2.98 (q, 2, $^3J_{HH} = 6.7$ Hz, C$_\beta$CH_2CH$_3$), 1.45 (d, 12, $^3J_{HH} = 7.4$ Hz, eq CHMe_2), 1.38 (t, 6, $^3J_{HH} = 7.6$ Hz, C$_\alpha$CH$_2$CH_3), 1.08 (d, 24, $^3J_{HH} = 6.7$ Hz, ax CHMe_2), 0.31 (t, 3, $^3J_{HH} = 6.7$ Hz, C$_\beta$CH$_2$CH_3); ^{13}C NMR (C$_6$D$_6$) δ 244.9 (s, $J_{CW} = 124$ Hz, C$_\alpha$), 162.3 (s, ax C$_{ipso}$), 159.5 (s, eq C$_{ipso}$), 137.6 (s, eq C$_o$), 136.9 (s, ax C$_o$), 136.6 (s, C$_\beta$), 123.3, 123.1, 122.3, 120.1 (each a d, $J_{CH} = 150-160$ Hz, C$_m$ and C$_p$), 29.5 (t, $J_{CH} = 130$ Hz, C$_\alpha$CH$_2$CH$_3$), 28.4 (d, $J_{CH} = 126$ Hz, eq CHMe$_2$), 27.3 (d, $J_{CH} = 126$ Hz, ax CHMe$_2$), 24.4 (t, $J_{CH} = 126$ Hz, C$_\beta$CH$_2$CH$_3$), 24.2 (q, $J_{CH} = 126$ Hz, eq CHMe_2), 23.6 (q, $J_{CH} = 126$ Hz, ax CHMe_2), 15.4 (q, $J_{CH} = 127$ Hz, C$_\alpha$CH$_2$CH$_3$), 12.6 (q, $J_{CH} = 130$ Hz, C$_\beta$CH$_2$CH$_3$). Anal. Calcd for WC$_{45}$H$_{66}$O$_3$: C, 64.43; H, 7.93. Found: C, 64.24; H, 7.90.

W(C$_3$Pr$_3$)[O-2,6-C$_6$H$_3$(i-Pr)$_2$]$_3$ (3). A sample of 1 (1.00 g, 1.27 mmol) was dissolved in pentane (15 mL), and 4-octyne (410 μL, 2.80 mmol) was added. The solution turned dark red immediately. After several minutes the solvent was removed in vacuo. The residue was recrystallized from pentane at −30 °C to give large, dark red prisms (two crops, 0.77 g, 69%): ^{1}H NMR (C$_6$D$_6$) δ 7.19 (d, 2, $^3J_{HH} = 7.7$ Hz, eq H$_m$), 6.97 (t, 1, $^3J_{HH} = 7.7$ Hz, eq H$_p$), 6.91 (d, 4, $^3J_{HH} = 7.6$ Hz, ax H$_m$), 6.73 (t, 2, $^3J_{HH} = 7.6$ Hz, ax H$_p$), 4.12 (sep, 2, $^3J_{HH} = 6.8$ Hz, eq CHMe$_2$), 3.82 (m, 4, C$_\alpha$CH_2CH$_2$CH$_3$), 3.20 (t, 2, $^3J_{HH} = 7.8$ Hz, C$_\beta$CH_2CH$_2$CH$_3$), 3.09 (sep, 4, $^3J_{HH} = 6.7$ Hz, ax CHMe$_2$), 2.06 (m, 4, C$_\alpha$CH$_2$CH_2CH$_3$),

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Table V. Final Parameters for $W(C_3Et_3)[O\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]_3$

atom	x	y	z	U_{iso}, Å^2
W	0.22716 (2)	0.46515 (3)	0.72187 (2)	
O(1)	0.2866 (3)	0.3797 (5)	0.7882 (4)	
O(2)	0.1548 (3)	0.3668 (5)	0.7527 (4)	
O(3)	0.3153 (3)	0.5261 (5)	0.6944 (4)	
C(1)	0.1772 (5)	0.4941 (8)	0.6192 (6)	
C(2)	0.1545 (5)	0.5761 (8)	0.6659 (6)	
C(3)	0.1815 (5)	0.5859 (8)	0.7488 (6)	
C(1A)	0.1549 (6)	0.4742 (10)	0.5330 (6)	
C(1B)	0.1901 (7)	0.5431 (13)	0.4795 (7)	
C(2A)	0.1008 (5)	0.6561 (9)	0.6322 (7)	
C(2B)	0.0273 (6)	0.6271 (10)	0.6529 (7)	
C(3A)	0.1658 (6)	0.6693 (9)	0.8060 (7)	
C(3B)	0.2269 (7)	0.6850 (10)	0.8706 (7)	
C(11)	0.3454 (5)	0.3206 (8)	0.8034 (6)	0.0438 (26)
C(12)	0.3428 (6)	0.2169 (9)	0.7830 (7)	0.0598 (32)
C(13)	0.4035 (7)	0.1567 (11)	0.8015 (8)	0.0826 (40)
C(14)	0.4621 (7)	0.2016 (11)	0.8412 (8)	0.0814 (40)
C(15)	0.4639 (7)	0.3028 (11)	0.8637 (8)	0.0791 (39)
C(16)	0.4036 (6)	0.3674 (9)	0.8446 (7)	0.0586 (31)
C(12A)	0.2731 (8)	0.1688 (12)	0.7423 (9)	0.0900 (43)
C(12B)	0.2498 (9)	0.0831 (15)	0.7931 (10)	0.1246 (60)
C(12C)	0.2872 (11)	0.1251 (17)	0.6639 (12)	0.1491 (73)
C(16A)	0.4019 (7)	0.4791 (11)	0.8693 (8)	0.0804 (39)
C(16B)	0.3787 (9)	0.4849 (14)	0.9532 (10)	0.1201 (57)
C(16C)	0.4744 (10)	0.5353 (16)	0.8661 (11)	0.1418 (69)
C(21)	0.0889 (5)	0.3825 (8)	0.7703 (6)	0.0440 (26)
C(22)	0.0780 (5)	0.4162 (8)	0.8462 (6)	0.0516 (29)
C(23)	0.0077 (7)	0.4327 (10)	0.8624 (7)	0.0713 (36)
C(24)	−0.0449 (7)	0.4159 (10)	0.8043 (8)	0.0779 (38)
C(25)	−0.0360 (6)	0.3800 (10)	0.7334 (7)	0.0690 (35)
C(26)	0.0336 (5)	0.3589 (8)	0.7155 (6)	0.0513 (29)
C(22A)	0.1418 (6)	0.4282 (9)	0.9092 (7)	0.0647 (33)
C(22B)	0.1654 (7)	0.3185 (11)	0.9389 (8)	0.0890 (43)
C(22C)	0.1262 (7)	0.4982 (11)	0.9787 (8)	0.0907 (44)
C(26A)	0.0481 (6)	0.3080 (9)	0.6390 (7)	0.0638 (33)
C(26B)	0.0634 (7)	0.1933 (11)	0.6545 (8)	0.0829 (40)
C(26C)	−0.0118 (8)	0.3204 (12)	0.5710 (9)	0.0955 (46)
C(31)	0.3376 (5)	0.5641 (8)	0.6277 (6)	0.0425 (26)
C(32)	0.3322 (5)	0.6709 (8)	0.6131 (6)	0.0504 (28)
C(33)	0.3545 (7)	0.7082 (10)	0.5428 (7)	0.0732 (36)
C(34)	0.3855 (7)	0.6442 (11)	0.4921 (8)	0.0796 (39)
C(35)	0.3927 (6)	0.5385 (10)	0.5082 (7)	0.0692 (35)
C(36)	0.3695 (5)	0.4976 (8)	0.5767 (6)	0.0511 (29)
C(32A)	0.3040 (6)	0.7415 (9)	0.6709 (7)	0.0635 (33)
C(32B)	0.2577 (8)	0.8298 (12)	0.6306 (9)	0.0986 (47)
C(32C)	0.3631 (8)	0.7865 (13)	0.7268 (9)	0.1028 (49)
C(36A)	0.3789 (7)	0.3827 (10)	0.5970 (8)	0.0744 (37)
C(36B)	0.4532 (10)	0.3657 (15)	0.6380 (11)	0.1362 (66)
C(36C)	0.3620 (11)	0.3145 (17)	0.5232 (12)	0.1506 (75)

1.42 (d, 12, $^3J_{HH}$ = 6.8 Hz, eq CHMe_2), 1.09 (d, 24, $^3J_{HH}$ = 6.7 Hz, ax CHMe_2), 1.08 (t, 6, $^3J_{HH}$ = 7.9 Hz, C_αCH$_2$CH$_2$CH_3), 0.92 (sext, 2, $^3J_{HH}$ = 7.8 Hz, C_βCH$_2$CH_2CH$_3$), 0.48 (t, 3, $^3J_{HH}$ = 7.8 Hz, C_βCH$_2$CH$_2$CH_3); ^{13}C NMR (C$_6$D$_6$) δ 237.1 (s, J_{CH} = 125 Hz, C_α), 162.2 (s, ax C_{ipso}), 159.5 (s, eq C_{ipso}), 137.8 (s, eq C_o), 137.2 (s, ax C_o), 134.8 (s, C_β), 123.4, 123.1, 122.3, 120.2 (each a d, J_{CH} = 150–160 Hz, C_m and C_p), 39.0 (t, J_{CH} = 130 Hz, C_αCH$_2$CH$_2$CH$_3$), 33.2 (t, J_{CH} = 136 Hz, C_βCH$_2$CH$_2$CH$_3$), 28.3 (d, J_{CH} = 130 Hz, eq CHMe_2), 27.4 (d, J_{CH} = 130 Hz, ax CHMe_2), 24.8 (t, J_{CH} = 125 Hz, C_αCH$_2$CH$_2$CH$_3$), 24.3 (q, J_{CH} = 126 Hz, eq CHMe_2), 23.7 (q, J_{CH} = 126 Hz, ax CHMe_2), 22.3 (t, J_{CH} = 127 Hz, C_βCH$_2$CH$_2$CH$_3$), 14.9 (q, J_{CH} = 125 Hz, C_αCH$_2$CH$_2$CH$_3$), 13.8 (q, J_{CH} = 126 Hz, C_βCH$_2$CH$_2$CH$_3$). Anal. Calcd for WC$_{48}$H$_{72}$O$_3$: C, 65.44; H, 8.24. Found: C, 64.91; H, 8.22.

W[C(CMe$_3$)C(Me)C(Me)][O-2,6-C$_6$H$_3$(i-Pr)$_2$]Cl$_2$ (6). W[C-(CMe$_3$)C(Me)C(Me)]Cl$_3$ (0.50 g, 1.2 mmol) was added to a solution of lithium 2,6-diisopropylphenoxide (0.22 g, 1.2 mmol) in ether (~15 mL) at room temperature. After 1 h the bright red solution was filtered and the solvent removed in vacuo. The product was recrystallized from ether at −30 °C, giving bright red crystals (two crops, 0.54 g, 81% yield): ^{1}H NMR (C$_6$D$_6$) δ 7.19 (d, 2, $^3J_{HH}$ = 7.6 Hz, H$_m$), 7.00 (t, 1, $^3J_{HH}$ = 7.6 Hz, H$_p$), 3.91 (sep, 2, $^3J_{HH}$ = 6.7 Hz, CHMe_2), 3.29 (s, 3, C_αCH$_3$), 2.24 (s, 3, C_βCH$_3$), 1.54 (d, 12, $^3J_{HH}$ = 6.7 Hz, CHMe_2), 1.43 (s, 9, CCMe_3); ^{13}C NMR (C$_6$D$_6$) δ 278.5 (s, C_α), 270.1 (s, C_α), 163.8 (s, C_{ipso}), 141.3 (s, C_β), 137.6

(s, C_o), 124.0 (d, J_{CH} = 159 Hz, C_p), 123.2 (d, J_{CH} = 157 Hz, C_m), 36.6 (s, C_αCMe$_3$), 22.5 (br d, J_{CH} = 121 Hz, CHMe_2), 21.5 (q, J_{CH} = 128 Hz, CHMe_2), 15.6 (q, J_{CH} = 128 Hz, C_αMe and C_αCMe$_3$), 4.2 (q, J_{CH} = 135 Hz, C_βMe). Anal. Calcd for WC$_{21}$H$_{32}$Cl$_2$O: C, 45.43; H, 5.81. Found: C, 45.31; H, 5.74.

W[C(CMe$_3$)C(Me)C(Me)][O-2,6-C$_6$H$_3$(i-Pr)$_2$]$_2$Cl (7). W[C-(CMe$_3$)C(Me)C(Me)]Cl$_3$ (0.50 g, 1.2 mmol) and 2 equiv of lithium 2,6-diisopropylphenoxide (0.45 g, 2.4 mmol) were dissolved in ether (25 mL), and the solution was stirred overnight. The resulting red solution was filtered and then stripped to dryness. Recrystallization of the residue from pentane at −30 °C gave small, dark red crystals (0.55 g, 65% yield): ^{1}H NMR (C$_6$D$_6$) δ 7.22 (d, 2, $^3J_{HH}$ = 7.6 Hz, H$_m$), 6.99 (t, 1, $^3J_{HH}$ = 7.6 Hz, H$_p$), 6.97 (d, 2, $^3J_{HH}$ = 7.8 Hz, H$_m$), 6.81 (t, 1, $^3J_{HH}$ = 7.8 Hz, H$_p$), 4.01 (sep, 2, $^3J_{HH}$ = 6.8 Hz, eq CHMe_2), 3.39 (s, 3, C_αMe), 3.09 (sep, 2, $^3J_{HH}$ = 6.8 Hz, ax CHMe_2), 2.41 (s, 3, C_βMe), 1.57 (d, 6, $^3J_{HH}$ = 6.8 Hz, eq CHMe_AMe$_B$), 1.52 (d, 6, $^3J_{HH}$ = 6.8 Hz, eq CHMe_AMe$_B$), 1.26 (s, 9, CMe_3), 1.18 (d, 6, $^3J_{HH}$ = 6.8 Hz, ax CHMe_CMe$_D$), 1.06 (d, 6, $^3J_{HH}$ = 6.8 Hz, CHMe_CMe$_D$); ^{13}C NMR (C$_6$D$_6$) δ 258.7 (s, C_α), 247.5 (s, C_α), 162.2, 160.8 (each a s, C_{ipso}), 137.2, 136.8 (each a s, C_o), 132.1 (s, C_β), 123.5, 123.3, 122.8, 121.3 (each a d, J_{CH} = 145–155 Hz, C_m and C_p), 43.2 (s, CMe_3), 30.5, 29.6, 27.8, 23.6, 23.1 (each a q, J_{CH} = 125 Hz, Me groups), 24.4 (d, J_{CH} = 131 Hz, CHMe_2), 24.2 (d, J_{CH} = 131 Hz, CHMe_2), 22.5 (q, J_{CH} = 130 Hz, C_αMe), 13.0 (q, J_{CH} = 134 Hz, C_βMe). Anal. Calcd for WC$_{33}$H$_{49}$ClO$_2$:

	T, K	equiv of C_6D_{10}	10^4k, s^{-1}
2	292.5	40	3.98 (5)
	292.5	20	3.91 (6)
	305.1	20	25.0 (4)
	282.8	20	0.78 (2)
3	282.4	40	4.45 (7)
	282.4	20	4.43 (7)
	291.7	20	17.8 (3)
	272.3	20	0.717 (20)

C, 56.85; H, 7.09. Found: C, 56.61; H, 7.12.

W(CCMe₃)(O-2,6-C₆H₃Me₂)₃(C₄H₈O) (8). W(CCMe₃)-(dme)Cl₃ (2.50 g, 5.56 mmol) was added to a tetrahydrofuran solution (50 mL) of lithium 2,6-dimethylphenoxide (2.14 g, 16.7 mmol) at −30 °C. After 15 min, the solution was stripped to dryness and the residue was extracted with ether. The mixture was filtered to remove LiCl, and the filtrate was then cooled to −30 °C to give orange, cubic crystals of 8 (2 crops, 2.45 g, 69% yield): ¹H NMR (C₆D₆) δ 7.03 (d, 6, ³J_{HH} = 7.4 Hz, H$_m$), 6.81 (t, 3, ³J_{HH} = 7.4 Hz, H$_p$), 3.87 (m, 4, OCH_2CH₂), 2.50 (s, 18, O-2,6-C₆H₃Me_2), 1.37 (m, 4, OCH₂CH_2), 0.41 (s, 9, CCMe₃); ¹³C NMR (C₆D₆) δ 291.4 (s, CCMe₃), 166.0 (s, C$_{ipso}$), 128.8 (d, J_{CH} = 162 Hz, C$_m$), 126.6 (s, C$_o$), 122.0 (d, J_{CH} = 161 Hz, C$_p$), 68.8 (t, J_{CH} = 149 Hz, OCH₂), 49.4 (s, CCMe₃), 31.5 (q, J_{CH} = 127 Hz, CCMe_3), 25.6 (t, J_{CH} = 130 Hz, OCH₂CH₂), 18.1 (q, J_{CH} = 127 Hz, O-2,6-C₆H₃Me_2). Anal. Calcd for WC₃₃H₄₄O₄: C, 57.56; H, 6.44. Found: C, 57.56; H, 6.69.

W(CHCMe₃)[O-2,6-C₆H₃(CMe₂CH₂)(CMe₃)][O-2,6-C₆H₃(CMe₃)₂]Cl (9). W(CCMe₃)(dme)Cl₃ (0.75 g, 1.7 mmol) was added to a solution of lithium 2,6-di-*tert*-butoxyphenoxide (0.71 g, 3.3 mmol) in ether (20 mL). The reaction was allowed to stir overnight. The resulting red solution was filtered and stripped. The residue was recrystallized from toluene/pentane at −30 °C. The dark orange crystals collected were dried for several hours in vacuo to remove toluene trapped in the crystal lattice (three crops, 0.81 g, 69% yield): ¹H NMR (C₆D₆) δ 9.68 (s, 1, J_{WH} = 17.1 Hz, CHCMe₃), 7.16 (m, 4, H$_m$), 6.85 (t, 1, ³J_{HH} = 7.8 Hz, H$_p$), 6.76 (t, 1, ³J_{HH} = 7.8 Hz, H$_p$), 2.31 (d, 1, ²J_{HH} = 13.7 Hz, CMe₂CH_AH$_B$W), 2.20 (d, 1, ²J_{HH} = 13.7 Hz, CMe₂CH$_A$$H_B$W), 1.62 (s, 9, CMe₃), 1.52 (s, 9, CMe₃), 1.44 (s, 6, CMe_2CH$_A$H$_B$W), 1.41 (s, 9, CMe₃), 1.35 (s, 9, CMe₃); ¹³C NMR (C₆D₆) δ 283.1 (d, J_{CH} = 125 Hz, J_{CW} = 175 Hz, CHCMe₃), 160.1 (s, C$_{ipso}$), 155.8 (s, C$_{ipso}$), 142.4 (s, C$_o$), 140.8 (s, C$_o$), 140.6 (s, C$_o$), 139.4 (s, C$_o$), 126.7, 125.8, 125.3, 125.1, 125.0, 124.8 (each a d, J_{CH} = 155–160 Hz, C$_m$ and C$_p$), 73.2 (t, J_{CH} = 119 Hz, J_{CW} = 87 Hz, CMe₂CH₂W), 47.0 (s, CHCMe₃), 37.9 (s,

CMe₂CH₂W), 35.7 (s, CMe₃), 35.5 (s, CMe₃), 35.4 (s, CCMe₃), 36.8, 34.0, 33.4, 32.6, 30.9, 30.6 (each a q, J_{CH} = 125–130 Hz, Me groups). Anal. Calcd for WC₃₃H₅₁ClO₂: C, 56.70; H, 7.35. Found: C, 57.31; H, 7.25.

Observation of 4 and 5. 2-Butyne (30 µL, 0.38 mmol) was added to a solution of 1 (0.30 g, 0.38 mmol) in pentane (5 mL) at −30 °C. After 1 min the solvent was removed in vacuo. An ¹H NMR spectrum of the residue revealed unreacted 1 and resonances characteristic of 4 and 5. 4: ¹H NMR (C₆D₆) δ 3.30 (s, 6, C$_α$Me), 2.02 (s, 3, C$_β$Me). 5: ¹H NMR (C₆D₆) δ 3.14 (s, 3, C$_α$Me), 2.51 (s, 3, C$_β$Me), 1.47 (s, 9, C$_α$CMe₃).

Kinetic Measurements. An excess (20 or 40 equiv) of 3-hexyne-d_{10} was injected into an NMR tube containing 400 µL of a stock solution of either 2 (32.2 mM) or 3 (61.3 mM) in toluene-d_8. The NMR tube was then placed into the probe of a Bruker WM-270 NMR spectrometer. Several minutes were allowed for temperature equilibration, and then spectra were accumulated. Typically, 10 spectra were recorded over a period of ~2 half-lives. The C$_β$CH₂CH_3 resonance of 2 and the C$_β$CH₂CH₂CH_3 resonance of 3 were integrated vs. an internal standard (PhSiMe₃). Correlation coefficients for first-order kinetics were >0.9995. The rates obtained are listed in Table VI, and an Arrhenius plot of the data shown in Figure 5.

During the reaction of 3 with excess 3-hexyne-d_{10} resonances corresponding to the first product W[C(Pr)C(CD₂CD₃)C-(CD₂CD₃)][O-2,6-C₆H₃(i-Pr)₂]₃ grew in with time. The relevant shift is δ 3.61 (m, C$_α$CH_2CH₂CH_3).

Metathesis of 4-Nonyne and 4-Heptyne. Twenty equivalents of either 4-nonyne or 3-heptyne were added to a solution of 1 (0.050 g, 0.064 mmol) in pentane or ether (5 mL). Undecane (27 µL, 0.13 mmol) was added as an internal standard. The extent of reaction and amount of cleavage products were determined by gas chromatography.

Supplementary Material Available: A table of anisotropic thermal parameters (Table VS) and a list of observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.