actual dissociation ($AD_2 \rightarrow AD + D$) in which the leaving molecule carries away the excess energy.

Summary

The emission properties of jet-cooled adducts between ethers and some aromatic hydrocarbons may be accounted for by assuming an excited state that is a superposition of a van der Waals locally excited (LE) state and a charge-transfer (CT) state. The direct optical transition from the ground state to the CT state is forbidden by either symmetry or Franck–Condon considerations. Thus, the excitation spectrum is dominated by the LE state, and emission from the CT state has a longer decay time. The CT character of the excited state is more prominent in anthracene and its derivatives than in perylene. This is particularly so when a hydrogen atom is bound to a C-9 or C-10 carbon. It is therefore proposed that this atom may serve as a bridge in transmitting the charge from the oxygen lone pair orbital of the ether. Geometric factors appear to be decisive in determining the interaction as shown by the fact that tetrahydrofuran, in which the oxygen atom is constrained to be away from the 9- or 10-position, does not show exciplex-type emission with anthracene.

Registry No. $(Et)_2O$, 60-29-7; PhOMe, 100-66-3; anthracene, 120-12-7; 2-methylanthracene, 613-12-7; 9-methylanthracene, 779-02-2; 9,10-dimethylanthracene, 781-43-1; perylene, 198-55-0; tetrahydrofuran, 109-99-9.

Preparation and Reactivity of Several Alkylidene Complexes of the Type $W(CHR')(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OR)_2$ and Related Tungstacyclobutane Complexes. Controlling Metathesis Activity through the Choice of Alkoxide Ligand

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Abstract: The reaction between $W(C\text{-}t\text{-}Bu)(dme)Cl_3$ and ArNH(TMS) ($Ar = 2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$) yields $W(C\text{-}t\text{-}Bu)(NHAr)(dme)Cl_2$. In the presence of a catalytic amount of triethylamine, $W(C\text{-}t\text{-}Bu)(NHAr)(dme)Cl_2$ is transformed into $W(CH\text{-}t\text{-}Bu)(NAr)(dme)Cl_2$ quantitatively. Derivatives of the type $W(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ [$OR = O\text{-}t\text{-}Bu$, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, and $OC(CF_3)_2(CF_2CF_2CF_3)$] have been prepared. The X-ray structure of $W(CHPh)(NAr)[OCMe(CF_3)_2]_2$ (prepared by treating $W(CHEt)(NAr)[OCMe(CF_3)_2]_2$ with *cis*-β-methylstyrene) showed it to be pseudotetrahedral with a W═C bond of 1.859 (22) Å and an alkylidene ligand turned so H_α and the phenyl ring lie in the C_α–W–N plane with the phenyl ring pointing toward the imido nitrogen atom. (Structure parameters: $a = 11.57$ (3) Å, $b = 12.719$ (2) Å, $c = 21.192$ (9) Å, $V = 3118.9$ Å^3, space group = $P2_12_12_1$, $Z = 4$, with $R_1 = 0.089$, and $R_2 = 0.096$.) Addition of $Me_3SiCH{=}CH_2$ to $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ yielded the tungstacyclobutane complex $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ whose crystal structure showed it to be a pseudo trigonal bipyramid with an axial imido ligand and an equatorial, bent (29.9°), tungstacyclobutane ring with W–C bond lengths of 2.099 (11) and 2.066 (11) Å. (Structure parameters: $a = 18.049$ (4) Å, $b = 12.224$ (4) Å, $c = 18.877$ (5) Å, $\beta = 114.86$ (2)°, $V = 3778.9$ Å^3, space group $P2_1/n$, $Z = 4$, with $R_1 = 0.054$, and $R_2 = 0.058$.) Vinyltrimethylsilane is not metathesized; $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ loses only vinyltrimethylsilane in solution to give $W(CHSiMe_3)(NAr)[OCMe(CF_3)_2]_2$. $W(CH\text{-}t\text{-}Bu)[(NAr)[OCMe(CF_3)_2]_2$ reacts rapidly with *cis*-3-hexene to give a mixture of $W(CHEt)(NAr)[OCMe(CF_3)_2]_2$ and $W[CHEtCHEtCHEt](NAr)[OCMe(CF_3)_2]_2$; the latter loses 3-hexene completely in solution at 25 °C to give the former. $W(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2$ reacts much more slowly with an equilibrium mixture of *trans*- and *cis*-3-hexene to give $W(CHEt)(NAr)[OCMe_2(CF_3)]_2$ in a reaction that is first order in tungsten and first order in 3-hexene. $W(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ reacts very slowly with vinyltrimethylsilane and virtually not at all with *cis*-3-hexene, while $W(CH\text{-}t\text{-}Bu)(NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ reacts slowly with each to give unstable products. $W(CH\text{-}t\text{-}Bu)(NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ will react rapidly with ethylene, however, to give an unsubstituted tungstacyclobutane complex whose structure is analogous to that of $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$, except that the WC_3 ring is absolutely planar. (Structure parameters: $a = 18.355$ (10) Å, $b = 9.513$ (11) Å, $c = 19.976$ (26) Å, $\beta = 96.75$ (8)°, $V = 3463.9$ Å^3, space group $P2_1/n$, $Z = 4$, with $R_1 = 0.076$, and $R_2 = 0.092$.) An analogous $W(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2$ complex can be prepared. $W(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ complexes (where $OR = O\text{-}t\text{-}Bu$ or $OCMe_2(CF_3)$) react with ethylene, but the ultimate products could not be characterized readily. Reactions involving 1-pentene in all cases are relatively complex. *cis*-2-Pentene is metathesized rapidly by $OCMe(CF_3)_2$ and $OCMe_2(CF_3)$ complexes. Unsubstituted tungstacycles react with PMe_3 to yield methylene complexes of the type $W(CH_2)(NAr)(OR)_2(PMe_3)$ [$OR = OCMe(CF_3)_2$ or $OC(CF_3)_2(CF_2CF_2CF_3)$].

For two decades the olefin metathesis reaction has elicited the sort of excitement that a totally new reaction deserves.[1] Since the classical catalyst systems based on Mo, W, or Re can be prepared easily, and in many cases exhibit extraordinarily high activity, classical catalysts found some applications relatively quickly, especially in the area of ring-opening metathesis polymerization of cyclic olefins. But olefin metathesis technology cannot be utilized fully until catalysts can be prepared systematically and their activity controlled by rational methods. Among the more frustrating of the problems is an incompatability of classical catalysts with a large number of functional groups.

The first evidence that the oxidation state of the metal in metathesis systems is probably the highest possible appeared in 1980; isolable complexes of the type $W(CH\text{-}t\text{-}Bu)(O)L_2Cl_2$ (L = a trialkylphosphine) were found to react with oridinary olefins in the presence of $AlCl_3$ to yield the expected new W(CHR′)-

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(O)L_2Cl_2 complexes.[2] Such systems would metathesize approximately 50 equiv of an internal olefin before they became inactive. Shortly therafter Osborn discovered that an oxo ligand in related tungsten oxo alkyl complexes can be removed by AlX_3 reagents and replaced by two halides to give complexes of the type W(CH-*t*-Bu)$(OR)_2X_2$.[3a] Such species are extraordinarily active olefin metathesis catalysts in the presence of AlX_3. Four-coordinate cationic species, $[W(CHR')(OR)_yX_{3-y}]^+$, are suspected to be the most active components of such systems.[3b,c] Basset has discovered related phenoxide catalysts.[4]

A further development in the metathesis area was the discovery of alkylidyne complexes of the type M(C-*t*-Bu)$(OR)_3$. Some of them are extremely active catalysts for the metathesis of internal acetylenes (e.g., when M = W and OR = O-*t*-Bu),[5] while others (e.g., W(C-*t*-Bu)(O-2,6-C_6H_3-*i*-Pr_2)$_3$) react with internal acetylenes to yield stable tungstacyclobutadiene complexes of the type $W(C_3R'_3)$(O-2,6-C_6H_3-*i*-Pr_2)$_3$ that are relatively poor catalysts by virtue of a slow rate-limiting loss of an acetylene from the WC_3 ring to give incipient W(CR')(O-2,6-C_6H_3-*i*-Pr_2)$_3$ complexes.[6a] The rate of acetylene metathesis also can be altered drastically by changing the metal. For example, Mo(CR')(O-*t*-Bu)$_3$ complexes[7] react extremely slowly with internal acetylenes, in contrast to the analogous tungsten species.[5] These results suggest that both the choice of metal and the choice of alkoxide greatly affect the rate of reaction of a metal center with an acetylene and the relative stability of various metallacyclobutadiene rings, and therefore metathesis activity. In one case[6b] upon changing the alkoxide even the mechanism changes (from rate-limiting dissociation of an acetylene from a tungstacycle to an associative reaction between a tungstacycle and an acetylene). Bulky alkoxide ligands are required in all cases in order to prevent deactivation of the metal centers by bridging alkoxide ligands.

On the basis of these most recent findings in olefin and acetylene metathesis systems we felt that we should be able to prepare an active *neutral, four-coordinate* olefin metathesis catalyst. (A neutral catalyst could alleviate some of the potential for complications in the presence of basic functional groups.) In order to maintain the high oxidation state of the metal, one of the ligands would have to be a dianion; a bulky imido ligand, N-2,6-C_6H_3-*i*-Pr_2 (NAr), seemed to be the best choice on the basis of our success with the O-2,6-C_6H_3-*i*-Pr_2 ligand in acetylene metathesis systems.[6a,7] Therefore we sought a route to complexes of the type W(CH-*t*-Bu)(NAr)$(OR)_2$. In this paper we report a series of complexes of this type where OR is varied from a relatively donating alkoxide (O-*t*-Bu) to a highly electron withdrawing alkoxide $[OC(CF_3)_2(CF_2CF_2CF_3) = OR_F]$, reactions of these complexes with simple olefins, several tungstacyclobutane complexes, and several five-coordinate monoadducts of alkylidene complexes including two methylene complexes. Some of these results have been communicated in preliminary form.[8,9]

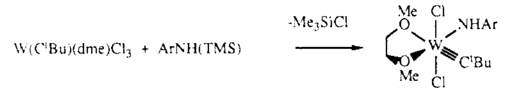
Results

Preparation of W(CH-*t*-Bu)(NAr)(OR)$_2$ Complexes. Several years ago we observed that neopentylidene complexes can be prepared from neopentylidyne complexes as shown in eq 1.[10] Although the mechanism of this reaction still is uncertain, we suspect that it is related to α-hydrogen abstraction reactions in d^0 alkyl complexes.[11] The α-hydrogen atom in the amido ligand

$$W(C\text{-}t\text{-}Bu)(NHPh)(PR_3)_2Cl_2 \xrightarrow{NEt_3 catalyst} W(CH\text{-}t\text{-}Bu)(NPh)(PR_3)_2Cl_2 \quad (1)$$

must be activated toward migration and may actually be removed by triethylamine and subsequently added back to the alkylidyne ligand. We felt that if we could design a system in which the same sort of reaction occurred, but one in which ligands more labile than phosphines were present, we might be able to gain a general entry into alkylidene chemistry.

The reaction between W(C-*t*-Bu)(dme)Cl_3[12] and ArNH(TMS) (Ar = 2,6-C_6H_3-*i*-Pr_2) proceeds smoothly as shown in eq 2. W(C-*t*-Bu)(NHAr)(dme)Cl_2 (**1**) can be isolated as yellow cubes in high yield. An important point is that the TMS reagent appears to be required, probably because it is a relatively mild method of introducing the NHAr ligand. If lithium or sodium salts of the amido anion are employed, then little or no W(C-*t*-Bu)(NHAr)(dme)Cl_2 is formed. We suspect that overamidation is a major problem, one that might be alleviated to some extent by using a bulky NHAr ligand. In a latter paper in this series we will show that few variations in the imido ligands are possible using *this* approach.



(2)

1

We propose that the neopentylidyne ligand is cis to the amido ligand in **1** since the π electrons of what is likely to be a planar amido ligand (about N) are best donated into a d orbital that is not used for π bonding to the alkylidyne ligand. (Similar reasoning explains why the neopentylidyne ligand is cis to the phosphido ligand in W(C-*t*-Bu)(PHPh)(PEt$_3$)$_2$Cl$_2$.[10]) In the NMR spectrum of **1** at 25 °C the dme resonances are broad, and added dme exchanges readily with coordinated dme. At low temperature the two ends of the dme are inequivalent, the isopropyl methine protons give rise to a single septet, and the isopropyl methyl groups give rise to two doublets. These data rule out a structure in which the amido and neopentylidyne ligands are trans to one another (if the phenyl ring rotates readily about the N–C bond). The structure of **1** shown in eq 2 is one possibility, if the plane of the phenyl ring of the amido ligand is oriented perpendicular to the N–W–C plane and does not rotate rapidly on the NMR time scale. Another possibility is a related molecule in which one end of the dme is trans to either N or C, and the other end trans to chloride, and in which the phenyl ring *does* rotate readily about the C–N bond.

Treating **1** with a catalytic amount of triethylamine in diethyl ether at −40 °C yields orange **2** (eq 3) in high yield. If the reaction is performed at 25 °C the major product is an as yet unidentified, relatively insoluble, yellow powder. In the absence of triethylamine **1** is not converted into **2** at 25 °C. Although we have not explored the mechanism of the reaction shown in eq 3, we do know that

$$\underset{\mathbf{1}}{W(C\text{-}t\text{-}Bu)(NHAr)(dme)Cl_2} \xrightarrow[ether]{NEt_3 \text{ catalyst}} \underset{\mathbf{2}}{W(CH\text{-}t\text{-}Bu)(NAr)(dme)Cl_2} \quad (3)$$

the rate is suppressed upon addition of dimethoxyethane, or if a bulkier amine such as NPr_2Et is employed. At room temperature the NMR spectrum shows broad dme resonances, but at low temperature the two ends of the dme are inequivalent, the isopropyl

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Table I. ^{1}H and ^{13}C NMR Data for Compounds of General Formula $W(CHR')(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)X_2$ and Related Alkylidene Complexes[a]

CHR′	X	δH_α	δC_α	J_{CH}	J_{CW}
CH-*t*-Bu (**2**)	Cl[b]	9.97	283.8	114	163
CH-*t*-Bu (**3a**)	$OCMe_3$	8.05	236.5	110	201
CH-*t*-Bu (**3b**)	$OCMe_2(CF_3)$	8.41	244.9	114	200
CH-*t*-Bu (**3c**)	$OCMe(CF_3)_2$	8.87	253.9	110	198
CH-*t*-Bu (**3d**)	OR_F	9.45	263.0	115	
CHPh (**4**)	$OCMe(CF_3)_2$	9.91	239.9[c]	121	202
$CHSiMe_3$ (**6**)	$OCMe(CF_3)_2$	9.97	242.8		
$CHSiMe_3$ (**7**)	$OCMe_2(CF_3)$	9.40	230.5	110	
$CHSiMe_3$ (**14**)	$OCMe(CF_3)_2$[d]	12.05	266.3		
CHEt	OR_F[e]	9.83			
CHEt (**8a**)	$OCMe(CF_3)_2$[e]	9.22	249.1	120	
CHEt (**8b**)	$OCMe(CF_3)_2$[f]	9.55	263.5	122	189
CHEt (**10**)	$OCMe_2(CF_3)$[e]	8.77			
CHEt (**11**)	$OCMe_3$[e]	8.40	229.0	110	203
CH_2 (**15**)	$OCMe(CF_3)_2$[e]	11.00	252.2	145	163[g]
CH_2 (**16**)	OR_F[e]	11.58 11.31	264.9	134	

[a] All spectra were recorded in C_6D_6 unless otherwise noted (see Experimental Section for further details); $OR_F = OC(CF_3)_2(CF_2CF_2CF_3)$. [b] Dimethoxyethane adduct. [c] In CD_2Cl_2. [d] PMe_3 adduct. [e] Observed in situ. [f] THF adduct. [g] J_{CP} = 14.5 Hz.

methine protons give rise to a single septet, and the isopropyl methyl groups give rise to two doublets, i.e., the spectrum of **2** at low temperature is analogous to that of **1**. Therefore the same arguments apply (see above), and we can be relatively certain only that the imido and neopentylidene ligands are cis to one another. We assume that the α-hydrogen atom of the neopentylidene ligand lies in the same plane as C, W, and N, an orientation that is required in order to maximize π bonding, and one which is found in a related molecule (see below). Although two isomers with the same overall geometry are possible (the other containing an alkylidene ligand that has been rotated by 180°), we see only one.

Preparation of complexes of the type W(CH-*t*-Bu)(NAr)(OR)$_2$ from W(CH-*t*-Bu)(NAr)(dme)Cl$_2$ is relatively straightforward (eq 4), although isolation of the products is complicated by their extreme solubility in pentane; also in one case ($OR = OC(CF_3)_2(CF_2CF_2CF_3) = OR_F$) the product can be purified only by distillation at 80 °C and 0.01 μm, after which it solidifies slowly to a waxy yellow-orange solid (mp ~25 °C). We assume that all four compounds are pseudotetrahedral molecules analogous

$$W(CH\text{-}t\text{-}Bu)(NAr)(dme)Cl_2 + 2MOR \xrightarrow{M = Li\text{ or }K} W(CH\text{-}t\text{-}Bu)(NAr)(OR)_2 + 2MCl \quad (4)$$

$$\begin{aligned} &\mathbf{3a},\ OR = OCMe_3\\ &\mathbf{3b},\ OR = OCMe_2(CF_3)\\ &\mathbf{3c},\ OR = OCMe(CF_3)_2\\ &\mathbf{3d},\ OR = OR_F \end{aligned}$$

to W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (see next section). Dimers that contain bridging alkoxide ligands (or an alkylidene or imido ligand) should be considered in the general case as plausible alternatives, especially if one or more of the three types of ligands is (are) not very bulky.

Proton and carbon NMR data for alkylidene complexes of the general formula W(CHR′)(NAr)X$_2$ are shown in Table I. The trends in chemical shift of H$_\alpha$ and C$_\alpha$ in **3a–d** are what one might expect on the basis of the relative electron-withdrawing ability of the alkoxide ligands, if we assume that the chemical shift is determined solely by changes in charge density as a result of the inductive effect of the alkoxide ligands. (Osborn has documented similar trends.[3c]) It is somewhat surprising to find that J_{CH} varies little with the nature of the alkoxides, although in the systems reported by Osborn J_{CH} also is relatively invariant. In contrast in related tantalum chemistry the value for J_{CH} varies markedly with the nature of the anionic ligand (e.g., X = Cl, Br, OR, etc.).[13]

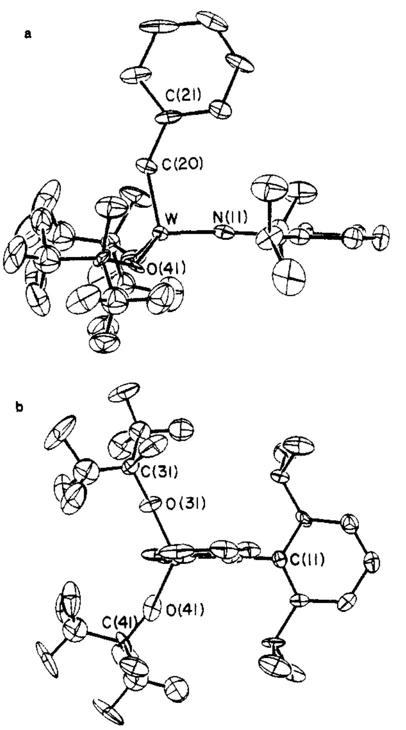

Figure 1. Two views of W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**4**) (a) looking down onto the C(20)–W–N(11) plane and (b) looking edge-on into the C(20)–W–N(11) plane.

Table II. Relevant Bond Lengths (Å) and Angles (deg) in W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**4**)

W–C(20)	1.859 (22)	W–N(11)–C(11)	175.6 (15)
W–N(11)	1.708 (17)	W–C(20)–C(21)	144.8 (18)
W–O(31)	1.903 (16)	W–O(31)–C(31)	140.7 (13)
W–O(41)	1.902 (14)	W–O(41)–C(41)	142.8 (14)
C(20)–W–N(11)	100.9 (9)	O(31)–W–O(41)	112.3 (7)
O(31)–W–N(11)	112.2 (7)	C(20)–W–O(31)	112.4 (8)
O(41)–W–N(11)	113.0 (8)	C(20)–W–O(41)	105.4 (8)

It is important to point out that migration of an α hydrogen from nitrogen to carbon appears to be slow when halides are not present, a trend that has been observed for migration of an α hydrogen from carbon to carbon.[13] For example, if W(C-*t*-Bu)(NHAr)(dme)Cl$_2$ is treated with LiOCMe(CF$_3$)$_2$ in ether, W(C-*t*-Bu)(NHAr)[OCMe(CF$_3$)$_2$]$_2$(dme) can be isolated in high yield. So far we have not been able to convert W(C-*t*-Bu)(NHAr)[OCMe(CF$_3$)$_2$]$_2$(dme) into W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ in a thermal or base-catalyzed process.

The X-ray Structure of W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (4). W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$ was prepared by reacting W(CHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$ with *cis*-β-methylstyrene (see later section). It is important to discuss its structure now in order to establish the basic features of pseudotetrahedral W(CHR′)(NAr)(OR)$_2$ complexes.

The overall geometry of W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (Figure 1) is close to tetrahedral. Only the C(20)–W–N(11) angle of 100.9 (9)° differs significantly from the tetrahedral value (Table II), and that not so much as to warrant any involved explanation. It can be compared to the C=W=O angle of 101.6 (8)° in W(O)(CH-*t*-Bu)(PMe$_3$)$_2$Cl$_2$[14] and 106.7 (6)° in W(O)(CH-*t*-Bu)(PEt$_3$)Cl$_2$.[15]

The two alkoxide ligands appear to be perfectly normal with W–O bond lengths of ~1.90 Å and W–O–C bond angles of

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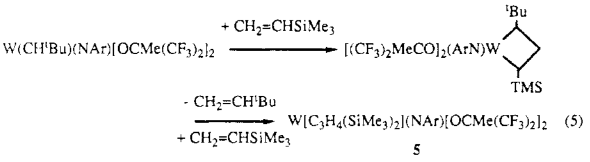
[15] (a) Wengrovius, J.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515. (b) Churchill, M. R.; Missert, J. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 3388.

141–143°. It is worth noting not only that the two alkoxide ligands are turned away from one another (and away from the imido ligand), as one would expect, but also that the two CF_3 groups in each $OCMe(CF_3)_2$ ligand are turned away from the benzylidene and imido ligands (Figure 1a). The CF_3 groups should turn away from the other ligands since each is larger than a methyl group, and also possibly because van der Waals interactions between a trifluoromethyl group and hydrocarbon groups should be diminished relative to interactions between hydrocarbons.[16]

The W–N bond length and W–N–C angle are what might be expected for an imido ligand bound to an electron-deficient metal as a result of the strong donation of the nitrogen lone pair and apparent sp hybridization about the N atom.[17] The orientation of the imido phenyl ring perpendicular to the C(20)–W–N(11) plane almost certainly is determined largely by steric considerations. The isopropyl groups fill the space above and below the C(20)–W–N(11) plane (Figure 1b), and the methyl groups in them are turned away from the metal. The C–C distances within the imido phenyl ring (not listed) are normal.

The most interesting feature of this molecule is the benzylidene ligand. The W–C(20) bond (1.859 (22) Å) is somewhat shorter than the W=C bond in $W(O)(CH\text{-}t\text{-}Bu)(PMe_3)_2Cl_2$ (2.006 (15) Å),[14] more comparable to the W=C bond in $W(O)(CH\text{-}t\text{-}Bu)(PEt_3)Cl_2$ (1.882 (14) Å).[15] Although shorter bonds in four- or five-coordinate species (relative to six-coordinate species) could be ascribed simply to the fact that the coordination number is lower (i.e., all metal–ligand bonds are shortened), it is certainly plausible that the electron-withdrawing alkoxide ligands also shorten the W=C bond compared to what it would be in a complex that contains normal (non-fluorinated) alkoxide ligands. The fact that C(21) lies in the same plane as C(20), W, and N(11) is to be expected since the W=C bond otherwise would compete with the W≡N pseudo triple bond for d orbitals involved in π bonding. The phenyl ring also lies in a position (in the C(20)–W–N(11) plane) consistent with conjugation of its π system with that of the W=C system. Finally, it should be noted that the phenyl ring is pointed toward the imido ligand, not away from it. This orientation actually appears to be the most favored sterically, since if the phenyl ring were to point away from the imido ligand, a CF_3 group from each alkoxide would appear to be close enough to interact significantly with it. It is possible that the orientation of the benzylidene ligand is determined by kinetic rather than thermodynamic factors, although we think that possibility is relatively unlikely.

Reactions of Neopentylidene Complexes with CH_2=$CHSiMe_3$ and the X-ray Structure of $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$. The reaction between 3c and excess vinyltrimethylsilane yields the tungstacyclobutane complex **5** (eq 5). No products of catalytic metathesis of vinyltrimethylsilane are detected at 25 °C, and neohexene is the only observed stoichiometric metathesis product. Therefore the initial WC_3 ring that contains an α *tert*-butyl group and an α trimethylsilylmethyl group breaks up to yield neohexene and $W(CHSiMe_3)(NAr)[OCMe(CF_3)_2]_2$ (**6**), which then scavenges a second equivalent of vinyltrimethylsilane to give **5**. The other possible initial WC_3 ring (α-*t*-Bu/β-TMS) may form, but it must not lose *t*-BuCH=CHSiMe$_3$ at a competitive rate.



(5)

$W[C_3H_4(SiMe_3)_2](NAr)[OCMe(CF_3)_2]_2$ (**5**) is a pale yellow crystalline solid that can be recrystallized only in the presence of excess vinyltrimethylsilane. In solution **5** is in equilibrium with vinyltrimethylsilane and **6**. In *dilute* solution at 25 °C as much as 60–70% of **5** is converted into **6**. (See Experimental Section for values of K_{eq}.) **6** can be isolated by treating **5** with THF to give $W(CHSiMe_3)(NAr)[OCMe(CF_3)_2]_2(THF)$ and then removing the THF in vacuo from $W(CHSiMe_3)(NAr)[OCMe(CF_3)_2]_2(THF)$ in the solid state. (See Experimental Section and Table I for NMR data.) The proton NMR spectrum of **6** is not completely straightforward; it is discussed along with that of a close relative below.

$$\underset{\mathbf{5}}{W[C_3H_4(SiMe_3)_2](NAr)[OCMe(CF_3)_2]_2} \underset{+\,CH_2=CHSiMe_3}{\overset{-\,CH_2=CHSiMe_3}{\rightleftharpoons}} \underset{\mathbf{6}}{W(CHSiMe_3)(NAr)[OCMe(CF_3)_2]_2} \qquad (6)$$

An X-ray study of **5** showed that the overall geometry of the core is best described as a trigonal bipyramid (Figure 2). One of the significant distortions of that core is the O(31)–W–N(21) angle of 97.3 (4)° (Table III). The tungsten therefore sits ~0.1 Å below the O(31)–C(11)–C(13) plane. Since the N(21)–W–C(11) and N(21)–W–C(13) angles are essentially 90°, we believe the large O(31)–W–N(21) angle can be ascribed largely to steric repulsion between the imido ligand and the "equatorial" hexafluoro-*tert*-butoxide ligand. The orientation of the imido ligand as a whole, and the isopropyl groups in it, appears to be the best compromise sterically. Note that C(31) points toward the imido ligand (between the isopropyl groups), while C(41) points away from Si(11). The entire axial ligand appears to be tipped slightly away from C(13) and Si(11) [O(41)–W–N(21) = 171.9 (4)°].

The imido and alkoxide ligands in **5** are similar to those in **4**. The W–O and W–N bond lengths in **5** tend to be somewhat longer than those in **4**, as one would expect in a compound of higher coordination number. The greatest difference (but still a relatively small one) is the somewhat larger W–O(41)–C(41) angle of 149.3

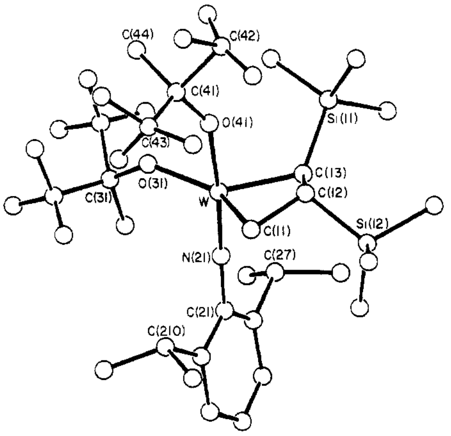


Figure 2. A drawing of $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ (**5**). For clarity, atoms are drawn as spheres of arbitrary radius and hydrogen atoms are omitted.

Table III. Relevant Bond Lengths (Å), Angles (deg), and Deviation from a Least-Squares Plane (Å) in $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ (**5**)

W–C(11)	2.099 (11)	O(31)–W–O(41)	82.8 (3)
W···C(12)	2.372 (11)	O(31)–W–N(21)	97.3 (4)
W–C(13)	2.066 (11	O(31)–W–C(11)	142.5 (4)
W–N(21)	1.738 (9	O(31)–W–C(13)	133.3 (4)
W–O(31)	1.960 (8)	O(41)–W–N(21)	171.9 (4)
W–O(41)	1.997 (7)	O(41)–W–C(11)	84.8 (4)
C(11)–C(12)	1.625 (15)	O(41)–W–C(13)	92.4 (4)
C(12)–C(13)	1.606 (16)	N(21)–W–C(11)	90.3 (4)
W–C(11)–C(12)	78.0 (6)	N(21)–W–C(13)	93.4 (4)
W–C(13)–C(12)	79.4 (6)	W–O(31)–C(31)	140.4 (9)
C(11)–C(12)–C(13)	116.1 (8)	W–O(41)–C(41)	149.3 (8)
C(11)–W–C(13)	82.3 (4)	W–N(21)–C(21)	172.0 (8)

W(−0.109)–C(11)(0.033)–C(13)(0.028)–O(31)(0.048)

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(16) (a) Reed, T. M., III In *Fluorine Chemistry*; Simons, J. H., Ed.; Academic: New York, 1964; Vol. 5, Chapter 2. (b) Hundlicky, M. *Chemistry of Organic Fluorine Compounds*; Macmillan: New York, 1962.

(17) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

Table IV. A Comparison of ^1H and ^{13}C NMR Data in Tungstacyclobutane Complexes[a]

compound	H_α	H_β	$C_\alpha(JCH)$	$C_\beta(JCH)$
$W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ (**5**)	5.66 4.36 4.04	−0.77	110.8 (155) 105.7 (134)	5.18 (141)
$W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe_2(CF_3)]_2$[b]	5.61 4.42 3.83	−0.74		
$W(C_3H_6)(NAr)[OCMe(CF_3)_2]_2$ (**12**)	4.66 4.51	−0.79 −1.39	100.7 (158)	−5.10 (157)
$W(C_3H_6)(NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ (**13**)	4.87 4.58	−0.95 −1.65	103.5 (158)	−6.79 (158)
$W[CH_2CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ (**17**)	5.04 4.36	−1.03	102.8 (155)	−0.55 (136)
$W[CHEtCHEtCHEt](NAr)[OCMe(CF_3)_2]_2$ (**9**)[c]	5.38	−0.56		

[a] See Experimental Section for complete data. [b] Observed in mixture along with **7**. [c] Observed in mixture along with **8a**.

(8)° in **5**, again what might be expected in a more crowded molecule.

The tungstacyclobutane ring in **5** is relatively symmetric. Three of the internal angles are close to 80° while the third [C(11)–C(12)–C(13)] is 116° (Figure 5). The W–C_α bond lengths are somewhat short relative to W–C single bonds in high oxidation state complexes (typically 2.15 Å), while the C–C bond lengths are longer than one might have expected in a small ring. The W···C(12) distance is 2.372 (11) Å, too long to be called a bonding interaction, but relatively short nevertheless. The dihedral angle between the C(13)–W–C(11) plane and the C(11)–C(12)–C(13) plane is 29.9°, almost enough to place the *transoid* α and β TMS groups in pseudoequatorial positions. It seems likely that interaction between the β TMS group and the imido ligand is what causes the ring to bend (cf. a flat unsubstituted tungstacycle described later). The TMS group bound to C(13) points away from the imido ligand's isopropyl group (C(27)) and the axial alkoxide therefore turns away from that TMS group. One can argue that a complex containing an α,α'-disubstituted ring would be of higher energy for steric reasons, although it probably still is accessible kinetically, since the initial α,α'-disubstituted metallacycle is that which forms and loses *tert*-butylethylene in the reaction shown in eq 5.

The NMR spectra of **5** are consistent with the results of the X-ray study (Table IV). Signals for three types of α protons are observed at 5.66, 4.36, and 4.04 ppm. The signal for the β proton is found at −0.77 ppm. Signals for the α carbon atoms are found at 110.8 (t, $J_{CH} = 155$, $J_{CW} = 61$) and 105.7 (d, $J_{CH} = 134$, $J_{CW} = 61$), while that for the β carbon atom is found at 5.18 ppm ($J_{CH} = 141$). Large CH coupling constants are found in other d^0 metallacyclobutane complexes[18] and are what one would expect for a small ring in general (e.g., $J_{CH} = 161$ Hz in cyclopropane[19]). We see no evidence that the compound whose NMR spectra we observe in solution is not the same as that found in the solid state. In particular the chemical shifts for α and β (carbon or hydrogen) atoms in the WC_3 ring are similar to those found in unsubstituted tungstacycles (Table IV; see later) and do not differ greatly from those in other d^0 metallacycle complexes.[18]

It is now clear why vinyltrimethylsilane is not metathesized by **5** or **6**. The intermediate tungstacyclobutane complex that is required for formation of 1,2-bis(trimethylsilyl)ethylene (**5**) breaks up to give *only* vinyltrimethylsilane, *never* 1,2-bis(trimethylsilyl)ethylene. This result could be ascribed to steric repulsion between TMS groups in the ground state (the α and β TMS groups, although trans to one another, weaken the C(12)–C(13) bond), or less obviously in a transition state, but electronic factors (stabilization of the $W{=}CHSiMe_3$ complex versus the $W{=}CH_2$ complex) could play a significant role as well. These findings also help explain why an initial α-*t*-Bu/β-TMS ring, *if* it forms, would likely lose vinyltrimethylsilane selectively, never $^tBuCH{=}CHTMS$, thereby allowing time for the α-*t*-Bu/α-TMS ring to form and lose *tert*-butylethylene (eq 5).

$W(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2$ reacts with a moderate excess of vinyltrimethylsilane (1.6 equiv) to give **7** (eq 7) in 75% yield, after recrystallization from pentane. If a toluene-d_8 solution of **7** and vinyltrimethylsilane is cooled, a metallacycle that appears to be analogous to **5** can be observed. NMR parameters for this metallacycle can be found in Table IV and equilibrium constants in the Experimental Section. At about −20 °C K_{eq} for the metallacycle breaking up to give **7** and vinyltrimethylsilane was found to be approximately *two orders of magnitude larger* than that in the analogous $OCMe(CF_3)_2$ system. This difference is easily observed qualitatively. At room temperature a mixture of **7** and vinyltrimethylsilane shows no trace of $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe_2(CF_3)]_2$, while an NMR spectrum of $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ (~0.1 M) shows little vinyltrimethylsilane and **6**. This result draws attention to the significantly greater instability of a metallacycle in a $OCMe_2(CF_3)$ complex versus that in a $OCMe(CF_3)_2$ complex. If >2 equiv of vinyltrimethylsilane is used in the preparation of **7**, ^1H NMR spectra of the product show a significant amount of vinyltrimethylsilane to be present. We propose that under the conditions of isolating **7** some $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe_2(CF_3)]_2$ forms, crystallizes out, and only slowly loses vinyltrimethylsilane at room temperature in the solid state. In solution, however, vinyltrimethylsilane is lost completely, and the sample of **7** therefore appears to contain vinyltrimethylsilane as an "impurity".

$$W(CH\text{-}t\text{-}Bu)(NAr)[OCMe_2(CF_3)]_2 \xrightarrow[-CH_2=CH\text{-}t\text{-}Bu]{+CH_2=CHSiMe_3} \underset{\mathbf{7}}{W(CHSiMe_3)(NAr)[OCMe_2(CF_3)]_2} \quad (7)$$

The proton NMR spectra of **7** and **6** (in C_6D_6 or toluene-d_8) are somewhat unusual. At room temperature the H_α, methine, and $SiMe_3$ resonances are broad. All others are sharp. All three broad resonances become sharp when a sample is heated to 80 °C, *or* when a sample is cooled to −60 °C. (At the low temperature the H_α resonance for **7** is sharp enough to observe coupling to tungsten.) Chemical shift differences at the high versus the low temperature are not significantly different for any resonance. At the present time we have no explanation.

Vinyltrimethylsilane reacts slowly with **3a**. A ^1H NMR spectrum of a 0.046 M solution of **3a** in C_6D_6 containing 5 equiv of vinyltrimethylsilane after 2 h at 25 °C shows that ~25% of **3a** is converted into a compound having a broad resonance at 9.01 ppm. After several more hours additional resonances can be observed at 9.52 and 10.55 ppm. No high-field resonances ascribable to a metallacyclobutane complex were observed. We presume that **3a** reacts slowly with vinyltrimethylsilane to give $W(CHSiMe_3)(NAr)(O\text{-}t\text{-}Bu)_2$, but that $W(CHSiMe_3)(NAr)(O\text{-}t\text{-}Bu)_2$ is relatively unstable. We assign the 9.01-ppm resonance to H_α in $W(CHSiMe_3)(NAr)(O\text{-}t\text{-}Bu)_2$ since a 9.01-ppm resonance is observed in the spectrum of the product formed when 2 equiv of potassium *tert*-butoxide are added to $W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ in C_6D_6. Other

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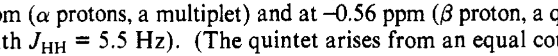
[18] (a) Gilliom, L. R.; Grubbs, R. H. *Organometallics* **1986**, *5*, 721. (b) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

[19] Wiberg, K. B.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749.

reactions of this type lead to *tert*-butoxide alkylidene complexes (see later).

Vinyltrimethylsilane (5 equiv) reacts slowly with **3d** (0.024 M in C_6D_6). After 1 h largely starting material (~80%) remained, but a resonance characteristic of H_β in a metallacyclobutane complex could be observed at −0.95 ppm. This metallacyclobutane complex appears to decompose at approximately the rate that **3d** is consumed, so after 16 h only a complex mixture of unidentifiable products was observed in the NMR sample.

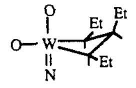
Reactions of Neopentylidene Complexes with *cis*-3-Hexene. When several equivalents of *cis*-3-hexene are added to W(CH-*t*-Bu)(NAr)[OCMe(CF_3)$_2$]$_2$ (**3c**) in pentane and the volatile components then removed in vacuo, golden orange crystals are obtained. When these are dissolved in C_6D_6 an NMR spectrum shows starting material, W(CHEt)(NAr)[OCMe(CF_3)$_2$]$_2$ (**8a**; δH_α = 9.22, t, J_{HH} = 6.0), and 3-hexene (85% trans). If treatment with *cis*-3-hexene is repeated twice more then an NMR spectrum of the golden orange product shows only W(CHEt)(NAr)[OCMe(CF_3)$_2$]$_2$ and 3-hexene (approximately 0.8 equiv, 85% trans) at 25 °C in deuteriobenzene. If an analogous toluene-d_8 solution containing W(CHEt)(NAr)[OCMe(CF_3)$_2$]$_2$ and *cis*-3-hexene is cooled to −60 °C then the intensities of the characteristic resonances for the propylidene complex decrease and new resonances arise that we can assign to the triethyltungstacyclobutane complex, W[CHEtCHEtCHEt](NAr)[OCMe(CF_3)$_2$]$_2$ (**9**). If the temperature is raised to 25 °C again, only signals for W(CHEt)(NAr)[OCMe(CF_3)$_2$]$_2$ and 3-hexene (85% trans) are observed. This behavior is totally reversible. A likely explanation is the following. The starting neopentylidene complex reacts rapidly with *cis*-3-hexene to yield **8a** and *trans*-2,2-dimethyl-3-hexene reversibly (eq 8). *cis*-3-Hexene is rapidly isomerized to *trans*-3-hexene, either by the back reaction of **8a** with *trans*-*t*-BuCH=CHEt, or (more likely we feel) by reversible reaction of **8a** with *cis*-3-hexene to form **9** (eq 9). When the volatile components are removed in vacuo in the first step much **3c** is reformed. However, since the reaction mixture cools down markedly when the volatile components are removed in vacuo in each step, **9** forms, crystallizes out, and then only slowly loses 3-hexene in the solid state at 25 °C. When treatment with *cis*-3-hexene is repeated, *trans*-2,2-dimethyl-3-hexene is eventually removed from the system by mass action, leaving a mixture of W(CHEt)(NAr)[OCMe(CF_3)$_2$]$_2$ (**8a**, ~20%) and W[CHEtCHEtCHEt](NAr)[OCMe(CF_3)$_2$]$_2$ (**9**, ~80%). In solution at 25 °C the mixture of 20% **8a** and 80% **9** becomes a mixture of W(CHEt)(NAr)[OCMe(CF_3)$_2$]$_2$ and ~0.8 equiv of *cis*- and *trans*-3-hexene.



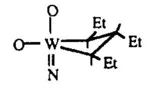
(8)

$$\mathbf{8a} + \textit{cis-} \text{ or } \textit{trans-}\text{3-hexene} \rightleftharpoons \underset{\mathbf{9}}{\text{W[CHEtCHEtCHEt](NAr)[OCMe(CF}_3)_2]_2} \quad (9)$$

^{1}H NMR resonances for the ring protons of **9** are found at 5.38 ppm (α protons, a multiplet) and at −0.56 ppm (β proton, a quintet with J_{HH} = 5.5 Hz). (The quintet arises from an equal coupling of H_β to the two apparently equivalent H_α protons and the two methylene protons in the β-ethyl group.) Unfortunately it is not possible to assign a structure to this metallacycle, since couplings between H_β and *cisoid* or *transoid* H_α protons in other metallacycles are of the same magnitude. For example, in W[CH_2CH($SiMe_3$)CH_2](NAr)[OCMe(CF_3)$_2$]$_2$ (**17**; see later) H_β is coupled to H_α by 8 Hz and to $H_{\alpha'}$ by 11 Hz. We can say at least that the metallacycle contains a plane of symmetry that passes through C_β and between the two α carbon atoms. Since α ethyl groups almost certainly would perfer to be in pseudoequatorial positions, the main question is whether the β-ethyl group is "axial" (in an "all cis" form) or "equatorial") (in an "all equatorial" form). (Another question, but not one we can concern ourselves with at this stage, is how the entire ring is oriented with respect to the two different axial ligands.) Since the TMS groups in **5** are both "equatorial" we speculate that the "all equatorial" form is the lowest energy isomer of **9**. Many researchers have made a similar assumption in discussions of classical systems.[1]



"all cis"



"all equatorial"

W(CHEt)(NAr)[OCMe(CF_3)$_2$]$_2$ (**8a**) can be isolated (see Experimental Section) although it is extremely sensitive to water. Even in the absence of air **8a** decomposes with a half-life of approximately 6 h in C_6D_6. Attempts to measure the rate of decomposition of **8a** yielded erratic results, perhaps in part because it is so sensitive to water. So far we have not been able to identify the decomposition product(s). When the mixture of W(CHEt)(NAr)[OCMe(CF_3)$_2$]$_2$ and W[CHEtCHEtCHEt](NAr)[OCMe(CF_3)$_2$]$_2$ is recrystallized from pentane in the presence of tetrahydrofuran then a relatively stable adduct, W(CHEt)(NAr)[OCMe(CF_3)$_2$]$_2$(THF) (**8b**), can be isolated as orange crystals in 75–80% yield. Even though **8b** is more stable thermally than **8a** we have not been able to analyze it entirely satisfactorily, we believe because some THF is lost in the solid state. In C_6D_6 **8b** does not decompose to any significant extent (<10%) in 1 day. It decomposes even more slowly in the presence of added THF. These observations suggest that dissociative loss of THF precedes decomposition.

As we noted in our preliminary communication,[8] sometimes a triplet resonance is observed slightly downfield from that which we ascribe to the alkylidene α proton in W(CHEt)(NAr)[OCMe(CF_3)$_2$]$_2$. Similar second H_α resonances have been observed sporadically in other W(CHEt)(NAr)(OR)$_2$ complexes reported here. For the moment we are ascribing such resonances to an isomer of W(CHEt)(NAr)(OR)$_2$ in which the propylidene ligand is rotated by 180° from a position analogous to that of the benzylidene ligand in W(CHPh)(NAr)[OCMe(CF_3)$_2$]$_2$. We hope to be able to address this subject in detail in future studies.

When W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF_3)]$_2$ (**3b**) is treated with *cis*-3-hexene (10 equiv) in C_6D_6 no observable amount of **3b** is consumed in the first 15 min at 25 °C, but the 10 equiv of *cis*-3-hexene is isomerized completely to an equilibrium mixture of *trans*- and *cis*-3-hexene. A triplet resonance characteristic of a propylidene complex then slowly appears (in hours) at 8.77 ppm along with resonances that can be ascribed to *trans*-2,2-dimethyl-3-hexene (identified by NMR comparison with an authentic sample). If such a mixture is heated for 7 h at 35 °C the ratio of the propylidene complex to the neopentylidene complex is 3.5:1, but the total amount of the two is only about half the amount of neopentylidene complex present initially. Since we know that the neopentylidene complex is stable under these conditions, W(CHEt)(NAr)[OCMe$_2$(CF_3)]$_2$ (**10**) must be decomposing slowly. Most likely *cis*-3-hexene reacts slowly with the starting neopentylidene complex (much more slowly than cis-3-hexene reacts with W(CH-*t*-Bu)(NAr)[OCMe(CF_3)$_2$]$_2$) to give an undetectable amount of W(CHEt)(NAr)[OCMe$_2$(CF_3)]$_2$ that then rapidly isomerizes *cis*-3-hexene to the *trans*/*cis* equilibrium mixture via metallacyclobutane intermediates. (A less likely alternative in our opinion is that some unidentified, very active metathesis catalyst is an impurity in the system, and this impurity isomerizes the olefin.) This proposal is consistent with the fact that **3b** is an extremely active catalyst for the metathesis of *cis*-2-pentene (see later).

The rate of the reaction of *cis*-3-hexene with W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF_3)]$_2$ (**3b**) was determined by following the disappearance of the neopentylidene α-proton resonance in deuteriobenzene employing *p*-dichlorobenzene as an internal standard in stock solutions of **3b** and *cis*-3-hexene. (Standard conditions can be found in Table V. For experimental reasons (NMR limitations) use of greater than 20 equiv of 3-hexene was impractical.) As mentioned above, *cis*-3-hexene is immediately isomerized to the equilibrium mixture of *cis*- and *trans*-3-hexene before any detectable amount of **3b** is consumed. Therefore, **3b** *is reacting with the equilibrium mixture of 3-hexenes*. First-order disappearance of **3b** was observed at temperatures between 35.6 and 65.7 °C (Table V) with correlation coefficients of greater than 0.997 over 3 half lives. An Arrhenius plot of the data

Table V. Rates of Reaction of W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (**3b**) with 3-Hexene (Equilibrium Mixture of Cis and Trans)[a]

T (°C)	10^4k (M^{-1} s^{-1})	$t_{1/2}$ (min)
35.6	2.52	125
44.4	3.17	100
54.0	4.02	79
54.4	4.29	74
62.7	6.56	48
65.7	7.19	44
35.4	2.57[b]	62[b]

[a] Unless otherwise noted, all runs employed 25 mg of **3b** (0.0366 mmol) in 1.00 mL of a C$_6$D$_6$ solution 0.366 M in *cis*-3-hexene and 0.367 M in *p*-C$_6$H$_4$Cl$_2$ (internal standard). [b] In this case the *cis*-3-hexene concentration was 0.732 M (cf. run 1).

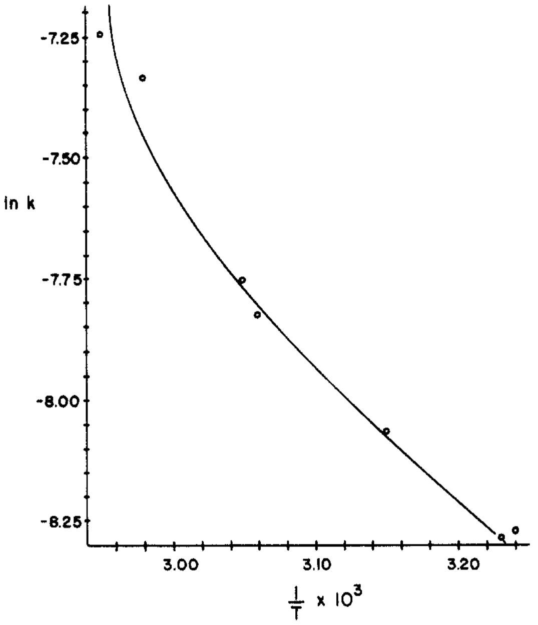


Figure 3. An Arrhenius plot of the data in Table V.

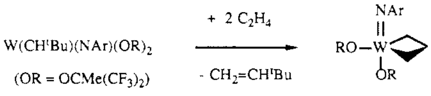
obtained between 35 and 55 °C is linear, but if the data at 65 °C is included the line is decidedly curved (Figure 3). We do not know why. One possibility is that both *cis*- and *trans*-3-hexene react with **3b**, but the temperature dependencies of the two rate constants are not identical. A more prosaic possibility is that the reaction at the higher temperatures is not well-behaved, e.g., W(CHEt)(NAr)[OCMe$_2$(CF$_3$)]$_2$ decomposes rapidly to give products that react rapidly with **3b**. In any case we feel that we have demonstrated unambiguously the expected second-order nature of the reaction between this metathesis catalyst and an olefin by virtue of the relatively slow reaction of the neopentylidene complex with 3-hexenes.

So far we have not been able to isolate W(CHEt)(NAr)[OCMe$_2$(CF$_3$)]$_2$ in pure form. Although the rate of decomposition of W(CHEt)(NAr)[OCMe$_2$(CF$_3$)]$_2$ appears to accelerate when solutions of its are concentrated, we are reluctant at this time to cite this qualitative observation as evidence that the propylidene complex decomposes in a bimolecular fashion. We believe that propylidene complexes are much less stable than neopentylidene complexes toward hydrolysis, so until we identify thermal decomposition products it will be difficult to distinguish thermal decomposition from hydrolysis.

W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (**3a**; 0.035 M in C$_6$D$_6$) reacts extremely slowly with *cis*-3-hexene (10 equiv). After four days there is no evidence for formation of W(CHEt)(NAr)(O-*t*-Bu)$_2$, although some decomposition is evident (estimated ~20%). The fact that only ~30% of the 10 equiv of *cis*-3-hexene has isomerized to *trans* in six days suggests that all reactions are slow. We prepared the expected product, W(CHEt)(NAr)(O-*t*-Bu)$_2$ (**11**), in situ by adding LiO-*t*-Bu to the mixture of W(CHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (20%) and W[CHEtCHEtCHEt](NAr)[OCMe(CF$_3$)$_2$]$_2$ (80%) described above. It *is* true that W(CHEt)(NAr)(O-*t*-Bu)$_2$ is not especially stable. It survives for a day or more in dilute solution but decomposes readily when solutions are concentrated. Therefore we have not been able to isolate it. We conclude that **11** forms extremely slowly from **3a** and decomposes before enough builds up to be observed. The fact that little *cis*-3-hexene is isomerized to *trans*-3-hexene confirms that all *tert*-butoxide complexes simply react very slowly with *cis*-3-hexene.

W(CH-*t*-Bu)(NAr)(OR$_F$)$_2$ (**3**; 0.018 M in C$_6$D$_6$) reacts more rapidly with 10 equiv of *cis*-3-hexene than **3a** does, but still relatively slowly. After 24 h 40% of the **3d** is consumed, 0.4 equiv of *trans-t*-BuCH=CHEt is observed, and the *trans*/*cis* equilibrium mixture of 3-hexenes is established. A small triplet resonance at 9.83 ppm can be assigned to the propylidene α proton in W(CHEt)(NAr)(OR$_F$)$_2$. After 39 h 70% of **3d** has been consumed and the ratio of **3d** to W(CHEt)(NAr)(OR$_F$)$_2$ is ~3:1. Therefore it appears that W(CHEt)(NAr)(OR$_F$)$_2$ decomposes at a rate that is approximately equal to the rate at which it forms from **3d** under these conditions. As we shall see below, W(CH-*t*-Bu)(NAr)(OR$_F$)$_2$ *does* react very rapidly with ethylene. Since a perfluoro alkoxide ligand is significantly larger than its hydrocarbon analogue[16] we suspect that steric problems limit the reactivity of **3d** with *cis*-3-hexene.

Reactions of Neopentylidene Complexes with Ethylene and the X-ray Study of W(CH$_2$CH$_2$CH$_2$)(NAr)[OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)]$_2$. W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ in pentane reacts rapidly with 2.4 equiv of ethylene to give *tert*-butylethylene and white, crystalline W(CH$_2$CH$_2$CH$_2$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**12**) quantitatively (eq 10). The proton NMR spectrum shows resonances of area two each at 4.66 and 4.51 ppm that can be assigned to two sets of α protons in the WC$_3$ ring, and two resonances of area one each at −0.79 and −1.39 ppm that can be assigned to two types of β protons in the WC$_3$ ring. Only one broadened resonance is observed for the methyl groups in the OCMe(CF$_3$)$_2$ ligands, however, suggesting that they are equilibrating in the NMR time scale at 25 °C. At 0 °C two OC*Me*(CF$_3$)$_2$ resonances are observed, while at temperatures in the range 50–80 °C a single sharp OC*Me*(CF$_3$)$_2$ resonance is observed. Changes in the imido ligand resonances are analogous; at low temperatures two isopropyl methyl resonances are observed (the phenyl ring evidently cannot rotate readily about the N–C bond in **12**), and at high temperatures one isopropyl resonance is observed. Carbon NMR spectra at 230 K show an α carbon resonance at 100.7 ppm with J_{CH} of 158 Hz and J_{CW} of 67 Hz and a β carbon resonance at −5.1 ppm with J_{CH} of 157 Hz. It is important to note that neither the α nor β tungstacycle ring protons equilibrate in this temperature range. The fluxional process involving the core of **12** is proposed to consist of formation of a square-pyramidal complex (eq 11) by moving *alkoxide* ligands (the WC$_3$ ring cannot flip). Proton and carbon NMR parameters for W(C$_3$H$_6$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ are compared in Table IV with those of W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe(CF$_3$)$_2$]$_2$.



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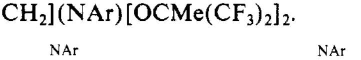


(11)

An analogous reaction between W(CH-*t*-Bu)(NAr)(OR$_F$)$_2$ and ethylene yields pale yellow crystalline W(C$_3$H$_6$)(NAr)(OR$_F$)$_2$ (**13**) virtually quantitatively. Proton and carbon NMR data for this species are analogous to those for W(C$_3$H$_6$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (Table IV). An X-ray study showed the molecule to be a pseudo-trigonal-bipyramidal molecule analogous to W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe(CF$_3$)$_2$]$_2$ (Figure 4). Details of the study can be found in the Experimental Section. Relevant bond distances and angles can be found in Table VI.

The overall structure of **13** is similar to that of **5**, so it will not be discussed in the same detail. Two features should be pointed

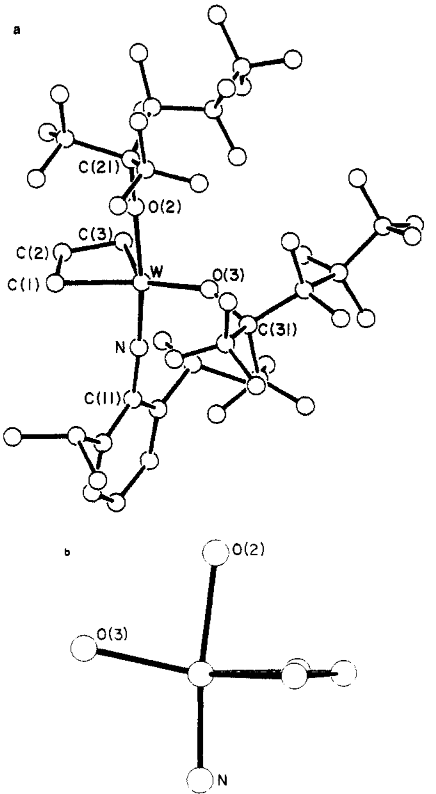


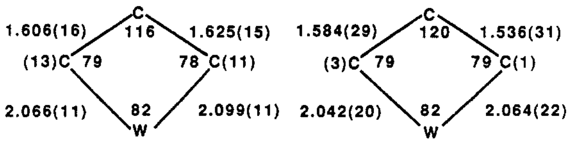
Figure 4. (a) A drawing of W($CH_2CH_2CH_2$)(NAr)[OC(CF_3)$_2$($CF_2CF_2CF_3$)]$_2$ (**13**) and (b) a side-on view of the WC_3O_2N core of W($CH_2CH_2CH_2$)(NAr)[OC(CF_3)$_2$($CF_2CF_2CF_3$)]$_2$.

Table VI. Relevant Bond Lengths (Å) and Angles (deg) in W($CH_2CH_2CH_2$)(NAr)[OC(CF_3)$_2$($CF_2CF_2CF_3$)]$_2$ (**13**)

W-C(1)	2.064 (22)	O(3)-W-O(2)	84.4 (5)
W···C(2)	2.323 (23)	O(3)-W-N	102.1 (6)
W-C(3)	2.042 (20)	O(3)-W-C(3)	134.1 (7)
W-N	1.748 (15)	O(3)-W-C(1)	140.2 (7)
W-O(2)	2.005 (13)	O(2)-W-N	173.0 (6)
W-O(3)	1.944 (11)	O(2)-W-C(3)	85.7 (7)
C(1)-C(2)	1.536 (31)	O(2)-W-C(1)	83.5 (7)
C(2)-C(3)	1.584 (29)	N-W-C(1)	89.8 (8)
W-C(1)-C(2)	78.9 (13)	N-W-C(3)	91.3 (7)
W-C(3)-C(2)	78.6 (12)	W-O(3)-C(31)	146.6 (11)
C(1)-C(2)-C(3)	120.1 (18)	W-O(2)-C(21)	172.4 (13)
C(1)-W-C(3)	82.4 (8)	W-N-C(11)	176.0 (13)

out. The first concerns the alkoxide ligand orientation and various bond lengths and angles within the alkoxide ligands. As can be seen in Figure 4b the equatorial alkoxide ligand is bent away from the imido ligand [O(3)-W-N = 102.1 (6)°] about 5° more than in **5**. Although both the axial and equatorial W-O bond lengths are approximately the same as what they are in **5**, there are two interesting differences. The first is that the axial alkoxide ligand in **13** is bent over the WC_3 ring (O(2)-W-N = 173.0 (6)°; Figure 4b). The second is that the W-O(2)-C(21) angle is 172.4 (13)°, approximately 25° greater than the W-O(3)-C(31) angle [146.6 (11)°] and either of the W-O-C angles [140.4 (9) and 149.3 (8)°] in **5**. There is no reason why the axial OR_F ligand in **13** should be a significantly better π electron donor than the axial OCMe(CF_3)$_2$ ligand in **5**. Therefore we suggest what is more plausible, that it is a poorer π electron donor as well as a "harder" anion whose W-C-O angle is especially sensitive to steric interactions. The large W-O(2)-C(21) angle could be taken as evidence that **13** is quite crowded, even though the WC_3 ring is not substituted.

The second feature that is worth discussing is the WC_3 ring itself. The bond lengths and angles are remarkably similar to those in **5**, as shown in Figure 5. The most important difference is that the WC_3 ring in **13** is absolutely flat. On the basis of experiment



5 13

Figure 5. A comparison of the bond lengths and angles in the WC_4 rings in **5** and **13**.

we can say now with some confidence what has been suspected for some time,[1] that bent rings (as in **5**) result from steric interactions between substituents on the ring, and probably also between those substituents and the ligands in the coordination sphere. What is still not known is whether the ring *must* bend in order that an olefin can be lost.

Both **3a** and **3b** react readily with ethylene. **3a** (0.04 M in C_6D_6) reacts with 5 equiv of ethylene to give 80% of the expected neohexene in 2 h. **3b** (0.03 M in C_6D_6) is completely consumed by 5 equiv of ethylene in 15 min. These reactions appear to be more complex ultimately than those involving **3c** or **3d**. They are still being investigated. Detailed studies will be reported in due course.

Reactions Involving Other Olefins Including Qualitative Metathesis Studies. *cis*-2-Pentene is metathesized readily by **3c**. The lower limit to the rate of this reaction is ~10^3 turnovers per minute at 25 °C for a catalyst concentration of 1 mM as judged from a reaction in which 4000 equiv of *cis*-2-pentene were metathesized to equilibrium in 5 min.[8] The initial reaction between **3c** and *cis*-2-pentene is rapid. We stress that the rate of metathesis of ordinary internal olefins by **3c** actually may be much higher than 10^3 turnovers per minute; we have not yet employed any techniques that would allow us to measure the rate accurately.

The reaction between **3b** (1.5 mM in toluene) and *cis*-2-pentene (500 equiv) has an induction period of ~4 min after which the *cis*-2-pentene is rapidly metathesized to equilibrium (6-8 min). The induction period can be ascribed to the relatively slow initial reaction of **3b** with *cis*-2-pentene relative to the rate of reaction of W(CHR)(NAr)[OCMe$_2$(CF_3)]$_2$ (R = Et, Pr) with *cis*-2-pentene. We are uncertain at this stage whether the difference in the rate of reaction of W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF_3)]$_2$ compared to analogous ethylidene and propylidene complexes is significantly larger than analogous relative rates in the OCMe(CF_3)$_2$ system or whether rate differences in the OCMe(CF_3)$_2$ system are simply masked because all alkylidene complexes are exceedingly reactive.

cis-2-Pentene is not metathesized or isomerized to any significant extent by W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ in C_6D_6 at 25 °C in a period of 1 day. This result is not surprising since we concluded earlier that *tert*-butoxide catalysts are inherently unreactive toward *cis*-3-hexene.

cis-2-Pentene does react with **3d**, but surprisingly slowly, as evidenced by the relatively slow rate of metathesis (50 equiv of equilibrium in 45 min with 4.6 mM **3d** in toluene). **3d** is consumed slowly (hours), but as in reactions involving *cis*-3-hexene described above, we believe these alkylidene complexes are too unstable to observe under these conditions.

We assume that other ordinary internal olefins will react with **3a-d** in ways similar to those discussed for *cis*-2-pentene and *cis*-3-hexene and that differences that do arise could be explained in terms of subtle steric and electronic factors. A case in point is the reaction between **3c** or **8a** and *cis*-β-methylstyrene. β-Methylstyrene, being a less nucleophilic and bulkier olefin than *cis*-2-pentene or *cis*-3-hexene, reacts relatively slowly with **3c**. After several hours only a small amount of W(CHPh)(NAr)[OCMe(CF_3)$_2$]$_2$ (**4**) is present. However, it does react readily with less sterically crowded **8a** to give **4**, the structure of which was described above. *cis*-4-Methyl-2-pentene also reacts quite slowly with **3c**, although it is metathesized quickly, we presume by W(CHMe)(NAr)[OCMe(CF_3)$_2$]$_2$ and W(CHCHMe$_2$)(NAr)[OCMe(CF_3)$_2$]$_2$ complexes.

We should point out that the difference in reactivity of O-*t*-Bu, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, and $OC(CF_3)_2(CF_2CF_2CF_3)$ complexes that we have noted here for ordinary internal olefins will not be true for more reactive internal olefins. For example, we have shown that norbornene reacts readily with **3a** to give living oligomers and polymers with the formula W-$[(CHC_5H_8CH)_xCH$-*t*-Bu](NAr)(O-*t*-Bu)$_2$.[9] The ability to fine tune the reactivity of these alkylidene complexes by changing the nature of the alkoxide ligand should have important implications in ring-opening polymerization reactions.

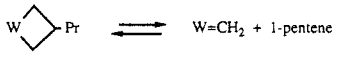
Reactions between **3a–d** and a typical metathesizeable ordinary terminal olefin (1-pentene) were investigated briefly. **3a** (0.04 M in C_6D_6) reacts with 1-pentene very slowly (70% in 8 h) to give neohexene. Roughly the same result is observed in the reaction between **3b** and 1-pentene, except that reaction is much faster than that involving **3a**. In neither case are more than a few turnovers to ethylene and 4-octenes observed in several hours. As with the reactions involving ethylene and **3a** or **3b**, no organometallic products have been identified. These reactions will be explored in more detail in the future.

In contrast, **3c** (0.03 M in C_6D_6) reacts rapidly with 5 equiv of 1-pentene at 25 °c (75% **3c** consumed in 10 min) to give (by NMR) ~15% of what we propose is W(CHPr)(NAr)[OCMe$(CF_3)_2]_2$, ~15% of what appears to be the β-substituted tungstacycle (H_β at -0.070 ppm (m)), and ~20% of the unsubstituted tungstacycle **12** (eq 12); these yields suggest that ~25% of the products have decomposed during this time period.

$$\mathbf{3c} + \text{1-pentene} \xrightarrow[\text{in 15 min}]{75\%} 15\%\ \underset{\mathbf{2}}{W(CHPr)(NAr)[OCMe(CF_3)_2]_2} + 15\%\ W(CH_2CHPrCH_2)(NAr)[OCMe(CF_3)_2]_2 + 20\%\ \mathbf{12} + 25\%\ \text{decomposition} \quad (12)$$

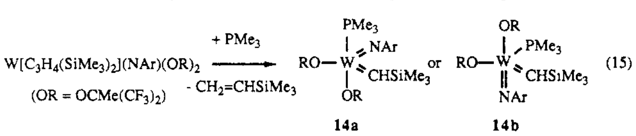
3d (0.024 M in C_6D_6) reacts completely with 1-pentene in <15 min to give two major products as shown in eq 13. The β-propyl metallacycle is a tentative proposal, as the evidence consists only of a broad H_β multiplet at -0.23 ppm; an α substituent could conceivably be present. Productive metathesis of 1-pentene (200 equiv) is extremely slow (a few turnovers per hour at best), most likely since it could be shown in a separate experiment that **13** reacts with 1-pentene to give only a trace of W-$(CH_2CHPrCH_2)(NAr)(OR_F)_2$ in 1 h. The β-propyl metallacycle also may be relatively stable toward loss of olefin, or for steric reasons virtually the only one that forms (eq 14).

$$\mathbf{3d} + \text{1-pentene} \xrightarrow{15\text{ min}} 70\%\ \mathbf{13} + 30\%\ W(CH_2CHPrCH_2)(NAr)(OR_F)_2 \quad (13)$$



(14)

Some Reactions of Tungstacyclobutane Complexes. W[CH$(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2$ reacts smoothly with PMe_3 to give pale yellow crystals of W$(CHSiMe_3)$-$(NAr)[OCMe(CF_3)_2]_2(PMe_3)$ (**14**) in high yield. This result is not unexpected given the fact that vinyltrimethylsilane is lost spontaneously from the WC_3 ring in W[CH$(SiMe_3)$CH-$(SiMe_3)(CH_2](NAr)[OCMe(CF_3)_2]_2$ in solution. NMR spectra suggest that PMe_3 is firmly bound ($\delta H_\alpha = 12.05$ ppm with $J_{HP} = 6.3$ Hz and $\delta_{C\alpha} = 266.3$ ppm with $J_{CP} = 10.6$ Hz), that the molecule is not fluxional on the NMR time scale (two different OC*Me*$(CF_3)_2$ resonances are observed), and that the molecule has no symmetry (resonances for four different types of Ar methyl groups are observed). We believe the structure of **14** is most likely one of the two shown in eq 15, the first being analogous to that observed for W(O)(CH-*t*-Bu)$(PEt_3)Cl_2$.[15] In **14b**, a molecule that has no structurally characterized analogue at this point, the alkylidene ligand substituents would be expected to point above and below the $WO_{eq}CP$ plane. As one might expect if PMe_3 is relatively nonlabile, **14** is virtually inactive as a metathesis catalyst for *cis*-2-pentene, very little metathesis being observed in 4 h at 25 °C.



(15)

14a **14b**

$W(C_3H_6)(NAr)[OCMe(CF_3)_2]_2$ and $W(C_3H_6)(NAr)(OR_F)_2$ each react readily with PMe_3 to give W$(CH_2)(NAr)[OCMe$-$(CF_3)_2]_2(PMe_3)$ (**15**) and $W(CH_2)(NAr)(OR_F)_2(PMe_3)$ (**16**), whose structures we believe are analogous to that for **14** (eq 16).

$$\underset{OR\ =\ OCMe(CF_3)_2\ \text{or}\ ORf}{W(C_3H_6)(NAr)(OR)_2} + PMe_3 \xrightarrow{-C_2H_4} W(CH_2)(PMe_3)(NAr)(OR)_2 \quad (16)$$

$$\mathbf{15}\text{: } OR = OCMe(CF_3)_2$$
$$\mathbf{16}\text{: } OR = OR_F$$

In **15** only one resonance is found for the two methylene protons at 11.00 ppm; the methylene carbon atom resonance is found at 252.2 ppm with $J_{CH} = 145$, $J_{CW} = 163$, and $J_{CP} = 14.5$ Hz. The ^{31}P NMR spectrum confirms that trimethylphosphine is not dissociating from the metal in **15** ($J_{PW} = 322$ Hz). We propose that the methylene protons *accidentally are coincident* in **15** since they are *inequivalent* in **16** (at 11.58 and 11.31 ppm). The evidence is against the possibility that the methylene ligand in **15** is rotating about the W=C bond at a rate of the order of the NMR time scale. The ^1H NMR spectrum of a sample of **15** in toluene-d_8 that had been cooled to -60 °C still showed the methylene protons to be equivalent and a sample of **16** at 100 °C in toluene-d_8 showed no evidence of broadening of the two methylene proton resonances. There *is* a fluxional process that can be observed in **15** (it is slow on the NMR time scale in **16**), rotation of the diisopropyl phenyl ring about the C_{ipso}–N bond. In **16** two C*H*Me$_2$ resonances and four CH*Me*$_2$ resonances are found. Although two broad C*H*Me$_2$ multiplets are observed in the spectrum of **15**, only one broad CH*Me*$_2$ doublet is observed. We presume that rotation of the phenyl ring is slow on the NMR time scale in $OC(CF_3)_2(CF_2CF_2CF_3)$ complex (**16**) for steric reasons.

Qualitative evidence suggests that W$(C_3H_6)(NAr)[OCMe$-$(CF_3)_2]_2$ (**12**) does lose ethylene in solution, but the back reaction is fast and K_{eq} small (eq 17). For example, C_2D_4 is incorporated into the ring in less than 1 min when solutions of **12** in C_6D_6 are exposed to C_2D_4. The exchange rate does not appear to be rapid enough to average the two β-ring protons or the α protons with the β protons. **12** also reacts virtually instantaneously with vinyltrimethylsilane to give the β-substituted tungstacyclobutane complex shown in eq 18. If only 1 eq of vinyltrimethylsilane is employed in a closed system (NMR tube) then an equilibrium is established immediately. If several equivalents of vinyltrimethylsilane are added to **12** in an open system then **17** can be isolated in good yield (see Table IV for NMR parameters). Finally it should be noted that **12** is an excellent catalyst for the metathesis of *cis*-2-pentene. An induction period is observed, presumably as **12** is consumed, ethylene is produced, and W(CHR)(NAr)-$[OCMe(CF_3)_2]_2$ complexes are formed. None of these qualitative observations is inconsistent with bimolecular displacement of ethylene from the tungstacycle, so more quantitative studies will be necessary before any definitive conclusions can be drawn.

$$\underset{(OR\ =\ OCMe(CF_3)_2)}{W(C_3H_6)(NAr)(OR)_2} \underset{+\ C_2H_4}{\overset{-\ C_2H_4}{\rightleftharpoons}} W(CH_2)(NAr)(OR)_2 \quad (17)$$

$$\underset{(OR\ =\ OCMe(CF_3)_2)}{W(C_3H_6)(NAr)(OR)_2} \underset{+\ C_2H_4\ -\ CH_2=CHSiMe_3}{\overset{+\ CH_2=CHSiMe_3\ -\ C_2H_4}{\rightleftharpoons}} \underset{\mathbf{17}}{W[CH_2CH(SiMe_3)CH_2](NAr)(OR)_2} \quad (18)$$

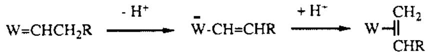
Discussion

A major finding of this study is the extent to which the reactivity of W(CHR′)(NAr)(OR)$_2$ complexes depends upon the electron-withdrawing power and the size of the OR ligand. If we assume that all $W(CHR')(NAr)(OR)_2$ complexes are monomeric, pseudotetrahedral species, then on steric grounds we would predict that the *tert*-butoxide complex would react with olefins the most rapidly. In fact, of the simple olefins, it reacts readily only with ethylene and slowly with terminal olefins. We propose that the metal simply is not electrophilic enough to overcome the steric problems encountered with internal olefins. Alkylidene complexes become more reactive as CF_3 groups are added in the OR ligand, but the steric properties of the OR ligand can become the dominant factor, as in the case of the $OC(CF_3)_2CF_2CF_2CF_3$ ligand where reactivity is limited to ethylene and 1-pentene. Recently both Osborn[3] and Basset[4] also have commented on the role of metal electrophilicity in olefin metathesis reactions, and Basset has correlated in a broad sense the relative reactivity of various phenoxide catalyst precursors with the electron-withdrawing ability of the substituents on the phenoxide ring.

We also now can discern some trends in stability of a tungstacyclobutane complex toward loss of an olefin. First, metallacyclobutane complex stability increases as the electron-withdrawing nature of the OR ligand increases. We have documented this trend for the $W[CH(TMS)CH(TMS)CH_2](NAr)(OR)_2$ complexes ($OR = OCMe_2(CF_3)$ or $OCMe(CF_3)_2$). The trend can be viewed as a consequence of a metal being more electrophilic, i.e., the olefin is less likely to be lost from the incipient olefin/alkylidene intermediate or transition state to give a species with a lower electron count if the OR ligand is relatively electron withdrawing. In the case of the $OC(CF_3)_2CF_2CF_2CF_3$ ligand, tungstacycles (unsubstituted and, we assume, monosubstituted) are the only relatively stable products that are formed upon reaction of **3d** with terminal olefins or ethylene. At the other extreme we have seen no evidence (so far) for any metallacycles in the *tert*-butoxide system. These findings are similar to those concerning stabilities of various metallacyclobutadiene intermediates in well-defined acetylene metathesis systems.[5] Second, we also have accumulated some qualitative evidence that a metallacyclobutane ring's stability depends upon the degree of substitution of the ring (decreasing in the order unsubstituted > β-substituted > α,β-disubstituted > trisubstituted), that pseudoequatorial substitution is probably preferred (certainly on the α-carbon atom, and probably also on the β-carbon atom), and that only substituted metallacycles are bent (slightly). These conclusions are not especially surprising, and have all been proposed in some form in order to interpret experimental findings in wholly "classical" systems where alkylidenes and metallacycles are not observable.[20] Our overall, working hypothesis is that in the most general sense MC_3 rings become less stable as one moves from group 4 to group 7 d^0 metal complexes and as electron withdrawing ligands are replaced with more electron donating ligands. To some extent the two parts of the hypothesis are linked since π-bonding ligands are required (the imido ligand in the cases reported here) as one moves from left to right in order to maintain the d^0 oxidation state in a neutral four-coordinate complex.

We also have documented in a qualitative way that the reactivity of an alkylidene complex greatly depends upon the size of the alkyl group in the alkylidene ligand. At this stage we can only guess that a neopentylidene complex will react more slowly than a propylidene complex by as many as two or three orders of magnitude, the extent depending upon the reactivity of the olefin and the size of OR. Even when an olefin as reactive as norbornene is employed the difference between the rate of initiation and the rate of propagation can be marked, i.e., conversion of the neopentylidene complex to the living alkylidene is good with the *tert*-butoxide complex and poor with the $OCMe(CF_3)_2$ complex.[9]

One topic that we have not yet touched upon is the stability of the alkylidene complexes. Unfortunately very little is known at this time. Two likely modes of decomposition are loss of an α hydrogen or loss of a β hydrogen (either intra- or intermolecularly). We have good evidence that alkylidyne complexes can be formed by deprotonating alkylidene complexes.[21b] In the systems we report here that is unlikely since the alkylidene complexes (at least the initial one) are formed *from* neopentylidyne complexes. In general, especially with more electron withdrawing ligands on the metal, α deprotonation could well be a significant problem. Loss of a β hydrogen probably is the more serious of the two problems in the systems we report here since rearrangement of an alkylidene ligand to an olefin is the mode by which some tantalum alkylidene complexes have been observed to decompose.[13c] If a β proton is lost (intramolecularly or intermolecularly) to some basic site (C_α, N, or O) then an intermediate vinyl ligand would form and ultimately probably be protonated at C_α (eq 19). Eventually we hope to be able to document the mode(s) of decomposition of this type of alkylidene complex. Although we can isolate five-coordinate adducts of methylene complexes we have observed reactions that suggest (not surprisingly) that four-coordinate methylene complexes are quite unstable.



$$W{=}CHCH_2R \xrightarrow{-H^+} \overset{-}{W}{-}CH{=}CHR \xrightarrow{+H^+} W{-}\begin{array}{c}CH_2\\ \Vert\\ CHR\end{array} \qquad (19)$$

The two main ideas that led to the work presented here had their origin in acetylene metathesis systems.[5,7] They are, first, that metathesis activity can be controlled by choice of the alkoxide ligand, and, second, the five-coordinate pseudo-trigonal-bipyramidal metallacyclic intermediates can be formed easily from four-coordinate precursors. We now know that analogous molybdenum complexes can be prepared and their activity controlled in a similar fashion,[22a] and there is good evidence that the systems that Osborn has been studying[3] also involve four-coordinate alkylidene catalysts. We can now entertain the possibility that four-coordinate, well-behaved, rhenium(VII) olefin metathesis catalysts can be prepared[22b] and that the most active complexes in classical catalyst systems are four-coordinate (neutral or cationic).

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres 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. Dichloromethane was distilled from calcium hydride under nitrogen. All deuteriated NMR solvents are passed through a column of activated alumina.

$W(C\text{-}t\text{-}Bu)(dimethoxyethane)Cl_3$[12] and $HOC(CF_3)_2(CF_2CF_2CF_3)$[23] were prepared as described in the literature. All other reagents were purchased from commercial sources and purified by standard techniques.

NMR data are listed in parts per million downfield from TMS for proton and carbon and relative to 85% phosphoric acid for phosphorus. Coupling constants are quoted in hertz. Obvious multiplicities and routine coupling constants usually are not listed. Spectra were obtained in benzene-d_6 at 25 °C unless otherwise noted. Usually the fluorocarbon resonances for the $OC(CF_3)_2(CF_2CF_2CF_3)$ ligands are not listed as part of the ^{13}C NMR data.

Preparation of Compounds. $W(C\text{-}t\text{-}Bu)(NHAr)(dme)Cl_2$ ($Ar = 2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$) (1). A solution of $W(C\text{-}t\text{-}Bu)(dimethoxyethane)Cl_3$ (4.0 g, 8.9 mmol) in diethyl ether was cooled to −40 °C and 2.22 g (8.9 mmol) of $Me_3SiNHAr$ in 10 mL of diethyl ether was added. The purple starting material dissolved to give a yellow-orange solution. After 30 min the solvent was removed in vacuo leaving a bright yellow powder that was recrystallized from a mixture of pentane and ether at −40 °C to give yellow cubes; crude yield > 95%; ^1H NMR δ 10.38 (br s, N*H*Ar),

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(20) (a) See a recent paper by Tanaka[20b] for a discussion of some of these points and for leading references to earlier work by the many contributors in this area. (b) Tanaka, K.; Tanaka, K.; Takeo, H.; Matsumura, C. *J. Am. Chem. Soc.* **1987**, *109*, 2422.

(21) (a) Kress, J.; Osborn, J. A.; Greene, R. M. E.; Ivin, K. J.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1985**, 874. (b) Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 1937.

(22) (a) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373. (b) So far it has been shown that four-coordinate Re(VII) complexes of the type $Re(CH\text{-}t\text{-}Bu)(NR)_2X$ do *not* react with ordinary olefins, or even norbornene.[22b] (b) Horton, A. D.; Schrock, R. R.; Freudenberger, J. H. *Organometallics* **1987**, *6*, 893.

(23) Sherer, K. V., Jr.; Terranova, T. F.; Lawson, D. D. *J. Org. Chem.* **1981**, *46*, 2379.

7.18–7.0 (m, 3, H$_{\mathrm{aryl}}$), 4.20 (sept, 2, *J* = 6.8, C*H*Me$_2$), 3.21 (br s, 6, *Me*O), 3.06 (s, 4, OCH$_2$CH$_2$O), 1.30 (br s, 6, CH*Me*$_2$), 1.20 (br s, 6, CH*Me*$_2$), 0.88 (CMe$_3$); ^{1}H NMR (toluene-*d*$_8$, −60 °C) δ 10.53 (N*H*Ar), 7.20–7.10 (H$_{\mathrm{aryl}}$), 4.24 (C*H*Me$_2$), 3.53 (3, MeO), 2.99 (2, OC*H*$_2$CH$_2$O), 2.90 (2, OCH$_2$C*H*$_2$O), 2.87 (3, MeO), 1.67 (6, CH*Me*$_2$), 1.30 (6, CH*Me*$_2$), 0.94 (CMe$_3$); ^{13}C NMR δ 304.5 (*C*CMe$_3$), 152.9 (C$_{\mathrm{ipso}}$), 144.1 (C$_o$), 126.7 (C$_p$), 123.2 (C$_m$), 72.3 (*C*H$_2$OMe), 63.7 (CH$_2$O*Me*), 49.9 (*C*Me$_3$), 31.2 (C*Me*$_3$), 27.7 (*C*HMe$_2$), 23.8 (CH*Me*$_2$). Anal. Calcd for WC$_{21}$H$_{37}$O$_2$Cl$_2$N: C, 42.72; H, 6.27. Found: C, 42.52; H, 6.44.

W(C-*t*-Bu)(NHAr)[OCMe(CF$_3$)$_2$]$_2$(dme). A solution of W(C-*t*-Bu)(NHAr)(dme)Cl$_2$ (400 mg, 0.68 mmol) in diethyl ether (10 mL) was cooled to −40 °C and LiOCMe(CF$_3$)$_2$ was added. The solution was allowed to warm to room temperature. After 60 min the solvent was removed in vacuo leaving a tan-colored solid which was recrystallized several times from pentane at −40 °C to give off-white crystals (275 mg, 40% yield): ^{1}H NMR δ 8.34 (br s, N*H*Ar), 7.16–7.05 (m, 3 H, H$_{\mathrm{aryl}}$), 3.29 (sept, 2, C*H*Me$_2$), 3.15 (s, 4, OCH$_2$CH$_2$O), 3.03 (s, 6, MeO), 1.78 (OCMe(CF$_3$)$_2$), 1.32 (d, 6, CH*Me*$_2$), 1.08 (d, 6, CH*Me*$_2$), 0.65 (CMe$_3$); ^{13}C NMR δ 291.6 (CCMe$_3$, J_{CW} = 279), 153.5 (C$_{\mathrm{ipso}}$), 143.2 (C$_o$), 132.8 (*C*F$_3$, J$_{\mathrm{CF}}$ = 270), 126.3 (C$_p$), 122.5 (C$_m$), 81.6 (*C*Me(CF$_3$)$_2$), 70.3 (MeOCH$_2$*C*H$_2$OMe), 58.1 (*Me*OCH$_2$CH$_2$O*Me*), 50.4 (C*C*Me$_3$), 32.1 (CC*Me*$_3$), 28.3 (*C*HMe$_2$), 24.8 (CC*Me*(CF$_3$)$_2$), 21.48 (CH*Me*$_2$), 20.0 (CH*Me*$_2$). Anal. Calcd for WC$_{29}$H$_{43}$F$_{12}$NO$_4$: C, 39.51; H, 4.92. Found: C, 38.85; H, 4.92.

W(CH-*t*-Bu)(NAr)(dme)Cl$_2$ (2). The crude product from the preparation of W(C-*t*-Bu)(NHAr)(dme)Cl$_2$ above was partially dissolved in 150 mL of ether and the mixture was cooled to −40 °C. Triethylamine (0.5 mL) in 3 mL of ether was added to the rapidly stirred mixture. After 1 h the volatile components of the now reddish solution were removed in vacuo to give an essentially pure product as an orange powder; yield > 95%. It can be recrystallized from ether by addition of pentane followed by cooling to give analytically pure orange crystals: ^{1}H NMR δ 9.97 (J_{HW} = 7.3, C*H*CMe$_3$), 7.12–6.98 (H$_{\mathrm{aryl}}$), 4.65 (C*H*Me$_2$), 3.19 (MeO), 3.13 (OCH$_2$CH$_2$O), 1.43 (CH*Me*$_2$, 1.38 (CMe$_3$); ^{1}H NMR (toluene-*d*$_8$, −50 °C) δ 10.03 (C*H*CMe$_3$), 7.08–6.98 (H$_{\mathrm{aryl}}$), 4.64 (C*H*Me$_2$), 3.26 (3, MeO), 3.14 (2, OC*H*$_2$CH$_2$O), 3.02 (3, OMe), 2.77 (2, OCH$_2$C*H*$_2$O), 1.48 (6, CH*Me*$_2$), 1.44 (6, CH*Me*$_2$), 1.40 (CMe$_3$); ^{13}C NMR δ 283.8 (J_{CH} = 114, J_{CW} = 163, *C*HCMe$_3$), 154.5 (C$_{\mathrm{ipso}}$), 149.2 (C$_o$), 123.5 and 123.0 (C$_m$ and C$_p$), 71.7 (CH$_2$O), 61.5 (OMe), 47.0 (*C*Me$_3$), 35.5 (C*Me*$_3$), 28.2 (*C*HMe$_2$), 24.8 (CH*Me*$_2$). Anal. Calcd for WC$_{21}$H$_{37}$O$_2$Cl$_2$N: C, 42.72; H, 6.27. Found: C, 42.45; H, 6.36.

W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (3a). LiO-*t*-Bu (484 mg, 6.05 mmol) was added to 1.78 g (3.02 mmol) of W(CH-*t*-Bu)(NAr)(dme)Cl$_2$ in 50 mL of ether at −30 °C. The solution was warmed to 25 °C and stirred for 45 min. LiCl was filtered off, and the ether was removed in vacuo. Recrystallization of the crude product from minimal pentane at −30 °C afforded 1.21 g of product as a bright yellow powder in three crops (70%): ^{1}H NMR δ 8.05 (J_{HW} = 12.9, C*H*-*t*-Bu), 7.18–7.06 (H$_{\mathrm{aryl}}$), 3.99 (C*H*Me$_2$), 1.35 (s, OC*Me*$_3$ and CHC*Me*$_3$), 1.34 (CH*Me*$_2$); ^{13}C NMR δ 236.5 (d, J_{CH} = 110, J_{CW} = 201, *C*H-*t*-Bu), 152.1 (C$_{\mathrm{ipso}}$), 145.2 (C$_o$), 125.7 (C$_p$), 122.8 (C$_m$), 78.0 (O*C*Me$_3$), 44.5 (CH*C*Me$_3$) 34.7 (CHC*Me*$_3$), 31.8 (OC*Me*$_3$), 28.0 (*C*HMe$_2$), 24.0 (CH*Me*$_2$). Anal. Calcd for WC$_{25}$H$_{45}$NO$_2$: C, 52.18; H, 7.88. Found: C, 51.67; H, 7.67.

W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (3b). LiOCMe$_2$(CF$_3$) (1.59 g, 11.86 mmol) was added to 3.50 g (5.93 mmol) of W(CH-*t*-Bu)-(NAr)(dme)Cl$_2$ in 100 mL of ether at −30 °C. The solution was warmed to 25 °C and stirred for 45 min. LiCl was filtered off, and the ether was removed in vacuo. Recrystallization of the crude product from minimal pentane gave, in three crops, 2.70 g of product as slightly oily, yellow-orange crystals (67%): ^{1}H NMR δ 8.41 (J_{HW} = 13.7, C*H*-*t*-Bu), 7.10–7.01 (H$_{\mathrm{aryl}}$), 3.72 (C*H*Me$_2$), 1.33 (OCMe$_2$CF$_3$), 1.27 (OCMe$_2$CF$_3$), 1.23 (CH*Me*$_2$), 1.15 (CHC*Me*$_3$); ^{13}C NMR δ 244.9 (d, J_{CH} = 114, J_{CW} = 200, *C*H-*t*-Bu), 151.6 (C$_{\mathrm{ipso}}$), 145.7 (C$_o$), 127.2 (J_{CF} = 286, CF$_3$), 126.9 (C$_p$), 122.9 (C$_m$), 79.5 (J_{CF} = 32, O*C*Me$_2$CF$_3$), 45.4 (CH*C*Me$_3$), 34.0 (CHC*Me*$_3$), 28.2 (*C*HMe$_2$), 24.4 (CH*Me*$_2$ or OC*Me*$_2$CF$_3$), 23.7 (CH*Me*$_2$ or OC*Me*$_2$CF$_3$). Anal. Calcd for WC$_{25}$H$_{39}$NO$_2$F$_6$: C, 43.94; H, 5.75. Found: C, 43.67; H, 5.60.

W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (3c). The crude product from the preparation of W(CH-*t*-Bu)(NAr)(dme)Cl$_2$ above was dissolved in 120 mL of diethyl ether and the solution was cooled to −30 °C. LiOCMe-(CF$_3$)$_2$ (3.35 g, 17.8 mmol) was added in small portions to the stirred solution. After all the LiOCMe(CF$_3$)$_2$ had been added the mixture was warmed to 25 °C and filtered through a pad of Celite. The solvent was removed from the filtrate in vacuo to give W(CH-*t*-Bu)(NAr)[OCMe-(CF$_3$)$_2$]$_2$ as what appears to be a weak dimethoxyethane adduct. Upon exposing the crude product to a vacuum (1 μm) for 36 h dimethoxyethane is lost; yield ~5.4 g, overall ~75% based on W(C-*t*-Bu)(dme)Cl$_3$: ^{1}H NMR δ 8.87 (J_{HW} = 12.8, C*H*CMe$_3$), 7.02 (H$_{\mathrm{aryl}}$), 3.54 (C*H*Me$_2$), 1.39 (OCMe(CF$_3$)$_2$), 1.19 (CH*Me*$_2$), 1.08 (CMe$_3$); ^{13}C NMR δ 253.9 (H_{CH} = 110, J_{CW} = 198, *C*HCMe$_3$), 151.4 (C$_{\mathrm{ipso}}$), 146.4 (C$_o$), 123.9 (J_{CF} = 288, CF$_3$), 123.1 (C$_m$ and C$_p$), 81.4 (O*C*Me(CF$_3$)$_2$), 46.3 (*C*Me$_3$), 33.5 (C*Me*$_3$), 28.2 (*C*HMe$_2$), 23.6 (CH*Me*$_2$), 18.7 (OC*Me*(CF$_3$)$_2$). Anal. Calcd for WC$_{25}$H$_{33}$NO$_2$F$_{12}$: C, 37.93; H, 4.17. Found: C, 37.93; H, 4.34.

W(CH-*t*-Bu)(NAr)[OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)]$_2$ (3d). KOC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$) (6.34 g, 16.9 mmol) was added over a period of ~3 min to 5.00 g (8.48 mmol) of W(CH-*t*-Bu)(NAr)(dme)Cl$_2$ in 200 mL of ether at −30 °C. The solution was warmed to 25 °C and stirred for 45 min. KCl was filtered off, and the solvent removed in vacuo to afford a dark red oil. This was combined with the crude product obtained in an analogous reaction by using 1.50 g of W(CH-*t*-Bu)(NAr)(dme)Cl$_2$. The sum was distilled at ~0.01 μm pressure and an oil bath temperature of 80–110 °C to afford 9.2 g of product (76% yield based on 6.50 g of W(CH-*t*-Bu)(NAr)(dme)Cl$_2$) as an orange-red oil. After standing for several days at −30 °C the product solidified into a waxy, yellow-orange solid that melts a few degrees above room temperature: ^{1}H NMR δ 9.45 (C*H*-*t*-Bu), 7.05–6.98 (H$_{\mathrm{aryl}}$), 3.52 (C*H*Me$_2$), 1.18 (CH*Me*$_2$), 1.08 (C*Me*$_3$); ^{13}C NMR δ 263.0 (d, J_{CH} = 115, *C*H-*t*-Bu), 151.6 (C$_{\mathrm{ipso}}$), 1473 (C$_o$), 129.1 (C$_p$), 123.5 (C$_m$), 87.1 (m, O*C*(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)), 47.6 (*C*Me$_3$), 33.1 (C*Me*$_3$), 28.3 (*C*HMe$_2$), 23.8 (CH*Me*$_2$). Anal. Calcd for WC$_{29}$H$_{27}$NO$_2$F$_{26}$: C, 31.68; H, 2.48; N, 1.27. Found: C, 31.41; H, 2.54, N, 1.42.

W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe(CF$_3$)$_2$]$_2$ (5). Vinyltrimethylsilane (124 μL) was added to a solution of 212 mg of W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ in 15 mL of pentane. The solvent was removed in vacuo after 2 h to give a light yellow product that can be recrystallized from pentane as light yellow crystals. The yield of crude product is essentially quantitative: ^{1}H NMR δ 6.88 (H$_m$), 6.68 (H$_p$), 5.71 (dd, 1, J_{HH} = 5 and 10, αC*H*H′), 4.36 (dd, 1, J_{HH} = 5 and 9, αCH*H*′), 4.04 (m, 1, αC*H*SiMe$_3$), 3.96 (C*H*Me$_2$), 1.75 (OCMe(CF$_3$)$_2$, 1.56 (OCMe(CF$_3$)$_2$), 1.18 (m, CH*Me*$_2$), 0.33 (SiMe$_3$), −0.13 (SiMe$_3$), −0.77 (m, 1, βC*H*SiMe$_3$); ^{13}C NMR (CF$_3$ and aryl carbon signals omitted) δ 110.8 (t, J_{CH} = 155, J_{CW} = 61, αCH$_2$), 105.7 (d, J_{CH} = 134, J_{CW} = 61, αCHSiMe$_3$), 28.0 (*C*HMe$_2$), 27.4 (*C*HMe$_2$), 26.4, 26.3, 24.5, and 24.1 (all CH*Me*$_2$), 18.9 (OC*Me*(CF$_3$)$_2$), 18.1 (OC*M*e(CF$_3$)$_2$), 5.2 (d, J_{CH} = 141, β*C*HSiMe$_3$), 1.3 (SiMe$_3$), 0.5 (SiMe$_3$). Anal. Calcd for WC$_{29}$H$_{45}$NO$_2$Si$_2$F$_{12}$: C, 38.37; H, 4.96. Found: C, 38.53; H, 5.11.

The equilibrium between **5** and W(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (**6**) in toluene-*d*$_8$ was measured by ^{1}H NMR: $K_{\mathrm{eq}} = 1.1 \times 10^{-4}$ M at −17 °C, 2.2×10^{-4} M at 3 °C, 1.4×10^{-3} M at 24 °C, 5.3×10^{-3} M at 41 °C, and 3.6×10^{-2} M at 61 °C.

W(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (6). A sample of W[CH-(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe(CF$_3$)$_2$]$_2$ (0.21 g, 0.23 mmol) was dissolved in THF (~5 mL) and the solution was concentrated in vacuo to give W(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$(THF) virtually quantitatively: ^{1}H NMR δ 10.11 (C*H*SiMe$_3$), 7.08–6.97 (H$_{\mathrm{aryl}}$), 3.60 (THF), 3.57 (C*H*Me$_2$), 1.36 (OCMe(CF$_3$)$_2$), 1.30 (THF), 1.22 (CH*Me*$_2$), 0.05 (CHSi*Me*$_3$). The coordinated THF can be removed from W-(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$(THF) by subjecting it to a vacuum (<0.05 μm) for 24 at 25 °C. Subsequent recrystallization from pentane affords **6** as yellow crystals (60 mg, 32% yield, not optimized): ^{1}H NMR δ 9.97 (C*H*SiMe$_3$), 7.07–6.98 (H$_{\mathrm{aryl}}$), 3.51 (C*H*Me$_2$), 1.34 (OC*Me*-(CF$_3$)$_2$), 1.20 (CH*Me*$_2$), 0.04 (CHSi*Me*$_3$); ^{13}C NMR δ 242.8 (*C*HSiMe$_3$), 152.0 (C$_{\mathrm{ipso}}$), 145.7 (C*o*), 127.9 (C$_p$), 123.7 (CF$_3$), 123.0 (C$_m$), 81.7 (sept, J_{CF} = 30, O*C*Me(CF$_3$)$_2$), 28.2 (*C*HMe$_2$), 23.7 (CH*Me*$_2$), 18.2 (OC*Me*(CF$_3$)$_2$), 1.8 (CHSi*Me*$_3$).

W(CHSiMe$_3$)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (7). Vinyltrimethylsilane (145 μL) was added to a solution of 400 mg (0.585 mmol) of W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ in 8 mL of pentane at 25 °C. After 2 h the solvent was removed in vacuo. The yellow product was recrystallized from pentane at −40 °C to afford 307 mg (75%) of a yellow, microcrystalline powder: ^{1}H NMR δ 9.40 (br, C*H*SiMe$_3$), 7.12–7.03 (H$_{\mathrm{aryl}}$), 3.67 (C*H*Me$_2$), 1.33 (6, OCMe$_2$CF$_3$), 1.24 (br, 12, CH*Me*$_2$), 1.23 (6, OCMe$_2$CF$_3$), 0.12 (SiMe$_3$); ^{1}H NMR (toluene-*d*$_8$, −50 °C) δ 9.47 (C*H*SiMe$_3$, J_{HW} = 11), 7.04 (H$_{\mathrm{aryl}}$), 3.65 (C*H*Me$_2$), 1.31 (OCMe$_2$CF$_3$), 1.25 (OCMe$_2$CF$_3$), 1.22 (CH*Me*$_2$), 0.13 (SiMe$_3$); ^{13}C NMR δ 230.5 (d, J_{CH} = 110, *C*HSiMe$_3$), 152.1 (C$_{\mathrm{ipso}}$), 144.8 (C$_o$), 127.1 (J_{CF} = 286, CF$_3$), 126.8 (C$_p$), 122.9 (C$_m$), 79.8 (J_{CF} = 29.9, O*C*Me$_2$CF$_3$), 28.2 (*C*HMe$_2$), 24.0 (OC*Me*$_2$CF$_3$ or CH*Me*$_2$), 23.7 (CH*Me*$_2$ or OC*Me*$_2$CF$_3$), 2.2 (SiMe$_3$).

Vinyltrimethylsilane (~1 equiv) was added to **7** in toluene-*d*$_8$ and the equilibrium between W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe$_2$-(CF$_3$)]$_2$ and **7** measured at several temperatures: K_{eq} = 0.12 M at 2 °C, 4.5×10^{-2} M at −8 °C, 1.7×10^{-2} M at −18 °C, 5.7×10^{-3} M at −28 °C, 3.0×10^{-3} M at −38 °C, 8.7×10^{-4} M at −48 °C. Another experiment yielded K_{eq} = 0.15 M at 3 °C, 4.6×10^{-2} M at −6 °C, 1.6×10^{-2} M at −17 °C, 5.6×10^{-3} M at −27 °C, and 1.9×10^{-3} M at −36 °C. ^{1}H NMR of W[CH(SiMe$_3$)CH(SiMe$_3$)CH$_2$](NAr)[OCMe(CF$_3$)]$_2$ (toluene-*d*$_8$) δ 6.85 (H$_m$), 6.69 (H$_p$), 5.61 (m, 1, C*H*H′), 4.42 (m, 1, CH*H*′), 4.07 (C*H*Me$_2$), 3.83 (d, 1, *J* = 11, αC*H*SiMe$_3$), 1.68, 1.61, 1.56, 1.42

(each a singlet, 3, $\mathrm{OCMe}\mathit{Me}\mathrm{(CF_3))}$), 1.24–1.13 (overlapping doublets, $\mathrm{CH}\mathit{Me}_2$), 0.39 ($\mathrm{SiMe_3}$), –0.083 ($\mathrm{SiMe_3}$), –0.74 (dd, 1, $\beta\mathrm{C}\mathit{H}\mathrm{SiMe_3}$); ^{1}H NMR of $\mathrm{W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe_2(CF_3)]_2}$ (toluene-d_8, –50 °C) δ 6.85 ($\mathrm{H_m}$), 6.68 ($\mathrm{H_p}$), 5.61 (dd, 1, J = 5 and 10, αCHH′), 4.42 (dd, 1, J = 5 and 9, αCHH′), 4.07 ($\mathrm{C}\mathit{H}\mathrm{Me_2}$), 3.83 (d, 1, J = 11, $\alpha\mathrm{C}\mathit{H}\mathrm{SiMe_3}$), 1.69, 1.61, 1.56, 1.43 (each a singlet, 3, $\mathrm{OCMe}\mathit{Me}\mathrm{(CF_3))}$), 1.24–1.13 (overlapping doublets, $\mathrm{CH}\mathit{Me}_2$), 0.39 ($\mathrm{SiMe_3}$), –0.081 ($\mathrm{SiMe_3}$), –0.74 (m, 1, J = 11, $\beta\mathrm{C}\mathit{H}\mathrm{SiMe_3}$).

W(CHEtCHEtCHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (9). A solution of $\mathrm{W(CHMe_3)(NAr)[OCMe(CF_3)_2]_2}$ (3.32 g, 4.19 mmol) in pentane (30 mL) was treated with *cis*-3-hexene (1.70 mL, 13.7 mmol) at –40 °C. The solution was allowed to warm to 25 °C. After 15 min the solvent was removed in vacuo. The residue was treated twice more with *cis*-3-hexene in a similar manner. The orange solid thus obtained was extracted with pentane and the solution was filtered. *cis*-3-Hexene (0.25 mL, 2.0 mmol) was added and the solution was cooled to –40 °C to afford thermally sensitive golden-orange crystals (2.60 g, 75% yield). By ^{1}H NMR the product consists of a mixture of **9** (80%) and $\mathrm{W(CHEt)(NAr)[OCMe(CF_3)_2]_2}$ (**8a**; 20%). The tungstacycle readily loses 3-hexene in solution at 25 °C or in the solid state when subjected to a vacuum. The tungstacycle also may be synthesized by using 2-pentene instead of 3-hexene: ^{1}H NMR ($\mathrm{CD_2Cl_2}$, –60 °C) δ 7.15 ($\mathrm{H_m}$), 6.98 ($\mathrm{H_p}$), 5.38 (m, 2, $\alpha\mathrm{C}\mathit{H}\mathrm{Et}$), 3.90 ($\mathrm{C}\mathit{H}\mathrm{Me_2}$), 3.57 (m, 2, $\alpha\mathrm{CHC}\mathit{H}_\mathrm{A}\mathrm{H_BCH_3}$), 2.60 (m, 2, $\alpha\mathrm{CHCH_A}\mathit{H}_\mathrm{B}\mathrm{CH_3}$), 1.57 (s, 3, $\mathrm{OCMe(CF_3)_2}$), 1.54 (m, 2, $\beta\mathrm{CHC}\mathit{H}_2\mathrm{CH_3}$), 1.38 (s, 3, $\mathrm{OCMe(CF_3)_2}$), 1.17 ($\mathrm{CH}\mathit{Me}_2$), 1.06 (t, J = 7.1, 9, α and $\beta\mathrm{CHCH_2CH_3}$), –0.56 (quint, J = 5.5, 1, βCHEt).

W(CHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (8a). An orange residue is obtained when an ether solution containing a mixture of $\mathrm{W(CHEtCHEtCHEt)(NAr)[OCMe(CF_3)_2]_2}$ and $\mathrm{W(CHEt)(NAr)[OCMe(CF_3)_2]_2}$ (see above) is concentrated in vacuo at a rate such that it does not cool much below 25 °C. If this procedure is repeated the residue consists of essentially pure **8a**. Unfortunately, **8a** not only has resisted all attempts to crystallize it but it is exceedingly sensitive to thermal decomposition. The ^{1}H NMR spectrum of **8a** isolated in this manner is the same as that for **8a** in a mixture of **8a** and **9** described above: ^{1}H NMR δ 9.22 (t, 1, J_HH = 6.0, $\mathrm{C}\mathit{H}\mathrm{CH_2CH_3}$), 7.02 (s, 3, $\mathrm{H_m}$ and $\mathrm{H_p}$), 4.10 (dq, 2, J_HH = 6.0, 7.5, $\mathrm{CHC}\mathit{H}_2\mathrm{CH_3}$), 3.49 ($\mathrm{C}\mathit{H}\mathrm{Me_2}$), 1.30 (s, 6, $\mathrm{OCMe(CF_3)_2}$), 1.19 ($\mathrm{CH}\mathit{Me}_2$), 0.78 (t, 3, J_HH = 7.5, $\mathrm{CHCH_2C}\mathit{H}_3$); ^{13}C NMR δ 249.1 (d, J_CH = 120, $\mathit{C}\mathrm{HCH_2CH_3}$), 151.0 ($\mathrm{C_{ipso}}$), 146.0 ($\mathrm{C_o}$), 128.0 ($\mathrm{C_p}$), 123.9 (q, J_CF = 289, $\mathrm{CF_3}$), 122.8 ($\mathrm{C_m}$), 81.7 (sept, J_CF = 30, $\mathrm{O}\mathit{C}\mathrm{Me(CF_3)_2}$), 38.8 ($\mathrm{CH}\mathit{C}\mathrm{H_2CH_3}$), 28.3 ($\mathit{C}\mathrm{HMe_2}$), 23.3 ($\mathrm{CH}\mathit{Me}_2$), 18.6 ($\mathrm{OC}\mathit{Me}\mathrm{(CF_3)_2}$); the $\mathrm{CHCH_2}\mathit{C}\mathrm{H_3}$ resonance could not be located in this spectrum.

W(CHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$(THF) (8b). A solution containing a mixture of **8a** and **9** (80%) (0.44 g, 0.54 mmol) in pentane (5 mL) was treated with tetrahydrofuran (0.44 mL, 5.3 mmol) at room temperature. After 5 min the volatile components were removed in vacuo and the resulting orange solid was recrystallized from pentane at –40 °C to give orange crystals of **8b** (0.34 g, 77% yield); ^{1}H NMR δ 9.55 (t, 1, J_HH = 7.0, $\mathrm{C}\mathit{H}\mathrm{CH_2CH_3}$), 7.07 ($\mathrm{H_m}$), 7.01 ($\mathrm{H_p}$), 4.47 (dq, 2, J_HH = 7.0 and 7.68 $\mathrm{CHC}\mathit{H}_2\mathrm{CH_3}$), 3.69 ($\mathrm{C}\mathit{H}\mathrm{Me_2}$), 3.63 (THF), 1.38 ($\mathrm{OCMe(CF_3)_2}$), 1.25 (THF), 1.23 ($\mathrm{CH}\mathit{Me}_2$), 0.82 (t, 3, J_HH = 7.6, $\mathrm{CHCH_2C}\mathit{H}_3$); ^{13}C NMR δ 263.5 (d, J_CH = 122, J_CW = 189, $\mathit{C}\mathrm{HCH_2CH_3}$), 151.2 ($\mathrm{C_{ipso}}$), 146.5 ($\mathrm{C_o}$), 127.7 ($\mathrm{C_p}$), 124.9 (q, J_CF = 286, $\mathrm{CF_3}$), 124.7 (q, J_CF = 288, $\mathrm{CF_3}$), 123.0 ($\mathrm{C_m}$), 81.3 (sept, J_CF = 30, $\mathrm{OCMe(CF_3)_2}$), 69.8 (THF), 39.8 ($\mathrm{CH}\mathit{C}\mathrm{H_2CH_3}$), 28.3 ($\mathit{C}\mathrm{HMe_2}$), 25.6 (THF), 23.9 ($\mathrm{CH}\mathit{Me}_2$), 20.1 ($\mathrm{CHCH_2}\mathit{C}\mathrm{H_3}$), 18.9 ($\mathrm{OC}\mathit{Me}\mathrm{(CF_3)_2}$). Anal. Calcd for $\mathrm{WC_{27}H_{37}F_{12}NO_3}$: C, 38.82; H, 4.46. Found: C, 38.14; H, 4.32.

W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (4). A 4:1 mixture of **9** and **8a** (1.00 g, 1.20 mmol) in pentane (10 mL) at –40 °C was treated with *cis*-β-methylstyrene (0.15 mL, 1.2 mmol) in pentane (2 mL). The solution was allowed to warm to ambient temperature. After 15 min the volatile components were removed in vacuo and the resulting red solid was recrystallized from pentane at –40 °C to give red-orange cubes (0.73 g, 75% yield): ^{1}H NMR δ 9.91 ($\mathrm{C}\mathit{H}\mathrm{Ph}$), 7.03–7.07 (m, 3, $\mathrm{H_{aryl}}$), 6.97–6.99 (m, 4, $\mathrm{H_{aryl}}$), 6.58 (m, 1, $\mathrm{H_{aryl}}$), 3.54 ($\mathrm{C}\mathit{H}\mathrm{Me_2}$), 1.29 ($\mathrm{OCMe(CF_3)_2}$), 1.14 ($\mathrm{CH}\mathit{Me}_2$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 239.9 ($J_\mathrm{CH}$ = 121, J_CW = 202, $\mathit{C}\mathrm{HPh}$), 151.4 (imido $\mathrm{C_{ipso}}$), 147.2 (imido $\mathrm{C_o}$), 143.5 (phenyl $\mathrm{C_{ipso}}$), 129.5, 129.0, 128.7, 127.9, and 123.4 (all $\mathrm{C_{aryl}}$), 124.0 (J_CF = 287, $\mathrm{CF_3}$), 123.9 (J_CF = 291, $\mathrm{CF_3}$), 82.4 (sept, J_CF = 30, $\mathrm{O}\mathit{C}\mathrm{Me(CF_3)_2}$), 28.9 ($\mathit{C}\mathrm{HMe_2}$), 23.8 ($\mathrm{CH}\mathit{Me}_2$), 19.4 ($\mathrm{OC}\mathit{Me}\mathrm{(CF_3)_2}$). Anal. Calcd for $\mathrm{WC_{27}H_{29}F_{12}NO_2}$: C, 39.97; H, 3.60. Found: C, 40.19; H, 3.79.

W(CH$_2$CH$_2$CH$_2$)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (12). A solution of W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (0.70 g, 0.89 mmol) in pentane (60 mL) in a 100-mL Schlenk flask was cooled to 0 °C and 2.4 equiv of ethylene was injected through a septum cap into the volume above the solution in a closed system. The solution was stirred vigorously for 20 min at 0 °C and the volatile components then removed in vacuo to give the essentialy pure product as a light yellow powder. An analytical sample was prepared by crystallization slowly from pentane: ^{1}H NMR δ 6.89 ($\mathrm{H_m}$), 6.73 ($\mathrm{H_p}$), 4.66 (m, 2, $\alpha\mathrm{CH_2}$), 4.51 (m, 2, $\alpha\mathrm{CH_2}$), 3.78 (sept, 2, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 1.54 (br s, $\mathrm{OC}\mathit{Me}\mathrm{(CF_3)_2}$), 1.04 (br s, $\mathrm{CH}\mathit{Me}_2$), –0.79 (br t, 1, $\beta\mathrm{CH_2}$), –1.39 (br t, 1, $\beta\mathrm{CH_2}$)); ^{13}C NMR (230 K) δ 147.9 ($\mathrm{C_o}$ or $\mathrm{C_{ips}}$*o*), 146.3 ($\mathrm{C_{ipso}}$ or $\mathrm{C_o}$), 127.7 ($\mathrm{C_p}$), 124.6 (J_CF = 216, $\mathrm{CF_3}$), 123.3 ($\mathrm{C_m}$), 100.7 (t, J_CH = 158, J_CW = 67, $\alpha\mathrm{CH_2}$), 83.7 (m, $\mathrm{O}\mathit{C}\mathrm{Me(CF_3)_2}$), 27.5 ($\mathit{C}\mathrm{HMe_2}$), 26.8, 23.3, 18.0, and 17.0 (Me groups), –5.1 (t, J_CH = 157, $\beta\mathrm{CH_2}$). Anal. Calcd for $\mathrm{WC_{23}H_{29}NO_2F_{12}}$: C, 36.18; H, 3.80. Found: C, 36.24; H, 3.48.

W(CH$_2$CH$_2$CH$_2$)(NAr)[OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)]$_2$ (13). W(CH-*t*-Bu)(NAr)[OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)]$_2$ (1.00 g, 0.910 mmol) was dissolved in 50 mL of pentane in a 100-mL Schlenk flask fitted with a rubber septum. Ethylene (60 mL, ~2.5 mmol) was injected above the solution. After the solution was stirred for 45 min at 0 °C the solvemt was removed in vacuo to afford an ivory colored solid. The crude product was recrystallized from pentane to afford 750 mg (77%) of product as a pale yellow solid: ^{1}H NMR δ 6.85 ($\mathrm{H_m}$), 6.68 ($\mathrm{H_p}$), 4.87 (m, 2, $\alpha\mathrm{CH_2}$), 4.58 (m, 2, $\alpha\mathrm{CH_2}$), 3.76 ($\mathrm{C}\mathit{H}\mathrm{Me_2}$), 1.06 (br d, 12, $\mathrm{CH}\mathit{Me}_2$), –0.95 (m, 1, $\beta\mathrm{CH_2}$), –1.65 (m, 1, $\beta\mathrm{CH_2}$); ^{13}C NMR δ 148.7 ($\mathrm{C_o}$), 145.5 ($\mathrm{C_{ipso}}$), 129.0 ($\mathrm{C_p}$), 123.3 ($\mathrm{C_m}$), 103.5 (t, J_CH = 158, J_CW = 66, $\alpha\mathrm{CH_2}$), 86.1 (m, $\mathrm{O}\mathit{C}\mathrm{(CF_3)_2(CF_2CF_2CF_3))}$, 27.9 ($\mathit{C}\mathrm{HMe_2}$), 25.0 (v br, $\mathrm{CH}\mathit{Me}_2$), –6.79 (t, J_CH = 158, $\beta\mathrm{CH_2}$). Anal. Calcd for $\mathrm{WC_{27}H_{23}NO_2F_{26}}$: C, 30.27; H, 2.16. Found: C, 30.38; H, 2.32.

W(CHSiMe$_3$)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$) (14). Excess trimethylphosphine (20 μL, 2.7 equiv) was added by syringe to a solution of $\mathrm{W[CH(SiMe_3)CH(SiMe_3)CH_2](NAr)[OCMe(CF_3)_2]_2}$ (60 mg) in 5 mL of pentane. The solvent and excess trimethylphosphine were removed after 2 h. A ^{1}H NMR spectrum of the crude reaction mixture showed it to contain <5% of the analogous methylene complex (**15**). Pure **14** was obtained by recrystallization of the crude product from pentane: ^{1}H NMR δ 12.05 (d, J_HP = 6.3, $\mathrm{C}\mathit{H}\mathrm{SiMe_3}$), 7.02 ($\mathrm{H_m}$), 6.88 ($\mathrm{H_p}$), 4.46 and 3.54 ($\mathrm{C}\mathit{H}\mathrm{Me_2}$), 2.09 and 1.50 ($\mathrm{CMe(CF_3)_2}$), 1.30, 1.28, 1.27, and 1.20 (eac 3, $\mathrm{CH}\mathit{Me}_2$), 0.95 (d, J_HP = 9.5, $\mathrm{PMe_3}$), 0.25 ($\mathrm{SiMe_3}$); ^{13}C NMR δ 266.3 (d, J_CH = 128, J_CP = 11, $\mathrm{CHSiMe_3}$), 150.7 ($\mathrm{C_{ipso}}$), 147.2 ($\mathrm{C_o}$), 127.6 ($\mathrm{C_m}$ or $\mathrm{C_p}$), 123.4 ($\mathrm{C_p}$ or $\mathrm{C_m}$), 80.9 ($\mathit{C}\mathrm{Me(CF_3)_2}$), 28.7 and 27.8 ($\mathit{C}\mathrm{HMe_2}$), 25.0, 24.4, 24.3, and 23.8 ($\mathrm{CH}\mathit{Me}_2$), 19.8 and 17.4 ($\mathrm{C}\mathit{Me}\mathrm{(CF_3)_2}$), 15.7 ($\mathrm{PMe_3}$), 1.9 ($\mathrm{SiMe_3}$). Anal. Calcd for $\mathrm{WC_{27}H_{42}NO_2PSiF_{12}}$: C, 36.70; H, 4.76. Found: C, 36.61; H, 4.67.

W(CH$_2$)(NAr)[OCMe(CF$_3$)$_2$]$_2$(PMe$_3$) (15). A solution of $\mathrm{W(CH_2CH_2CH_2)(NAr)[OCMe(CF_3)_2]_2}$ (100 mg) in pentane (5 mL) was cooled to 0 °C and 40 μL of $\mathrm{PMe_3}$ was added. After 15 min the solvent and excess $\mathrm{PMe_3}$ were removed in vacuo leaving pure product as a yellow powder. An analytical sample was crystallized from pentane: ^{1}H NMR δ 11.00 (d, 2, J_HP = 6.4, J_HW = 25, $\mathrm{CH_2}$), 7.03 ($\mathrm{H_m}$), 6.90 ($\mathrm{H_p}$), 4.22 (br m, 1, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 3.40 (br m, 1, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 2.05 (s, 3, $\mathrm{OC}\mathit{Me}\mathrm{CF_3)_2}$), 1.44 (s, 3, $\mathrm{OC}\mathit{Me}\mathrm{(CF_3)_2}$), 1.27 (br d, 12, $\mathrm{CH}\mathit{Me}_2$), 0.93 (d, 98 $\mathrm{J_{HP}}$ = 9.5, $\mathrm{PMe_3}$); ^{13}C NMR δ 252.2 (J_CP = 14.5, J_CW = 163, J_CH = 145, $\mathrm{CH_2}$), 150.0 ($\mathrm{C_{ipso}}$), 146.2 (br s, $\mathrm{C_o}$), 128.0 (C*m* or $\mathrm{C_p}$), 126.2 (J_CF = 188, $\mathrm{CF_3}$), 123.1 $\mathrm{C_p}$ or $\mathrm{C_m}$), 81.6 (m, $\mathrm{O}\mathit{C}\mathrm{Me(CF_3)_2}$), 29.4 (br, $\mathit{C}\mathrm{HMe_2}$), 28.0 (br, $\mathit{C}\mathrm{HMe_2}$), 24.0 (br, $\mathrm{CH}\mathit{Me}_2$), 19.5 ($\mathrm{OC}\mathit{Me}\mathrm{(CF_3)_2}$), 17.6 ($\mathrm{OC}\mathit{Me}\mathrm{(CF_3)_2}$), 15.7 ($J_\mathrm{CP}$ = 30, $\mathrm{PMe_3}$); ^{31}P NMR (tol-d_8) δ 9.7 (J_PW = 322). Anal. Calcd for $\mathrm{WC_{24}H_{34}NO_2F_{12}P}$: C, 35.52; H, 4.19. Found: C, 35.37; H, 4.36.

W(CH$_2$)(NAr)[OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)]$_2$(PMe$_3$) (16). $\mathrm{PMe_3}$ (80 μL, 1.0 mmol) was added to 400 mg of $\mathrm{W(CH_2CH_2CH_2)(NAr)[OC(CF_3)_2(CF_2CF_2CF_3)]_2}$ in 20 mL of pentane at 25 °C. After 60 m the solvent was removed in vacuo to afford an orange solid. The crude product was recrystallized from a mixture of ether and pentane (~1:1) at –40° to afford 312 mg of product as orange crystals (75%): ^{1}H NMR δ 11.58 (dd, 1, J = 8 and 6, $\mathrm{CH_AH_B}$), 11.31 (dd, 1, J_HH = J_PH = 8, $\mathrm{CH_AH_B}$), 6.99 (1 $\mathrm{H_m}$), 6.93 (1, $\mathrm{H_m}$), 6.85 (1, $\mathrm{H_p}$), 4.32 (1, $\mathrm{CHMe_i}$), 3.34 (1, $\mathrm{CHMe_2}$), 1.31, 1.26, 1.21, 1.09 (each 3, $\mathrm{CHMe_2}$), 0.8 (d, J_HP = 9.9, 9, $\mathrm{PMe_3}$); ^{13}C NMR δ (THF-d_8) 264.9 (J_CP = 16.3, J_CH = 134.6, $J_\mathrm{CH'}$ = 162.4, $\mathrm{CH_AH_B}$), 150.6 ($\mathrm{C_{ipso}}$), 148.0 ($\mathrm{C_{ortho}}$), 128.9 ($\mathrm{C_p}$), 124.4 ($\mathrm{C_m}$), 123.7 ($\mathrm{C_m}$), 30.1 ($\mathrm{CHMe_2}$), 28.2 ($\mathrm{CHMe_2}$), 17.6 (J_CP = 32, $\mathrm{PMe_3}$). The isopropyl methyl resonances were obscured by THF-d_8 resonances. Anal. Calcd for $\mathrm{WC_{28}H_{28}NO_2F_{26}P}$: C, 30.05; H, 2.52. Found: C, 30.22; H, 2.71.

W[CH$_2$CH(SiMe$_3$)CH$_2$](NAr)[OCMe(CF$_3$)$_2$]$_2$ (17). $\mathrm{W(C_3H_6)(NAr)[OCMe(CF_3)_2]_2}$ (0.30 g, 0.39 mmol) was dissolved in 15 mL of pentane and 300 μL (5 equiv) of vinyltrimethylsilane was added. After 30 min the volatile components were removed in vacuo to give an orange oil. This oil was dissolved in ~1 mL of pentane and the solution was stored at –30 °C for 2 days to give the product as a light yellow powder (75% yield): ^{1}H NMR δ 6.88 ($\mathrm{H_p}$), 6.69 ($\mathrm{H_o}$), 5.04 (dd, 2, J = 11 and 6, $\alpha\mathrm{C}\mathit{H}_\mathrm{A}\mathrm{H_B}$), 4.36 (dd, 2, J = 6 and 8, $\alpha\mathrm{CH_A}\mathit{H}_\mathrm{B}$), 3.94 ($\mathrm{C}\mathit{H}\mathrm{Me_2}$), 1.66 (v br, 3, $\mathrm{OCMe(CF_3)_2}$), 1.55 (v br, 3, $\mathrm{OCMe(CF_3)_2}$), 1.12 ($\mathrm{CH}\mathit{Me}_2$), –0.17 ($\mathrm{SiMe_3}$), –1.03 (tt, 1, J = 11 and 8, $\mathrm{C}\mathit{H}\mathrm{SiMe_3}$); ^{13}C NMR (toluene-$d_8$, 240 K) δ 147.9 ($\mathrm{C_o}$), 127.6 ($\mathrm{C_m}$ or $\mathrm{C_p}$), 124.7 ($\mathrm{CF_3}$), 124.5 ($\mathrm{CF_3}$), 123.4 ($\mathrm{C_p}$ or $\mathrm{C_m}$), 102.8 (t, J_CH = 155, J_CW = 68, $\alpha\mathrm{CH_2}$), 84.2 (m, $\mathrm{O}\mathit{C}\mathrm{MenCF_3)_2}$), 80.8 (m, $\mathrm{O}\mathit{C}\mathrm{Me(CF_3)_2}$), 27.5 ($\mathit{C}\mathrm{HMe_2}$), 26.5 ($\mathrm{CH}\mathit{Me}_2$), 26.1 ($\mathrm{CH}\mathit{Me}_2$), 18.5 ($\mathrm{OC}\mathit{Me}\mathrm{(CF_3)_2}$), 17.0 ($\mathrm{OC}\mathit{Me}\mathrm{(CF_3)_2}$), –0.33

($SiMe_3$), −0.55 (d, J_{CH} = 136, C*H*$SiMe_3$). Anal. Calcd for $WC_{26}H_{37}NO_2F_{12}Si$: C, 37.37; H, 4.43. Found: C, 37.05; H, 4.55.

The product could not be isolated in crystalline form on a scale less than that reported here. The C_{ipso} resonance was not found in the ^{13}C NMR spectrum.

X-ray Structure of W(CHPh)(NAr)[OCMe$(CF_3)_2]_2$ (4). Data were collected at −65 °C on an Enraf-Nonius CAD4F-11 diffractometer equipped with a liquid nitrogen low-temperature device and with Mo Kα radiation. Data collection, reduction, and refinement procedures have been detailed elsewhere.[24] A total of 4019 reflections were collected in the range $3° \leq 2\theta \leq 55°$ with the 3421 having $F_o > 4\sigma(F_o)$ being used in the structure refinement which was by full-matrix least-squares techniques (368 variables) with SHELX-76; final R_1 = 0.089 and R_2 = 0.096. The alternate hand of the structure was refined and resulted in slightly higher R values. The OCMe$(CF_3)_2$ ligands behaved poorly in the refinement so C(33), C(34), C(43), and C(44) were refined isotropically. All remaining non-hydrogen atoms were refined anisotropically. A final difference-Fourier map showed no chemically significant features. The crystal data are the following: a = 11.571 (3) Å, b = 12.719 (2) Å, c = 21.192 (9) Å, V = 3118.9 Å^3, space group $P2_12_12_1$, Z = 4, mol wt = 811.37, ρ(calcd) = 1.728 g cm^{-3}, μ = 36.0 cm^{-1}. A semiempirical absorption corrections was applied. A drawing of **4** is shown in Figure 1. Relevant bond distances and angles are listed in Table II.

X-ray Structure of W[CH$(SiMe_3)$CH$(SiMe_3)CH_2$](NAr)[OCMe$(CF_3)_2]_2$ (5). Data were collected at −22 °C as described above. A total of 6623 reflections were collected in the range $3° \leq 2\theta \leq 50°$ with the 4209 having $F_o > 4\sigma(F_o)$ being used in the structure refinement which was by full-matrix least-squares techniques (424 variables) with SHELX-76; final R_1 = 0.054 and R_2 = 0.058. The axial OCMe$(CF_3)_2$ ligand behaved poorly in the refinement so C(43) and C(44) were refined isotropically and hydrogen atoms were not included on C(44). The result is a poor geometry for the CF_3 group containing C(42). All remaining non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å) and were constrained to ride on their respective carbon atoms. A final difference-Fourier map showed no significant features. The crystal data are the following: a = 18.049 (4) Å, b = 12.224 (4) Å, c = 18.877 (5) Å, β = 114.86 (2)°, V = 3778.9 Å^3, space group $P2_1/n$, Z = 4, mol wt = 907.69, ρ(calcd) = 1.594 g cm^{-3}, μ = 30.3 cm^{-1}. A semiempirical absorption correction was applied. A drawing of **5** is shown in Figure 2. Relevant bond distances and angles are listed in Table III.

X-ray Structure of W$(CH_2CH_2CH_2)$(NAr)[OC$(CF_3)_2(CF_2CF_2CF_3)]_2$ (13). X-ray data were collected at −65 °C as described above. A total of 6126 reflections ($+h,+k,\pm l$) were collected in the range $3° < 2\theta < 50°$ with the 3827 having $I_o > 2\sigma(I_o)$ being used in the structure refinement which was by full-matrix least-squares techniques (365 variables) with SHELX-76; final R_1 = 0.076 and R_2 = 0.092. Hydrogen atoms in the imido ligand were placed in calculated positions (C–H = 0.95 Å) and were constrained to ride on their respective carbon atoms while hydrogen atoms on the tungstacyclobutane ring were ignored. Only the W and F atoms were refined anisotropically and the final difference-Fourier map showed no chemically significant features. The W atom was located from a Patterson map. The program DIRDIF[25] was found useful in assigning the light atom structure since the heavy atom lies on a pseudospecial position. The crystal data are the following: a = 18.355 (10) Å, b = 9.513 (11) Å, c = 19.976 (26) Å, β = 96.75 (8)°, V = 3463.9 Å^3, space group $P2_1/n$, Z = 4, mol wt = 1071.3, ρ(calcd) = 2.054 g cm^{-3}, μ = 33.1 cm^{-1}. A semiempirical absorption correction was applied. A drawing of the molecule can be found in Figure 4. Relevant bond distances and angles are listed in Table VI.

Kinetic Study of the Reaction between W(CH-*t*-Bu)(NAr)[OCMe$_2(CF_3)]_2$ and an Equilibrium Mixture of *cis*- and *trans*-3-Hexene. W(CH-*t*-Bu)(NAr)[OCMe$_2(CF_3)]_2$ (25 mg, 0.0366 mmol) was dissolved in 1.00 mL of a stock solution that was 0.366 M in *cis*-3-hexene and 0.0367 M in *p*-$C_6H_4Cl_2$ in C_6D_6. The change in volume was considered negligible compared to other errors. The above solution was transferred to an NMR tube and the tube sealed under a partial vacuum of dinitrogen (~700 mm). The solution was kept frozen until the kinetics run was begun. The tube was placed inside the probe of a 300-MHz spectrometer which had been preheated to the desired temperature. After 15 min the first spectrum was acquired and subsequent spectra recorded at timed intervals thereafter. First-order plots of the concentration of W(CH-*t*-Bu)(NAr)[OCMe$_2CF_3]_2$ (determined by integration vs *p*-$C_6H_4Cl_2$) as a function of time yielded straight lines ($R > 0.997$) over at least 3 half-lives (~15 data points).

In addition to resonances corresponding to 3-hexene (*cis*/*trans* mixture) and the cleavage product *trans*-2,2-dimethyl-3-hexene, the following resonances characteristic of the propylidene complex were observed during the reaction: δ 8.77 (t, J = 6.2, CHEt), 7.10–7.00 (3, H_{aryl}), 4.10 (m, CHC*H*$_2CH_3$), 3.73 (C*H*Me_2), 1.32 (6, OCMe$_2(CF_3)$), 1.26 (6, OCMe$_2$ (CF_3)). The γ CH_3 resonance in the propylidene ligand is obscured by the 3-hexene CH_3 resonance, but if 3-hexene is removed the γ CH_3 resonance can be observed at δ 0.94 (t, J = 7.4).

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Supplementary Material Available: Listings of final positional and thermal parameters for all three structures (6 pages); listings of final observed and calculated structure factors for all three structures (56 pages). Ordering information is given on any current masthead page.

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