

Metathesis of Acetylenes by (Fluoroalkoxy)tungstenacyclobutadiene Complexes and the Crystal Structure of $W(C_3Et_3)[OCH(CF_3)_2]_3$. A Higher Order Mechanism for Acetylene Metathesis

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The reaction of 3 equiv of $LiOR$ ($R = CH(CF_3)_2$) or $LiOR'$ ($R' = CMe(CF_3)_2$) with $W(CMe_3)(dme)Cl_3$ yields $W(CMe_3)(OR)_3(dme)$ and $W(CMe_3)(OR')_3(dme)$, respectively ($dme = 1,2$ -dimethoxyethane). Each reacts with disubstituted acetylenes ($R''C\equiv CR''$) to give tungstenacyclobutadiene complexes $W(C_3R''_3)(OR)_3$ and $W(C_3R''_3)(OR')_3$. Both tungstenacyclobutadiene complexes are catalysts for the metathesis of disubstituted acetylenes. $W(C_3Et_3)(OR')_3$ metathesizes acetylenes extremely rapidly by a dissociative mechanism, i.e., via formation of putative $W(CEt)(OR')_3$. $W(C_3Et_3)(OR)_3$, on the other hand, slowly metathesizes acetylenes by an associative mechanism in relatively noncoordinating solvents (pentane, benzene, or toluene; $\Delta H^\ddagger = 14.4$ (6) kcal mol⁻¹; $\Delta S^\ddagger = -22.8$ (2) eu). In diethyl ether or in the presence of dme the rate of metathesis is much higher due (it is postulated) to the solvent assisted dissociation of an acetylene from the WC_3 ring to give $W(CEt)(OR)_3(ether)_x$ ($x = 1$ or 2) or $W(CEt)(OR)_3(dme)$ intermediates. $W(C_3Et_3)[OCH(CF_3)_2]_3$ crystallizes in the triclinic space group $P\bar{1}$ [No. 2] with $a = 9.949$ (3) Å, $b = 16.419$ (4) Å, $c = 18.485$ (4) Å, $\alpha = 112.81$ (2)°, $\beta = 93.53$ (6)°, $\gamma = 98.60$ (2)°, and $Z = 4$. Diffraction data were refined to $R_F = 8.00\%$ and $R_{wF} = 7.78\%$ for 511 parameters refined against all 6439 unique data and $R_F = 5.04\%$ and $R_{wF} = 5.55\%$ for those 4540 data with $|F_o| > 3\sigma(|F_o|)$. Two independent molecules define the crystallographic asymmetric unit. Each is a trigonal bipyramid containing a planar WC_3 ring system in the equatorial plane. The two molecules differ primarily in the orientation of the β -ethyl group. In one molecule the $W-C_\alpha$ bond lengths are 1.902 (16) and 1.864 (14) Å with $W-C_\beta = 2.093$ (14) Å and $C_\alpha-C_\beta = 1.429$ (18) and 1.437 (21) Å. Axial and equatorial alkoxy ligands show similar $W-O-C$ angles of 129.4 (9), 133.6 (8), and 138.6 (10)° and $W-O$ distances of 1.982 (11), 1.962 (12), and 1.932 (10) Å, consistent with a poor π -electron-donating ability by the hexafluoroisopropoxide ligand.

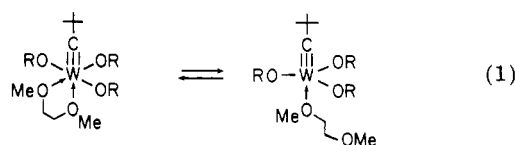
Introduction

In the preceding paper² we explore the fine balance between a tungstenacyclobutadiene complex and an alkylidyne complex formed by loss of an acetylene from the WC_3 ring. We proposed that steric bulk of the phenoxide ligands, steric bulk of the metallacycle's α substituents, and donation of π -electron density to the metal by the equatorial phenoxide ligand all lead to destabilization of the metallacyclic ring, i.e., ejection of an acetylene. Our search for new examples of tungstenacyclobutadiene complexes and our interest in further understanding the factors that determine whether a system will catalyze acetylene metathesis or not led us to study fluoroalkoxide complexes. In this paper we report the preparation of tungsten alkylidyne and tungstenacyclobutadiene complexes containing hexafluoroisopropoxide and hexafluoro-*tert*-butoxide ligands and their reactions with simple disubstituted acetylenes. We will show that both electronic and steric effects subtly control the metathesis reaction and, furthermore, that a mechanism significantly different from that shown to be operative in the phenoxide system² obtains in the hexafluoroisopropoxide system.

Results

Preparation of $W(CMe_3)[OCH(CF_3)_2]_3(dme)$ and $W(C_3Et_3)[OCH(CF_3)_2]_3$. Treating $W(CMe_3)(dme)Cl_3$ ³

with 3 equiv of lithium hexafluoroisopropoxide in ether yields a bright yellow, crystalline complex of composition $W(CMe_3)[OCH(CF_3)_2]_3(dme)$ (1) ($dme = 1,2$ -dimethoxyethane). Below 0 °C the ¹H NMR spectrum of 1 is consistent with the *mer* octahedral structure shown in eq 1. At 25 °C the signals for coordinated dme consist of



three broad resonances that do not change upon adding dme to the sample, and the signals for the added dme remain sharp, consistent with an intramolecular exchange of the two ends of the dme ligand. The most likely intermediate is the *fac* isomer. Although dissociation of one end of the dme ligand to give the TBP complex shown in eq 1 is reasonable—TBP monoadducts of $W(CMe_3)(OCMe_3)_3$ are known^{4,5}—this or any related $\eta^2 \rightarrow \eta^1$ process alone does not exchange the two ends of the dme ligand. At 100 °C coordinated dme does rapidly exchange with free dme . In view of the highly electrophilic nature of the metal center the intermolecular exchange process most likely consists of attack by dme on a five-coordinate species (e.g., that shown in eq 1) to give intermediate *fac*- W -

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(2) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R., preceding paper in this issue.

(3) Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. A.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* 1982, 1, 1645.

(4) Listemann, M. L., unpublished results.

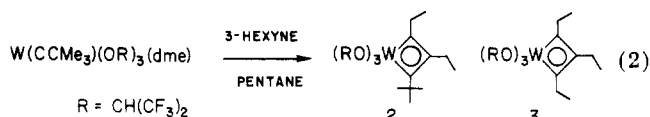
(5) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* 1983, 22, 2903.

(CCMe₃)(OR)₃(dme)₂ rather than by complete loss of dme to give intermediate W(CCMe₃)(OR)₃. The fact that 1 sublimes cleanly at 60 °C (0.1 μm) with dme intact is good evidence that W(CCMe₃)(OR)₃ is not readily formed. These qualitative results suggest that at least one metal coordination site in 1 is likely to be made available at some rapid rate on the chemical time scale at 25 °C and that an acetylene ligand could in principle compete with the dimethoxyethane ligand for that site.

One concern about the six-coordinate structure proposed in eq 1 is the fact that only one ¹⁹F NMR signal is observed at 0 °C. We suspected this was accidental. In a bis(pyridine) adduct, prepared straightforwardly from 1 and pyridine, the pyridine ligands are inequivalent at 25 °C, the hexafluoroisopropoxides' methyne proton resonances appear as two overlapping septets of ratio 2:1, and the ¹⁹F spectrum (84.26 MHz) shows two signals in a ratio of 2:1 separated by only 0.9 ppm. Under ideal conditions three ¹⁹F peaks actually should be observed in a ratio of 1:1:1 since the CF₃ groups in the two mutually trans hexafluoroisopropoxide ligands should be diastereotopic. Therefore we feel our suspicion was correct; in spite of the large chemical shift differences generally observed in ¹⁹F NMR spectra, peaks for the different CF₃ groups in hexafluoroisopropoxide ligand(s) are often accidentally coincident.

It should be noted that the reaction between W(CCMe₃)(dme)Cl₃ and 3 equiv of LiOCHMe₂ produces a dme-free species with the formulation W(CCMe₃)(OCHMe₂)₃.⁶ NMR studies at low temperature suggest that this complex is dimeric, probably with a structure analogous to that of [W(CMe)(OCMe₃)₂]₂.⁵ Since the hexafluoroisopropoxide ligand is a much poorer base than the isopropoxide ligand and for this reason also less likely to bridge between metals, the fact that dimethoxyethane is retained in 1 is not altogether surprising.

W(CCMe₃)[OCH(CF₃)₂]₃(dme) (1) reacts readily with 3-hexyne to produce a mixture of two metallacyclobutadiene complexes (eq 2). The relative amount of each

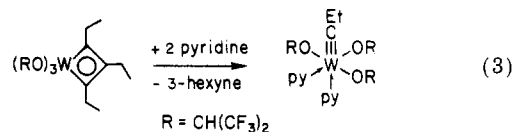


metallacycle depends upon the quantity of 3-hexyne added. The triethyl metallacycle 3 can be prepared in pure form by selectively crystallizing it from a pentane solution containing a large excess of 3-hexyne (see Experimental Section). The α-tert-butyl metallacycle 2 cannot be obtained in pure form by this method; some 3 is formed even when only 1 equiv of 3-hexyne is added to 1. However, 2 can be prepared by reacting W[C(CMe₃)C(Et)C(Et)]Cl₃⁷ with 3 equiv of lithium hexafluoroisopropoxide in toluene.

In a reaction analogous to that shown in eq 2, W(C₃-Pr₃)[OCH(CF₃)₂]₃ (4) can be prepared from 1 and excess 4-octyne. It is important to note that the C_αCH₂CH₂CH₃ signal in 4 is a normal 1:2:1 triplet, not a second-order pattern as it was in W(C₃Pr₃)[O-2,6-C₆H₃(i-Pr)₂]₃ as a result of restricted rotation of the C_α-propyl group.²

No mixed (propyl/ethyl) metallacycles are formed when 3 and 4 are combined in benzene. We conclude that in benzene 3 and 4 do not readily lose 3-hexyne or 4-octyne, respectively. However, when 3 and 4 are dissolved in ether and then all solvent is removed in vacuo, an ¹H NMR

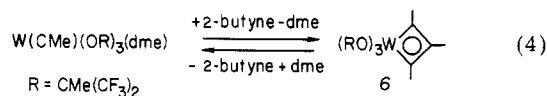
spectrum of the residue in C₆D₆ is consistent with a mixture of many, if not all, possible metallacycles. (The spectrum is too complicated for exact analysis.) We propose that ether is a good enough donor to "displace" acetylene from the WC₃ ring to form small amounts of complexes of the type W(CR)[OCH(CF₃)₂]₃(ether)_x (x = 1 or 2), which then react with any available acetylene to give (ultimately) all possible metallacycles. A result that supports this proposal is shown in eq 3 (see Experimental



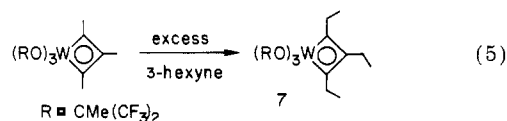
Section for details). Therefore it is not surprising that 2 is not stable in ether. After 1 h a mixture containing ~20% 3 is obtained. The remainder consists largely of 2 and a small amount of an unidentified tert-butyl-containing material.

Hexafluoro-tert-butoxide Complexes. W(CCMe₃)[OCMe(CF₃)₂]₃(dme) (5) can be prepared by treating W(CCMe₃)(dme)Cl₃ with 3 equiv of lithium hexafluoro-tert-butoxide in ether. In C₆D₆ 5 appears to have the same structure as 1. A significant difference, however, is that the ends of the dme exchange more readily intramolecularly (the coalescence temperature for the intramolecular exchange process in 5 is -5 °C compared to ~45 °C in 1) and coordinated dme exchanges more readily with free dme (exchange is rapid at 60 °C in 5 vs. ~100 °C in 1). One could argue that increased steric crowding by the hexafluoro-tert-butoxide ligands favors formation of a five-coordinate species containing η¹-dme and that both exchange processes are for that reason faster. In spite of sterically induced greater lability of one end of the dme ligand in 5, it, like 1, sublimes with the dme ligand intact at 60 °C and 0.1 μm. The reaction of 5 with pyridine also gives a bis(pyridine) adduct in which the two pyridine ligands are inequivalent and two types of alkoxide ligands are observed (cf. eq 3).

If 2–8 equiv of 2-butyne are added to a solution of 5 in pentane, W(CMe)[OCMe(CF₃)₂]₃(dme) can be isolated in good yield. If, however, 20–30 equiv are used, W(C₃Me₃)[OCMe(CF₃)₂]₃ crystallizes from solution. This result can be explained in terms of the equilibrium in eq 4. Surprisingly, a similar reaction between 5 and 3-hexyne



failed to yield the analogous triethyl metallacycle 7 even when 40 equiv of 3-hexyne were used: only W(CEt)[OCMe(CF₃)₂]₃(dme) could be isolated. We propose that for steric reasons alone 3-hexyne simply cannot compete as successfully with dme as 2-butyne can. W(C₃Et₃)[OCMe(CF₃)₂]₃ can be prepared by treating 6 with an excess of 3-hexyne in pentane (eq 5, OR = OCMe(CF₃)₂).



As expected, addition of 1 equiv of dme to 7 in C₆D₆ yields W(CEt)[OCMe(CF₃)₂]₃(dme) quantitatively (by ¹H NMR). Likewise 6 and 7 yield complexes of the type W(CR)[OCMe(CF₃)₂]₃(THF)₂ upon dissolving them in THF and removing all volatile components in vacuo. Peculiarly, both

(6) Pedersen, S. F. Ph.D. Thesis, Massachusetts Institute of Technology, 1983.

(7) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W., following paper in this issue.

Table I. Kinetic Data for the Reaction between $W(C_3Et_3)[OCH(CF_3)_2]_3$ and 3-Hexyne- d_{10}

T, K	[3-hexyne- d_{10}], M	$10^4 k_{obsd}$, s^{-1}	$10^4 k$, $M^{-1} s^{-1}$
314.2	0.366 ± 3%	24.7 (10)	68 (3)
307.7	0.366 ± 3%	12.9 (5)	35.2 (17)
304.7	0.366 ± 3%	11.2 (4)	30.6 (14)
295.0	0.366 ± 3%	4.12 (12)	11.3 (5)
295.0	0.630 ± 3%	6.75 (18)	10.7 (4)
295.0	0.982 ± 3%	10.4 (3)	10.6 (4)
278.0	0.366 ± 3%	1.07 (4)	2.92 (14)

Table II. Interatomic Distances (Å) for $W(C_3Et_3)[OCH(CF_3)_2]_3$

3a		3b	
(A) Distances about the Tungsten Atoms			
W(1)-O(1)	1.982 (11)	W(2)-O(4)	1.970 (11)
W(1)-O(2)	1.932 (10)	W(2)-O(5)	1.934 (10)
W(1)-O(3)	1.962 (12)	W(2)-O(6)	1.969 (11)
W(1)-C(1)	1.902 (16)	W(2)-C(13)	1.885 (15)
W(1)-C(2)	2.093 (14)	W(2)-C(14)	2.100 (15)
W(1)-C(3)	1.864 (14)	W(2)-C(15)	1.860 (17)

(B) Distances within C_3Et_3 Ligands

C(1)-C(2)	1.429 (18)	C(13)-C(14)	1.348 (27)
C(2)-C(3)	1.437 (21)	C(14)-C(15)	1.492 (23)
C(1)-C(1A)	1.499 (25)	C(13)-C(13A)	1.567 (20)
C(1A)-C(1B)	1.491 (26)	C(13A)-C(13B)	1.505 (43)
C(2)-C(2A)	1.548 (22)	C(14)-C(14A)	1.572 (25)
C(2A)-C(2B)	1.575 (30)	C(14A)-C(14B)	1.594 (36)
C(3)-C(3A)	1.509 (21)	C(15)-C(15A)	1.502 (30)
C(3A)-C(3B)	1.447 (34)	C(15A)-C(15B)	1.390 (38)

(C) O-C Distances within $OCH(CF_3)_2$ Ligands

O(1)-C(4)	1.403 (23)	O(4)-C(16)	1.385 (20)
O(2)-C(7)	1.399 (18)	O(5)-C(19)	1.428 (20)
O(3)-C(10)	1.391 (22)	O(6)-C(22)	1.415 (19)

(D) C-C Distances within $OCH(CF_3)_2$ Ligands

C(4)-C(5)	1.507 (29)	C(16)-C(17)	1.520 (35)
C(4)-C(6)	1.461 (26)	C(16)-C(18)	1.469 (26)
C(7)-C(8)	1.516 (22)	C(19)-C(20)	1.514 (35)
C(7)-C(9)	1.511 (24)	C(19)-C(21)	1.427 (37)
C(10)-C(11)	1.529 (23)	C(22)-C(23)	1.527 (30)
C(10)-C(12)	1.448 (31)	C(22)-C(24)	1.510 (22)

(E) C-F Distances

C(5)-F(5A)	1.292 (23)	C(17)-F(17A)	1.260 (36)
C(5)-F(5B)	1.327 (22)	C(17)-F(17B)	1.322 (27)
C(5)-F(5C)	1.268 (29)	C(17)-F(17C)	1.274 (24)
C(6)-F(6A)	1.387 (35)	C(18)-F(18A)	1.349 (31)
C(6)-F(6B)	1.319 (36)	C(18)-F(18B)	1.259 (42)
C(6)-F(6C)	1.291 (25)	C(18)-F(18C)	1.261 (36)
C(8)-F(8A)	1.262 (31)	C(20)-F(20A)	1.326 (38)
C(8)-F(8B)	1.315 (24)	C(20)-F(20B)	1.331 (29)
C(8)-F(8C)	1.328 (26)	C(20)-F(20C)	1.321 (38)
C(9)-F(9A)	1.262 (22)	C(21)-F(21A)	1.393 (27)
C(9)-F(9B)	1.320 (24)	C(21)-F(21B)	1.394 (35)
C(9)-F(9C)	1.298 (31)	C(21)-F(21C)	1.227 (35)
C(11)-F(11A)	1.291 (23)	C(23)-F(23A)	1.279 (26)
C(11)-F(11B)	1.346 (29)	C(23)-F(23B)	1.290 (23)
C(11)-F(11C)	1.293 (32)	C(23)-F(23C)	1.267 (19)
C(12)-F(12A)	1.299 (27)	C(24)-F(24A)	1.311 (24)
C(12)-F(12B)	1.307 (29)	C(24)-F(24B)	1.312 (26)
C(12)-F(12C)	1.319 (25)	C(24)-F(24C)	1.280 (32)

6 and 7 appear to decompose in diethyl ether. (Note that 3 and 4 do not.) Perhaps ether is simply too poor a ligand in these more crowded molecules, and "W(CR)[OCMe(CF₃)₂]₃" decomposes.

Mixing 6 and 7 in C₆D₆ at 25 °C immediately yields a mixture whose ¹H NMR is consistent with the presence of all six possible metallacycles. This result contrasts markedly with that obtained for the analogous hexafluoroisopropoxide complexes; a mixture of 3 and 4 is

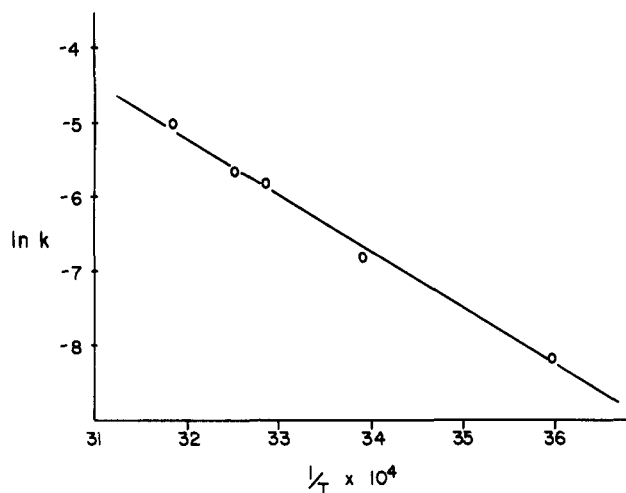


Figure 1. Arrhenius plot for the reaction of $W(C_3Et_3)[OCH(CF_3)_2]_3$ with 3-hexyne- d_{10} .

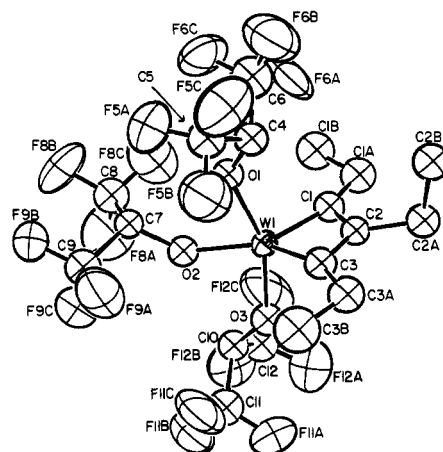


Figure 2. Labeling of atoms in $W(C_3Et_3)[OCH(CF_3)_2]_3$ —molecule 3a.

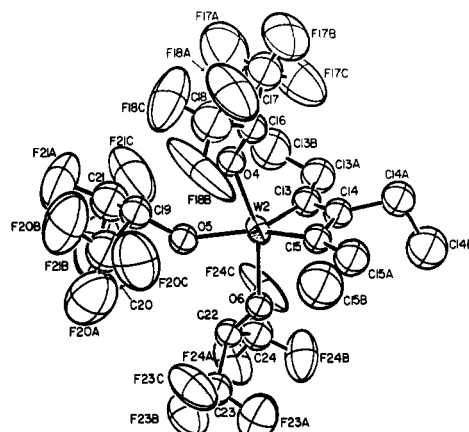


Figure 3. Labeling of atoms in $W(C_3Et_3)[OCH(CF_3)_2]_3$ —molecule 3b.

stable in C₆D₆ and ether is required for the scrambling process. The most reasonable explanation, one which is consistent with other results discussed below, is that 6 and 7 lose 3-hexyne and 4-octyne in C₆D₆ to give small amounts of the putative alkylidyne complexes, whereas 3 and 4 do not in the absence of donor solvents.

Metathesis of Alkynes. Both 6 and 7, or any of the hexafluoro-*tert*-butoxide alkylidyne complexes, will catalyze the metathesis of 20 equiv of 3-heptyne to equilibrium in less than 5 min in pentane or ether. (The rates are qualitatively the same in the two solvents.) We attempted

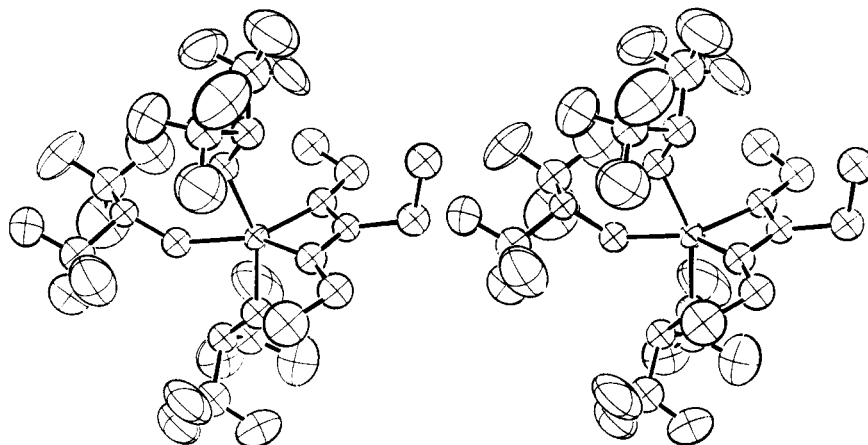


Figure 4. Stereoscopic view of molecule 3a.

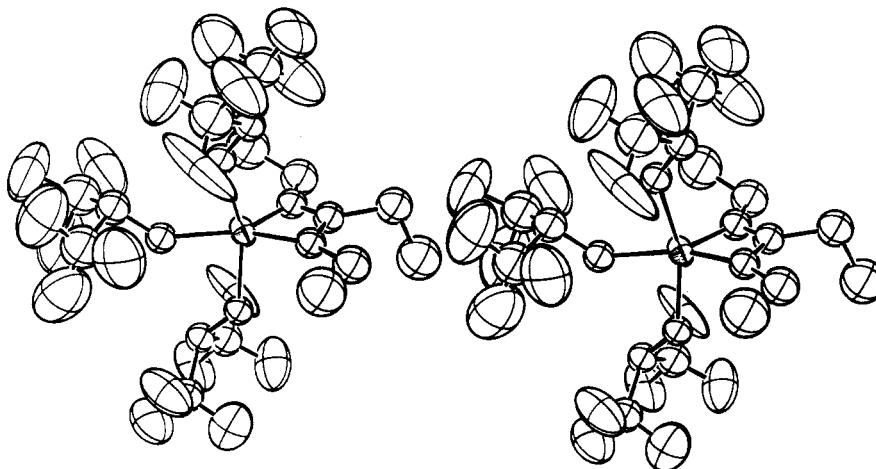


Figure 5. Stereoscopic view of molecule 3b.

to determine the order of the reaction by measuring the rate of incorporation of 3-hexyne- d_{10} into 6. Unfortunately, the reaction is too fast (even at $-50\text{ }^{\circ}\text{C}$) to measure by routine NMR methods. In spite of the lack of kinetic proof we feel comfortable in proposing that the rate-limiting step for acetylene metathesis by 6 or 7 in noncoordinating solvents consists of loss of an acetylene from the WC_3 ring to give putative alkylidyne complex $\text{W}(\text{CR})[\text{OCMe}(\text{CF}_3)_2]_3$. In the presence of dimethoxyethane, tetrahydrofuran, or other donor solvents that may compete with alkynes for metal coordination sites, the reaction could be considerably more complex mechanistically; the result might depend upon the relative concentration of the solvent vs. free acetylenes, and the solvent's donor ability. At least we can say that in noncoordinating hydrocarbons the hexafluoro-*tert*-butoxide tungstenacyclobutadiene complexes catalyze metathesis in a manner analogous to that we were able to document fully in the previous paper for 2,6-diisopropylphenoxide derivatives. What is important is how these results in noncoordinating hydrocarbons differ with those employing 1, 3, or 4 as the metathesis catalyst in noncoordinating hydrocarbons.

$\text{W}(\text{CCMe}_3)[\text{OCH}(\text{CF}_3)_2]_3(\text{dme})$ (1) will catalyze the metathesis of 3-heptyne in ether ($t_{1/2} \approx 10$ min for 20 equiv of 3-heptyne). Approximately the same rate is observed when metallacycle 3 is used as the catalyst. If the reaction is run in pentane by using the same concentrations of 3 and 3-heptyne, the rate drops dramatically ($t_{1/2} \approx 21$ h). Adding 1 equiv of dme to the pentane yields an intermediate rate of metathesis ($t_{1/2} \approx 4.5$ h). It should be noted that in all cases a significant amount of polymer is observed after a day at room temperature. The main

point, however, is the large qualitative difference in rate of reaction in ether and in pentane vs. similar rates for 6 and 7 in the two solvents.

The reaction between 3 and 3-hexyne- d_{10} in toluene- d_8 was monitored by following the disappearance of the $\text{C}_6\text{H}_2\text{CH}_3$ signal in the ^1H NMR spectrum. From 10 to 40 equiv of 3-hexyne- d_{10} were employed in each experiment. During each reaction a small amount of what is probably acetylene polymer was formed. The rate of incorporation of 3-hexyne- d_{10} was first order in tungsten. At the highest concentrations of 3-hexyne- d_{10} we followed the reaction for ~ 3 half-lives. Surprisingly, the rate was first order in 3-hexyne- d_{10} (Table I). A variable-temperature study yielded $\Delta H^\ddagger = +14.4$ (6) kcal mol^{-1} and $\Delta S^\ddagger = -22.8$ (20) $\text{cal mol}^{-1} \text{K}^{-1}$ (see Figure 1), consistent with an *associative* mechanism. Although we will defer proposing any details of this bimolecular reaction until the Discussion, we do want to point out one potential problem that we touched upon in the previous paper, i.e., whether 3 reacts with 3-hexyne to give only $\text{W}[(\text{CH}_2\text{CH}_3)\text{C}(\text{CD}_2\text{CD}_3)\text{C}(\text{C}-\text{D}_2\text{CD}_3)][\text{OCH}(\text{CF}_3)_2]_3$ or whether some $\text{W}[(\text{CD}_2\text{CD}_3)\text{C}(\text{CH}_2\text{CH}_3)\text{C}(\text{CD}_2\text{CD}_3)][\text{OCH}(\text{CF}_3)_2]_3$ forms. In this case we cannot tell, but the answer is not necessary for our purposes here. What is important is that acetylenes are metathesized by 3 in toluene- d_8 in a *relatively slow, bimolecular reaction*.

X-ray Crystal Structure of $\text{W}(\text{C}_3\text{Et}_3)[\text{OCH}(\text{CF}_3)_2]_3$. Crystals of $\text{W}(\text{C}_3\text{Et}_3)[\text{OCH}(\text{CF}_3)_2]_3$ (3) are composed of discrete monomeric molecular units separated by normal van der Waals' distances; there are no abnormally short intermolecular contacts. The crystallographic asymmetric unit consists of two complete, approximately trigonal-bi-

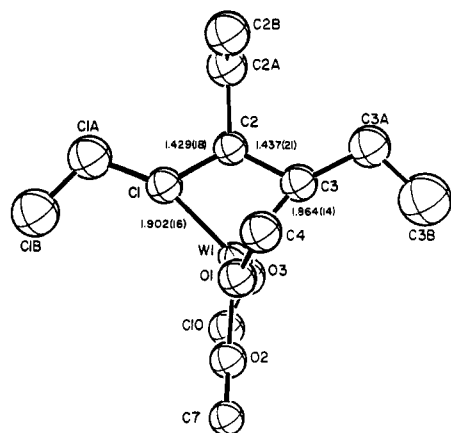


Figure 6. Molecule **3a**, projected onto its WC_3 plane.

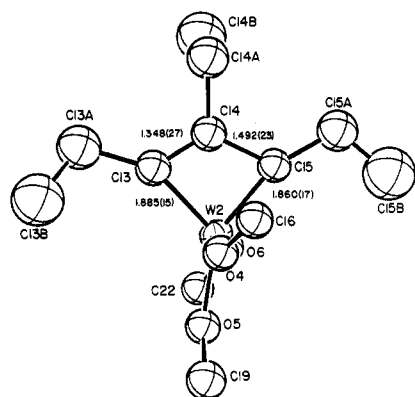


Figure 7. Molecule **3b**, projected onto its WC_3 plane.

pyramidal molecules (designated **3a** and **3b**). Labeling of atoms in these two molecules is shown in Figures 2 and 3; stereoscopic view of the molecules are provided by Figures 4 and 5; a projection onto the WC_3 plane in each molecule is shown in Figures 6 and 7. Interatomic distances and angles are collected in Tables II and III, respectively. Note that the two crystallographically independent molecules are virtually identical, the principal difference being the conformation of the ethyl group on the β -carbon atom of the WC_3 systems. In **3a** both the ethyl group's C(2B) and the alkoxide's C(7) atoms are above the equatorial coordination plane. In **3b**, the ethyl group on the β -carbon atom points down (C(14B) is below the equatorial coordination plane) while C(19) of the equatorial alkoxide ligand is above this plane.

Let us first consider the tungstenacyclobutadiene ring systems in **3a** and **3b**. In each of the two crystallographically independent molecules the WC_3 systems are planar within the limits of experimental error (see planes A and D of Table IV); root-mean-square deviations from planarity are 0.010 Å for atoms of the WC_3 system in **3a** and 0.005 Å for atoms of the WC_3 system in **3b**. The $W-C_\alpha$ distances for **3a** are $W(1)-C(1) = 1.902(16)$ Å and $W(1)-C(3) = 1.864(14)$ Å; corresponding distances in **3b** are $W(2)-C(13) = 1.885(15)$ Å and $W(2)-C(15) = 1.860(17)$ Å. The average $W-C_\alpha$ distance is $1.878[20]$ Å.⁸ The $W\cdots C(\beta)$ distances in the two molecules are $W(1)\cdots C(2) = 2.093(14)$ Å and

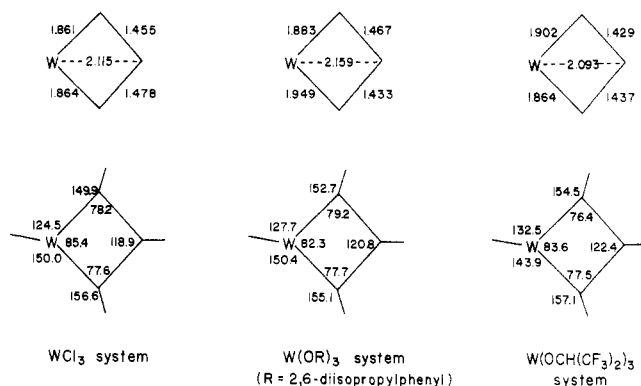


Figure 8. A comparison of bond lengths and angles in several tungstenacyclobutadiene complexes.

$W(2)\cdots C(14) = 2.100(15)$ Å. Carbon-carbon distances within the WC_3 systems appear to be equivalent in **3a** ($C(1)-C(2) = 1.429(18)$ Å and $C(2)-C(3) = 1.437(21)$ Å) and inequivalent in **3b** ($C(13)-C(14) = 1.348(27)$ Å and $C(14)-C(15) = 1.492(23)$ Å); however, the central atom is common to the two measurements in each case and errors in this atom's coordinates can affect the difference in the two C-C distances by an unusual amount. Therefore we attribute no great significance to the discrepancy in the C-C distances in **3b**. The more accurately known W-C distances suggest that 3-hexyne is not about to be lost from these WC_3 ring systems. Other notable features of the WC_3 systems include the internal angles at the β -carbon atoms [$C(1)-C(2)-C(3) = 122.4(13)^\circ$ and $C(13)-C(14)-C(15) = 121.4(14)^\circ$], the $C_\alpha-W-C_\alpha$ angles [$C(1)-W(1)-C(3) = 83.6(6)^\circ$ and $C(13)-W(2)-C(15) = 82.8(7)^\circ$], and the large external angles at the α -carbon atoms [$W(1)-C(1)-C(1A) = 154.5(12)^\circ$, $W(1)-C(3)-C(3A) = 157.1(13)^\circ$, $W(2)-C(13)-C(13A) = 148.8(14)^\circ$, and $W(2)-C(15)-C(15A) = 158.8(13)^\circ$].

The axial alkoxide ligands are all essentially equivalent [$W(1)-O(1) = 1.982(11)$ Å, $W(1)-O(3) = 1.962(12)$ Å, $W(2)-O(4) = 1.970(11)$ Å, $W(2)-O(6) = 1.969(11)$ Å] and have W-O-C angles close to 130° [viz., $W(1)-O(1)-C(4) = 129.4(9)^\circ$, $W(1)-O(3)-C(10) = 133.6(8)^\circ$, $W(2)-O(4)-C(16) = 130.9(10)^\circ$, and $W(2)-O(6)-C(22) = 130.8(11)^\circ$]. The equatorial alkoxide ligands are associated with only slightly shorter tungsten-oxygen distances [$W(1)-O(2) = 1.932(10)$ Å and $W(2)-O(5) = 1.934(10)$ Å] and slightly more obtuse W-O-C angles [$W(1)-O(2)-C(7) = 138.6(10)^\circ$ and $W(2)-O(5)-C(19) = 135.9(11)^\circ$], indicative of only a slightly greater amount of donation of π -electron density from the equatorial alkoxide oxygens to tungsten than from the axial alkoxide oxygens to tungsten. The difference between axial and equatorial W-O-C angles is nowhere near as dramatic as that found in the phenoxide derivative $W(C_3Et_3)[O-2,6-C_6H_3(i-Pr)_2]_3$,² where relatively strong π -electron donation from the oxygen of an equatorial phenoxide ligand causes a discrepancy of $\sim 25^\circ$ between the axial and equatorial W-O-C angles.

Two other points of interest relative to the alkoxide ligands are, first, that the equatorial alkoxide ligands take up a conformation such that the W-O-C plane is approximately perpendicular to the WC_3 system. (Dihedral angles are $W(1)-C(1)-C(2)-C(3)/W(1)-O(2)-C(7) = 86.5^\circ$ and $W(2)-C(13)-C(14)-C(15)/W(2)-O(5)-C(19) = 77.5^\circ$.) In $W(C_3Et_3)[O-2,6-C_6H_3(i-Pr)_2]_3$ the equatorial phenoxide ligand is approximately coplanar with the WC_3 system,² most likely in order to delocalize π -electron density throughout the aromatic ring. Second, in the two axial alkoxide ligands in $W(C_3Et_3)[OCH(CF_3)_2]_3$ the W-O-C systems essentially parallel one another; in $W(C_3Et_3)[O-$

(8) Esd's of average values, shown in square brackets, are calculated by using the scatter formula, viz.

$$[\sigma] = \frac{\sum_{i=1}^N (x_i - \bar{x})^2}{(N-1)^{1/2}}$$

Here, x_i is the i th of N equivalent measurements and \bar{x} is the mean of these N measurements.

Table III. Interatomic Angles (deg) for $W(C_3Et_3)[OCH(CF_3)_2]_3$

3a		3b	
(A) Angles about the Tungsten Atoms			
O(1)-W(1)-O(2)	79.4 (4)	O(4)-W(2)-O(5)	80.3 (4)
O(1)-W(1)-O(3)	157.6 (4)	O(4)-W(2)-O(6)	158.3 (4)
O(1)-W(1)-C(1)	98.5 (6)	O(4)-W(2)-C(13)	99.8 (6)
O(1)-W(1)-C(3)	97.3 (6)	O(4)-W(2)-C(15)	96.8 (6)
O(1)-W(1)···C(2)	101.3 (5)	O(4)-W(2)···C(14)	100.8 (6)
O(2)-W(1)-O(3)	80.2 (5)	O(5)-W(2)-O(6)	82.0 (4)
O(2)-W(1)-C(3)	143.9 (6)	O(5)-W(2)-C(15)	148.4 (6)
O(2)-W(1)···C(2)	174.0 (5)	O(5)-W(2)···C(14)	167.8 (6)
O(3)-W(1)-C(1)	102.0 (6)	O(6)-W(2)-C(13)	101.0 (6)
O(3)-W(1)-C(3)	93.8 (6)	O(6)-W(2)-C(15)	91.8 (6)
O(3)-W(1)···C(2)	99.9 (5)	O(6)-W(2)···C(14)	99.2 (6)
C(1)-W(1)-C(3)	83.6 (6)	C(13)-W(2)-C(15)	82.8 (7)
C(1)-W(1)···C(2)	41.6 (5)	C(13)-W(2)···C(14)	39.1 (8)
C(3)-W(1)···C(2)	42.1 (6)	C(15)-W(2)···C(14)	43.8 (7)
C(1)-W(1)-O(2)	132.5 (5)	C(13)-W(2)-O(5)	128.7 (7)
(B) Angles Involving the C_3Et_3 Ligands			
C(1)-C(2)-C(3)	122.4 (13)	C(13)-C(14)-C(15)	121.4 (14)
W(1)-C(1)-C(2)	76.4 (9)	W(2)-C(13)-C(14)	79.1 (10)
W(1)-C(3)-C(2)	77.5 (8)	W(2)-C(15)-C(14)	76.7 (10)
C(1)-C(1A)-C(1B)	111.7 (17)	C(13)-C(13A)-C(13B)	108.7 (17)
C(2)-C(2A)-C(2B)	108.5 (14)	C(14)-C(14A)-C(14B)	106.8 (18)
C(3)-C(3A)-C(3B)	108.7 (16)	C(15)-C(15A)-C(15B)	111.1 (20)
W(1)···C(2)-C(2A)	179.3 (12)	W(2)···C(14)-C(14A)	175.7 (12)
W(1)-C(1)-C(1A)	154.5 (12)	W(2)-C(13)-C(13A)	148.8 (14)
W(1)-C(3)-C(3A)	157.1 (13)	W(2)-C(15)-C(15A)	158.8 (13)
C(1)-C(2)-C(2A)	117.7 (13)	C(13)-C(14)-C(14A)	121.5 (16)
C(3)-C(2)-C(2A)	119.8 (12)	C(15)-C(14)-C(14A)	117.1 (16)
C(2)-C(1)-C(1A)	128.9 (14)	C(14)-C(13)-C(13A)	132.0 (15)
C(2)-C(3)-C(3A)	124.8 (14)	C(14)-C(15)-C(15A)	124.2 (14)
(C) W-O-C Angles			
W(1)-O(1)-C(4)	129.4 (9)	W(2)-O(4)-C(16)	130.9 (10)
W(1)-O(2)-C(7)	138.6 (10)	W(2)-O(5)-C(19)	135.9 (11)
W(1)-O(3)-C(10)	133.6 (8)	W(2)-O(6)-C(22)	130.8 (11)
(D) O-C-C Angles			
O(1)-C(4)-C(5)	109.2 (15)	O(4)-C(16)-C(17)	109.5 (16)
O(1)-C(4)-C(6)	108.0 (15)	O(4)-C(16)-C(18)	109.1 (16)
O(2)-C(7)-C(8)	109.5 (14)	O(5)-C(19)-C(20)	106.4 (19)
O(2)-C(7)-C(9)	109.2 (12)	O(5)-C(19)-C(21)	105.2 (15)
O(3)-C(10)-C(11)	106.2 (13)	O(6)-C(22)-C(23)	107.9 (14)
O(3)-C(10)-C(12)	112.0 (15)	O(6)-C(22)-C(24)	109.2 (13)
(E) C-C-C Angles within $OCH(CF_3)_2$ Ligands			
C(5)-C(4)-C(6)	105.4 (18)	C(17)-C(16)-C(18)	110.0 (19)
C(8)-C(7)-C(9)	112.3 (14)	C(20)-C(19)-C(21)	113.9 (19)
C(11)-C(10)-C(12)	110.6 (17)	C(23)-C(22)-C(24)	115.1 (15)
(F) C-C-F Angles			
C(4)-C(5)-F(5A)	116.8 (16)	C(16)-C(17)-F(17A)	113.3 (21)
C(4)-C(5)-F(5B)	105.8 (18)	C(16)-C(17)-F(17B)	111.0 (21)
C(4)-C(5)-F(5C)	114.2 (18)	C(16)-C(17)-F(17C)	106.2 (21)
C(4)-C(6)-F(6A)	106.6 (20)	C(16)-C(18)-F(18A)	112.4 (21)
C(4)-C(6)-F(6B)	113.6 (18)	C(16)-C(18)-F(18B)	110.6 (24)
C(4)-C(6)-F(6C)	119.7 (21)	C(16)-C(18)-F(18C)	112.3 (25)
C(7)-C(8)-F(8A)	111.1 (15)	C(19)-C(20)-F(20A)	116.0 (19)
C(7)-C(8)-F(8B)	109.4 (18)	C(19)-C(20)-F(20B)	107.7 (25)
C(7)-C(8)-F(8C)	105.9 (16)	C(19)-C(20)-F(20C)	107.7 (20)
C(7)-C(9)-F(9A)	110.1 (16)	C(19)-C(21)-F(21A)	107.1 (19)
C(7)-C(9)-F(9B)	110.4 (14)	C(19)-C(21)-F(21B)	114.5 (27)
C(7)-C(9)-F(9C)	110.6 (18)	C(19)-C(21)-F(21C)	118.9 (24)
C(10)-C(11)-F(11A)	113.8 (17)	C(22)-C(23)-F(23A)	111.7 (16)
C(10)-C(11)-F(11B)	108.8 (14)	C(22)-C(23)-F(23B)	111.9 (18)
C(10)-C(11)-F(11C)	112.1 (19)	C(22)-C(23)-F(23C)	112.4 (17)
C(10)-C(12)-F(12A)	115.4 (17)	C(22)-C(24)-F(24A)	111.4 (16)
C(10)-C(12)-F(12B)	115.1 (18)	C(22)-C(24)-F(24B)	109.8 (18)
C(10)-C(12)-F(12C)	108.6 (21)	C(22)-C(24)-F(24C)	110.9 (17)
(G) F-C-F Angles			
F(5A)-C(5)-F(5B)	104.2 (17)	F(17A)-C(17)-F(17B)	110.5 (23)
F(5A)-C(5)-F(5C)	109.0 (19)	F(17A)-C(17)-F(17C)	107.6 (24)
F(5B)-C(5)-F(5C)	105.6 (16)	F(17B)-C(17)-F(17C)	108.0 (19)
F(6A)-C(6)-F(6B)	107.1 (21)	F(18A)-C(18)-F(18B)	103.7 (25)
F(6A)-C(6)-F(6C)	102.5 (18)	F(18A)-C(18)-F(18C)	108.6 (24)
F(6B)-C(6)-F(6C)	106.1 (21)	F(18B)-C(18)-F(18C)	108.7 (27)

Table III (Continued)

3a		3b	
F(8A)-C(8)-F(8B)	111.4 (18)	F(20A)-C(20)-F(20B)	113.9 (22)
F(8A)-C(8)-F(8C)	111.1 (21)	F(20A)-C(20)-F(20C)	110.6 (28)
F(8B)-C(8)-F(8C)	107.8 (17)	F(20B)-C(20)-F(20C)	99.6 (21)
F(9A)-C(9)-F(9B)	110.8 (20)	F(21A)-C(21)-F(21B)	100.4 (20)
F(9A)-C(9)-F(9C)	105.8 (17)	F(21A)-C(21)-F(21C)	113.2 (29)
F(9B)-C(9)-F(9C)	109.0 (17)	F(21B)-C(21)-F(21C)	101.2 (23)
F(11A)-C(11)-F(11B)	107.2 (20)	F(23A)-C(23)-F(23B)	105.6 (18)
F(11A)-C(11)-F(11C)	105.5 (16)	F(23A)-C(23)-F(23C)	106.9 (20)
F(11B)-C(11)-F(11C)	109.1 (18)	F(23B)-C(23)-F(23C)	108.0 (15)
F(12A)-C(12)-F(12B)	106.8 (22)	F(24A)-C(24)-F(24B)	106.1 (18)
F(12A)-C(12)-F(12C)	106.0 (19)	F(24A)-C(24)-F(24C)	110.6 (20)
F(12B)-C(12)-F(12C)	104.0 (16)	F(24B)-C(24)-F(24C)	107.9 (18)

2,6-C₆H₃(*i*-Pr)₂]₃ these two systems are perpendicular to one another, possibly in order to optimize π bonding between oxygen and tungsten at each coordination site. Both points further illustrate the dramatic difference between the fluoralkoxide ligands in **3** and the phenoxide ligands in W(C₃Et₃)[O-2,6-C₆H₃(*i*-Pr)₂]₃.

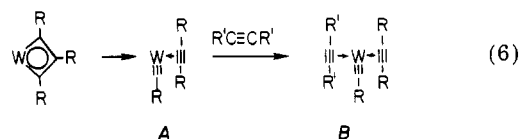
Discussion

The structures of the two independent molecules of W(C₃Et₃)[OCH(CF₃)₂]₃ are overall quite similar to those of W(C₃Et₃)[O-2,6-C₆H₃(*i*-Pr)₂]₃² and W[C(CMe₃)C(Me)-C(Me)]Cl₃.⁹ The bond distances and angles in the equatorial plane in the four complexes fall within a narrow range, and in each case the L_{ax}-W-L_{ax} angle is $\sim 160^\circ$. Since the three complexes react rather differently with acetylenes, we must conclude that at least among TBP complexes containing a planar WC₃R₃ ring system, we cannot accurately predict reactivity on the basis of small structural differences in the WC₃ rings. We should note that planar WC₃R₃ ring systems have so far been observed *only* in TBP molecules. In W(η^5 -C₅H₅)[C(Ph)C(CMe₃)C(Ph)Cl₂]¹⁰ the WC₃ ring is "bent", and in W(η^5 -C₅H₅)[C₃(CMe₃)₂Me](PMe₃)Cl₂¹¹ and W[C₃(CMe₃)₂Me]Cl₃(tmeda)^{7,12} a fairly symmetric WC₃ tetrahedron is observed. We are beginning to suspect that planar WC₃R₃ ring systems may be of lowest energy relative to other WC₃ arrangements only in complexes of trigonal-bipyramidal geometry.

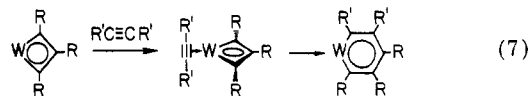
One property of a hexafluoroisopropoxide ligand that the structure of **3** emphasizes is its poor ability to donate π -electron density to the metal, even when it is located in an equatorial position, as judged by the similarity of the W-O_{ax}-C and W-O_{eq}-C bond angles (*all* within the range 130–135°). In marked contrast the W-O_{ax}-C and W-O_{eq}-C angles differ by $\sim 25^\circ$ in the O-2,6-C₆H₃(*i*-Pr)₂ complex discussed in the previous paper, the W-O_{eq}-C angle being the larger. On the basis of this structural result, one that is reinforced by the fact that fluoroalkoxide ions are poor Brønsted bases, one would predict that the metal is relatively electrophilic in hexafluoroalkoxide complexes compared to analogous fluoride-free alkoxide complexes. One might be tempted also to suggest that donation of π electrons by an equatorial alkoxide ligand is required for labilization of an acetylene in the WC₃ ring were it not for the fact that an acetylene is forced out of the WC₃ ring in the hexafluoro-*tert*-butoxide system. We think that the metal's electrophilicity in **7** does not differ significantly

from what it is in **3** and that changing the metathesis mechanism from associative (for **3**) to dissociative (for **7**) is a fairly clear-cut illustration of how a reaction mechanism can be altered significantly by subtly changing steric interactions within the coordination sphere. Electronic factors, at least among the types of molecules we have been talking about here, eventually lose out to steric factors. We think it worth pointing out that in general it should be easier to document and control the steric influence of an anionic, relatively nonlabile ligand in catalytic reactions vs. that of a neutral, relatively labile ligand such as a phosphine.

One of the most surprising results of this study is that an associative reaction between a tungstenacyclobutadiene complex and an acetylene can result in metathesis. Although at this point any details of the bimolecular reaction between **3** and an acetylene are speculative, we believe it constructive to think about two likely possibilities. The first is a "displacement" of an acetylene from a "bent tungstenacyclobutadiene"¹⁰ or an "acetylene alkylidyne" complex (eq 6). In the lowest energy form of A the W \equiv



CR bond axis should be perpendicular to the RC \equiv CR axis (in order to maximize π bonding of each ligand), while in B the π bonding of the three ligands can no longer be mutually independent. One acetylene therefore will be relatively labile. Almost certainly B will be a high, if not the highest, energy intermediate or transition state in the "displacement" reaction. The second possibility is a ring expansion to give a planar tungstenabenzene intermediate (eq 7). The structure of a derivatized osmabenzene com-



plex has been reported recently¹³ and others have been postulated.¹⁴ In actuality it is likely to be difficult to describe the higher order metathesis reaction in such detail—bonding in the species in eq 6 and 7 is unlikely to be as ideal as shown and there are even other possibilities, as we shall see in the next paper. The most interesting point to make now is that whatever the bimolecular reaction, the end result is not reduction of the metal to give a cyclopentadienyl complex.⁷

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Table IV. Least-Squares Planes for the Two $W(C_3Et_3)[OCH(CF_3)_2]_3$ Molecules 3a and 3b

atom	dev, Å	atom	dev, Å
(A) WC_3 Plane, 3a			
$-0.3739X + 0.4981Y - 0.7824Z - 3.354 = 0$			
W(1)*	0.006	O(2)	0.019
C(1)*	-0.008	C(7)	-0.898
C(2)*	0.011	O(1)	-1.940
C(3)*	-0.009	O(3)	1.927
(B) W(1)-O(2)-C(7) Plane, 3a			
$-0.5821X - 0.7617Y - 0.2844Z + 13.80 = 0$			
W(1)*	0.000		
O(2)*	0.000		
C(7)*	0.000		
(C) O(1)-W(1)-O(3) Plane, 3a			
$-0.1938X - 0.8882Y - 0.4166Z + 15.02 = 0$			
W(1)*	0.000		
O(1)*	0.000		
O(3)*	0.000		
(D) WC_3 Plane, 3b			
$-0.7595X + 0.3046Y - 0.5748Z + 6.974 = 0$			
W(2)*	0.003	O(5)	-0.017
C(13)*	-0.004	C(19)	0.943
C(14)*	0.006	O(4)	1.936
C(15)*	-0.004	O(6)	-1.929
(E) W(2)-O(5)-C(19) Plane, 3b			
$0.2120X + 0.9667Y - 0.1433Z - 7.378 = 0$			
W(2)*	0.000		
O(5)*	0.000		
C(19)*	0.000		
(F) O(4)-W(2)-O(6) Plane, 3b			
$0.6505X + 0.6057Y - 0.4582Z - 7.119 = 0$			
W(2)*	0.000		
O(4)*	0.000		
O(6)*	0.000		
Dihedral Angles (deg)			
A/B	86.51	D/E	77.53
A/C	92.52	D/F	92.64
B/C	24.78	E/F	37.90

Experimental Section

General Data. General procedures were the same as in the previous paper.² Hexafluoro-2-propanol was purchased and the alkoxide prepared by deprotonating it with *n*-butyllithium in pentane. Lithium hexafluoro-*tert*-butoxide was prepared by adding hexafluoroacetone to methylolithium in ether.

We were unable to obtain good analytical data for compounds containing the hexafluoro-*tert*-butoxide ligand. Analyses for six different compounds were typically 1–3% low in carbon. For a given compound analyses varied significantly from sample to sample. We are continuing to attempt to come up with an adequate explanation.

Collection of X-ray Diffraction Data and Solution of the Crystal Structure of $W(C_3Et_3)[OCH(CF_3)_2]_3$. A crystal of $W(C_3Et_3)[OCH(CF_3)_2]_3$ with approximate dimensions $0.2 \times 0.1 \times 0.3$ mm was mounted along its extended direction in a thin-walled glass capillary under an inert (Ar) atmosphere. It was aligned on the Syntex P2₁ automated four-circle diffractometer, and 2θ data collection was carried out by using the previously described techniques of this laboratory (Table IV).¹⁵

All data were corrected for decay, absorption ($\mu = 46.2 \text{ cm}^{-1}$), and Lorentz and polarization effects and were converted to unscattered $|F_o|$ values. Those reflections with $I(\text{net}) < 0$ were assigned a value of $|F_o| = 0$. A Wilson plot was used to place the data on an approximate absolute scale.

Table V. Experimental Data for X-ray Diffraction Study of $W(C_3Et_3)[OCH(CF_3)_2]_3$ (3)

(A) Crystal Parameters at 23 °C (296 K)	
crystal system:	triclinic $V = 2728.7 (11) \text{ \AA}^3$
space group:	$P\bar{1}$ [No. 2] $Z = 4$
$a = 9.949 (3) \text{ \AA}$	mol wt = 808.2
$b = 16.419 (4) \text{ \AA}$	$\rho(\text{calcd}) = 1.96 \text{ g cm}^{-3}$
$c = 18.485 (4) \text{ \AA}$	
$\alpha = 112.81 (2)^\circ$	
$\beta = 93.53 (6)^\circ$	
$\gamma = 98.60 (2)^\circ$	
(B) Data Collection	
diffractometer:	Syntex P2 ₁
radiation:	Mo $K\alpha$ ($\lambda = 0.710730 \text{ \AA}$)
monochromator:	pyrolytic graphite
scan type:	coupled $\theta(\text{crystal})-2\theta(\text{counter})$
scan width:	symmetrical, $[1.8 + \Delta(\alpha_2 - \alpha_1)]^\circ$
scan speed:	$2.50 \text{ deg min}^{-1}$
reflections collected:	$+h, \pm k, \pm l$ for $2\theta = 4.5-45.0$, 7661
	total yielding 6439 unique reflections
abs coeff:	$\mu = 46.2 \text{ cm}^{-1}$

The positions of the two crystallographically independent tungsten atoms (which are related by pseudosymmetry) were finally located, after considerable difficulty, using the SHELXTL system. All subsequent calculations were performed on the SUNY—Buffalo CDC Cyber 173 computer using the SHELX76 program set. The remaining non-hydrogen atoms for both molecules were located from a series of difference Fourier syntheses. At convergence, discrepancy indices were $R_F = 8.00\%$ and $R_{wF} = 7.78\%$ for 511 parameters refined against all 6439 unique data and $R_F = 5.04\%$ and $R_{wF} = 5.55\%$ for those 4540 data with $|F_o| > 3\sigma(|F_o|)$. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, where $1/w = \{ \sigma(|F_o|) \}^2 + \{ 0.002|F_o| \}^2$. A final difference Fourier synthesis was featureless.

Final positional parameters are listed in Table VI; anisotropic thermal parameters (Table VIS) and a table of observed and calculated structure factors appear as supplementary material. Hydrogen atom contributions were not included in the refinement.

$W(\text{CCMe}_3)[OCH(\text{CF}_3)_2]_3(\text{dme})$ (1). $W(\text{CCMe}_3)(\text{dme})\text{Cl}_3^3$ (4.00 g, 8.90 mmol) was added as a solid to 3 equiv of lithium hexafluoroisopropoxide (4.64 g, 26.7 mmol) in ether (50 mL). After 30 min the bright yellow solution was filtered and the solvent removed in vacuo. Recrystallization of the residue from ether at -30°C gave 1 as large, bright yellow prisms (two crops, 6.59 g, 88% yield): $^1\text{H NMR}$ (C_6D_6) δ 5.75 (br, 3, $\text{CH}(\text{CF}_3)_2$), 3.56 (br, 3, CH_2O), 2.87 (br, 5, CH_3O and CH_2O), 2.58 (br, 2, CH_2O), 0.82 (s, 9, CCMe_3); $^{13}\text{C NMR}$ (C_6D_6) δ 296.1 (s, CCMe_3), 123.6 (q, $J_{\text{CF}} = 284 \text{ Hz}$, CF_3), 86.1 (dsep, $J_{\text{CH}} = 143 \text{ Hz}$, $^2J_{\text{CCF}} = 32 \text{ Hz}$, $\text{CH}(\text{CF}_3)_2$), 74.7 (br t, $J_{\text{CH}} = 143 \text{ Hz}$, OCH_2), 72.2 (br q, $J_{\text{CH}} = 149 \text{ Hz}$, OCH_3), 69.5 (br t, $J_{\text{CH}} = 141 \text{ Hz}$, OCH_2), 59.3 (br q, $J_{\text{CH}} = 149 \text{ Hz}$, OCH_3), 50.1 (s, CCMe_3), 34.0 (q, $J_{\text{CH}} = 126 \text{ Hz}$, CCMe_3). Anal. Calcd for $W_{16}H_{22}F_{18}O_5$: C, 25.61; H, 2.63. Found: C, 25.12; H, 2.75.

$W(\text{CCMe}_3)[OCH(\text{CF}_3)_2]_3(\text{py})_2$. Pyridine (228 μL , 2.83 mmol) was added to a solution of 1 (1.00 g, 1.13 mmol) in ether (20 mL). After 10 min the solvent was removed in vacuo, leaving a quantitative yield of yellow crystalline product. For analysis purposes a sample was recrystallized from ether at -30°C : $^1\text{H NMR}$ (C_6D_6) δ 8.76 (d, 2, $^3J_{\text{HH}} = 4.9 \text{ Hz}$, H_b), 8.54 (d, 2, $^3J_{\text{HH}} = 4.9 \text{ Hz}$, H_c), 6.75 (t, 1, $^3J_{\text{HH}} = 7.1 \text{ Hz}$, H_d), 6.73 (t, 1, $^3J_{\text{HH}} = 7.1 \text{ Hz}$, H_e), 6.54 (t, 2, $^3J_{\text{HH}} = 7.1 \text{ Hz}$, H_m), 6.32 (t, 2, $^3J_{\text{HH}} = 7.1 \text{ Hz}$, H_n), 6.03 (sep, 1, $^3J_{\text{HF}} = 6.1 \text{ Hz}$, $\text{CH}(\text{CF}_3)_2$), 5.95 (sep, 2, $^3J_{\text{HF}} = 6.1 \text{ Hz}$, $\text{CH}(\text{CF}_3)_2$), 1.01 (s, 9, CCMe_3); $^{13}\text{C NMR}$ (C_6D_6) δ 299.5 (s, CCMe_3), 153.0 (d, $J_{\text{CH}} = 186 \text{ Hz}$, py), 149.1 (d, $J_{\text{CH}} = 186 \text{ Hz}$, py), 138.6 (d, $J_{\text{CH}} = 165 \text{ Hz}$, py), 137.8 (d, $J_{\text{CH}} = 162 \text{ Hz}$, py), 124.2 (d, $J_{\text{CH}} = 167 \text{ Hz}$, py), 123.8 (q, $J_{\text{CF}} = 285 \text{ Hz}$, CF_3), 86.3 (d m, $^2J_{\text{CCF}} = 29 \text{ Hz}$, $J_{\text{CH}} = 146 \text{ Hz}$, $\text{OCH}(\text{CF}_3)_2$), 49.9 (s, CCMe_3), 34.2 (q, $J_{\text{CH}} = 127 \text{ Hz}$, CCMe_3). Anal. Calcd for $W_{24}H_{22}F_{18}N_2O_3$: C, 31.60; H, 2.43. Found: C, 31.95; H, 2.66.

$W(C_3Et_3)[OCH(\text{CF}_3)_2]_3$ (3). A sample of 1 (1.50 g, 1.78 mmol) was suspended in pentane (20 mL) at room temperature, and an excess of 3-hexyne (2.00 mL, 17.6 mmol, 10 equiv) was added. After several minutes all of 1 had dissolved, and the solution was

(15) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* 1977, 16, 265.

Table VI. Final Parameters for $W(C_3Et_3)[OCH(CF_3)_2]_2$ (3)

atom	x	y	z	$U_{iso}, \text{\AA}^2$
Molecule 3a				
W(1)	0.55680 (6)	0.99312 (4)	0.21503 (3)	
O(1)	0.6073 (10)	0.9845 (6)	0.3169 (6)	0.0714 (26)
O(2)	0.4379 (10)	1.0648 (6)	0.2803 (6)	0.0728 (27)
O(3)	0.4422 (11)	1.0102 (7)	0.1337 (6)	0.0841 (30)
C(1)	0.7365 (15)	1.0230 (10)	0.1917 (9)	0.0713 (41)
C(2)	0.6996 (14)	0.9281 (9)	0.1468 (8)	0.0621 (36)
C(3)	0.5709 (16)	0.8764 (10)	0.1487 (9)	0.0747 (43)
C(1A)	0.8637 (20)	1.0864 (13)	0.1944 (12)	0.1056 (59)
C(1B)	0.8723 (23)	1.1775 (15)	0.2585 (13)	0.1263 (72)
C(2A)	0.8063 (17)	0.8801 (11)	0.0972 (10)	0.0873 (48)
C(2B)	0.8984 (19)	0.8489 (12)	0.1502 (11)	0.1009 (56)
C(3A)	0.5225 (19)	0.7774 (12)	0.0988 (11)	0.0955 (53)
C(3B)	0.3820 (28)	0.7520 (17)	0.1097 (15)	0.1564 (95)
C(4)	0.6764 (17)	0.9231 (11)	0.3319 (10)	0.0815 (46)
C(5)	0.5860 (20)	0.8735 (12)	0.3700 (11)	0.1047 (59)
C(6)	0.7949 (25)	0.9743 (15)	0.3915 (14)	0.1353 (79)
C(7)	0.4064 (15)	1.0921 (9)	0.3580 (8)	0.0638 (37)
C(8)	0.4598 (20)	1.1923 (13)	0.4026 (11)	0.1062 (60)
C(9)	0.2533 (20)	1.0673 (12)	0.3561 (11)	0.1025 (58)
C(10)	0.3654 (16)	1.0750 (10)	0.1354 (9)	0.0777 (44)
C(11)	0.2308 (21)	1.0239 (13)	0.0816 (12)	0.1116 (63)
C(12)	0.4357 (22)	1.1395 (14)	0.1082 (12)	0.1179 (67)
F(5A)	0.5349 (15)	0.9221 (9)	0.4312 (7)	
F(5B)	0.4774 (17)	0.8274 (10)	0.3165 (10)	
F(5C)	0.6388 (19)	0.8156 (9)	0.3856 (8)	
F(6A)	0.8798 (13)	1.0211 (13)	0.3581 (11)	
F(6B)	0.8675 (16)	0.9234 (12)	0.4114 (11)	
F(6C)	0.7784 (16)	1.0371 (9)	0.4571 (7)	
F(8A)	0.4079 (20)	1.2365 (8)	0.3693 (10)	
F(8B)	0.4344 (19)	1.2172 (8)	0.4764 (6)	
F(8C)	0.5949 (17)	1.2037 (10)	0.4033 (11)	
F(9A)	0.2126 (15)	0.9842 (10)	0.3154 (11)	
F(9B)	0.2214 (12)	1.0900 (11)	0.4287 (7)	
F(9C)	0.1885 (14)	1.1079 (12)	0.3212 (8)	
F(11A)	0.2462 (16)	0.9797 (11)	0.0087 (8)	
F(11B)	0.1505 (13)	1.0833 (11)	0.0826 (9)	
F(11C)	0.1662 (14)	0.9651 (12)	0.1039 (11)	
F(12A)	0.4701 (18)	1.1055 (12)	0.0374 (9)	
F(12B)	0.3711 (17)	1.2041 (9)	0.1110 (9)	
F(12C)	0.5511 (17)	1.1817 (11)	0.1560 (13)	
Molecule 3b				
W(2)	0.98790 (6)	0.52927 (4)	0.28137 (4)	
O(4)	0.8405 (10)	0.5151 (6)	0.1988 (6)	0.0751 (28)
O(5)	1.0634 (10)	0.4587 (7)	0.1883 (6)	0.0794 (29)
O(6)	1.1360 (10)	0.4974 (6)	0.3349 (5)	0.0696 (26)
C(13)	1.0204 (17)	0.6552 (11)	0.3374 (10)	0.0821 (46)
C(14)	0.9324 (17)	0.6291 (11)	0.3803 (10)	0.0802 (45)
C(15)	0.8767 (15)	0.5320 (10)	0.3593 (9)	0.0733 (41)
C(13A)	1.0914 (24)	0.7506 (15)	0.3450 (14)	0.1280 (74)
C(13B)	1.1194 (31)	0.7447 (18)	0.2642 (17)	0.179 (11)
C(14A)	0.8796 (21)	0.6995 (14)	0.4527 (12)	0.1131 (64)
C(14B)	0.9900 (30)	0.7249 (19)	0.5280 (17)	0.174 (10)
C(15A)	0.7873 (21)	0.4978 (14)	0.4079 (12)	0.1125 (63)
C(15B)	0.7609 (32)	0.4043 (21)	0.3771 (18)	0.191 (12)
C(16)	0.7013 (17)	0.5140 (11)	0.2010 (9)	0.0780 (44)
C(17)	0.6633 (24)	0.5919 (15)	0.1844 (13)	0.1323 (75)
C(18)	0.6247 (29)	0.4282 (18)	0.1410 (16)	0.1615 (99)
C(19)	1.0155 (20)	0.4120 (13)	0.1057 (11)	0.1000 (56)
C(20)	1.0059 (26)	0.3128 (17)	0.0869 (15)	0.1537 (89)
C(21)	1.1149 (27)	0.4464 (17)	0.0671 (15)	0.1515 (92)
C(22)	1.2705 (16)	0.4873 (10)	0.3171 (9)	0.0767 (43)
C(23)	1.3025 (19)	0.4063 (12)	0.3316 (11)	0.0994 (55)
C(24)	1.3684 (21)	0.5749 (13)	0.3642 (12)	0.1108 (62)
F(17A)	0.6969 (20)	0.5924 (16)	0.1199 (13)	
F(17B)	0.5311 (13)	0.5933 (11)	0.1870 (10)	
F(17C)	0.7302 (17)	0.6634 (10)	0.2399 (15)	
F(18A)	0.4884 (13)	0.4189 (11)	0.1442 (12)	
F(18B)	0.6564 (16)	0.3631 (11)	0.1537 (19)	
F(18C)	0.6457 (20)	0.4181 (17)	0.0717 (10)	
F(20A)	1.1227 (25)	0.2872 (13)	0.0984 (12)	
F(20B)	0.9382 (26)	0.2670 (14)	0.0144 (11)	
F(20C)	0.9150 (25)	0.2907 (11)	0.1285 (13)	
F(21A)	1.0823 (19)	0.3942 (16)	-0.0138 (9)	
F(21B)	1.2465 (16)	0.4310 (21)	0.0801 (11)	
F(21C)	1.1384 (20)	0.5275 (14)	0.0834 (14)	

Table VI (Continued)

atom	x	y	z	$U_{iso}, \text{\AA}^2$
F(23A)	1.3041 (17)	0.4193 (11)	0.4045 (9)	
F(23B)	1.4221 (12)	0.3904 (9)	0.3141 (9)	
F(23C)	1.2152 (14)	0.3353 (8)	0.2922 (11)	
F(24A)	1.4959 (10)	0.5669 (10)	0.3541 (9)	
F(24B)	1.3620 (14)	0.5978 (11)	0.4400 (8)	
F(24C)	1.3372 (13)	0.6382 (9)	0.3463 (12)	

red. The solution was stirred for 40 minutes before it was filtered through Celite and cooled to -30°C . Red plates crystallized from solution. This crude product contained from 3 to 5% $W[\text{C}(\text{CMe}_3)\text{C}(\text{Et})\text{C}(\text{Et})][\text{OCH}(\text{CF}_3)_2]_3$. Therefore the above procedure was repeated. The crude product was dissolved in pentane (15 mL), and 3-hexyne (1.00 mL, 8.80 mmol) and 1,2-dimethoxyethane (200 μL , 1.92 mmol) were added. After 40 min the solution was filtered through Celite and cooled to -30°C . Red plates crystallized from solution (0.70 g, 47%): $^1\text{H NMR}$ (C_6D_6) δ 5.98 (sep, 1, $J_{\text{HF}} = 6.3$ Hz, eq $\text{CH}(\text{CF}_3)_2$), 4.36 (sep, 2, $J_{\text{HF}} = 6.1$ Hz, ax $\text{CH}(\text{CF}_3)_2$), 3.58 (q, 4, $^3J_{\text{HH}} = 7.5$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_3$), 3.01 (q, 2, $^3J_{\text{HH}} = 7.7$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_3$), 1.32 (t, 6, $^3J_{\text{HH}} = 7.5$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_3$), 0.50 (t, 3, $^3J_{\text{HH}} = 7.7$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_3$); $^{13}\text{C NMR}$ (C_6D_6) δ 242.9 (s, $J_{\text{CW}} = 127$ Hz, C_α), 147.3 (s, C_β), 122.9 (q, $J_{\text{CF}} = 284$ Hz, CF_3), 78.9 (d m, $^2J_{\text{CCF}} = 32$ Hz, $J_{\text{CH}} = 146$ Hz, $\text{CH}(\text{CF}_3)_2$), 29.7 (t, $J_{\text{CH}} = 132$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_3$), 25.4 (t, $J_{\text{CH}} = 138$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_3$), 14.3 (q, $J_{\text{CH}} = 129$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_3$), 12.0 (q, $J_{\text{CH}} = 130$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_3$). Anal. Calcd for $\text{WC}_{22}\text{H}_{18}\text{F}_{18}\text{O}_3$: C, 26.75; H, 2.24. Found: C, 27.25; H, 2.34.

$W[\text{C}(\text{CMe}_3)\text{C}(\text{Et})\text{C}(\text{Et})][\text{OCH}(\text{CF}_3)_2]_3$ (2). $W[\text{C}(\text{CMe}_3)\text{C}(\text{Et})\text{C}(\text{Et})]\text{Cl}_3$ (0.50 g, 1.1 mmol) was added to a solution of lithium hexafluoroisopropoxide (0.59 g, 3.4 mmol) in toluene (20 mL). The solution turned light red after 2 h. It was then filtered and stripped to dryness. The residue was recrystallized from pentane to give red crystals of 2 (0.61 g, 64% yield): $^1\text{H NMR}$ (C_6D_6) δ 5.96 (sep, 1, $^3J_{\text{HF}} = 6.2$ Hz, eq $\text{OCH}(\text{CF}_3)_2$), 4.44 (sep, 2, $^3J_{\text{HF}} = 6.2$ Hz, ax $\text{OCH}(\text{CF}_3)_2$), 3.51 (q, 2, $^3J_{\text{HH}} = 7.5$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_3$), 3.29 (q, 2, $^3J_{\text{HH}} = 7.6$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_3$), 1.38 (t, 3, $^3J_{\text{HH}} = 7.5$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_3$), 1.21 (s, 9, CMe_3), 0.51 (t, 3, $^3J_{\text{HH}} = 7.6$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_3$); $^{13}\text{C NMR}$ (C_6D_6) δ 250.4 (s, C_α), 245.8 (s, C_β), 147.4 (s, C_β), 123.0 (q, $J_{\text{CF}} = 284$ Hz, $\text{CH}(\text{CF}_3)_2$), 79.2 (d sep, $^2J_{\text{CCF}} = 34$ Hz, $J_{\text{CH}} = 144$ Hz, ax $\text{CH}(\text{CF}_3)_2$), 77.7 (d sep, $^2J_{\text{CCF}} = 34$ Hz, $J_{\text{CH}} = 138$ Hz, eq $\text{CH}(\text{CF}_3)_2$), 42.6 (s, CMe_3), 31.1 (q, $J_{\text{CH}} = 127$ Hz, CMe_3), 30.4 (t, $J_{\text{CH}} = 127$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_3$), 23.5 (t, $J_{\text{CH}} = 132$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_3$), 14.3 (q, $J_{\text{CH}} = 127$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_3$), 12.9 (q, $J_{\text{CH}} = 130$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_3$). Anal. Calcd for $\text{WC}_{20}\text{H}_{22}\text{F}_{18}\text{O}_3$: C, 28.73; H, 2.65. Found: C, 28.55; H, 2.72.

$W(\text{C}_3\text{Pr}_3)[\text{OCH}(\text{CF}_3)_2]_3$ (4). A sample of 1 (0.50 g, 0.59 mmol) was suspended in pentane (15 mL) and an excess of 4-octyne (600 μL , 4.1 mmol, ~ 7 equiv) was added. After several minutes all the starting material had dissolved and the solution was dark red. This mixture was stirred for 1 h and then stripped slowly to dryness in vacuo. This procedure was repeated with 1 equiv of dme (61 μL , 0.59 mmol) added to promote metathesis. The resulting residue was then recrystallized from pentane at -30°C to yield red cubes that melt near room temperature (0.29 g, 58%): $^1\text{H NMR}$ (C_6D_6) δ 5.98 (sep, 1, $^3J_{\text{HF}} = 6.1$ Hz, eq $\text{CH}(\text{CF}_3)_2$), 4.43 (sep, 2, $^3J_{\text{HF}} = 6.1$ Hz, ax $\text{CH}(\text{CF}_3)_2$), 3.64 (t, 4, $^3J_{\text{HH}} = 7.2$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_2\text{CH}_3$), 3.08 (t, 2, $^3J_{\text{HH}} = 7.7$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_2\text{CH}_3$), 1.82 (sex, 4, $^3J_{\text{HH}} = 7.2$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_2\text{CH}_3$), 1.04 (t, 6, $^3J_{\text{HH}} = 7.2$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_2\text{CH}_3$), ~ 1.02 (m, 2, $\text{C}_\beta\text{CH}_2\text{CH}_2\text{CH}_3$), 0.55 (t, 3, $^3J_{\text{HH}} = 7.3$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_2\text{CH}_3$); $^{13}\text{C NMR}$ (C_6D_6) δ 241.9 (s, $J_{\text{CW}} = 127$ Hz, C_α), 146.3 (s, C_β), 123.1 (q, $J_{\text{CF}} = 281$ Hz, eq $\text{OCH}(\text{CF}_3)_2$), 123.0 (q, $J_{\text{CF}} = 286$ Hz, ax $\text{OCH}(\text{CF}_3)_2$), 78.5 (d, mult, $^2J_{\text{CCF}} = 35$ Hz, $J_{\text{CH}} = 146$ Hz, ax $\text{OCH}(\text{CF}_3)_2$), 77.4 (d mult, $^2J_{\text{CCF}} = 33$ Hz, $J_{\text{CH}} = 150$ Hz, eq $\text{OCH}(\text{CF}_3)_2$), 38.3 (t, $J_{\text{CH}} = 132$ Hz), 33.6 (t, $J_{\text{CH}} = 142$ Hz), 23.6 (t, $J_{\text{CH}} = 126$ Hz), 21.7 (t, $J_{\text{CH}} = 126$ Hz), 13.9 (q, $J_{\text{CH}} = 125$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_2\text{CH}_3$), 13.4 (q, $J_{\text{CH}} = 126$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_2\text{CH}_3$).

$W(\text{CCH}_2\text{CH}_3)[\text{OCH}(\text{CF}_3)_2]_3(\text{py})_2$. Pyridine (88 μL , 1.09 mmol) was added to a solution of 3 (0.40 g, 0.49 mmol) in pentane (10 mL). The solution turned yellow immediately, and the microcrystalline product that fell from solution was collected and dried in vacuo (0.35 g, 80% yield): $^1\text{H NMR}$ (C_6D_6) δ 8.83 (d, 2, $^3J_{\text{HH}} = 4.7$ Hz, H_α), 8.36 (d, 2, $^3J_{\text{HH}} = 5.3$ Hz, H_α), 6.78 (t, 2, $^3J_{\text{HH}} = 7.7$ Hz, H_β or H_γ), 6.57 (t, 2, $^3J_{\text{HH}} = 6.8$ Hz, H_β or H_γ), 6.37

(t, 2, $^3J_{\text{HH}} = 6.9$ Hz, H_β or H_γ), 5.94 (sep, 1, $^3J_{\text{HF}} = 6.2$ Hz, $\text{OCH}(\text{CF}_3)_2$), 5.75 (sep, 2, $^3J_{\text{HF}} = 6.2$ Hz, $\text{OCH}(\text{CF}_3)_2$), 4.31 (q, 2, $^3J_{\text{HH}} = 7.5$ Hz, CCH_2CH_3), 0.77 (t, 3, $^3J_{\text{HH}} = 7.5$ Hz, CCH_2CH_3); $^{13}\text{C NMR}$ (C_6D_6) δ 293.6 (s, CCH_2CH_3), 152.8 (d, $J_{\text{CH}} = 180$ Hz, C_α), 149.1 (d, $J_{\text{CH}} = 183$ Hz, C_α'), 138.6 (d, $J_{\text{CH}} = 167$ Hz, C_β), 137.9 (d, $J_{\text{CH}} = 167$ Hz, C_β'), 124.6 (d, $J_{\text{CH}} = 170$ Hz, C_m), 124.4 (d, $J_{\text{CH}} = 165$ Hz, C_m'), 123.8 (q, $J_{\text{CF}} = 287$ Hz, CF_3), 87.0 (d m, $^2J_{\text{CCF}} = 32$ Hz, $J_{\text{CH}} = 146$ Hz, $\text{CH}(\text{CF}_3)_2$), 85.9 (d m, $^2J_{\text{CCF}} = 31$ Hz, $J_{\text{CH}} = 146$ Hz, $\text{CH}(\text{CF}_3)_2$), 37.2 (t, $J_{\text{CH}} = 128$ Hz, CCH_2CH_3), 17.6 (q, $J_{\text{CH}} = 128$ Hz, CCH_2CH_3). Anal. Calcd for $\text{WC}_{22}\text{H}_{18}\text{F}_{18}\text{N}_2\text{O}_3$: C, 29.88; H, 2.05. Found: C, 30.32; H, 2.23.

$W(\text{CCMe}_3)[\text{OCMe}(\text{CF}_3)_2]_3(\text{dme})$ (5). $W(\text{CCMe}_3)(\text{dme})\text{Cl}_3$ (1.00 g, 2.22 mmol) was added to a solution of lithium hexafluoro-*tert*-butoxide (1.25 g, 6.67 mmol) in ether (50 mL). After several minutes the orange solution was filtered and the solvent removed in vacuo. The residue was recrystallized from a mixture of ether and pentane at -30°C (2 crops, 1.58 g, 80% yield): $^1\text{H NMR}$ (C_6D_6) δ 3.34 (br, 6, OCH_3), 3.00 (br, 4, $\text{O}(\text{CH}_2)_2\text{O}$), 1.84 (br s, 9, $\text{OCMe}(\text{CF}_3)_2$), 0.98 (s, 9, CCMe_3); $^{13}\text{C NMR}$ (C_6D_6) δ 294.7 (s, CCMe_3), 124.9 (q, $J_{\text{CF}} = 290$ Hz, CF_3), 81.9 (m, $\text{OCMe}(\text{CF}_3)_2$), 72.1 (br, dme), 65.5 (br, dme), 49.5 (s, CCMe_3), 34.7 (q, $J_{\text{CH}} = 127$ Hz, CCMe_3), 19.3 (q, $J_{\text{CH}} = 130$ Hz, $\text{OCMe}(\text{CF}_3)_2$).

$W(\text{CCMe}_3)[\text{OCMe}(\text{CF}_3)_2]_3(\text{py})_2$. Pyridine (228 μL , 2.83 mmol) was added to a solution of 5 (1.00 g, 1.13 mmol) in ether (20 mL). After several minutes the solution was stripped in vacuo to give a light orange powder. The powder was pure by $^1\text{H NMR}$, and the yield was quantitative: $^1\text{H NMR}$ (C_6D_6) δ 8.82 (br, 2, H_α), 8.56 (br, 2, H_α'), 6.95 (br, 1, H_β), 6.79 (br, 3, H_β' and H_γ), 6.38 (br, 2, H_γ'), 1.88 (br s, 3, $\text{OCMe}(\text{CF}_3)_2$), 1.84 (br s, 6, $\text{OCMe}(\text{CF}_3)_2$), 1.17 (s, 9, CMe_3); $^{13}\text{C NMR}$ (C_6D_6) δ 296.0 (s, CCMe_3), 153.7 (d, $J_{\text{CH}} = 183$ Hz, C_α), 149.9 (d, $J_{\text{CH}} = 183$ Hz, C_α'), 138.6 (d, $J_{\text{CH}} = 165$ Hz, C_β), 136.4 (d, $J_{\text{CH}} = 136.4$ Hz, C_β), 124.8 (q, $J_{\text{CF}} = 289$ Hz, CF_3), 124.5 (q, $J_{\text{CF}} = 289$ Hz, CF_3), 124.1 (d, $J_{\text{CH}} = 170$ Hz, C_m), 123.5 (d, $J_{\text{CH}} = 162$ Hz, C_m'), 82.0 (br, $\text{OCMe}(\text{CF}_3)_2$), 50.4 (s, CCMe_3), 34.4 (q, $J_{\text{CH}} = 126$ Hz, CCMe_3), 19.6 (q, $J_{\text{CH}} = 130$ Hz, $\text{OCMe}(\text{CF}_3)_2$).

$W(\text{C}_3\text{Me}_3)[\text{OCMe}(\text{CF}_3)_2]_3$ (6). $W(\text{CCMe}_3)[\text{OCMe}(\text{CF}_3)_2]_3$ -
(dme) (1.00 g, 1.13 mmol) was placed into 40 mL of pentane and then cooled to -30°C . An excess of 2-butyne (1.77 mL, 22.6 mmol, 20 equiv) was added. The solution was stirred vigorously and allowed to warm until all of the starting material had dissolved. The solution was then filtered through Celite and cooled to -30°C . Large, red crystals of 4 were isolated (0.59 g, 65% yield): $^1\text{H NMR}$ (C_6D_6) δ 3.22 (s, 6, C_αMe), 2.16 (s, 3, C_βMe), 1.79 (s, 3, eq $\text{OCMe}(\text{CF}_3)_2$), 0.80 (s, 6, ax $\text{OCMe}(\text{CF}_3)_2$); $^{13}\text{C NMR}$ (C_6D_6) δ 239.9 (s, C_α), 133.5 (s, C_β), 124.5 (q, $J_{\text{CF}} = 287$ Hz, $\text{OCMe}(\text{CF}_3)_2$), 124.1 (q, $J_{\text{CF}} = 292$ Hz, $\text{OCMe}(\text{CF}_3)_2$), 21.5 (q, $J_{\text{CH}} = 130$ Hz, CH_3), 17.5 (q, $J_{\text{CH}} = 129$ Hz, CH_3), 17.1 (q, $J_{\text{CH}} = 131$ Hz, CH_3), 14.1 (q, $J_{\text{CH}} = 135$ Hz, CH_3).

$W(\text{C}_3\text{Et}_3)[\text{OCMe}(\text{CF}_3)_2]_3$ (7). Excess 3-hexyne (1.52 mL, 13.4 mmol, 12 equiv) was added to a solution of 5 (0.90 g, 1.11 mmol) in pentane (25 mL). The solution was allowed to stir for 3 min and then stripped in vacuo. This procedure was repeated. The residue was dissolved in ~ 20 mL of pentane and filtered through Celite to remove a small amount of polymer. Cooling this solution to -30°C gave thin red plates of 7 (0.73 g, 77% yield): $^1\text{H NMR}$ (C_6D_6) δ 3.81 (q, 4, $^3J_{\text{HH}} = 7.4$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_3$), 2.86 (q, 2, $^3J_{\text{HH}} = 7.7$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_3$), 1.82 (s, 3, eq $\text{OCMe}(\text{CF}_3)_2$), 1.45 (t, 6, $^3J_{\text{HH}} = 7.4$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_3$), 0.82 (s, 6, ax $\text{OCMe}(\text{CF}_3)_2$), 0.79 (t, 3, $^3J_{\text{HH}} = 7.7$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_3$); $^{13}\text{C NMR}$ (C_6D_6) δ 256.2 (s, $J_{\text{CW}} = 119$ Hz, C_α), 134.4 (s, C_β), 124.1 (q, $J_{\text{CF}} = 287$ Hz, eq $\text{OCMe}(\text{CF}_3)_2$), 123.8 (q, $J_{\text{CF}} = 289$ Hz, ax $\text{OCMe}(\text{CF}_3)_2$), 81.0 (m, $^2J_{\text{CCF}} = 29$ Hz, eq $\text{OCMe}(\text{CF}_3)_2$), 76.6 (m, $^2J_{\text{CCF}} \approx 29$ Hz, ax $\text{OCMe}(\text{CF}_3)_2$), 22.4 (t, $J_{\text{CH}} = 130$ Hz, $\text{C}_\alpha\text{CH}_2\text{CH}_3$), 16.9 (t, $J_{\text{CH}} = 134$ Hz, $\text{C}_\beta\text{CH}_2\text{CH}_3$), 8.2 (q, $J_{\text{CH}} = 131$ Hz, CH_3), 7.9 (q, $J_{\text{CH}} = 132$ Hz, CH_3), 4.8 (q, $J_{\text{CH}} = 128$ Hz, CH_3), 2.1 (q, $J_{\text{CH}} = 130$ Hz, CH_3).

W(CCH₃)[OCMe(CF₃)₂]₃(THF)₂. A sample of **6** (0.30 g, 0.37 mmol) was dissolved in tetrahydrofuran (~5 mL). The color of the solution changed rapidly from red to yellow. The solvent was removed in vacuo and the residue recrystallized from a mixture of ether and pentane at -30 °C to give large, yellow crystals (0.22 g, 67% yield): ¹H NMR (C₆D₆) δ 3.71 (s, 3, CCH₃), 3.69 (m, 8, OCH₂CH₂), 1.67 (s, 9, OCMe(CF₃)₂), 1.36 (m, 8, OCH₂CH₂); ¹³C NMR (C₆D₆) δ 277.5 (s, CCH₃), 124.4 (q, J_{CF} = 289 Hz, CF₃), 83.9 (br, OCMe(CF₃)₂), 69.4 (t, J_{CH} = 149 Hz, OCH₂CH₂) 31.7 (q, J_{CH} = 128 Hz, CCH₃), 25.6 (t, J_{CH} = 133 Hz, OCH₂CH₂), 19.3 (q, J_{CH} = 131 Hz, OCMe(CF₃)₂).

W(CCH₂CH₃)[OCMe(CF₃)₂]₃(dme). 3-Hexyne (193 μL, 1.70 mmol) was added to a solution of **6** (0.75 g, 0.85 mmol) partially dissolved in pentane (6 mL) at -30 °C. The mixture was stirred and allowed to warm to room temperature. All starting material dissolved. The solution was then filtered through Celite and cooled to -30 °C. Large, yellow plates crystallized from solution (0.52 g, 71% yield): ¹H NMR (C₆D₆) δ 4.31 (q, 2, ³J_{HH} = 7.6 Hz, ³J_{HW} = 7.8 Hz, CCH₂CH₃), 3.6-3.0 (br, 6, OCH₃), 2.94 (br, 4, O(CH₂)₂O), 1.73 (s, 9, OCMe(CF₃)₂), 0.66 (t, 3, ³J_{HH} = 7.6 Hz, CCH₂CH₃); ¹³C NMR (C₆D₆) δ 286.7 (s, J_{CW} = 265 Hz, CCH₂CH₃), 124.9 (q, J_{CF} = 288 Hz, CF₃), 82.8 (m, OCMe(CF₃)₂), 72.1 (br, dme), 38.9 (t, J_{CH} = 130 Hz, ²J_{CCW} = 42.5 Hz, CCH₂CH₃), 18.7 (q, J_{CH} = 130 Hz, OCMe(CF₃)₂), 16.8 (q, J_{CH} = 130 Hz, CCH₂CH₃).

W(CCH₃)[OCMe(CF₃)₂]₃(dme). A sample of **5** (0.75 g, 0.85 mmol) was partially dissolved in pentane (~6 mL) and cooled to -30 °C. 2-Butyne (130 μL, 1.7 mmol) was added. The mixture was stirred and allowed to warm at room temperature. After several minutes all starting material dissolved. The solution was filtered through Celite and cooled to -30 °C to give yellow crystals (0.55 g, 77% yield): ¹H NMR (C₆D₆) δ 3.94 (s, 3, ³J_{HW} = 9.3, CCH₃), 3.5-3.0 (br, 6, OCH₃), 2.93 (br, 4, O(CH₂)₂O), 1.71 (s, 9, OCMe(CF₃)₂); ¹³C NMR (C₆D₆) δ 279.0 (s, CCH₃), 124.9 (q, J_{CF} = 291 Hz, CF₃), 82.5 (br, OCMe(CF₃)₂), 71.4 (br, dme), 30.0 (q, J_{CH} = 128 Hz, CCH₃), 18.7 (q, J_{CH} = 131 Hz, OCMe(CF₃)₂).

Metathesis of 3-Heptyne. The compound of interest (50 mg) was dissolved in either 5 mL of pentane or ether. Two equivalents of undecane were added as an internal standard. Twenty equivalents of 3-heptyne were added and aliquots removed at

predetermined intervals. The aliquots were analyzed by gas chromatography. A ratio of 1:2:1 (3-hexyne:3-heptyne:4-octyne) was taken to be equilibrium.

Kinetic Measurements. Samples were prepared by injecting a stock solution of 3-hexyne-*d*₁₀ (10-40 equiv) in toluene-*d*₈ into a solution of **2** in toluene-*d*₈. The tube was then placed in a Bruker WM-270 NMR spectrophotometer. Several minutes were allowed for the temperature to equilibrate, and then accumulation of spectra was begun. The reaction was followed by integrating the β-CH₂CH₃ resonance vs. a standard (PhSi(CH₃)₃). The data were manipulated according to normal first-order methods. Runs with 10 equiv of 3-hexyne-*d*₁₀ (0.366 M) could only be followed for ~1 half-life before curvature became significant. A run with 40 equiv (0.982 M) was linear for slightly over 3 half-lives. The linear correlation coefficients for each plot were all >0.999. Volume change due to temperature change was small compared to other errors and was disregarded. The results are listed in Table I. An Arrhenius plot is given in Figure 1. Error terms for the reaction parameters were calculated from the actual scatter of the data.

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Registry No. 1, 91202-86-7; 2, 91202-81-2; 3, 91202-82-3; 4, 91202-83-4; 5, 91208-75-2; 6, 91202-84-5; 7, 91208-74-1; W-(CCMe₃)[OCH(CF₃)₂]₃(py)₂, 91202-87-8; W(CCH₂CH₃)[OCH(CF₃)₂]₃(py)₂, 91202-88-9; W(CCMe₃)[OCMe(CF₃)₂]₃(py)₂, 91202-89-0; W(CCH₃)[OCMe(CF₃)₂]₃(THF)₂, 91202-90-3; W-(CCH₂CH₃)[OCMe(CF₃)₂]₃(dme), 91202-91-4; W(CCH₃)[OCMe(CF₃)₂]₃(dme), 91202-92-5; W(CCMe₃)(dme)Cl₃, 83416-70-0; W[C(CMe₃)C(Et)C(Et)]Cl₃, 83487-36-9; 3-hexyne, 928-49-4; 4-octyne, 1942-45-6; 2-butyne, 503-17-3; 3-heptyne, 2586-89-2; 3-hexyne-*d*₁₀, 91202-85-6.

Supplementary Material Available: A table of anisotropic thermal parameters (Table VIS) and a list of observed and calculated structure factor amplitudes (29 pages). Ordering information is given on any current masthead page.