Further Studies of Imido Alkylidene Complexes of Tungsten, Well-Characterized Olefin Metathesis Catalysts with Controllable Activity

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An alternative synthesis of W(CH-*t*-Bu)(NAr)(dme)Cl_2 (Ar = 2,6-C_6-H_3-*i*-Pr_2) consists of the five steps WCl_6 → W(O)Cl_4 → W(NAr)Cl_4 → W(NAr)(O-*t*-Bu)$_2Cl_2$(THF) → W(NAr)(O-*t*-Bu)$_2$(CH_2-*t*-Bu)$_2$ → W-(CH-*t*-Bu)(NAr)(dme)Cl_2, in which *tert*-butoxide "protecting groups" are replaced by chlorides in the last step upon addition of PCl_5. The easiest synthesis to a catalyst precursor consists of the three steps WO_2Cl_2 → W(NAr)$_2Cl_2$(dme) → W(NAr)$_2$(CH_2R)$_2$ → W(CHR)(NAr)(OTf)$_2$(dme) (R = *t*-Bu, CMe_2Ph; OTf = OSO_2CF_3), in which an imido ligand protecting group is ultimately replaced by two triflate ligands upon addition of triflic acid in the last step. An X-ray study of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ shows it to be a pseudotetrahedral complex in which the *tert*-butyl group points toward the imido ligand (syn conformation; space group $P\bar{1}$, a = 14.050 (5) Å, b = 18.885 (5) Å, c = 11.123 (5) Å, α = 92.22 (3)°, β = 108.30 (3)°, γ = 79.25 (2)°, V = 2752 (2) Å^3, Z = 4, M_r 572.46, ρ = 1.381 g cm^{-3}, μ = 43.03 cm^{-1}; R = 0.039, R_w = 0.043). Complexes of the type W(CH-*t*-Bu)(NAr')(OR)$_2$ (NAr' = N-2,6-$C_6H_3Me_2$; OR = O-*t*-Bu, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, $OC(CF_3)_2(CF_2CF_2CF_3)$) were prepared by methods analogous to those used originally to prepare NAr complexes. Reactions between NAr' complexes and olefins in general yield less stable organometallic products than when the NAr ligand is present. In one case (addition of internal olefins to W(CH-*t*-Bu)(NAr')[$OCMe(CF_3)_2$]$_2$) a product was isolated that was consistent with the formation {W(NAr')-[$OCMe(CF_3)_2$]$_2$}$_2$. Some of the W(CH-*t*-Bu)(NAr)X_2 variations that were prepared include X = OAr, $OCEt_3$, $OCMe_2Ph$, SAr, and CH_2-*t*-Bu. Other variations include W(CHEt)(NAr)X_2 complexes (X = $OCEt_3$, NPh_2), W($CHSiMe_3$)(NAr)X_2 complexes (X = OAr, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, and W[$CHSi(OMe)_3$](NAr)X_2 complexes (X = OAr, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$). Syn and anti rotamers of W($CHSiMe_3$)(NAr)(OAr)$_2$ were observed and found to interconvert on the NMR time scale ($\Delta G^{\ddagger}_{298}$ = 15.0 (1) kcal mol^{-1}). None of the variations have any obvious advantage over known alkoxide/NAr complexes for metathesis of ordinary or strained cyclic olefins. An attempt to prepare a derivative containing the $OC(CF_3)_2$(tolyl) ligand yielded W[$OC(C_6H_3Me)(CF_3)_2$](NAr)[$OC(CF_3)_2$(tolyl)](CH_2-*t*-Bu), formed by addition of an ortho CH bond to the W=C bond (space group $P2_1/c$, a = 16.821 (2) Å, b = 11.951 (1) Å, c = 19.455 (4) Å, β = 93.852 (8)°, V = 3920.5 Å^3, Z = 4, M_r 943.6, ρ(calcd) = 1.606 g cm^{-3}, μ = 31.09 cm^{-1}; R = 0.038, R_w = 0.043).

Introduction

The activity of complexes of the type W(CH-*t*-Bu)-(NAr)(OR)$_2$[1] (Ar = 2,6-diisopropylphenyl; OR = O-*t*-Bu, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, $OC(CF_3)_2(CF_2CF_2CF_3)$) in the metathesis of olefins[2] depends critically upon the nature of OR. For example, the complex in which OR = $OCMe(CF_3)_2$ is an active catalyst for the metathesis of ordinary olefins at rates that may be as high as 10^3 turnovers per minute at 25 °C in a hydrocarbon solvent, while analogous W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ complexes do not react readily with internal olefins.[3] Tungstacyclobutane complexes have been observed and isolated in some cases,[1,4] and the required new alkylidene complexes in active metathesis catalyst systems have been observed.[1] On the other hand, W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ *will* react readily with more reactive monomers such as norbornenes,[3,5] benzvalene,[6] 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]-deca-3,7,9-triene,[7] and acetylene,[8] a circumstance that allows one to prepare essentially monodisperse living polymers and block copolymers.[8,9] Analogous molybdenum catalysts also have been prepared[10] and seem to have important advantages over tungsten catalysts for polymerizing functionalized norbornenes[11] and norbornadienes.[12] In the latter case some remarkable stereoselectivities have been observed (proposed >98% trans and tactic). Tungsten and especially molybdenum ring-opening metathesis polymerization catalysts appear to be more tolerant of functionalities and have activities that are more controllable than those that contain more oxophilic metals such as titanium[13] and tantalum[14] or Lewis acids.[15]

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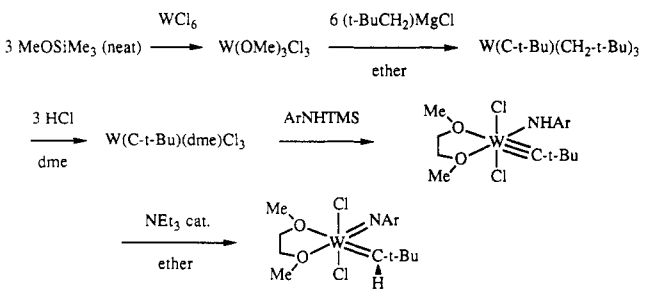
Scheme I



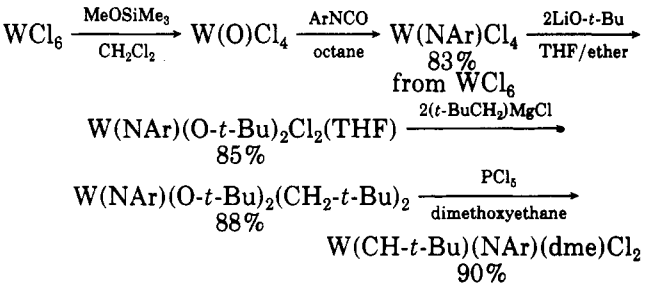
Among the several important questions that one might ask are as follows: Can simpler catalyst syntheses be developed, can related four-coordinate catalysts that contain imido ligands other than the (2,6-diisopropylphenyl)imido ligands be prepared, and can anionic ligands other than electron-withdrawing alkoxides yield active catalysts? In this paper we answer some of these questions for the tungsten catalyst system, present a simple synthesis of a versatile catalyst precursor, and report the crystal structures of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$, one of the most successful catalysts for controlled ring-opening metathesis polymerizations, and W[OC(C_6H_3Me)(CF_3)$_2$](NAr)[O-(CF_3)$_2$(tolyl)](CH_2-*t*-Bu). Some of the results reported here have appeared in preliminary versions.[5,16]

Results

New Preparations of Catalyst Precursors. The original preparation of W(CH-*t*-Bu)(NAr)(dme)Cl_2 (NAr = N-2,6-C_6H_3-*i*-Pr_2; dme = 1,2-dimethoxyethane)[16] consists of the sequence of reactions shown in Scheme I. Unfortunately, WCl_6 is usually contaminated by W(O)Cl_4 and therefore must be purified, a process that is relatively inconvenient on a large scale in the laboratory. The preparation of W(C-*t*-Bu)(CH_2-*t*-Bu)$_3$[17] in the next step consumes 6 equiv of Grignard reagent, requires a tedious distillation of the product, and gives only a 50–60% yield. Removal of the neopentyl groups, addition of the amido ligand, and proton transfer to generate the imido neopentylidene complex all take place in high yield.[1]

A more convenient route to W(CH-*t*-Bu)(NAr)(dme)Cl_2 was developed that also involves five steps, but simpler ones (Scheme II). One convenience is that the normal W(O)Cl_4 impurity in WCl_6 need not be removed; impure WCl_6 virtually can be titrated to an orange end point characteristic of W(O)Cl_4. Addition of only 1 equiv of $MeOSiMe_3$ to WCl_6 presumably yields Me_3SiCl and unstable W(OMe)Cl_5, which decomposes to give W(O)Cl_4 and methyl chloride. A recent improvement of this step

Scheme II



employs more readily available and purer $Me_3SiOSiMe_3$.[18] Crude W(O)Cl_4 may be used in the second step, which proceeds smoothly to give brown W(NAr)Cl_4 in 83% overall yield from WCl_6. Subsequent reactions to give W(NAr)(O-*t*-Bu)$_2$$Cl_2$(THF) and W(NAr)(O-*t*-Bu)$_2$(CH_2-*t*-Bu)$_2$ take place smoothly and can be scaled up readily. We can be confident that they are monomers but do not know structural details.

The last reaction in Scheme II is unusual in transition-metal chemistry, but is probably related to the preparation of alkyl halides from alcohols and various phosphorus reagents.[19] Only 1 equiv of PCl_5 is required. We speculate that the oxygen atom of the first *tert*-butoxide ligand is attacked by PCl_4^+, followed by attack by chloride at the metal. The ultimate fate of the *tert*-butyl group (e.g., *tert*-butyl chloride or isobutylene) was not investigated. The second *tert*-butoxide must be attacked similarly by a phosphorus product of the first step (e.g., P(O)Cl_3) or by HCl (if isobutylene and HCl are formed). W(NAr)-(CH_2-*t*-Bu)$_2$$Cl_2$ is a likely intermediate, one that must be unstable toward α-hydrogen abstraction, at least in the presence of a donor solvent such as dimethoxyethane, to give W(CH-*t*-Bu)(NAr)(dme)Cl_2 and neopentane (cf. α-hydrogen abstraction in Ta(CH_2-*t*-Bu)$_2$$Cl_3$ induced by THF to give Ta(CH-*t*-Bu)Cl_3(THF)$_2$[20]). These proposals are supported by reaction of W(NAr)(O-*t*-Bu)$_2$(norbornyl)$_2$ with PCl_5 to give W(NAr)(norbornyl)$_2$$Cl_2$[21] and by the reaction between W(C-*t*-Bu)(O-*t*-Bu)$_3$ and PCl_5 in dimethoxyethane to give W(C-*t*-Bu)Cl_3(dme).[22] In effect the *tert*-butoxide are "protecting groups" for halides in syntheses of alkyl halide complexes that undergo rapid α-hydrogen abstraction and that in general cannot be prepared by selective alkylation (see below). In the past α-hydrogen abstraction has been induced by the steric bulk of more than two alkyl groups in an alkyl or alkyl halide complex or by the addition of donor ligands to alkyl/halide complexes.[23]

Imido ligands have been used as protecting groups in rhenium(VII) chemistry recently, ultimately being replaced by two chlorides upon protonation by HCl and removal of the imido ligand as the ammonium salt.[24] This approach has led to the most convenient preparation of a precursor to tungsten catalysts, one that is analogous to the recently published synthesis of Mo(CHCMe_2Ph)-

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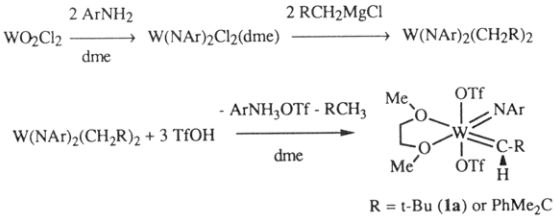
Scheme III



(NAr)(triflate)$_2$(dme) (Scheme III).[25] WO_2Cl_2 can be purchased commercially, or it can be prepared readily from WCl_6 by employing $Me_3SiOSiMe_3$ in refluxing toluene.[18] It reacts slowly with ArNCO in refluxing toluene to give $W(NAr)_2Cl_2$ or more rapidly with ArNH(TMS) or $ArNH_2$ in dimethoxyethane to give $W(NAr)_2Cl_2(dme)$. $W(NAr)_2Cl_2(dme)$ reacts smoothly with RCH_2MgCl (R = *t*-Bu, CMe_2Ph) to give $W(NAr)_2(CH_2R)_2$. Neophyl (CH_2CMe_2Ph) is advantageous for several reasons: (i) neophyl chloride is inexpensive ($\sim^1/_{50}$th the cost of neopentyl chloride), (ii) neophyl complexes tend to be slightly more crystalline and more easily handled than neopentyl complexes, and (iii) the methyl groups in the neophyl or neophylidene ligand offer an additional stereochemical NMR probe. Both $W(NAr)_2(CH_2R)_2$ complexes are formed in high yield and are nicely crystalline.

The final step in the synthesis of a catalyst precursor is the virtually quantitative reaction between $W(NAr)_2(CH_2R)_2$ and triflic acid. The most logical intermediate in this reaction is $W(NAr)(CH_2R)_2(OTf)_2$, formed by multiple protonation of an imido ligand and removal of it as the anilinium salt. $W(NAr)(CH_2R)_2(OTf)_2$ should be quite unstable with respect to loss of alkane to generate "$W(CHR)(NAr)(OTf)_2$", given the ionic nature of the triflate ligand[26] and the relative instability of dineopentyl complexes when the metal is relatively positively charged.[23] A surprising turn of events that makes this reaction successful is that $W(CHR)(NAr)(OTf)_2(dme)$ is relatively stable to triflic acid, in spite of the potential for protonating either the alkylidene or the imido ligand, perhaps largely because of the remaining relatively high positive charge on the metal and tightly bound dme. (NMR studies suggest that the bound dme in the pseudooctahedral species does not exchange with free dme on the NMR time scale.) Although the isopropyl groups in the N-2,6-C_6H_3-*i*-Pr_2 ligand are equivalent, the methyl groups in them are not; i.e., the phenyl ring does not rotate rapidly about the N–C bond. The structure of **1** is proposed to be that shown in Scheme III on the basis of the structure of $Mo(CH\text{-}t\text{-}Bu)(NAr)(OTf)_2(dme)$.[25] The chemical shifts for H_α and C_α in **1a** and **1b** are consistent with the metal being relatively positively charged (Table I).

A great deal of work has gone into attempting to prepare $W(NAr)(CH_2\text{-}t\text{-}Bu)_2Cl_2$ or $W(CH\text{-}t\text{-}Bu)(NAr)(dme)Cl_2$ by selectively alkylating $W(NAr)Cl_4$ with a variety of alkylating agents under a variety of conditions. $W(CH\text{-}t\text{-}Bu)(NAr)(dme)Cl_2$ is produced in low yield (up to ~20%), but mostly $W(CH\text{-}t\text{-}Bu)(NAr)(CH_2\text{-}t\text{-}Bu)_2$ (see later) and $W(NAr)(CH_2\text{-}t\text{-}Bu)_3Cl$ are the products, in addition to unidentified insoluble materials. In short, selective dialkylation of $W(NAr)Cl_4$ for some time now in our hands has not been successful. Some conditions still may be devised that will yield $W(CH\text{-}t\text{-}Bu)(NAr)(dme)Cl_2$ directly from $W(NAr)Cl_4$ by partial alkylation, but that possibility is appearing more and more remote. Similar problems were noted in the $W(NPh)Cl_4$ system.[27] We are still operating under the assumption that $W(NAr)(CH_2\text{-}t\text{-}Bu)_2Cl_2$ is relatively reactive toward addition of another group and also relatively unstable toward loss of neopentane to give "$W(NAr)(CH\text{-}t\text{-}Bu)Cl_2$", a species that is likely to be susceptible to further alkylation.

Table I. NMR Data for Alkylidene Complexes[a]

compd	$\delta(H_\alpha)$ (J_{HW}, Hz)	$\delta(C_\alpha)$	J_{CH}, Hz	J_{CW}, Hz
$W(CH\text{-}t\text{-}Bu)(NAr)(OTf)_2(dme)$ (**1a**)	11.20	292.7		
$W(CHCMe_2Ph)(NAr)(OTf)_2(dme)$ (**1b**)	11.35	291.1		
$W(CH\text{-}t\text{-}Bu)(NAr')(dme)Cl_2$ (**2**)	10.03	283.9	111	
$W(CH\text{-}t\text{-}Bu)(NAr')(O\text{-}t\text{-}Bu)_2$ (**3a**)	8.11	236.5	113	202
$W(CH\text{-}t\text{-}Bu)(NAr')[OCMe_2(CF_3)]_2$ (**3b**)	8.47	245.1	113	200
$W(CH\text{-}t\text{-}Bu)(NAr')[OCMe(CF_3)_2]_2$ (**3c**)	8.91	254.1	115	196
$W(CH\text{-}t\text{-}Bu)(NAr')[OC(CF_3)_2(CF_2CF_2CF_3)]$ (**3d**)	9.50	263.0[b]	115	193
$W(CHEt)(NAr')[OCMe(CF_3)_2]_2$ (**4**)[c]	9.25			
$W(CH\text{-}t\text{-}Bu)(NAr)(OAr)_2$ (**6**)	8.41 (16)	243.4	121	197
$W(CH\text{-}t\text{-}Bu)(NAr)(OCMe_2Ph)_2$ (**7**)	7.55			
$W(CH\text{-}t\text{-}Bu)(NAr)(OCEt_3)_2$ (**8**)	7.91 (14)			
$W(CH\text{-}t\text{-}Bu)(NAr)(CH_2\text{-}t\text{-}Bu_2)$ (**11**)	6.74 (15)	247.2	102	
$W(CH\text{-}t\text{-}Bu)(NAr)(SAr)_2$ (**12**)	8.35 (11)	274.4	106	173
$W(CHEt)(NAr)(OCEt_3)_2$ (**9**)	8.24			
$W(CHEt)(NAr)(NPh_2)_2$ (**10**)	8.36 (15)	262.6	114	194
$W(CHSiMe_3)(NAr)(OAr)_2$ (**14a**)	9.35 (15)[f] 10.46[f]	220.4[g] 223.3[g]	110 135	
$W(CHSiMe_3)(NAr)[OCMe_2(CF_3)]_2$[d] (**14b**)	9.47 (11)[e]	230.5	110	
$W(CHSiMe_3)(NAr)[OCMe(CF_3)_2]_2$[d] (**14c**)	9.97	242.8		
$W[CHSi(OMe)_3](NAr)(OAr)_2$ (**15a**)	9.55	195.7	160	154
$W[CHSi(OMe)_3](NAr)[OCMe_2(CF_3)]_2$ (**15b**)	9.46	194.6		
$W[CHSi(OMe)_3](NAr)[OCMe(CF_3)_2]_2$ (**15c**)	9.93	206.1	160	150

[a] All spectra were run in C_6D_6 at 25 °C unless otherwise noted. [b] Solvent CD_2Cl_2. [c] Contaminated with $\{W(NAr')[OCMe(CF_3)_2]_2\}_2$; see text. [d] See ref 1. [e] −50 °C. [f] −20 °C. [g] −40 °C.

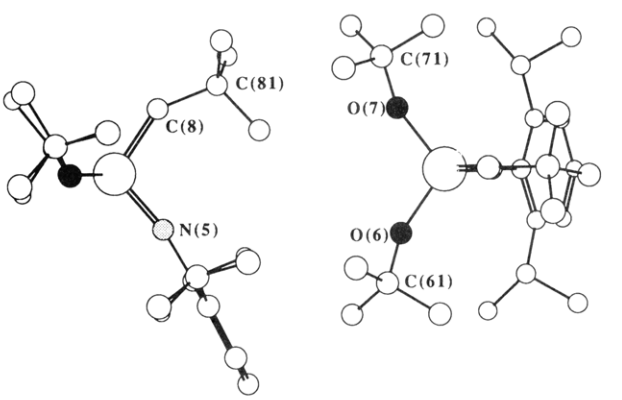


Figure 1. Two views of $W(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(O\text{-}t\text{-}Bu)_2$.

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Table II. Summary of Crystal Data, Data Collection, and Structure Refinement

	W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$	13
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a, Å	14.050 (5)	16.821 (2)
b, Å	18.885 (5)	11.951 (1)
c, Å	11.123 (5)	19.455 (4)
α, deg	92.22 (3)	90
β, deg	108.30 (3)	93.852 (8)
γ, deg	79.25 (2)	90
V, Å^3	2752 (2)	3902 (2)
Z	4	4
ρ(calcd), g cm^{-3}	1.381	1.61
temp, °C	−65	20
μ, cm^{-1}	43.03	31.09
diffractometer	Rigaku AFC6R	Enraf-Nonius CAD 4
radiation (λ, Å)	Mo Kα (0.71069)	Mo Kα (0.71069)
monochromator	graphite cryst	graphite cryst
scan type	ω–2θ	ω–2θ
scan range, deg	$0 < 2\theta < 55$	$1.05 < \theta < 27.34$
rflns measd	$+h,+k,\pm l$	$\pm h,+k,+l$
no. of rflns collected	11 367 (unique), 6716 ($I > 3\sigma(I)$)	8805 (unique), 6254 ($I > 2\sigma(I)$)
R	0.039	0.038
R_w	0.043	0.043

X-ray Study of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$. An important question is whether the structure of a complex that is virtually inactive for the metathesis of ordinary internal olefins (W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$[1,3]) is analogous to that of W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$,[1] a very active metathesis catalyst for internal olefins, or whether there is some structural reason W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ is relatively inactive, e.g., that it is actually a dimer. An X-ray study of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (Table II) shows that it is, in fact, a pseudotetrahedral monomer. Two views are shown in Figure 1, and relevant bond distances and angles are listed in Table III. Two virtually identical molecules of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ were found in the unit cell. We will discuss only molecule 2. Bond distances and angles should be compared with those in W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (also listed in Table II); there are no significant differences.

The overall geometry of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ is close to tetrahedral, the range of interligand angles being 104–113°, with the smallest being C(8)–W–N(5). The C(8)–W–N(5) and (~104°) compares favorably with the C=W=O angle of 101.6 (8)° in W(O)(CH-*t*-Bu)(PMe$_3$)$_2$Cl$_2$[28] and 106.7 (6)° in W(O)(CH-*t*-Bu)(PEt$_3$)Cl$_2$[29] and the C=Mo=N angle of 101.4 (5)° in Mo(CH-*t*-Bu)(NAr)(triflate)$_2$(dme).[25]

The two *tert*-butoxide ligands appear to be normal with W–O bond lengths of ~1.90 Å and W–O–C bond angles of 144–148°. Although the differences in W–O bond length and W–O–C bond angles in the *tert*-butoxide complex versus those in the OCMe(CF$_3$)$_2$ complex are not statistically significant, they are at least in the direction that one would expect for what is likely to be a more basic (in both a σ and a π sense) *tert*-butoxide ligand (relative to a OCMe(CF$_3$)$_2$ ligand). Note that the two *tert*-butoxide ligands are turned away from one another and away from the imido ligand, as one would expect on the basis of steric interactions.

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 sp hybridization about the N atom and likely donation of the nitrogen lone pair to the metal.[30] 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(8)–W–N(5) plane, 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 just significantly smaller W–N–C angle in the *tert*-butoxide complex versus that in the hexafluoro-*tert*-butoxide complex may result from the somewhat greater steric interactions in the hexafluoro-*tert*-butoxide complex.

The three features of the structure of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ that are virtually identical with those found in W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$ are the W=C bond length, the W–C$_\alpha$–C$_\beta$ angle, and the syn orientation of the alkylidene ligand. (The fact that C(81), C(8), W, and N(5) all lie in the same plane is now what is to be expected in such circumstances.[23]) The phenyl ring of the imido ligand lies perpendicular to the C(8)–W–N(5) plane, thereby forcing the *tert*-butyl groups of the *tert*-butoxide ligands to turn away from the isopropyl methyl groups. The *tert*-butyl groups in the *tert*-butoxide ligands in turn force the *tert*-butyl group in the neopentylidene ligand to point toward the imido ligand, which probably forces the W–N(5)–C$_{ipso}$ bond to bend slightly, thereby bringing the series of steric interactions full circle. One might conclude that the imido ligand is a powerful steric force on the entire molecule and that the sterically most open "pocket" for the alkylidene substituent is in the region between C(8) and N(5).

Preparation of N-2,6-C$_6$H$_3$Me$_2$ (NAr′) Complexes. We chose to base the chemistry of alkylidene complexes around the (2,6-diisopropylphenyl)imido ligand[1] not only because we felt that an imido ligand would be less likely than an oxo or relatively small imido ligand (e.g., phenyl or *tert*-butyl) to bridge between metals or to be attacked or displaced by alkylating agents or other strong nucleophiles but also because the O-2,6-C$_6$H$_3$-*i*-Pr$_2$(OAr) ligand was so successful in the development of well-characterized acetylene metathesis catalysts.[31] Other alkoxides (e.g., *tert*-butoxide or OCMe$_2$(CF$_3$)) also were successful to varying degrees in acetylene metathesis, but the 2,6-C$_6$H$_3$-*i*-Pr$_2$ group seemed to be the largest, most readily available one that could be found in an imido ligand. (2,6-Diisopropylaniline is commercially available.) That choice may prove to be important for other reasons that are now only beginning to be elucidated through X-ray studies.

We decided to try to establish the extent to which the N-2,6-C$_6$H$_3$-*i*-Pr$_2$(NAr) ligand is required. A readily accessible minimal variation of that ligand is one that contains methyl groups in the ortho positions instead of isopropyl groups. Since this work was done before the development of the new synthetic routes, the initial route (Scheme I) was followed. Ongoing studies are concerned with determining the generality of the synthesis shown in Scheme III for a variety of imido ligands.

Orange W(NHAr′)(C-*t*-Bu)(dme)Cl$_2$ (Ar′ = 2,6-C$_6$H$_3$Me$_2$) can be prepared virtually quantitatively from

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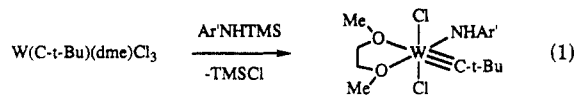
(31) (a) Murdzek, J. S.; Schrock, R. R. In *Carbyne Complexes*; Verlag Chemie: Weinheim, New York, 1988. (b) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342.

Table III. Selected Bond Distances (Å) and Angles (deg) in W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$ Compared with the Equivalent Bond Distances and Angles in W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$[a]

W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$		W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$		
			molecule 2	molecule 1
W-C(20)	1.859 (22)	W-C(8)	1.892 (7)	1.863 (8)
W-N(11)	1.708 (17)	W-N(5)	1.748 (6)	1.731 (6)
W-O(31)	1.903 (16)	W-O(6)	1.863 (5)	1.879 (5)
W-O(41)	1.902 (14)	W-O(7)	1.877 (5)	1.866 (5)
C(20)-W-N(11)	100.9 (9)	C(8)-W-N(5)	103.7 (3)	104.4 (3)
O(31)-W-N(11)	112.2 (7)	O(6)-W-N(5)	113.4 (3)	110.5 (3)
O(41)-W-N(11)	113.0 (8)	O(7)-W-N(5)	111.3 (2)	113.1 (3)
W-N(11)-C(11)	175.6 (15)	W-N(5)-C(51)	167.4 (5)	169.1 (5)
W-C(20)-C(21)	144.8 (18)	W-C(8)-C(81)	144.1 (6)	146.1 (6)
W-O(31)-C(31)	140.7 (13)	W-O(6)-C(61)	147.8 (5)	145.0 (5)
W-O(41)-C(41)	142.8 (14)	W-O(7)-C(71)	144.4 (5)	147.8 (5)
O(31)-W-O(41)	112.3 (7)	O(6)-W-O(7)	108.1 (2)	108.9 (2)
C(20)-W-O(31)	112.4 (8)	C(8)-W-O(6)	109.6 (3)	110.6 (3)
C(20)-W-O(41)	105.4 (8)	C(8)-W-O(7)	110.7 (3)	109.3 (3)

[a] Molecules 1 and 2; the notation refers to molecule 2.

W(C-*t*-Bu)(dme)Cl$_3$ (eq 1) in ether that contains some dimethoxyethane. Its NMR and IR spectra are entirely



(1)

1

analogous to those for W(NHAr)(C-*t*-Bu)(dme)Cl$_2$;[1] the neopentylidyne α-carbon resonance is found at 303.9 ppm (304.5 ppm in the NAr analogue) and the NH stretch at 3220 cm^{-1}. ^{1}H NMR spectra in the presence of dme suggest that free and coordinated dme exchange rapidly at 25 °C. The structure shown in eq 1 is proposed by analogy with related NAr compounds; it is not known whether Ar′ points toward or away from the neopentylidyne ligand.

Triethylamine catalyzes the conversion of W(NHAr′)(C-*t*-Bu)(dme)Cl$_2$ into W(CH-*t*-Bu)(NAr′)(dme)Cl$_2$ (**2**; eq 2) smoothly in high yield (86% isolated). As we have

$$\text{W(NHAr')(C-}t\text{-Bu)(dme)Cl}_2 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{NEt}_3\text{ cat.}} \underset{\mathbf{2}}{\text{W(CH-}t\text{-Bu)(NAr')(dme)Cl}_2} \quad (2)$$

observed before,[1] this type of catalyzed proton transfer reaction is relatively slow for a complex that contains alkoxides in place of chlorides. Consistent with this trend is the fact that W(NHAr′)(C-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$·0.5dme can be prepared readily in high yield from W(NHAr′)(C-*t*-Bu)(dme)Cl$_2$, and it cannot be transformed into W(CH-*t*-Bu)(NAr′)[OCMe(CF$_3$)$_2$]$_2$, a known compound (see later). It is not known whether the dme is weakly bound or is present only in the crystal lattice. We speculate that Et$_3$N actually dehydrohalogenates the amido ligand and then NEt$_3$HCl reprotonates the neopentylidyne ligand. All indications are that dme also is labile in **2**. The structure of **2** probably is analogous to that of W(CH-*t*-Bu)(NAr)(dme)Cl$_2$ (Scheme I).

From **2** the series of alkoxide complexes (**3a–d**) shown in eq 3 can be prepared. The isolated yields of the yellow

$$\text{W(CH-}t\text{-Bu)(NAr')(dme)Cl}_2 \xrightarrow[\text{2MCl, -dme}]{\text{+2MOR}} \underset{\mathbf{3a}\text{: M = Li, OR = O-}t\text{-Bu}\quad \mathbf{3b}\text{: M = Li, OR = OCMe}_2\text{(CF}_3\text{)}\quad \mathbf{3c}\text{: M = Li, OR = OCMe(CF}_3\text{)}_2\quad \mathbf{3d}\text{: M = K, OR = OC(CF}_3\text{)}_2\text{(CF}_2\text{CF}_2\text{CF}_3\text{)}}{\text{W(CH-}t\text{-Bu)(NAr')(OR)}_2} \quad (3)$$

to yellow-orange products are as low as 60% because of their high solubility, even in pentane. We assume that they are all pseudotetrahedral complexes closely analogous to W(CHPh)(NAr)[OCMe(CF$_3$)$_2$]$_2$ and W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$. Proton and carbon NMR data shown in Table I differ little from the data for the analogous NAr compounds. The most important feature is the progressively larger chemical shift for H$_\alpha$ and C$_\alpha$ as OR varies in the series OR = O-*t*-Bu, OCMe$_2$(CF$_3$), OCMe(CF$_3$)$_2$, OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$), as one would now expect as the electron-withdrawing ability of the alkoxides increases.

We have tried to prepare many other W(CH-*t*-Bu)(NR)(dme)Cl$_2$ complexes (e.g., those in which R = Ph, 3,5-C$_6$H$_3$Me$_2$, *t*-Bu) via routes analogous to that shown in Scheme I but so far have not been able to do so. The synthetic route shown in Scheme III may prove to be more amenable to further variations of the imido ligand, although it does not seem likely at this stage that catalysts that are active, yet more stable, than those containing the NAr ligand will result.

At the other end of the scale one might expect the N-2,6-C$_6$H$_3$-*t*-Bu$_2$ imido ligand to be the most sterically protected of all. Although O-2,6-C$_6$H$_3$-*t*-Bu$_2$ ligands are prone to undergo CH cleavage reactions in the *t*-Bu group,[32] the linear nature of the imido ligand might reduce the rate of intramolecular CH cleavage reactions. However, so far neither the route shown in Scheme I nor that shown in Scheme II has allowed us to prepare a species containing a W-N-2,6-C$_6$H$_3$-*t*-Bu$_2$ bond. Presumably steric problems are too severe under conditions similar to those used to prepare analogous N-2,6-C$_6$H$_3$-*i*-Pr$_2$ and N-2,6-C$_6$H$_3$Me$_2$ complexes.

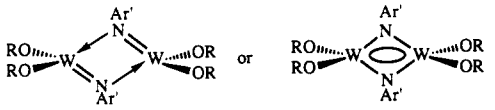
The activity of the NAr′ complexes prepared here roughly parallels that for the NAr complexes[1] as the OR ligand becomes more electron withdrawing. The reaction between **3c** and *cis*-3-hexene occurs readily, and with care a mixture of largely orange platelets of what appears to be **4** (by NMR studies) mixed with chocolate brown nuggets (**5**; eq 4) can be obtained. If this mixture is redissolved

$$\mathbf{3c} \xrightarrow[\text{cis-3-hexene (excess)}]{} \underset{\mathbf{4}}{\text{W(CHEt)(NAr')[OCMe(CF}_3\text{)}_2\text{]}_2} \rightarrow \underset{\mathbf{5}\ (\sim 60\%)}{\text{“W(NAr')[OCMe(CF}_3\text{)}_2\text{]}_2\text{”}} \quad (4)$$

in pentane and left at room temperature for 2 h, then **5** is isolated in good yield; no **4** remains. The preferred preparation of **5** is to treat **3c** with a mixture of *cis*- and *trans*-2-pentene. We could not obtain **4** in pure form, but

(32) (a) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502. (b) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177. (c) Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153.

its ^1H NMR spectrum ($\delta(H_\alpha)$ at 9.25 ppm, a triplet with J_{CH} = 5.6 Hz) is what one would expect for a propylidene complex, the propylidene H_α resonance always being found at slightly lower field than H_α in an analogous neopentylidene complex (8.91 ppm in **3c**). We propose that **5** is a dimer which contains bridging N-2,6-$C_6H_3Me_2$ ligands:



5 [OR = $OCMe(CF_3)_2$]

Unfortunately, crystals that have been obtained so far have not been suitable for a complete X-ray study, although the tungsten atoms could be located and their positions were consistent with the dimeric formulation. NMR spectra and elemental analyses show clearly that no organic product of decomposition of the propylidene complex is present in the solid product, but we have not yet been able to determine the fate of the propylidene ligand. A working hypothesis is that **4** decomposes bimolecularly more readily than the analogous NAr complex because the NAr′ ligand is less sterically demanding than the NAr ligand. A plausible alternative is that tungstacyclobutane intermediates rearrange to olefins more readily in less crowded molecules.

Variations of the X Ligand in W(CH-*t*-Bu)(NAr)X_2. One of the fundamental requirements for synthesizing stable W(CHR)(NAr)X_2 complexes appears to be that X be relatively large, especially if R is not *tert*-butyl or the approximate equivalent (e.g., CMe_2Ph). It is suspected that intermolecular reactions (most simply formation of a dimer, possibly followed by ligand transfer and/or subsequent decomposition) otherwise would lead to deactivation or decomposition. Therefore, we set out to prepare examples of stable W(CH-*t*-Bu)(NAr)X_2 complexes where X is not *tert*-butoxide or a partially fluorinated relative[1] and to explore their reactions with olefins. Most of these syntheses begin with W(CH-*t*-Bu)(NAr)(dme)Cl_2 for historical reasons, although there is no obvious reason why more readily accessible W(CHR)(NAr)$(OTf)_2$(dme) (R = *tert*-butyl or CMe_2Ph) would not work equally well. One piece of evidence to date suggests that to be the case. Addition of 2 equiv of $LiOCMe(CF_3)_2$ to W(CH-*t*-Bu)-(NAr)$(OTf)_2$(dme) in diethyl ether gives W(CH-*t*-Bu)-(NAr)$[OCMe(CF_3)_2]_2$, which does not retain dimethoxyethane and which therefore can be isolated in crystalline form directly from the reaction mixture.[33] Presumably dimethoxyethane binds to lithium in LiOTf more readily than to lithium in LiCl or tungsten in W(CH-*t*-Bu)-(NAr)$[OCMe(CF_3)_2]_2$ and thereby allows W(CH-*t*-Bu)-(NAr)$[OCMe(CF_3)_2]_2$ to be isolated in dme-free crystalline form directly upon workup.

Phenoxide complexes are important variations because of the ready availability of phenoxide ligands with a wide variety of steric and electronic properties. Some of these properties have been exploited by Basset in order to control tungsten alkylidene activity for olefin metathesis.[34] One phenoxide ligand that has been used in acetylene metathesis systems is O-2,6-C_6H_3-*i*-Pr_2(OAr). **6a** (eq 5) is a highly crystalline orange complex formed in high yield. It does not react readily with *cis*-2-pentene but will slowly

$$\text{W(CH-}t\text{-Bu)(NAr)(dme)Cl}_2 \xrightarrow[-2\text{LiCl, -dme}]{2\text{LiOAr}} \underset{\mathbf{6a}}{\text{W(CH-}t\text{-Bu)(NAr)(OAr)}_2} \quad (5)$$

isomerize *cis*-2-pentene to *trans*-2-pentene. No new alkylidene complexes are observed, consistent with conversion of a small percentage of **6a** to a more reactive (less crowded) ethylidene or propylidene complex. However, **6a** will react readily with ethylene and some terminal olefins. Studies of this type are reported separately.[35]

One might have expected to be able to isolate a variety of other alkoxide complexes, but in general we have not found this to be the case. Among the alkoxides we have not yet successfully employed to make W(CH-*t*-Bu)-(NAr)$(OR)_2$ complexes are O-2,6-$C_6H_3Me_2$, O(adamantyl), $OC(CH_2Ph)_3$, OCH_2-*t*-Bu, and $OCHMe_2$, although at least O(adamantyl) and $OC(CH_2Ph)_3$ would seem to be bulky enough to produce stable species. We feel confident that some ultimately will be successful, especially if donor solvents such as THF are employed, in which case five-coordinate THF adducts most likely would be formed. Yellow-orange W(CH-*t*-Bu)(NAr)$(OCMe_2Ph)_2$ (**7**) was obtained only as an oil that appeared to decompose slowly. Ortho metalation of the phenyl ring could be a significant problem, as it is in the attempted synthesis of the analogous $OC(CF_3)_2Ph$ complex (see next section).

An alkoxide ligand that should have approximately the same donor ability as *tert*-butoxide, but is considerably more bulky, is $OCEt_3$. W(CH-*t*-Bu)(NAr)$(OCEt_3)_2$ (**8**) can be prepared straightforwardly, but as expected, it is even less reactive than W(CH-*t*-Bu)(NAr)$(O\text{-}t\text{-Bu})_2$ toward olefins. A propylidene complex (**9**) has been prepared as shown in eq 6, according to ^1H NMR spectra of the crude

$$\text{W(CHEt)(NAr)[OCMe(CF}_3)_2]_2\text{(EtCHCHEt)}_{0.8} \xrightarrow[-0.8\ \text{3-hexene}]{2\text{KOCEt}_3} \underset{\mathbf{9}}{\text{W(CHEt)(NAr)(OCEt}_3)_2} \quad (6)$$

product. (W(CHEt)(NAr)$[OCMe(CF_3)_2]_2$(EtCHCHEt)$_{0.8}$ is the approximate stoichiometry of a mixture of W-(CHEtCHEtCHEt)(NAr)$[OCMe(CF_3)_2]_2$ and W(CHEt)-(NAr)$[OCMe(CF_3)_2]_2$ that is usually obtained.[1]) Unfortunately **9** also appears to be an oil (~90% pure by NMR spectroscopy), which does not sublime without decomposition and which does not survive chromatography. However, it is worth noting that it is stable in the condensed state, whereas W(CHEt)(NAr)$(O\text{-}t\text{-Bu})_2$ can only be observed in solution and appears to decompose rapidly when such solutions are concentrated.[1] **9** reacts more readily than **8** with olefins, but we have not pursued that chemistry, in part because of the oily nature of the $OCEt_3$ complexes and because there is no obvious advantage to employing them in metathesis reactions.

Amido ligands could be valuable as a means of adding more electron density to the metal and thereby further deactivating it toward reaction with an olefin. Because the chemistry of primary amido complexes might be complicated by proton-transfer reactions, we chose to prepare a secondary amido complex. The reaction shown in eq 7

$$\text{W(CHEt)(NAr)[OCMe(CF}_3)_2]_2\text{(EtCH=CHEt)}_{0.8} \xrightarrow[-\text{LiCl, -0.8 3-hexene}]{+2\text{LiNPh}_2} \underset{\mathbf{10}}{\text{W(CHEt)(NAr)(NPh}_2)_2} \quad (7)$$

yields orange crystalline **10** in high yield. **10** does not react with ordinary internal olefins, and although norbornene

(33) Thomas, J. Unpublished observations, Massachusetts Institute of Technology.

(34) (a) Quignard, F.; Leconte, M.; Basset, J.-M. *J. Mol. Catal.* **1986**, *36*, 13. (b) Quignard, F.; Leconte, M.; Basset, J.-M.; Hus, L.-Y.; Alexander, J. J.; Shore, S. G. *Inorg. Chem.* **1987**, *26*, 4272.

(35) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R.; Thomas, J. *Organometallics*, in press.

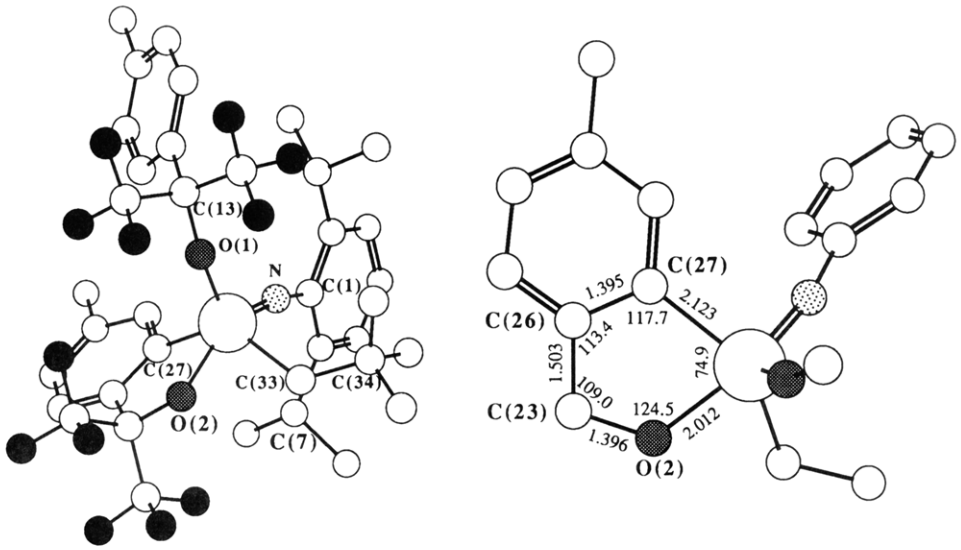


Figure 2. Structure of W[OC(C_6H_3Me)(CF_3)$_2$](NAr)[OC(CF_3)$_2$(tolyl)](CH_2-*t*-Bu) (**13**).

is polymerized to high-molecular-weight polynorbornene, we have not observed the alkylidene at the end of the living polynorbornene by proton NMR spectroscopy, a surprising result since the rate of initiation should be greater than the rate of propagation for steric reasons. Therefore, we believe that some other complex present in an undetectable amount is actually polymerizing norbornene. The fact that the H_α resonance in **10** is found at approximately the same position as it is in W(CHEt)(NAr)(O-*t*-Bu)$_2$ (8.40 ppm[1]) suggests that electronically the metal in **10** (assuming it is isostructural with W(CHEt)(NAr)(O-*t*-Bu)$_2$) is at least as deactivated toward ordinary olefins as is W(CHEt)(NAr)(O-*t*-Bu)$_2$. Apparently, however, **10** is simply too crowded to be useful in metathesis. The same is likely to be true of analogous NMe_2 derivatives. The possibility of preparing bulky *primary* amido complexes (e.g., NH(*t*-Bu)) remains to be explored.

An example of a W(CHR)(NAr)(alkyl)$_2$ complex has been prepared as shown in eq 8. **11** appears to form in

$$\text{W(CH-}t\text{-Bu)(NAr)(dme)Cl}_2 \xrightarrow[-2\text{MgCl}_2,\ -\text{dme}]{2t\text{-BuCH}_2\text{MgCl}} \underset{\mathbf{11}}{\text{W(CH-}t\text{-Bu)(NAr)(CH}_2\text{-}t\text{-Bu)}_2} \quad (8)$$

high yield, but it is difficult to isolate in high yield because of its extreme solubility in pentane. Its ^{1}H NMR spectrum shows an H_α resonance at 7.13 ppm, the highest field shift of any neopentylidene complex. It does not react readily with *cis*-3-hexene, although it (or possibly some impurity in it) will slowly isomerize *cis*-3-hexene. A small percentage of it (or some impurity) does polymerize norbornene to high-molecular-weight polynorbornene. It reacts slowly (minutes) with ethylene and very slowly (days) with 1-pentene to give as yet unidentified products. Like **10**, **11** simply appears to be too crowded to react readily with small molecules. Attempts to prepare benzyl and 2,4,6-trimethylbenzyl analogues of **11** were not successful. Attempts to prepare W(CHEt)(NAr)(CH$_2$-*t*-Bu)$_2$ from W(CHEt)(NAr)[OC(CF_3)$_2$Me]$_2$(EtCHCHEt)$_{0,8}$ (eq 6) appeared promising ($\delta(H_\alpha)$ at 6.79 ppm), but a stable crystalline product could not be obtained.

The reaction shown in eq 9 (Ar = 2,6-C_6H_3-*i*-Pr$_2$) gives orange crystalline **12** in good yield. Its proton NMR

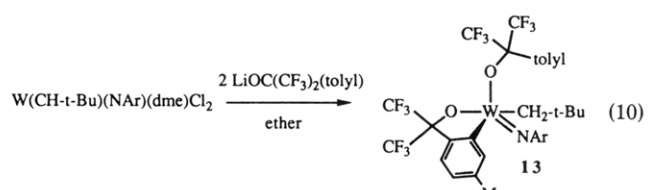
$$\text{W(CH-}t\text{-Bu)(NAr)(dme)Cl}_2 \xrightarrow{2\text{LiSAr}} \underset{\mathbf{12}}{\text{W(CH-}t\text{-Bu)(NAr)(SAr)}_2} \quad (9)$$

Table IV. Selected Bond Distances (Å) and Angles (deg) in 13

W–N	1.746 (5)	W–C(33)	2.159 (7)
W–O(1)	1.866 (4)	O(1)–C(13)	1.408 (7)
W–O(2)	2.012 (4)	O(2)–C(23)	1.396 (7)
W–C(27)	2.123 (6)		
W-C(33)-C(34)	126.7 (5)	C(27)–W–O(2)	74.9 (2)
W–O(1)–C(13)	162.0 (4)	C(27)–W–O(1)	110.5 (2)
W–N–C(1)	165.7 (4)	C(27)–W–N	89.3 (2)
C(33)–W–C(27)	130.3 (2)	O(2)–W–O(1)	101.9 (2)
C(33)–W–O(2)	75.4 (2)	O(2)–W–N	145.4 (2)
C(33)–W–O(1)	114.0 (2)	O(1)–W–N	112.5 (2)
C(33)–W–N	93.4 (2)		

spectrum is invariant down to −90 °C; thus, the thiolates do not bridge strongly. It is interesting to note that the H_α resonance in **12** is found at 8.35 ppm, close to that for W(CH-*t*-Bu)(NAr)(OAr)$_2$ (8.41 ppm). This is somewhat surprising if the SAr ligand is actually a significantly better σ donor than the OAr ligand and if better σ donor lead to complexes in which the H_α resonance is found at higher field. **12** reacts with terminal olefins, ethylene, and norbornene, although the reactions have not yet been explored in detail. On the basis of the greater stability of tantalum alkylidene complexes containing the triisopropylbenzenethiolate ligand versus that of the analogous diisopropylphenoxide complexes,[36] tungsten SAr complexes should be good candidates for ROMP reactions involving strained olefins.

X-ray Study of W[OC(C_6H_3Me)(CF_3)$_2$](NAr)[OC(CF_3)$_2$(tolyl)](CH_2-*t*-Bu). One of the most active metathesis catalysts in the W(CH-*t*-Bu)(NAr)(OR)$_2$ class is that where OR = OC(CF_3)$_2$Me.[1] An attempt to prepare the OC(CF_3)$_2$(tolyl) derivative yielded the complex shown in eq 10, formed by adding an ortho C—H bond in the tolyl



(10)

group across the W=C bond. Selected bond distances and

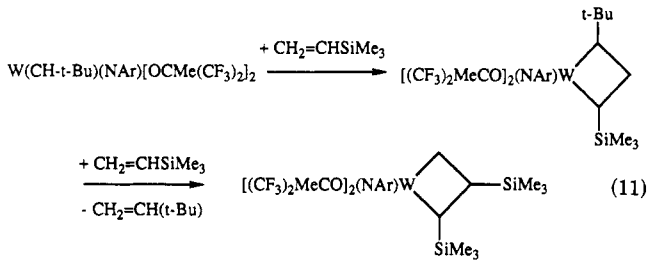
(36) (a) Ehrenfeld, D.; Kress, J.; Moore, B. D.; Osborn, J. A.; Schoettel, G. *J. Chem. Soc., Chem. Commun.* **1987**, 129. (b) Schoettel, G.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1989**, 1062.

angles are listed in Table IV. Views of the molecule can be found in Figure 2.

The structure of **13** is far from an ideal trigonal bipyramid or square pyramid. It is perhaps best described as a square pyramid with O(1) at the apical position (Figure 2, left side). The smallest apical/basal angle is O(1)–W–O(2) (101.9 (2)°), the others being more normal (110.5 (2), 114.0 (23), 112.5 (2)°). The tungsten atom is located 0.69 Å above the best basal plane defined by O(2), C(27), C(33), and N, while O(1) is 2.55 Å above this plane. The WOC_3 ring is virtually planar with bond distances and angles (Figure 2, right side) that are not unusual. The long W–O(2) bond length (2.012 (4) Å) and small W–O(2)–C(23) angle (124.5 (3)°) compared to those in the other alkoxide ligand (1.866 (4) Å, 162.0 (4)°) are consistent with the enforced sp^3 or sp^2 hybridization at O(2) and possibly also less donation of π electron density from O(2) to W. Bond distances and angles in the imido, neopentyl, and OC-$(CF_3)_2$(tolyl) ligands are all normal. One somewhat unusual feature of the structure of **13** is the relatively short distance between tungsten and the methine proton on C(7) (3.03 Å).

Activation of an aryl C–H bond to make a five-membered ring is not surprising in view of the number of related activations of a C–H bond in a *tert*-butyl group in 2,6-di-*tert*-butylphenoxide complexes of tantalum.[32] After one chloride is replaced by an $OC(CF_3)_2$(tolyl) ligand, dimethoxyethane probably is lost from the coordination sphere to create a relatively coordinatively unsaturated metal. We propose that the relatively electrophilic metal then interacts with the C–H_{ortho} electron pair and activates H_{ortho} toward migration to the nucleophilic alkylidene α-carbon atom.

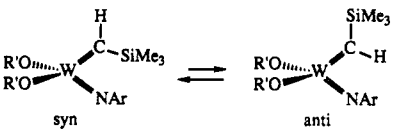
Silyl-Substituted Methylene Complexes. W(CH-*t*-Bu)(NAr)$[OCMe(CF_3)_2]_2$ reacts with excess vinyltrimethylsilane to give *tert*-butylethylene and the α,β-disubstituted tungstacyclobutane complex shown in eq 11.[1]



(11)

No products of catalytic metathesis of vinyltrimethylsilane are detected at 25 °C, and *tert*-butylethylene is the only observed olefin product (in stoichiometric yield). Therefore, the initial WC_3 ring that contains an α-*t*-Bu group and an α'-TMS group breaks up to yield W$(CHSiMe_3)$-(NAr)$[OCMe(CF_3)_2]_2$, which then scavenges a second equivalent of vinyltrimethylsilane. The other possible initial WC_3 ring (α-*t*-Bu/β-TMS) probably forms, but this metallacycle does not lose *t*-BuCH=$CHSiMe_3$, probably for the same reason that the α-*t*-TMS/β-TMS tungstacyclobutane complex does not lose Me_3SiCH=$CHSiMe_3$; i.e., steric repulsion between the substituents forces loss of the monosubstituted olefin. Reactions involving Me_3SiCH=CH_2 therefore are not complicated by catalytic olefin metathesis.

W(CH-*t*-Bu)(NAr)$(OAr)_2$ reacts with excess vinyltrimethylsilane to give W$(CHSiMe_3)$(NAr)$(OAr)_2$ (**14a**) in ~80% yield after recrystallization from pentane. In the room-temperature proton NMR spectrum of **14a** *two* broad H_α resonances are observed at 10.42 and 9.32 ppm in a ratio of 45:55, which sharpen at −20 °C (^{183}W satellite peaks are observed on the peak at 9.32 ppm; J_{WH} = 15 Hz) and broaden and coalesce (at 58 °C) to give a single H_α resonance at higher temperatures, all reversibly. these data suggest that **14a** is a mixture of interconverting syn and anti rotamers (eq 12). The ^{13}C NMR spectrum supports



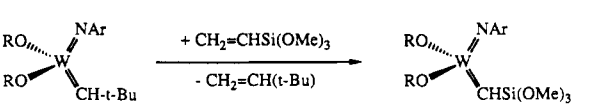
(12)

this view, two C_α resonances being observed at 223.3 ppm (d, J_{CH} = 135 Hz) and 220.4 ppm (d, J_{CH} = 110 Hz) at low temperatures. A complete line-shape analysis of the temperature-dependent alkylidene H_α resonances for the interconverting rotamers of W$(CHSiMe_3)$(NAr)$(OAr)_2$ gave $\Delta H^\ddagger$ = 12.7 (3) kcal mol^{-1}, $\Delta S^\ddagger$ = −7.6 (9) eu, and $\Delta G^\ddagger_{298}$ = 15.0 (1) kcal mol^{-1}. When a mixture of W-$(CHSiMe_3)$(NAr)$(OAr)_2$ and vinyltrimethylsilane in toluene-d_8 was cooled to −60 °C, no tungstacyclobutane complex could be observed by proton NMR spectroscopy.

We have already reported the syntheses of W-$(CHSiMe_3)$(NAr)$[OCMe_2(CF_3)]_2$ (**14b**) and W-$(CHSiMe_3)$(NAr)$[OCMe(CF_3)_2]_2$ (**14c**). Although the proton NMR spectrum of **14c** was sharp and unambiguous, that for **14b** was peculiar. At room temperature the H_α, C*H*Me_2, and $SiMe_3$ resonances were broad. All others were sharp. All three broad resonances became sharp when a sample was heated to 80 °C *or* cooled to −60 °C. At low temperature ^{183}W satellites could be observed on the H_α resonance (J_{CW} = 11 Hz). Chemical shift differences at high versus low temperatures were not significant. At the time no explanation of these observations were offered.[1] On the basis of the results obtained for **14a** we can postulate now that the variable-temperature NMR behavior of **14b** can be ascribed to the interconversion of syn and anti rotamers in a mixture where one rotamer predominates and where the difference in chemical shift for the two alkylidene protons is insufficient to resolve the resonances for each. At low temperature the equilibrium would shift more in favor of the predominant rotamer and only one sharp resonance might be observable. At high temperature the major and minor resonances would coalesce and sharpen to give one virtually unshifted resonance. Primarily one rotamer of **14c** must be present since no temperature-dependent behavior was observed.

A proton NMR spectrum of W(CH-*t*-Bu)(NAr)$(O\text{-}t\text{-}Bu)_2$ (C_6D_6, 0.046 M, 25 °C) containing 5 equiv of vinyltrimethylsilane after 2 h showed that ~25% of it had been converted into a compound having a broad resonance at 9.01 ppm. The 9.01 ppm resonance is also observed in the spectrum of the product formed when 2 equiv of potassium *tert*-butoxide is added to W$[CH(SiMe_3)CH(SiMe_3)$-$CH_2]$(NAr)$[OCMe_2(CF_3)]_2$. Therefore, we tentatively assign it to H_α in W$(CHSiMe_3)$(NAr)$(O\text{-}t\text{-}Bu)_2$. It seems likely that rotamers are present and are possibly interconverting on the NMR time scale, since rotamers were found for Mo(CH-*t*-Bu)(NAr)$(O\text{-}t\text{-}Bu)_2$.[25] Unfortunately, W$(CHSiMe_3)$(NAr)$(O\text{-}t\text{-}Bu)_2$ appears to be unstable under these conditions and could not be fully characterized.

Other examples of silicon-substituted alkylidene complexes may be prepared as shown in eq 13. The NMR



(13)

15a, OR = OAr
15b, OR = $OCMe_2(CF_3)$
15c, OR = $OCMe(CF_3)_2$

spectra of the resulting trimethoxysilyl-substituted alkylidene complexes **15** are dramatically different from those of **14**. The room-temperature ^1H NMR spectrum of bright yellow **15a** contains only a single sharp resonance (9.55 ppm), and the spectrum does not change significantly with temperature (−40 to +100 °C in toluene-d_8). Therefore, either rotamers of **15a** are present and interconvert rapidly on the NMR time scale or only one rotamer is present under all conditions. In the ^{13}C NMR spectrum of **15a**, a single C_α resonance is found relatively far upfield at 195.7 ppm. The CH coupling constant is relatively large (160 Hz), and J_{CW} (154 Hz) is approximately 50 Hz smaller than is typically observed (see Table I). Since J_{HW} is too small to be observed (≤5 Hz; J_{HW} in the anti isomer of **14a** is small), we propose that **15a** is entirely the anti form. The proton NMR spectra of W[CHSi(OMe)$_3$](NAr)[OCMe$_2$(CF$_3$)]$_2$ (**15b**) and W[CHSi(OMe)$_3$](NAr)[OCMe(CF$_3$)$_2$]$_2$ (**15c**), which can be prepared straightforwardly (eq 12), are similar to that of **15a** in all respects.

Discussion

The synthetic scheme shown in Scheme III is a significant advance in catalyst synthesis since all reactions take place in high yield, starting materials are all readily available, the reactions can be scaled up readily, and any catalyst can be prepared from W(CHR)(NAr)(OTf)$_2$(dme). An analogous approach has been successful for preparing molybdenum catalysts.[25] Synthesis of a related molybdenum *tert*-butylimido neopentylidene complex also relies on use of an imido ligand as a protecting group,[36] and synthesis of rhenium(VII) organometallic complexes has succeeded to a large extent because imido ligands were used as protecting groups.[24,37] It remains to be determined whether other strong acids (e.g., methanesulfonic or *p*-toluenesulfonic) can be used in the last step. There has been no incentive for doing so yet, since triflate ligands are easily displaced, even with relatively weak nucleophiles such as OCMe(CF$_3$)$_2$, and the yield of **1** is high. It would be highly desirable to be able to prepare catalysts that contain a smaller alkylidene ligand as shown in Scheme III, but preliminary experiments where CH$_2$R is CH$_2$CHMe$_2$ were not immediately successful. Although α-elimination is faster then β-elimination in one tantalum system,[38] formation of an alkylidene ligand by α-abstraction in the presence of a β-proton is still unknown.

The failure to prepare certain types of alkoxide complexes is still puzzling. However, observation of C–H activation in an OC(CF$_3$)$_2$(tolyl) complex increases the likelihood that an aryl C–H bond will be activated in other circumstances (e.g., in OCMe$_2$Ph or OC(CH$_2$Ph)$_3$ complexes) and that activation of a C–H bond could be a more general phenomenon. An example of the latter might be aliphatic C–H bond cleavage in the methyl group of an O-2,6-C$_6$H$_3$Me$_2$ complex. The fact that isopropyl methine protons are less accessible than protons in a methyl group would account for the relative stability of O-2,6-C$_6$H$_3$-*i*-Pr$_2$ complexes, although the long-range interaction of an isopropyl methine proton in an isopropyl group in the NAr ligand in **13** could be taken as evidence that even *o*-isopropyl groups under some circumstances might be susceptible to C–H bond cleavage.

An important finding is that both syn and anti alkylidene rotamers can be formed in pseudotetrahedral alkylidene imido complexes and that they can interconvert readily on the NMR time scale. The existence of rotamers could have important consequences in olefin metathesis mechanisms. Evidence has appeared recently elsewhere in the literature that rotamers are present in systems of this type.[12,25] It is rare that both rotamers can be observed, i.e., that their energies differ by less than ~2 kcal mol^{-1}. At this stage it would appear that the syn rotamer is favored in most circumstances, and one could argue on the basis of the reported X-ray studies that steric interactions are minimized in this rotamer. Therefore, the syn rotamer should be favored when the substituent on the alkylidene ligand is large or when the alkoxide ligand is large. Whether the converse is true (a smaller alkylidene prefers the anti conformation) is not clear at this stage, although it can be argued that **15** is all anti if the NMR parameters for syn and anti rotamers are distinctive. (In the syn rotamers for which data are available J_{HW} = 11–15 Hz, J_{CH} = 102–121 Hz, and J_{CW} = 173–202 Hz, while in the anti rotamers J_{HW} is too small to observe, J_{CH} is larger (160 Hz), and J_{CW} is smaller (150–154 Hz).) An intriguing possibility is that the stability of either the syn or anti rotamer is also enhanced for electronic reasons. For example, the electrons in the C–H$_\alpha$ bond in the syn rotamer could be donated to the metal, a circumstance that would account for the relatively high values for J_{HW}, low values for J_{CH}, and high values for J_{CW}.[39] Experiments designed to probe for answers to these questions are under way.

Indirect evidence for facile alkylidene ligand rotation in other tungsten alkylidene complexes has been obtained recently.[40] Alkylidene ligands in bis(cyclopentadienyl) alkylidene complexes of tantalum investigated some time ago were found to be relatively resistant to rotation, probably because no orbitals are available to form a π bond to an alkylidene ligand after it has rotated 90°. In contrast, "distorted alkylidene" ligands in reduced tantalum complexes rotate readily.[23] Alkylidene ligand rotation is likely to be relatively facile in circumstances where metal orbitals that are not involved to any significant extent in bonding to another ligand can stabilize the rotated alkylidene ligand in the transition state. In the case of the tetrahedral species discussed here formation of a square-planar core geometry in the process of interconverting syn and anti rotamers cannot be ruled out but seems less likely than retention of the tetrahedral geometry for steric reasons. Future studies will be directed toward a further understanding of the mechanism of alkylidene ligand rotation and the connection, if any, between alkylidene ligand rotation and reactivity of the metal complex with olefins and other substrates.

Conclusions

A variety of W(CH-*t*-Bu)(NAr)X$_2$ complexes now can be prepared relatively conveniently via W(CH-*t*-Bu)(NAr)(OTf)$_2$(dme). Although there are now examples of X = alkyl, amide, and thiolate, in addition to alkoxide, the most common and versatile X, only X = thiolate holds any promise as a metathesis catalyst (for strained rings). Steric factors must be finely balanced in W(CH-*t*-Bu)(NAr)(OR)$_2$ complexes, since replacing the NAr ligand by an N-2,6-C$_6$H$_3$Me$_2$ ligand yields species that are significantly less stable toward bimolecular decomposition. C–H bond activation within an alkoxide ligand has now been documented and could be a significant problem in a variety of circumstances, especially when the metal is relatively electrophilic. Readily interconvertible syn and anti rotamers have been observed in W(CHSiMe$_3$)(NAr)(OR)$_2$ complexes; all evidence suggests that they are present in

(37) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448.
(38) Turner, H. W.; Schrock, R. R.; Fellmann, J. D.; Holmes, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4942.
(39) We thank W. E. Crowe for pointing out this possibility.
(40) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 3953.

a wide variety of circumstances.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres 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 deuterated NMR solvents were passed through a column of activated alumina.

W(C-*t*-Bu)Cl_3(dme),[17] W(CHEt)(NAr)[OCMe$(CF_3)_2]_2$(3-hexene)$_{0.8}$ (a mixture of W(CHEt)(NAr)[OCMe$(CF_3)_2]_2$ and W(CHEtCHEtCHEt)(NAr)[OCMe$(CF_3)_2]_2$),[1] W(CHSiMe_3)(NAr)[OCMe$_2(CF_3)]_2$,[1] and W(CHSiMe_3)(NAr)[OCMe$(CF_3)_2]_2$[1] were prepared as described in the literature. Me_3SiNHAr (Ar = 2,6-C_6H_3-*i*-Pr_2) was prepared from Me_3SiCl and LiNHAr in ether at room temperature and was distilled prior to use. All other reagents were purchased from commercial sources and purified by standard techniques. Neophyl Grignard reagent (~1 M) was prepared straightforwardly from neophyl chloride in ether. Neopentyl chloride was treated with concentrated sulfuric acid for several hours until the acid layer was clear and was washed, dried, and purified as described in the literature.[41]

NMR data are listed in parts per million downfield from TMS for proton and carbon and are 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.

Preparation of Compounds. W(O)Cl_4. A solution of Me_3SiOMe (26.5 g) in 80 mL of dichloromethane was added dropwise over 6 h to a rapidly stirred suspension of tungsten hexachloride (101 g, 255 mmol) in 750 mL of dichloromethane. The reaction mixture was stirred for 20 h. The volatile components were removed to give an orange-red solid weighing 86.9 g. This material is pure enough to be used in the next step of the synthesis. If desired, it may be sublimed at 80 °C ($<0.1 \times 10^{-3}$ mmHg). A recent improvement of this procedure employs $Me_3SiOSiMe_3$.[18]

W(NAr)Cl_4. Freshly distilled 2,6-diisopropylphenyl isocyanate (49.4 g, 243 mmol) was added to a suspension of crude W(O)Cl_4 (83.0 g, 243 mmol) from the preceding reaction in 800 mL of octane. This mixture was heated to reflux for several hours until CO_2 evolution ceased. The dark brown precipitate was filtered, washed with pentane, and dried to give 106 g (211 mmol, 83% from WCl_6) of the product: ^{1}H NMR δ 7.08 (H_m), 6.19 (H_p), 4.67 (C*H*Me_2), 1.21 (CH*Me*$_2$).

W(NAr)Cl_4 is sufficiently pure for further use but cannot be recrystallized from noncoordinating solvents because of its low solubility. It can be dissolved in either diethyl ether or THF and crystallized as the dark green monoadducts in ~75% overall yield based on $WOCl_4$: W(NAr)Cl_4(THF) ^{1}H NMR (CD_2Cl_2) δ 7.69 (d, 2, H_m), 6.70 (t, 1, H_p), 4.72 (br m, 4, THF), 4.56 (sept, 2, C*H*Me_2), 2.17 (br m, 4, THF), 1.37 (d, 12, *Me*$_2$CH). Anal. Calcd for $WC_{16}H_{25}NOCl_4$: C, 33.54; H, 4.40; N, 2.44. Found: C, 33.69; H, 4.32; N, 2.24.

W(NAr)(O-*t*-Bu)$_2Cl_2$(THF). A chilled suspension (−35 °C) of LiO-*t*-Bu (33.4 g, 422 mmol in 150 mL of ether) was added over 30 min to a chilled (−35 °C) solution of W(NAr)Cl_4 (106 g, 211 mmol) in a mixture of tetrahydrofuran (150 mL) and ether (600 mL). The resulting mixture was stirred at room temperature for 20 h. The color turned from the green characteristic of W(NAr)Cl_4 in THF, to an intense red that we believe is the color of W(NAr)(O^{t}Bu)Cl_3(THF) (the analogous NPh complex has been isolated[27]), to orange-yellow. The reaction mixture was filtered through Celite and concentrated in vacuo. Recrystallization of the resulting solid from minimal pentane by cooling to −30 °C gave 116 g (180 mmol, 85%) of yellow crystals: ^{1}H NMR δ 7.14 (H_m), 6.75 (H_p), 4.61 (C*H*Me_2), 4.14 (THF), 1.47 (*t*-Bu), 1.41 (CH*Me*$_2$), 1.39 (THF). Anal. Calcd for $WC_{24}H_{43}NO_3Cl_2$: C, 44.46; H, 6.68; N, 2.16. Found: C, 44.95; H, 6.63; N, 2.06.

W(NAr)(CH_2-*t*-Bu)$_2$(O-*t*-Bu)$_2$. A prechilled (−35 °C) ethereal solution of neopentylmagnesium chloride (1.86 M, 24.8 mL, 26.2 mmol) was added over 15 min to a chilled solution of W(NAr)(O-*t*-Bu)Cl_2(THF) (15 g, 23.1 mmol) in 50 mL of ether. The resulting solution was stirred at room temperature for 24 h. The orange-yellow mixture was filtered through Celite, and the filter cake was washed thoroughly with ether. Orange flakes formed upon concentrating the filtrate in vacuo. These were collected and recrystallized from pentane to give 13.24 g (20.4 mmol, 88%) of the product as bright orange crystals: ^{1}H NMR δ 7.09 (H_m), 6.84 (H_p), 3.95 (C*H*Me_2), 1.89 (br s, 4, CH_2-*t*-Bu), 1.42 (s, 18, *t*-Bu), 1.32 (s, 18, *t*-Bu), 1.30 (CH*Me*$_2$). Anal. Calcd for $WC_{30}H_{57}NO_2$: C, 55.64; H, 8.87. Found: C, 55.22; H, 8.66.

W(NAr)(CH-*t*-Bu)(dme)Cl_2. Finely ground phosphorus pentachloride (2.25 g, 10.8 mmol) was added to a chilled (−35 °C) suspension of W(NAr)(CH_2-*t*-Bu)$_2$(O-*t*-Bu)$_2$ (7.00 g, 10.8 mmol) in 120 mL of dimethoxyethane. The mixture was warmed to room temperature and stirred for an additional 1 h after all the solids had disappeared. The mixture was then concentrated in vacuo until an orange powder formed. This material was washed with cold pentane to give 5.75 g (90%) of the product as a yellow-orange powder that was identical with a sample prepared by the other method.[1] This synthesis can fail virtually completely if the dimethoxyethane is not scrupulously dry and the PCl_5 not rigorously pure.

WO_2Cl_2. This preparation is a variation of that reported by Gibson.[18] (Commercially available material is also suitable for subsequent reactions presented here.) WCl_6 (5.0 g, 12.6 mmol) was dissolved in 45 mL of toluene. A solution of hexamethyldisiloxane (5.36 mL, 25.2 mmol) was added slowly over 45 min, and the mixture was stirred at room temperature for an additional 1 h. A reflux condenser was attached and the mixture heated at reflux overnight to give an orange solution containing a white precipitate of WO_2Cl_2, which was collected on a glass frit and washed with dichloromethane to yield 3.1 g (86%) of the product.

W(NAr)$_2Cl_2$(dme) (2). (a) From WO_2Cl_2. (i) 2,6-Diisopropylphenyl isocyanate (7.09 g, 34.9 mmol) was added to a suspension of WO_2Cl_2 (5.00 g, 17.4 mmol), and minimal toluene (~10 mL) was added. The mixture was heated at reflux for 10 days, during which time the yellow suspension dissolved. Enough toluene was added to dissolve any red-brown precipitate, any unreacted WO_2Cl_2 was filtered off, and the solvent was removed from the filtrate in vacuo. Ether (50 mL) containing dimethoxyethane (2.0 mL, 19.2 mmol) was added, and the solution was stirred for 1 h, during which time an orange precipitate began to form. The solvent was again removed in vacuo, and the crude product was washed with cold (−40 °C) pentane to yield 7.67 g (65%) of orange microcrystals that were sufficiently pure for further use. An analytically pure sample was recrystallized from a mixture of toluene and pentane: ^{1}H NMR δ 7.13 (H_m), 6.85 (H_p), 4.28 (sept, 2, C*H*Me_2), 3.45 (s, 6 *Me*OCH_2CH_2O*Me*), 3.05 (s, 4, MeOC*H*$_2$C*H*$_2$OMe), 1.30 (d, 12, CH*Me*$_2$); ^{13}C NMR δ 150.90 (C_{ipso}), 144.98 (C_o), 126.23 (C_m), 122.84 (C_p), 71.11 (t, MeO*C*H$_2$CH$_2$OMe), 63.66 (q, *Me*OCH$_2$CH$_2$O*Me*), 27.60 (d, *C*HMe$_2$), 25.13 (q, CH*Me*$_2$). Anal. Calcd for $WC_{28}H_{44}N_2Cl_2O_2$: C, 48.36; H, 6.38; N, 4.03. Found: C, 47.95; H, 6.29; N, 4.15.

(ii) WO_2Cl_2 (3.00 g, 10.4 mmol) was suspended in dimethoxyethane (30 mL), and Me_3SiCl (6.78 g, 62 mmol), 2,6-lutidine (2.31 g, 21.6 mmol), and ArNH(TMS) (5.24 g, 20.8 mmol) were added. Upon addition of ArNH(TMS) the solution turned dark red and a white precipitate formed. After 15 h the solution was filtered through Celite and the cake washed with ether until the washings were colorless. The solvent was removed from the filtrate in vacuo, and the resulting dark orange solid was washed with pentane to give 4.62 g (64%) of the product as a bright orange powder.

(iii) WO_2Cl_2 (3.011 g, 10.5 mmol) was suspended in dme (5 mL), and chlorotrimethylsilane (11.5 g), 2,6-lutidine (4.6 g, 43 mmol), and 2,6-diisopropylaniline (3.9 g, 22 mmol) were added. The orange, cloudly mixture was refluxed under argon for 16 h and was then filtered to remove lutidine hydrochloride. Solvents were removed from the filtrate in vacuo to give a red oil containing some crystalline solids, to which pentane was added in order to precipitate the product; yield 5.08 g (70%).

(b) From W(NAr)Cl_4(THF). Dimethoxyethane (3.15 g, 34.9 mmol) was added to a suspension of W(NAr)Cl_4(THF) (10.0 g,

(41) The acid wash procedure was one of many contributions by the checkers of the synthesis of W(C-*t*-Bu)(CH_2-*t*-Bu)$_3$.[17b]

17.5 mmol) in cold ether (−40 °C; 50 mL). A solution of 2,6-diisopropylaniline (3.09 g, 17.5 mmol) and triethylamine (3.53 g, 34.9 mmol) in 15 mL of cold ether was added dropwise. The mixture was stirred overnight and filtered through Celite, and the solvent was removed in vacuo. The product was extracted into ether, and the solution was filtered. Removing the solvent in vacuo yielded orange microcrystals (9.32 g, 79%).

(c) From $WOCl_4$. Chlorotrimethylsilane (7.95 g, 73.17 mmol) and dimethoxyethane (2.64 g, 29.3 mmol) were added to a suspension of $WOCl_4$ (5.0 g, 14.7 mmol) in 100 mL of ether. 2,6-Diisopropylaniline (5.19 g, 29.3 mmol) and 2,6-lutidine (7.27 g, 58.5 mmol) were added, and the solution turned dark red. The mixture was stirred overnight, during which time the color changed to a bright orange. The product was isolated as in (b); yield 4.2 g (41%).

$W(NAr)_2(CH_2$-t-$Bu)_2$. Neopentylmagnesium chloride (1.48 M, 7.8 mL, 11.5 mmol in ether) was added to a cold (−40 °C) solution of $W(NAr)_2Cl_2$(dme) (4.00 g, 5.75 mmol) in ether. The orange solution immediately turned bright yellow, and a white precipitate began to form. The mixture was warmed to room temperature over 75 min and was filtered. The solvent was removed in vacuo, and the crude product was recrystallized from a mixture of ether and pentane at −40 °C in yield 3.04 g (78%) of yellow crystals: ^{1}H NMR δ 7.04 (H_m), 6.94 (H_p), 3.70 (sept, 2, C*H*Me$_2$), 2.14 (s, 2, CH_2CMe$_3$), 1.15 (d, 6, CH*Me*$_2$); ^{13}C NMR δ 152.27 (C_{ipso}), 142.86 (C_o), 125.53 (C_m), 122.84 (C_p), 91.19 (t, J = 105, CH_2CMe$_3$), 34.05 (q, CH$_2$C*Me*$_3$), 28.24 (d, CHMe$_2$), 23.37 nq, CH*Me*$_2$). Anal. Calcd for $WC_{34}H_{56}N_2$: C, 60.35; H, 8.34; N, 4.14. Found: C, 60.06; H, 8.12; N, 4.13.

W(CH-t-Bu)(NAr)(OSO$_2$CF$_3$)$_2$(dme) (1a). Triflic acid (0.137 mL, 1.55 mmol) in 2 mL of cold dimethoxyethane was added over a period of 1 min to a cold (−40 °C) solution of $W(NAr)_2(CH_2$-t-Bu$)_2$ (0.35 g, 0.517 mmol) in 5 mL of dimethoxyethane. The solution was warmed to room temperature and was stirred for 2 h, during which time the color changed from dark yellow to light yellow. The solvent was removed in vacuo. (It is important to remove any excess dme, since it solubilizes the anilinium triflate.) The crude product was extracted into 10 mL of cold toluene, and the mixture was filtered to yield 0.320 g (76%) of light orange-yellow powder, which was used without further purification: ^{1}H NMR δ 11.20 (s, C*H*CMe$_3$), 7.07 (H_m), 6.94 (H_p), 3.88 (sept, 2, C*H*Me$_2$), 3.85 (s, 3, *Me*$_A$OCH$_2$CH$_2$OMe$_B$), 3.07 (t, 2, Me$_A$OCH_2CH$_2$OMe$_B$), 2.81 (s, 3, Me$_A$OCH$_2$CH$_2$O*Me*$_B$), 2.65 (t, 2, Me$_A$OCH$_2$CH_2OMe$_B$), 1.46 (s, 9, CHC*Me*$_3$), 1.42 (d, 6, CH*Me*$_A$), 1.24 (d, 6, CH*Me*$_B$); ^{13}C NMR δ 292.72 (C_α), 149.98, 149.50, 129.18, 123.84, 73.64, 70.41, 67.13, 62.95, 49.22, 33.82, 27.98, 25.46, 23.64, 23.46.

$W(NAr)_2(CH_2CMe_2Ph)_2$. This compound was prepared by a method analogous to that used to prepare $W(NAr)_2(CH_2$-t-Bu$)_2$; yield 90%. An analytically pure sample was prepared by recrystallization from the minimum amount of pentane: ^{1}H NMR δ 7.42 (d, 2), 7.23 (t, 2), 7.1 (t, 1), 7.04 (d, 2), and 6.95 (t, 1) are all assigned to aryl protons, 3.66 (sept, 2, C*H*Me$_2$), 1.58 (s, 2, CH_2CMe$_2$Ph), 1.44 (s, 6, CH$_2$C*Me*$_2$Ph), 1.12 (d, 12, CH*Me*$_2$); ^{13}C NMR δ 152.17 (C_{ipso}), 150.83 (C_{ipso}), 142.82 (C_o), 128.65 (C_o), 126.86 (C_m), 126.47 (C_p), 125.43 (C_m), 122.94 (C_p), 88.88 (t, J = 118, CH_2CMe$_2$Ph), 39.74 (CH$_2$CMe$_2$Ph), 32.81 (CH$_2$C*Me*$_2$Ph), 27.88 (CH*Me*$_2$), 23.60 (CH*Me*$_2$). Anal. Calcd for $WC_{44}H_{60}N_2$: C, 65.99; H, 7.55; N, 3.50. Found: C, 65.78; H, 7.57; N, 3.35.

W(CHCMe$_2$Ph)(NAr)(OSO$_2$CF$_3$)$_2$(dme) (1b). A solution of triflic acid (0.377 mL, 4.26 mmol) in 5 mL of cold dme was added over a period of 1 min to a cold (−40 °C) solution of $W(NAr)_2$-$(CH_2CMe_2Ph)_2$ (1.10 g, 1.37 mmol) in 40 mL of dme. The solution was warmed to room temperature and was stirred for 7 h. The solvent was removed in vacuo—it is important to remove any excess dme, as it appears to solubilize the anilinium triflate—and the crude product extracted into 20 mL of cold toluene and the extract filtered to yield 0.95 g (78%) of light yellow powder, which was used without further purification: ^{1}H NMR (except aryl) δ 11.35 (s, 1, C*H*CMe$_2$Ph), 3.86 (sept, 2, C*H*Me$_2$), 3.69 (s, 3 *Me*$_A$OCH$_2$CH$_2$OMe$_B$), 3.05 (t, 2, Me$_A$OCH_2CH$_2$OMe$_B$), 2.81 (s, 3, Me$_A$OCH$_2$CH$_2$O*Me*$_B$), 2.67 (t, 2 Me$_A$OCH$_2$CH_2OMe$_B$), 1.94 (s, 6, CHC*Me*$_2$Ph), 1.40 (d, 6 CH(*Me*$_A$)$_2$), 1.23 (d, 6, CH(*Me*$_B$)$_2$); ^{13}C NMR δ 291.11 (C_α), 151.90, 150.25, 149.19, 137.83, 129.26, 126.56, 125.63, 123.85, 73.706, 70.387, 67.087, 63.175, 54.93, 33.99, 27.95, 23.56, 23.30. Anal. Calcd for $WC_{28}H_{39}NO_8F_6S_2$: C, 38.24; H, 4.47; N, 1.59. Found: C, 38.32; H, 4.43; N, 1.50.

W(C-t-Bu)(NAr')(dme)Cl$_2$. 1,2-Dimethoxyethane (0.52 mL, 5.0 mmol) and *N*-(trimethylsilyl)-2,6-dimethylaniline (1.94 g, 10.0 mmol) were added to a stirred solution of W(C-t-Bu)(dme)Cl$_3$ (4.49 g, 9.99 mmol) in ether (110 mL) at −40 °C. The mixture was stirred as it was warmed to ambient temperature. After 1 h the solvents were removed from the dark red-brown solution to give an orange foam. Recrystallization of the orange solid at −40 °C from a minimal amount of ether containing a few drops of dimethoxyethane afforded orange crystals (5.17 g, 97% yield): ^{1}H NMR δ 10.10 (NH), 7.03 (H_m), 6.93 (H_p), 3.24 (s, 6, OCH$_3$), 3.09 (s, 4, OCH$_2$), 2.70 (s, 6, CH$_3$), 0.94 (s, 9, t-Bu); ^{13}C NMR δ 303.9 (C-t-Bu), 155.9 (C_{ipso}), 134.0 (C_o), 128.0 (C_m), 125.7 (C_p), 72.4 (t, J_{CH} = 147, OCH$_2$), 64.0 (q, J_{CH} = 148, OCH$_3$), 49.8 (CMe$_3$), 31.1 (C*Me*$_3$), 20.8 (aryl Me); IR (Nujol) 3220 (NH) cm^{-1}. Anal. Calcd for $WC_{17}H_{29}Cl_2NO_2$: C, 38.22; H, 5.47. Found: C, 38.31; H, 5.52.

W(C-t-Bu)(NHAr')[OCMe(CF$_3$)$_2$]$_2$·0.5dme. A solution of LiOCMe(CF$_3$)$_2$ (0.38 g, 2.0 mmol) in ether (5 mL) was added to a solution of W(C-t-Bu)(NHAr')(dme)Cl$_2$ (0.54 g, 1.0 mmol) in ether (25 mL) at −40 °C. The solution was stirred as it was warmed to room temperature. After 45 min the solvent was removed in vacuo and the residue was extracted with pentane. The extracts were filtered through Celite and concentrated in vacuo to give an oily orange solid that was exposed to a high vacuum for 2 days at ambient temperature. The resulting orange solid was recrystallized twice from pentane at −40 °C to afford pale yellow platelets (0.56 g, 72% yield): ^{1}H NMR δ 7.63 (NH), 6.99 (H_m), 6.87 (H_p), 3.22 (s, 2, OCH$_2$), 3.05 (s, 3, OCH$_3$), 2.18 (aryl Me), 1.74 (OCMe(CF$_3$)$_2$), 0.66 (t-Bu); ^{13}C NMR δ 291.9 (C-t-Bu), 155.4 (C_{ipso}), 132.9 (C_o), 128.0 (C_m), 125.6 (C_p), 124.4 (q, J_{CF} = 287, CF$_3$), 123.9 (q, J_{CF} = 288, CF$_3$), 82.0 (sept, $^2J_{CF}$ = 29, OCMe(CF$_3$)$_2$), 70.8 (t, J_{CH} = 143, OCH$_2$), 58.9 (q, J_{CH} = 140, OCH$_3$), 50.8 (CMe$_3$), 31.6 (C*Me*$_3$), 20.2 (OC*Me*(CF$_3$)$_2$), 19.1 (aryl Me); IR (Nujol) 3270 (NH), 3295 (NH) cm^{-1}. Anal. Calcd for $WC_{23}H_{30}F_{12}NO_3$: C, 35.40; H, 3.88. Found: C, 35.47; H, 3.99.

W(CH-t-Bu)(NAr')(dme)Cl$_2$ (2). Dimethoxyethane (0.60 mL, 5.8 mmol) and NEt$_3$ (0.18 mL, 1.3 mmol) were added to a solution of W(C-t-Bu)(NHAr')(dme)Cl$_2$ (3.05 g, 5.71 mmol) in methylene chloride (100 mL) at −40 °C. The solution was warmed to 0 °C, stirred for 3–4 h, and then concentrated in vacuo without warming it above 0 °C. The resulting red-orange solid was extracted with ether, and the extracts were filtered through Celite. The filtrate was concentrated in vacuo, and a few drops of dimethoxyethane were added. Cooling the solution to −40 °C afforded a burnt orange powder (2.61 g, 86% yield). This material can be recrystallized from a mixture of methylene chloride and pentane, but it is pure enough to use in subsequent reactions. It also can be made from W(C-t-Bu)(dme)Cl$_3$ without isolating and purifying W(C-t-Bu)(NHAr')(dme)Cl$_2$: ^{1}H NMR δ 10.03 (C*H*-t-Bu), 6.88 (H_m), 6.78 (H_p), 3.20 (s, 6, OCH$_3$), 3.10 (s, 4, OCH$_2$), 2.88 (aryl Me), 1.37 (t-Bu); ^{13}C NMR δ 283.9 (d, J_{CH} = 111, C*H*-t-Bu), 153.5 (C_{ipso}), 139.3 (C_o), 128.2 (C_m), 126.5 (C_p), 71.7 (OCH$_2$), 62.2 (OCH$_3$), 46.3 (CHCMe$_3$), 33.1 (C*Me*$_3$), 20.7 (aryl Me). Anal. Calcd for $WC_{17}H_{29}Cl_2NO_2$: C, 38.22; H, 5.47. Found: C, 37.84; H, 5.31.

W(CH-t-Bu)(NAr')(O-t-Bu)$_2$ (3a). A solution of LiO-t-Bu (0.15 g, 1.9 mmol) in ether (2–3 mL) was added to a solution of W(CH-t-Bu)(NAr')(dme)Cl$_2$, and the mixture was warmed to room temperature. After 1 h the mixture was filtered and the solvent removed from the filtrate in vacuo. The residue was extracted with pentane and the extract filtered and concentrated in vacuo to give an oily red solid. Recrystallization of the oily solid from minimal pentane at −40 °C afforded yellow-orange crystals (0.31 g, 64%): ^{1}H NMR δ 8.11 (C*H*-t-Bu), 7.00 (H_m), 6.88 (H_p), 2.45 (aryl Me), 1.30 (O-t-Bu), 1.28 (C-t-Bu); ^{13}C NMR δ 236.5 (d, J_{CH} = 113, J_{CW} = 202, *C*H-t-Bu), 154.9 (C_{ipso}), 134.9 (C_o), 127.7 (C_m), 124.7 (C_p), 78.1 (OCMe$_3$), 44.0 (CCMe$_3$), 34.8 (CC*Me*$_3$), 31.9 (OC*Me*$_3$), 19.9 (aryl Me). Anal. Calcd for $WC_{21}H_{37}NO_2$: C, 48.56; H, 7.18. Found: C, 48.70; H, 6.93.

W(CH-t-Bu)(NAr')[OCMe$_2$(CF$_3$)]$_2$ (3b). An ether solution (2–3 mL) of LiOCMe$_2$CF$_3$ (0.26 g, 1.9 mmol) was added to a stirred solution of W(CH-t-Bu)(NAr')(dme)Cl$_2$ (0.50 g, 0.94 mmol) in ether (10 mL) at −40 °C. The mixture was warmed to ambient temperature. After 1 h the mixture was filtered, the solvent was removed from the filtrate in vacuo, and the residue was recrystallized from pentane at −40 °C to give yellow-orange crystals (0.36

g, 61%): ^{1}H NMR δ 8.47 (C*H*-*t*-Bu), 6.93 (H_m), 6.85 (H_p), 2.27 (aryl Me), 1.30 (s, 6, $OCMe_2(CF_3)$), 1.23 (s, 6, $OCMe_2(CF_3)$), 1.12 (*t*-Bu); ^{13}C NMR δ 245.1 (d, J_{CH} = 113, J_{CW} = 200, *C*H-*t*-Bu), 154.5 (C_{ipso}), 135.4 (C_o), 127.8 (C_m), 127.2 (CF_3), 125.9 (C_p), 79.5 (q, $^2J_{CF}$ = 29, $OCMe_2(CF_3)$), 44.7 (*C*CMe$_3$), 34.1 (CC*Me*$_3$), 24.6 (OC*Me*$_2(CF_3)$, 24.5 (OC*Me*$_2(CF_3)$), 19.3 (aryl Me). Anal. Calcd for $WC_{21}H_{31}F_6NO_2$: C, 40.21; H, 4.98. Found: C, 40.35; H, 4.96.

W(CH-*t*-Bu)(NAr′)[OCMe(CF$_3$)$_2$]$_2$ (3c). A solution of W(CH-*t*-Bu)(NAr′)(dme)Cl$_2$ (3.03 g, 5.67 mmol) in ether (40 mL) at −40 °C was treated with an ether solution (10 mL) of LiOCMe(CF$_3$)$_2$ (2.17 g, 11.5 mmol). The mixture was warmed to ambient temperature and after 1 h was filtered through Celite. The solvent was removed from the filtrate in vacuo and the residue recrystallized from pentane at −40 °C to give golden crystals (3.61 g, 87%): ^{1}H NMR δ 8.91 (C*H*-*t*-Bu), 6.85 (m, 3, H_{aryl}), 2.17 (aryl Me), 1.31 (OCMe(CF$_3$)$_2$), 1.00 (*t*-Bu); ^{13}C NMR δ 254.1 (d, J_{CH} = 115, J_{CW} = 196, *C*H-*t*-Bu), 154.5 (C_{ipso}), 135.9 (C_o), 127.8 (C_m), 127.1 (C_p), 123.9 (OCMe(*C*F$_3$)$_2$ 81.6 (sept, $^2J_{CF}$ = 30, O*C*Me(CF$_3$)$_2$), 45.6 (*C*Me$_3$), 33.4 (CC*Me*$_3$), 18.8 (OC*Me*(CF$_3$)$_2$ and aryl Me). Anal. Calcd for $WC_{21}H_{25}F_{12}NO_2$: C, 34.30; H, 3.43. Found: C, 34.41; H, 3.48.

W(CH-*t*-Bu)(NAr′)[OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)]$_2$ (3d). A solution of W(CH-*t*-Bu)(NAr′)(dme)Cl$_2$ (0.50 g, 0.94 mmol) in ether (10 mL) at −40 °C was treated with an ether solution (3–4 mL) of KOC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$) (0.70 g, 1.9 mmol). The mixture was warmed to room temperature. It was stirred for 1 h and filtered through Celite. Solvent was removed from the filtrate in vacuo, and the residue was recrystallized from pentane at −40 °C to give golden crystals (0.78 g, 79% yield): ^{1}H NMR δ 9.50 (C*H*-*t*-Bu), 6.79 (m, 3 H_m and H_p), 2.24 (aryl Me), 1.04 (*t*-Bu); ^{13}C NMR (CD_2Cl_2) δ 263.0 (d, J_{CH} = 115, J_{CW} = 193, *C*H-*t*-Bu), 155.0 (C_{ipso}), 136.8 (C_o), 128.2 (C_m), 128.1 (C_p), 121.4 (q, J_{CF} = 293, OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)), 121.2 (q, J_{CF} = 292, OC(*C*F$_3$)$_2$(CF$_2$CF$_2$CF$_3$)), 118.2 (qt, J_{CF} = 284, $^2J_{CF}$ = 34, CF$_2$CF$_2$CF$_3$), 114.4 (tt, J_{CF} = 272, $^2J_{CF}$ = 32, *C*F$_2$CF$_2$CF$_3$), 109.8 (tqt, J_{CF} = 270, $^2J_{CF}$ = 34, 32, CF$_2$*C*F$_2$CF$_3$), 87.1 (m, $^2J_{CF}$ = 29, O*C*(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)), 47.4 (*C*HCMe$_3$), 33.2 (CHC*Me*$_3$), 18.8 (aryl Me). Anal. Calcd for $WC_{25}H_{19}F_{26}NO_2$: C, 28.78; H, 1.84. Found: C, 29.09; H, 1.93.

Observation of W(CHEt)(NAr′)[OCMe(CF$_3$)$_2$]$_2$ (4). A golden suspension of W(CH-*t*-Bu)(NAr′)[OCMe(CF$_3$)$_2$]$_2$ (0.20 g, 0.27 mmol) in pentane (5 mL) at −40 °C was treated with *cis*-3-hexene (0.26 mL, 2.1 mmol). The solution was warmed to room temperature and then was taken to dryness in vacuo. The orange residue was treated in an identical fashion with more *cis*-3-hexene. The orange solid obtained after the second cycle was recrystallized from pentane at −40 °C to give a mixture of orange platelets contaminated with some brown crystals of {W(NAr′)[OCMe(CF$_3$)$_2$]$_2$}$_2$ (total 0.12 g, 60%). W(CHEt)(NAr′)[OCMe(CF$_3$)$_2$]$_2$ largely decomposes to {W(NAr′)[OCMe(CF$_3$)$_2$]$_2$}$_2$ after 2–3 h in noncoordinating solvents: ^{1}H NMR δ 9.25 (t, *J* = 5.6, C*H*Et), 6.85 (m, 3, H_m and H_p), 4.00 (dq, 2, *J* = 5.6, 7.6, CHC*H*$_2$CH$_3$), 2.20 (aryl Me), 1.26 (OCMe(CF$_3$)$_2$), 0.81 (t, 3, *J* = 7.6, CHCH$_2$C*H*$_3$).

{W(NAr′)[OCMe(CF$_3$)$_2$]$_2$}$_2$ (5). An orange suspension of W(CH-*t*-Bu)(NAr′)[OCMe(CF$_3$)$_2$]$_2$ (0.50 g, 0.68 mmol) in pentane (10 mL) was treated with 2-pentene (0.80 mL, 7.4 mmol, cis/trans mixture) at room temperature. After 2 h the dark brown solution was filtered and concentrated to dryness in vacuo. The residue was recrystallized from pentane at −40 °C to give chocolate brown crystals (0.26 g, 56%): ^{1}H NMR δ 6.96 (s, 3, H_m and H_p), 2.49 (aryl Me), 1.27 (s, 6, OCMe(CF$_3$)$_2$); ^{13}C NMR (CD_2Cl_2) δ 156.7 (C_{ipso}), 136.1 (C_o), 128.3 (C_m), 128.0 (C_p), 123.3 (CF_3), 123.2 (CF_3'), 83.5 (sept, $^2J_{CF}$ = 30, O*C*Me(CF$_3$)$_2$), 19.8 (OC*Me*(CF$_3$)$_2$), 19.6 (aryl Me). Anal. Calcd for $WC_{16}H_{15}F_{12}NO_2$: C, 28.89; H, 2.27. Found: C, 29.37; H, 2.51.

W(CH-*t*-Bu)(NAr)(OAr)$_2$ (6). The lithium salt of 2,6-diisopropylphenoxide (1.60 g, 6.19 mmol) was added to 1.82 g (3.09 mmol) of W(CH-*t*-Bu)(NAr)(dme)Cl$_2$ in 50 mL of diethyl ether at −40 °C. The solution was warmed to 25 °C and stirred for 45 min. The reaction mixture was filtered, and the filtrates were concentrated to afford an orange solid. Recrystallization of this material from minimal pentane afforded 1.74 g of product as a bright yellow solid in two crops (72%): ^{1}H NMR δ 8.41 (s, J_{HW} = 16, H_α), 7.11–6.95 (H_{aryl}), 3.71 (sept, 4, C*H*Me$_2$ (OAr)), 3.58 (sept, 2, C*H*Me$_2$ (NAr)), 1.33 (d, 12, CH*Me*$_2$), 1.27 (d, 12, CH*Me*$_2$), 1.13 (s, 9, *t*-Bu), 1.09 (d, 12, CH*Me*$_2$); ^{13}C NMR δ 243.4 (J_{CH} = 121, J_{CW} = 197, C_α), 160.1 (C_{ipso} (OAr)), 151.7 (C_{ipso} (NAr)), 145.6 (C_o (OAr), 137.7 (C_o (NAr)), 127.2, 123.6, 123.2, 123.0 (C_m and C_p for OAr and NAr), 45.6 (CHCMe$_3$), 34.1 (C*Me*$_3$, CH*Me*$_2$ (OAr), or CH*Me*$_2$ (NAr)), 28.8 (CHMe$_2$ (NAr)), 27.4 (CHMe$_2$ (OAr)), 24.0 (C*Me*$_3$, CH*Me*$_2$ (OAr), or CH*Me*$_2$ (NAr)), 23.7 (C*Me*$_3$, CH*Me*$_2$ (OAr), or CH*Me*$_2$ (NAr)), 23.5 (C*Me*$_3$, CH*Me*$_2$ (nOAr), or CH*Me*$_2$ (NAr)). Anal. Calcd for $WC_{41}H_{61}NO_2$: C, 62.85; H, 7.25. Found: C, 62.68; H, 8.01.

W(CH-*t*-Bu)(NAr)(OCMe$_2$Ph)$_2$ (7). LiOCMe$_2$Ph (241 mg, 1.70 mmol) was added to W(CH-*t*-Bu)(NAr)(dme)Cl$_2$ (500 mg, 0.848 mmol) in 25 mL of ether at −40 °C. The solution was stirred and warmed to room temperature over a period of 45 min. LiCl was filtered off and the ether removed in vacuo to afford a yellow-orange oil. This material could not be crystallized from minimal pentane at −40 °C, but by ^{1}H NMR spectroscopy it appeared to be ≥95% pure: ^{1}H NMR δ 7.55 (s, 1, H_α), 7.50–7.05 (m, 3, H_{aryl}), 4.00 (sept, 2, C*H*Me$_2$), 1.66 (s, 6, Me), 1.60 (s, 6, Me), 0.901 (d, 12, CH*Me*$_2$), 1.19 (s, 9, *t*-Bu); ^{1}H NMR (CD_2Cl_2) δ 7.57, 7.35, 7.15, 3.78, 1.76, 1.64, 1.24, 1.12; ^{13}C NMR (CD_2Cl_2) δ 239.8 (*C*H-*t*-Bu), 149.4, 145.5, 128.4, 126.5, 125.5, 122.8, 81.7, 44.8, 34.4, 33.8, 31.7, 28.0, 24.9, 23.9.

W(CH-*t*-Bu)(NAr)(OCEt$_3$)$_2$ (8). LiOCEt$_3$ (124 mg, 1.02 mmol) was added to W(CH-*t*-Bu)(NAr)(dme)Cl$_2$ (300 mg, 0.509 mmol) in 25 mL of ether at −40 °C. The solution was warmed to room temperature while it was stirred for 30 min. LiCl was filtered off and the ether removed in vacuo to afford a yellow-orange oil. This material could not be crystallized from minimal pentane at −40 °C, but it appeared to be ≥95% pure by NMR spectroscopy: ^{1}H NMR δ 7.91 (s, 1, J_{HW} = 14, H_α), 7.18–7.06 (3, H_{aryl}), 4.10 (sept, 2, C*H*Me$_2$), 1.61 (q, 12, C*H*$_2$CH$_3$), 1.34 (overlapping doublet and singlet, 21, CH*Me*$_2$ and *t*-Bu), 0.90 (t, 18, CH$_2$*Me*).

W(CHEt)(NAr)(OCEt$_3$)$_2$. LiOCEt$_3$ (10 mg, 0.0819 mmol) was added to W(CHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$(3-hexene)$_{0.8}$ (31 mg, 0.0406 mmol) in 1 mL of ether at −40 °C. The solution was stirred for 30 min and the ether removed in vacuo to afford a yellow oil whose proton NMR spectrum was consistent with the proposed product: ^{1}H NMR δ 8.24 (t, J_{HH} = 7, 1, H_α), 7.2–7.08 (3, H_{aryl}), 4.28 (sept, 2, C*H*Me$_2$ or CHC*H*$_2$CH$_3$), 4.18 (sept, 2, C*H*Me$_2$ or CHC*H*$_2$CH$_3$), 1.58 (q, 12, OC(C*H*$_2$CH$_3$)$_3$), 1.35 (d, CH*Me*$_2$), 0.87 (t, 18, OC(CH$_2$C*H*$_3$)$_3$), 1.13 (CHCH$_2$C*H*$_3$).

W(CHEt)(NAr)(NPh$_2$)$_2$ (10). A solution of W(CHEt)(NAr)[OCMe(CF$_3$)$_2$]$_2$(3-hexene)$_{0.8}$ (1.05 g, 1.27 mmol) in ether (15 mL) at −40 °C was treated with 2 equiv of LiNPh$_2$(ether)$_{0.5}$ (0.54 g, 2.6 mmol). The solution was warmed to ambient temperature. After 1 h the solvent was removed in vacuo and the orange residue recrystallized from a mixture of ether and pentane at −40 °C to give golden orange crystals (0.68 g, 73% yield): ^{1}H NMR (CD_2Cl_2) δ 8.36 (t, C*H*Et), 7.17–7.25 (m, 8, phenyl protons), 7.07 (s, 3, imido H_m, H_p), 6.96–7.03 (m, 12, phenyl protons), 3.75 (dq, $^3J_{HH}$ = 5.9, 7.4, CHC*H*$_2$CH$_3$), 3.44 (sept, 2, C*H*Me$_2$), 1.02 (d, 12, CH*Me*$_2$), 0.77 (t, 3, *J* = 7.4, CHCH$_2$C*H*$_3$); ^{13}C NMR (CD_2Cl_2) δ 262.6 (d, J_{CH} = 114, J_{CW} = 194, *C*HEt), 154.0 (phenyl C_{ipso}), 152.1 (imido C_{ipso}), 144.6 (imido C_o), 129.6 (phenyl C_m), 125.6 (imido C_p), 124.8 (phenyl C_o), 123.7 (phenyl C_p), 122.7 (imido C_m), 39.2 (*C*HCH$_2$CH$_3$), 28.3 (*C*HMe$_2$), 23.8 (CH*Me*$_2$), 17.3 (CHCH$_2$CH$_3$). Anal. Calcd for $WC_{39}H_{43}N_3$: C, 63.50; H, 5.88. Found: C, 63.37; H, 5.91.

W(CH-*t*-Bu)(NAr)(CH$_2$-*t*-Bu)$_2$ (11). W(CH-*t*-Bu)(NAr)(dme)Cl$_2$ (1.00 g, 1.69 mmol) was dissolved in ~70 mL of diethyl ether, and the solution was chilled to −40 °C. While this solution was stirred, 2.0 mL of *t*-BuCH$_2$MgCl (1.78 M in ether, 3.56 mmol, 2.10 equiv) was added. This solution was warmed to room temperature. The resulting yellow-brown reaction mixture was filtered through Celite, and the solids were rinsed with ether. The solvents were removed from the filtrate in vacuo to give a brown residue from which analytically pure orange crystals can be obtained by repeated recrystallization from pentane at −40 °C (0.69 g, 71%): ^{1}H NMR δ 7.13 (m, H_{aryl}), 6.74 (s, J_{HW} = 15, C*H*-*t*-Bu), 3.9 (sept, C*H*Me$_2$), 2.72 (d, CH_aH$_b$CMe$_3$), 1.29 (d, CH*Me*$_2$), 1.18 (s, C*Me*$_3$), 0.41 (d, CH$_a$*H*$_b$CMe$_3$); ^{13}C NMR δ 247.2 (d, J_{CH} = 102, *C*H-*t*-Bu), 153.1 (C_{ipso}), 143.6 (C_o), 125.7 (C_m), 122.9 (C_p), 89.9 (t, J_{CH} = 115, *C*H$_2$CMe$_3$), 46.4 (CH*C*Me$_3$), 37–31 (overlapping, CH$_2$*C*Me$_3$, CH$_2$C*Me*$_3$, and CHC*Me*$_3$), 28.2 (dd, *C*HMe$_2$), 24.1 (CH*Me*$_2$). Anal. Calcd for $WC_{27}H_{49}N$: C, 56.74; H, 8.64. Found: C, 56.44; H, 8.56.

W(CH-*t*-Bu)(NAr)(SAr)$_2$ (12). A solution of W(CH-*t*-Bu)(NAr)(dme)Cl$_2$ (0.900 g, 1.52 mmol) in ether (20 mL) at −40 °C was treated with NaSAr (0.663 g, 3.06 mmol). The solution

was warmed to room temperature. After 1.5 h the solution was filtered and the volatiles were removed in vacuo to give an orange foam. This was extracted with pentane, filtered through Celite, and recrystallized at −40 °C to afford orange crystals (0.82 g, 66%): ^{1}H NMR δ 8.35 (s, 1, J_{HW} = 11.5, C*H*-*t*-Bu), 7.12–6.98 (m, 9, aryl), 4.07 (sept, 4, J = 6.8, S–C*H*Me$_2$), 3.95 (sept, 2, J = 6.7, N–C*H*Me$_2$), 1.32, 1.28, 1.24 (d, 12, S–CH*Me*Me′, S–CHMe*Me*′, N–CH*Me*$_2$), 0.85 (s, 9, CHC*Me*$_3$); ^{13}C NMR δ 274.4 (d, J_{CH} = 106, J_{CW} = 173, *C*H-*t*-Bu), 152.5 (N–C$_{ipso}$), 149.8 (S–C$_o$), 144.3 (N–C$_o$), 140.6 (S–C$_{ipso}$), 128.1 (S–C$_p$), 126.9 (N–C$_p$), 124.0 (S–C$_m$), 122.9 (N–C$_m$), 47.7 (*C*HCMe$_3$), 33.8 (S–*C*HMe$_2$), 31.5 (CHC*Me*$_3$), 28.6 (N–*C*HMe$_2$), 24.2, 24.0, 23.9 (S–CH*Me*Me′, S–CHMe*Me*′, N–CH*Me*$_2$). Anal. Calcd for $WC_{41}H_{61}NS_2$: C, 60.36; H, 7.54. Found: C, 60.59; H, 7.69.

W[OC(C$_6$H$_3$Me)(CF$_3$)$_2$](NAr)[OC(CF$_3$)$_2$(tolyl)](CH$_2$-*t*-Bu) (13). The synthesis was carried out on a 1-mmol scale in ether (30 mL) in a manner analogous to that described for related compounds (reaction time 30 min) and isolated by recrystallization from minimal pentane at −40 °C (75% yield): ^{1}H NMR (CD_2Cl_2) δ 7.75 (d, 1, H$_{aryl}$), 7.71 (d, 1, H$_{aryl}$), 7.61 (d, 2, H$_{aryl}$), 7.29 (m, 6, H$_{aryl}$), 3.70 (d, 1 C*H*$_A$H$_B$-*t*-Bu), 3.19 (sept, 2, C*H*Me$_2$), 2.50 (d, 1, CH$_A$*H*$_B$-*t*-Bu), 2.38 (s, 3, Me$_{aryl}$), 2.16 (s, 3, Me$_{aryl}$), 1.50 (s, 9, *t*-Bu), 1.05 (d, 6, CH*Me*$_2$), 0.80 (d, 6, CH*Me*$_2$); ^{13}C NMR δ 21.3, 23.8, 24.5, 29.1, 33.8, 37.3, 95 (m), 90.5 (m), 99.8, 124.2, 125.0, 127.5, 129.7, 130.5, 132.1, 139.0, 198. Anal. Calcd for $C_{37}H_{41}F_{12}NO_2W$: C, 47.09; H, 4.39; N, 1.48. Found: C, 46.97; H, 4.29; N, 1.50.

W(CHSiMe$_3$)(NAr)(OAr)$_2$ (14a). W(CH-*t*-Bu)(NAr)(OAr)$_2$ (150 mg, 0.191 mmol) and vinyltrimethylsilane (296 μL, 1.92 mmol) were dissolved in 2.5 mL of pentane and the solution was stirred for 20 h at room temperature. Solvents were then removed in vacuo to yield a bright yellow-orange foam. The residue was recrystallized from minimum pentane at −40 °C to afford 125 mg of a bright yellow microcrystalline solid (82%). NMR data are for the mixture of syn and anti isomers: ^{1}H NMR δ 10.46 (br, ∼0.45, H$_\alpha$), 9.36 (br, ∼0.55, H$_\alpha$), 7.08–6.88 (9, H$_{aryl}$), 3.90 (br, 1, C*H*Me$_2$), 3.68 (br, 4, C*H*Me$_2$), 3.31 (br, 1, C*H*Me$_2$), 1.27 (br, 30, CH*Me*$_2$), 1.00 (br, 6, CH*Me*$_2$), 0.16 (9, SiMe$_3$); ^{1}H NMR (toluene-d_8, −20 °C) δ 10.46 (∼0.45, H$_\alpha$), 9.35 (J_{HW} = 15, ∼0.55, H$_\alpha$), 7.09–6.87 (9, H$_{aryl}$), 3.85 (sept, 1, C*H*Me$_2$), 3.67 (sept, J_{HH} = 7, 4, C*H*Me$_2$), 3.20 (sept, 1, C*H*Me$_2$), 1.34–1.19 (5 overlapping doublets, 30, CH*Me*$_2$), 0.93 (d, 6, J_{HH} = 7, CH*Me*$_2$), 0.18 (9, SiMe$_3$); ^{1}H NMR (toluene-d_8, 100 °C) δ 9.85 (br, H$_\alpha$), 7.05–6.89 (9, H$_{aryl}$), 3.64 (sept, 6, C*H*Me$_2$), 1.23 (d, 30, CH*Me*$_2$), 1.12 (d, 6, CH*Me*$_2$), 0.12 (9, SiMe$_3$); ^{13}C NMR (toluene-d_8, −40 °C) δ 223.3 (J_{CH} = 136, C$_\alpha$), 220.4 (J_{CH} = 110, C$_\alpha$), 158.7, 158.4, 152.2, 151.6, 144.6, 143.1, 137.7, 136.5 (C$_{ipso}$ and C$_o$ for NAr and OAr in the two isomers), 123.5, 122.9, 122.6, 122.3 (C$_m$ and C$_p$ for NAr and OAr in the two isomers; some reasonances are obscured by the toluene-d_8 resonances), 27.1, 24.1, 23.6, 23.4, 23.3, 23.2, 22.9 (*C*HMe$_2$ and CH*Me*$_2$ for NAr and OAr in the two isomers), 2.74 (SiMe$_3$), 1.45 (SiMe$_3$). Anal. Calcd for $WC_{40}H_{61}NO_2Si$: C, 60.07; H, 7.69. Found: C, 59.74; H, 7.80.

The rate at which the syn and anti rotomers interconvert at T_c was estimated by using the equation $k = \pi(\nu_a - \nu_b)2^{-1/2}$. The activation energy for the exchange process was estimated by using the Arrhenius equation and the preexponential factor $A = 10^{11}$.

W[CHSi(OMe)$_3$](NAr)(OAr)$_2$ (15a). W(CH-*t*-Bu)(NAr)(OAr)$_2$ (150 mg, 0.191 mmol) and vinyltrimethoxysilane (44 μL, 0.288 mmol) were dissolved in 4 mL of pentane. The solution was stirred for 4.5 h at 25 °C. The solvents were then removed in vacuo to afford a slightly oily yellow solid that was recrystallized from minimal pentane to afford 119 mg of a bright yellow crystalline solid (73%): ^{1}H NMR δ 9.62 (H$_\alpha$), 7.06 (H$_m$), 6.99 (H$_m$), 6.91 (H$_p$), 6.85 (H$_p$), 3.86 (sept, 2, C*H*Me$_2$), 3.74 (sept, 4, C*H*Me$_2$), 3.42 (9, OMe), 1.29 (d, 12, CH*Me*$_2$), 1.21 (d, 12, CH*Me*$_2$), 1.18 (d, 12, CH*Me*$_2$); ^{13}C NMR δ 195.7 (J_{CW} = 154, J_{CH} = 159, C$_\alpha$), 159.7, 151.0, 145.5, 137.0 (C$_{ipso}$ and C$_o$ for NAr and OAr), 126.9, 123.3, 122.4, 122.3 (C$_m$ and C$_p$), 50.9 (OMe), 28.8, 26.9, 23.9 (*C*HMe$_2$ and CH*Me*$_2$; we assume some resonances are accidentally coincident). Anal. Calcd for $WC_{40}H_{61}NO_5Si$: C, 56.66; H, 7.25. Found: C, 56.49; H, 7.37.

W[CHSi(OMe)$_3$](NAr)[OCMe$_2$(CF$_3$)]$_2$ (15b). W(CH-*t*-Bu)(NAr)[OCMe$_2$(CF$_3$)]$_2$ (150 mg, 0.219 mmol) and vinyltrimethoxysilane (50 μL, 0.327 mmol) were dissolved in 8.0 mL of pentane. After the solution had been stirred for 2.5 h at 25 °C, the solvents were removed in vacuo to afford a yellow powder that was recrystallized from minimal pentane at −40 °C to afford 127 mg of a slightly oily, bright yellow, crystalline solid (78%): ^{1}H NMR δ 9.46 (s, 1, H$_\alpha$), 7.11 (H$_m$), 6.97 (H$_p$), 4.22 (sept, 2, C*H*Me$_2$), 3.54 (s, 9, OMe), 1.37 (s, 6, OCMe$_2$(CF$_3$)), 1.31 (18, OCMe$_2$(CF$_3$) and CH*Me*$_2$); ^{13}C NMR δ 194.6 (C$_\alpha$), 145.4 (C$_o$), 127.2 (C$_p$), 123.1 (C$_m$), 81.0 (J_{CF} = 33, O*C*Me$_2$(CF$_3$)), 50.3 (OMe), 27.5, 23.9, 23.2 (*C*HMe$_2$, CH*Me*$_2$, and OC*Me*$_2$(CF$_3$)). Anal. Calcd for $WC_{24}H_{39}NO_5F_6Si$: C, 38.56; H, 5.26. Found: C, 38.64; H, 5.50.

W[CHSi(OMe)$_3$](NAr)[OCMe(CF$_3$)$_2$]$_2$ (15c). W(CH-*t*-Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (150 mg, 0.190 mmol) and vinyltrimethoxysilane (32 μL, 0.209 mmol) were dissolved in 5.0 mL of pentane. After the solution was stirred for 30 min at 25 °C, the solvents were removed in vacuo to afford an oily orange solid. This residues was recrystallized from minimal pentane at −40 °C to afford 81 mg of a yellow, crystalline solid (50%): ^{1}H NMR δ 9.93 (s, J_{HW} = 6, H$_\alpha$), 7.08 (H$_m$), 6.93 (H$_p$), 4.13 (sept, 2, C*H*Me$_2$), 3.49 (s, 9, OMe), 1.47 (s, 6, OCMe(CF$_3$)$_2$), 1.27 (d, 12, CH*Me*$_2$); ^{13}C NMR δ 206.1 (J_{CH} = 160, J_{CW} = 150, C$_\alpha$), 150.1 (C$_{ipso}$), 147.3 (C$_o$), 128.3 (C$_p$), 126.2 (br m, CF$_3$), 123.3 (C$_m$), 82.8 (sept, J_{CF} = 29, OCMe(CF$_3$)$_2$), 50.9 (Si(OMe)$_3$), 28.1 (*C*HMe$_2$), 24.5 (CH*Me*$_2$), 18.0 (C*Me*(CF$_3$)$_2$). Anal. Calcd for $WC_{24}H_{33}NO_5F_{12}Si$: C, 33.70; H, 3.89. Found: C, 33.93; H, 4.20.

X-ray Study of W(CHCMe$_3$)(NAr)(O-*t*-Bu)$_2$. A pale prismatic crystal of W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ was mounted on a glass fiber under a stream of cold nitrogen. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement with the setting angles of 25 carefully centered reflections in the range $8.79 < 2\theta < 17.37°$, corresponded to a triclinic cell. On the basis of packing considerations and a statistical analysis of the intensity distribution, the space group was determined to be $P\bar{1}$. The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of eight rescans), and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1.

Of the 11 802 reflections that were collected, 11 367 were unique (R_{int} = 0.047); equivalent reflections were merged. The intensities of three representative reflections that were measured after every 150 reflections remained constant throughout the data collection time, indicating crystal and electronic stability (no decay correction was applied).

The linear absorption coefficient for Mo Kα is 43.0 cm^{-1}. An empirical absorption correction, with use of the program DIFABS,[42] was applied, which resulted in transmission factors ranging from 0.83 to 1.20. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.[43] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions (d_{C-H} = 0.95 Å) and were assigned isotropic thermal parameters that were 20% greater than the B_{equiv} value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement[44] were based on 7361 observed reflections ($I > 3.00\sigma(I)$) and 523 variable parameters and converged (largest parameter

(42) DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166.

(43) PHASE: Calbrese, J. C. PHASE-Patterson Heavy Atom Solution Extractor. Ph.D. Thesis, University of Wisconsin—Madison, 1972. DIRDIF: Beurskens, P. T. DIRDIF: Direct Methods for Difference Structures-an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors; Technical Report 1984/1; Crystallography Laboratory: Toernooiveld, 6525 Ed Nijmegen, The Netherlands.

(44) Function minimized in least-squares refinement:

$$\sum w(|F_o| - |F_c|)^2$$

where

$$w = \frac{4F_o^2}{\sigma^2(F_o^2)}$$

$$\sigma^2(F_o^2) = \frac{S^2(C + R^2B) + (pF_o^2)^2}{(Lp)^2}$$

S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, Lp = Lorentz–polarization factor, and p = p factor.

shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = 0.039$ and $R_w = 0.043$.[45]

The standard deviation of an observation of unit weight was 1.65.[46] The weighting scheme was based on counting statistics and includes a factor ($p = 0.02$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, $(\sin J)/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map correspond to 2.67 and −1.71 e/Å^3, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[47] Anomalous dispersion effects were included in F_{calc};[48] the values of $\Delta F'$ and $\Delta F''$ were those of Cromer.[49] All calculations were performed with use of the TEXSAN crystallographic software package of Molecular Structure Corp.[50]

X-ray Study of W[OC(C_6H_3Me)(CF_3)$_2$][NAr][OC(CF_3)$_2$-(tolyl)](CH_2-*t*-Bu). The brown-yellow prisms of **13** chosen for data collection had approximate dimensions 0.28 × 0.26 × 0.28 mm. The unit cell parameters were obtained by a least-squares fit to the J values of 75 automatically centered reflections ($10.64 \le \theta \le 21.41°$); 9485 intensity data ($-21 < h < 21$, $0 < k < 15$, $0 < l < 25$) were measured within the range $1.05 < \theta < 27.34°$ on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects. An absorption correction was performed by Gaussian integration over 49 points. Correction factors were $A_{max} = 2.411$ and $A_{min} = 1.944$. $\sigma(F)$ was calculated from $\sigma(F) = [\sigma(I)^2 + (Ik)^2]^{1/2}/2F$, where $k = 0.02$. Of a total of 8805 unique measured intensities, 6254 satisfied the criterion $I > 2.0\sigma(I)$, and only these were used in the solution and refinement of the structure.

The structure was solved by the heavy-atom method. Refinement was by blocked least-squares methods (two blocks), where the function minimized was $\sum w(\Delta F)^2$ with $w = 1/\sigma(F)^2$ and $\Delta F = ||F_o| - |F_c||$. The positions of the hydrogen atoms were calculated (d(C–H) = 0.95 Å) and included in the refinement with fixed positions and fixed isotropic thermal parameters ($U_H = 0.8$ Å^2). Refinement converged at $R = 0.038$ and $R_w = 0.043$ for 478 variables and 6254 reflections. Important bond distances and angles are listed in Table IV.

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Supplementary Material Available: Labeled drawings and tables of final positional parameters and final anisotropic thermal parameters for W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ and **13** (20 pages); listings of final observed and calculated structure factors (105 pages). Ordering information is given on any current masthead page.

(45)

$$R = \frac{\sum||F_o| - |F_c||}{\sum|F_o|}$$

$$R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum wF_o^2}\right]^{1/2}$$

(46) Standard deviation of an observation of unit weight:

$$\left[\frac{\sum w(|F_o| - |F_c|)^2}{N_o - N_v}\right]^{1/2}$$

N_o = number of observations

N_v = number of variables

(47) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

(48) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(49) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

(50) TEXSAN is the TEXRAY Structure Analysis Package of the Molecular Structure Corp., College Station, TX, 1985.