$Co(C_5H_4PPh_2)_2$ are given in Table VIII.

Registry No. 1, 67292-47-1; $1^+ \cdot PF_6^-$, 67292-48-2; 2, 99920-72-6; $2^+ \cdot PF_6^-$, 67292-27-7; 3, 101835-52-3; $TlC_5H_4PPh_2$, 85320-10-1; TlOEt, 20398-06-5; $Mo(CO)_4$(norbornadiene), 12146-37-1; $Co(C_5H_5)_2$, 1277-43-6; $Fe(C_5H_4PPh_2)_2$, 12150-46-8; $[Fe(C_5H_4PPh_2)_2][Mo(Co)_4]$, 95408-43-8; NaC_5H_5, 4984-82-1; $ClPPh_2$, 1079-66-9; $CoCl_2$, 7646-79-9; $[Fe(C_5H_5)_2]PF_6$, 11077-24-0; $Mo(Co)_6$, 13939-06-5.

Supplementary Material Available: Tables of hydrogen coordinates and temperature factors, anisotropic temperature factors, least-squares planes, and observed and calculated structure factors for 1 (25 pages). Ordering information is given on any current masthead page.

Formation of Tungstenacyclobutadiene Complexes Containing a Proton in the Ring and Their Conversion to "Deprotio" Tungstenacyclobutadiene Complexes[1]

John H. Freudenberger and Richard R. Schrock*

Department of Chemistry, 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The reaction between W(C-*t*-Bu)[$OCH(CF_3)_2$]$_3$(dme) (dme = 1,2-dimethoxyethane) and *tert*-butylacetylene or phenylacetylene yields the tungstenacyclobutadiene complexes W(C-*t*-BuCHCR)(HFIP)$_3$ (R = *t*-Bu or Ph; HFIP = hexafluoroisopropoxide). In the presence of triethylamine and dme the R = Ph species is converted into a "deprotio" tungstenacyclobutadiene complex, W(C_3-*t*-BuPh)(HFIP)$_2$(dme). Addition of dme to W(C-*t*-BuCHCR)(HFIP)$_3$ results in formation of W(C_3-*t*-BuR)(HFIP)$_2$(dme) in equilibrium with W(C-*t*-BuCHCR)(HFIP)$_3$. Addition of phenylacetylene to W(CPh)(HFIP)$_3$(dme) yields only W(C_3Ph_2)(HFIP)$_2$(dme). Addition of *tert*-butylacetylene to W(C-*t*-Bu)(DIPP)$_3$ (DIPP = 2,6-diisopropylphenoxide) yields isolable red W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$ that slowly and irreverisbly is converted in solution into W(C_3-*t*-Bu_2)(DIPP)$_2$. The reaction is greatly accelerated by addition of triethylamine or LiDIPP; it is believed that the base removes the ring proton directly. The pyridine adduct W(C_3-*t*-Bu_2)(DIPP)$_2$(py) has been fully characterized. W(C_3-*t*-Bu_2)(DIPP)$_2$ reacts with excess *tert*-butylacetylene to give a compound with the formula W(C_5H-*t*-Bu_3)(DIPP)$_2$ that can be isolated as its monopyridine adduct. The planar C_5H-*t*-Bu_3 ligand system is formed (it is proposed) by regiospecific reaction of *tert*-butylacetylene with the W–C_α bond in the "deprotio" tungstenacyclobutadiene complex. The alkylidene-like carbon atom in W(C_5H-*t*-Bu_3)(DIPP)$_2$ can be protonated by CF_3CO_2H or $PhCO_2H$ to give complexes of the type W(C_5H_2-*t*-Bu_3)(DIPP)$_2$(RCO_2). The chemistry of the analogous DMP complexes (DMP = 2,6-dimethylphenoxide) is analogous to that of the DIPP complexes. Isolated characterized complexes include W(C-*t*-BuCHC-*t*-Bu)(DMP)$_3$, W(C_3-*t*-Bu_2)(DMP)$_2$(py), W(C_5H-*t*-Bu_3)(DMP)$_2$(py), W(C-*t*-BuCHC-*t*-Bu)(DMP)$_2$Cl, and W(C_3-*t*-Bu_2)(DMP)$_2$.

Introduction

The metathesis of internal acetylenes is now reasonably well understood.[2] The key requirement of a practical metathesis catalyst is a crowded alkoxide coordination sphere that, first, sterically prevents further reaction of the metallacyclobutadiene complex with an acetylene and, second, sterically and electronically destabilizes the metallacycle toward loss of an acetylene from the ring to reform an alkylidyne complex. It is also now clear that the metal center must be reasonably electrophilic, a property that can be controlled by the nature of the alkoxide ligand (e.g., $OCMe_3$ vs. $OCMe_2(CF_3)$ vs. $OCMe(CF_3)_2$).

Terminal acetylenes, on the other hand, have never been metathesized successfully. The first hint that a proton can be lost from a presumed intermediate metallacyclobutadiene ring was the formation of W(η^5-C_5H_5)(C_3-*t*-Bu_2)Cl upon addition of *t*-BuC≡CH to W(η^5-C_5H_5)(C-*t*-Bu)Cl_2.[3] More recently, alkoxy molybdenum alkylidyne complexes have been found to react with terminal acetylenes to give other examples of isolable "deprotiometallacyclobutadiene" complexes.[2e] We then turned to analogous alkoxy tungsten alkylidyne complexes. We felt that we would more likely observe intermediate metallacyclobutadiene complexes since tungstenacyclobutadiene complexes[2b,c] are more stable than their molybdenum analogues[2e] toward loss of an acetylene from the ring. Secondly, the proton in a tungstenacycle should be less acidic than that in an analogous molybdenacycle on the basis of the fact that tungsten alkylidyne complexes appear to be more easily protonated to give alkylidene complexes than molybdenum alkylidyne complexes.[4] The results of this investigation are reported here.

Results

Studies Involving Hexafluoroisopropoxide Complexes. Yellow, crystalline W(C-*t*-Bu)(HFIP)$_3$(dme) (dme

(1) Multiple Metal–Carbon Bonds. 42. For part 41 see: Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1986**, *5*, 398.

(2) (a) Schrock, R. R.; Freudenberger, J. H.; Listemann, M. L.; McCullough, L. G. *J. Mol. Catal.* **1985**, *28*, 1. (b) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554. (c) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; and Ziller, J. W. *Organometallics* **1984**, *3*, 1563. (d) McCullough, L. G.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 4067. (e) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. S. *J. Am. Chem. Soc.* **1985**, *107*, 5987.

(3) McCullough, L. G.; Listemann, M. L.; Schrock, R. R.; Churchill, M. R.; Ziller, J. W. *J. Am. Chem. Soc.* **1983**, *105*, 6729.

(4) Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 1937.

(5) Churchill, M. R.; Ziller, J. W. *J. Organomet. Chem.* **1985**, *286*, 27.

0276-7333/86/2305-1411$01.50/0

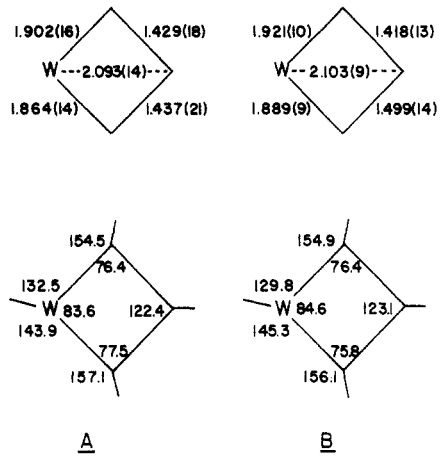
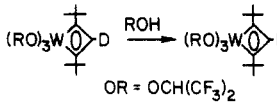


Figure 1. Bond distances and angles in the WC_3 ring in $W(C_3Et_3)[OCH(CF_3)_2]_3$[2c] (A) and $W(CBu\text{-}t\text{-}CHC\text{-}t\text{-}Bu)[OCH(CF_3)_2]_3$[5] (B).

= 1,2-dimethoxyethane, HFIP = $OCH(CF_3)_2$) has been shown to react with internal acetylenes to give tungstenacyclobutadiene complexes.[2c] One of these, a triethyl metallacycle, has been structurally characterized.[2c] A similar reaction between $W(C\text{-}t\text{-}Bu)(HFIP)_3(dme)$ and *tert*-butylacetylene gives dark red $W(C\text{-}t\text{-}BuCHC\text{-}t\text{-}Bu)(HFIP)_3$, a tungstenacyclobutadiene complex whose structure is similar to that of $W(C_3Et_3)(HFIP)_3$, as shown recently by Churchill and Ziller.[5] The virtually symmetric ring systems in these two distorted trigonal-bipyramidal complexes are compared in Figure 1. In each the $W\text{–}C_\alpha$ bond length is far shorter than one would expect for a bond of roughly 1.5 order, and the $W\cdots C_\beta$ distance is less than that of a typical W–C single bond. In each complex the equatorial alkoxide is not in a symmetric position relative to the ring, a fact that suggests that a distorted square-pyramidal description of the structure is equally valid. In the two independent molecules of $W(C_3Et_3)(HFIP)_3$ the W–O–C angles are 138.6 (10) and 135.9 (11)° (O_{eq}), 129.4 (9) and 130.9 (10)° (O_{ax}), and 133.6 (8)° and 130.8 (11)° (O_{ax}), while in $W(C_3\text{-}t\text{-}Bu_2H)(HFIP)_3$ they are 138.7 (9)° (O_{eq}), 135.3 (6)° (O_{ax}), and 137.9 (7)° (O_{ax}).

In the ^1H and ^{13}C NMR spectra of $W(C_3\text{-}t\text{-}Bu_2H)(HFIP)_3$ the H_β resonance is found at 10.01 ppm (J_{HW} = 15.3 Hz), the C_α resonance is found at 252.7 ppm (J_{CW} = 122 Hz), and the C_β resonance is found at 128.3 ppm ($J_{CW} \approx 0$ Hz; J_{CH} = 202 Hz). The relatively high value for J_{HW} is characteristic of systems containing short tungsten–carbon bonds with a good deal of π character. Examples are J_{HW} = 6–13 Hz in neopentylidene complexes of the type $W(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2X_2$ (X = halide, carboxylate, phenoxide)[4] and J_{HW} = 90 Hz in the methylidyne complex $W(CH)(O\text{-}t\text{-}Bu)_3$(quinuclidine).[6] The $J_{CH\beta}$ value (202 Hz) is also characteristic of a bond with a relatively high s content somewhere between that in an arene ($J_{CH} \approx 160$ Hz) and that in an acetylene ($J_{CH} \approx 250$ Hz). The chemical shifts for C_α and C_β are roughly similar to what they are in $W(C_3Et_3)(HFIP)_3$ (242.9 and 147.3 ppm, respectively).

$W(C_3\text{-}t\text{-}Bu_2D)(HFIP)_3$ was prepared straightforwardly and exposed to excess $(CF_3)_2CHOH$ at room temperature in C_6D_6. Within minutes D_β exchanged completely (eq 1).



(1)

It seems unlikely that $(CF_3)_2CHOH$ is a strong enough acid to protonate C_β, and in any case we have found that one tungstenacyclobutadiene complex is protonated at C_α not C_β.[3] Nor does it seem likely that $(CF_3)_2CHOH$ is a strong enough base to remove D_β to give "$W(C_3\text{-}t\text{-}Bu_2)(HFIP)_3^-$". Therefore, we propose that $W(C_3\text{-}t\text{-}Bu_2H)(HFIP)_3$ is in equilibrium with $W(C_3\text{-}t\text{-}Bu_2)(HFIP)_2$, perhaps via an intermediate weak adduct, $W(C_3\text{-}t\text{-}Bu_2)[OCH(CF_3)_2]_2[HOCH(CF_3)_2]$.

Some evidence for the equilibrium between "protio" and "deprotio" complexes comes from ^1H NMR studies of $W(C_3\text{-}t\text{-}Bu_2H)(HFIP)_3$ in C_6D_6 in the presence of 1 equiv of dme. Minor components of the mixture are $(CF_3)_2CHOH$ and, in an equimolar amount, what appears to be $W(C_3\text{-}t\text{-}Bu_2)(HFIP)_2(dme)$. The ratio of $W(C_3\text{-}t\text{-}Bu_2H)(HFIP)_3$ to $W(C_3\text{-}t\text{-}Bu_2)(HFIP)_2(dme)$ is 7:1. If $W(C_3\text{-}t\text{-}Bu_2)(HFIP)_2(dme)$ is present, then it should be possible to shift the equilibrium toward a "deprotio" complex with a better ligand than dme, e.g., pyridine. Indeed, treating $W(C_3\text{-}t\text{-}Bu_2H)(HFIP)_3$ with pyridine yields $W(C_3\text{-}t\text{-}Bu_2)(HFIP)_2(py)_2$ as a well-characterized crystalline species (eq 2). In it the pyridine ligands exchange readily (we assume dissociatively) with free pyridine. The resonance for C_α in the ring of $W(C_3\text{-}t\text{-}Bu_2)(HFIP)_2(py)_2$ is found at

$$W(C_3\text{-}t\text{-}Bu_2H)(HFIP)_3 \xrightarrow[-(CF_3)_2CHOH]{+2py} W(C_3\text{-}t\text{-}Bu_2)(HFIP)_2(py)_2 \quad (2)$$

219.2 ppm and that for C_β at 206.7 ppm. Similar chemical shifts for C_α and C_β have been observed in other deprotiocycles, including structurally characterized $Mo(C_3\text{-}t\text{-}Bu_2)(HFIP)_2(py)_2$.[2e] We assume that $W(C_3\text{-}t\text{-}Bu_2)(HFIP)_2(py)_2$ is isostructural with $Mo(C_3\text{-}t\text{-}Bu_2)(HFIP)_2(py)_2$. We cannot be certain that pyridine serves only to trap the deprotiocycle in the reaction shown in eq 2. As we shall see later, there are circumstances where actual deprotonation of the $WC_3\text{-}t\text{-}Bu_2H$ ring by a suitably strong Brønsted base such as triethylamine is the most likely explanation of how the deprotiocycle is formed.

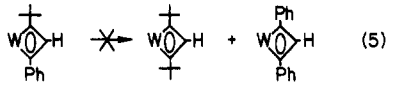
The ease of forming a deprotiocycle should depend sensitively upon the substituents on the ring. We have been able to demonstrate this proposal for phenyl-substituted systems. When $W(C\text{-}t\text{-}Bu)(HFIP)_3(dme)$ is treated with phenylacetylene at −40 °C, $W(C\text{-}t\text{-}BuCHCPh)(HFIP)_3$ can be isolated in good yield if one works rapidly. (Since PhC≡CH is polymerized more readily than *t*-BuC≡CH, a better method of preparing $W(C\text{-}t\text{-}BuCHCPh)(HFIP)_3$ is to add *t*-BuC≡CH to $W(CPh)(HFIP)_3(dme)$—see later.) If $W(C\text{-}t\text{-}BuCHCPh)(HFIP)_3$ is dissolved in C_6D_6 and 1 equiv of dme added, then over a period of about 3 h the ~1:1 equilibrium shown in eq 3 is established. $W(C_3\text{-}t\text{-}BuPh)(HFIP)_2(dme)$ actually can be isolated (in ~40% yield) by adding excess dme to $W(C\text{-}t\text{-}BuCHCPh)(HFIP)_3$ followed by triethylamine to speed up conversion (eq 4). Addition of 1 equiv of $(CF_3)_2CHOH$ to isolated $W(C_3\text{-}t\text{-}BuPh)(HFIP)_2(dme)$ in C_6D_6 yields the same 1:1 equilibrium shown in eq 3 after ~3 h. At equilibrium a small amount of $W(C\text{-}t\text{-}Bu)(HFIP)_3(dme)$ is observed, presumably due to loss of PhC≡CH from $W(C\text{-}t\text{-}BuCHCPh)(HFIP)_3$. (If $W(CPh)(HFIP)_3(dme)$ were formed in trace quantities, it would be difficult to identify with any certainty.) It should be noted, however, that no ring systems containing two

$$W(C\text{-}t\text{-}BuCHCPh)(HFIP)_3 + dme \rightleftharpoons W(C_3\text{-}t\text{-}BuPh)(HFIP)_2(dme) + (CF_3)_2CHOH \quad (3)$$

$$W(C\text{-}t\text{-}BuCHCPh)(HFIP)_3 \xrightarrow[NEt_3]{dme} W(C_3\text{-}t\text{-}BuPh)(HFIP)_2(dme) \quad (4)$$

(6) Listemann, M. L.; Schrock, R. R. *Organometallics* **1985**, *4*, 74.

tert-butyl groups (see above) or two phenyl groups (see below) are observed (eq 5), a fact that allows us to conclude



(5)

that only a negligible amount of terminal acetylene can be lost from a tungstenacyclobutadiene ring system in the time frame (up to 3 h) of the reactions we will be talking about here.

Let us return briefly to W(C_3-*t*-BuPh)(HFIP)$_2$(dme). Its ^{1}H NMR spectrum shows only one type of OCH(CF$_3$)$_2$ ligand and two singlets for the dme ligand. Addition of free dme leads to an average dme signal, indicative of rapid exchange of free and coordinated dme. Addition of pyridine immediately yields W(C_3-*t*-BuPh)(HFIP)$_2$(py)$_2$. In this complex the two pyridine ligands also exchange rapidly with free pyridine on the NMR time scale. The fact that W(C_3-*t*-BuPh)(HFIP)$_2$(dme) is formed rapidly upon addition of triethylamine, a poor ligand, to W(C-*t*-BuCHCPh)(HFIP)$_3$ suggests that it may be possible for a base to remove the ring proton directly and thereby catalyze the loss of (CF$_3$)$_2$CHOH. We will see more evidence that such a reaction is possible later.

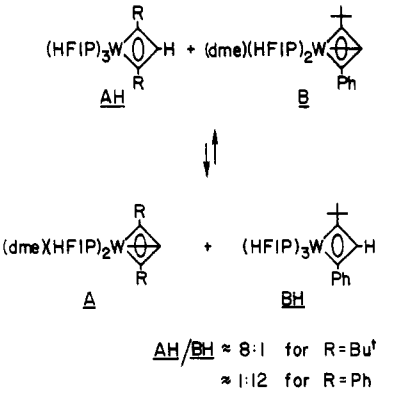
W(CPh)(HFIP)$_3$(dme) can be prepared readily as shown in eq 6.[2c] Treating W(CPh)(HFIP)$_3$(dme) with phenylacetylene at −40 °C yields W(C_3Ph$_2$)(HFIP)$_2$(dme) as the only isolated product. When a sample of W(C_3Ph$_2$)-(HFIP)$_2$(dme) is dissolved in C_6D_6 and 1 equiv of (CF$_3$)$_2$CHOH is added, an ^{1}H NMR spectrum indicates that W(C_3Ph$_2$H)(HFIP)$_3$ and W(C_3Ph$_2$)(HFIP)$_2$(dme) are present in a ratio of ~1:7, i.e., the ratio of protio- to deprotiocycle changes from ~7:1 for the di-*tert*-butyl ring system to ~1:1 for the *tert*-butyl phenyl ring system to ~1:7 for the diphenyl ring system. Addition of ~5 equiv of (CF$_3$)$_2$CHOH to the 1:7 diphenyl ring mixture changed the ratio to ~1:1, thereby allowing the protiometallacycle to be identified unambiguously by its ^{1}H NMR spectrum.

$$\text{W(C-}t\text{-Bu)(HFIP)}_3\text{(dme)} \xrightarrow[-\text{PhC}\equiv\text{C-}t\text{-Bu}]{+\text{PhC}\equiv\text{CPh}} \text{W(CPh)(HFIP)}_3\text{(dme)} \quad (6)$$

The relative stabilities of two different protiometallacycles can be determined by equilibrating a protiometallacycle of one type with an equal amount of a deprotiometallacyle of another type. Two examples are shown in Scheme I. In the case where R = *t*-Bu an 8:1 ratio of AH to BH was observed, and when R = Ph a 1:12 ratio of AH to BH was observed, as one would expect on the basis of the findings above for each of the three systems individually. These results clearly illustrate the tendency for phenyl-substituted ring systems to lose H$_\beta$ more readily. They also show that no added alcohol or dme is necessary for the equilibration to proceed to equilibrium.

Studies Involving 2,6-Diisopropylphenoxide (DIPP) Complexes. Addition of *tert*-butylacetylene to W(C-*t*-Bu)(DIPP)$_3$ gives W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$ as large, dark red prisms. Over a period of several days at 25 °C ($t_{1/2} \approx 12$ h) a red solution of W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$ fades to yellow and the ^{1}H NMR spectrum is consistent with the sample now being a mixture of W(C_3-*t*-Bu$_2$)(DIPP)$_2$ and DIPPH (along with traces of unidentified decomposition product). According to the ^{1}H NMR spectrum the yield of each is >90%. W(C_3-*t*-Bu$_2$)(DIPP)$_2$ cannot be isolated from this mixture due to the presence of DIPPH, but it can be prepared pure via another route (see below). At ~50 °C the decomposition of W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$ produces significantly lower yields of W(C_3-*t*-Bu)$_2$(DIPP)$_2$.

Scheme I. Approximate Equilibrium Ratios in Reactions between Different *tert*-Butyl- and Phenyl-Substituted Metallacycles[a]



AH/BH ≈ 8:1 for R = Bu^t
≈ 1:12 for R = Ph

[a] [AH] = [B] and [A] = [BH].

If the decomposition of W(C-*t*-BuCDC-*t*-Bu)(DIPP)$_3$ is followed by ^{1}H NMR in the presence of DIPPH (5–10 equiv), no W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$ is observed at the point where 20% W(C_3-*t*-Bu$_2$)(DIPP)$_2$ has formed. This result suggests that the loss of DIPPH from W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$ is essentially irreversible (eq 7) and,

$$\text{W(C-}t\text{-BuCHC-}t\text{-Bu)(DIPP)}_3 \underset{+\text{DIPPH}}{\overset{-\text{DIPPH}}{\rightleftharpoons}} \text{W}(C_3\text{-}t\text{-Bu}_2)\text{(DIPP)}_2 \quad (7)$$

in view of the likely extremely crowded nature of W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$ (cf. W(C_3Et$_3$)(DIPP)$_3$[2b]), that it is an intramolecular reaction. In this respect the DIPP system differs markedly from the hexafluoroisopropoxide system where the deprotiocycle can be converted back to the protiocycle by addition of hexafluoro-2-propanol. So far our efforts to confirm that the decomposition of W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$ is intramolecular have been hampered by experimental problems believed to be caused by traces of LiDIPP (see below).

The conversion of W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$ to W(C_3-*t*-Bu$_2$)(DIPP)$_2$ is complete in minutes if a catalytic amount of LiDIPP is added (~0.1 equiv). An alternative is to add a catalytic amount of triethylamine (eq 8). Since

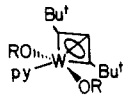
$$\text{W(C-}t\text{-BuCHC-}t\text{-Bu)(DIPP)}_3 \xrightarrow[\text{or NEt}_3]{\text{LiDIPP}} \text{W}(C_3\text{-}t\text{-Bu}_2)\text{(DIPP)}_2 + \text{DIPPH} \quad (8)$$

we feel it is unlikely that either DIPP or NEt$_3$ could coordinate to W in a molecule as crowded as W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$, we are forced to conclude that the proton is removed directly from the ring and probably delivered to the oxygen atom of the DIPP ligand shortly thereafter (eq 9).

$$\text{W(C-}t\text{-BuCHC-}t\text{-Bu)(DIPP)}_3 \xrightarrow[\text{base}]{-\text{H}^+} [\text{W}(C_3\text{-}t\text{-Bu}_2)\text{(DIPP)}_3]^- \xrightarrow{-\text{DIPP}} \text{W}(C_3\text{-}t\text{-Bu}_2)\text{(DIPP)}_2 \quad (9)$$

Pyridine reacts rapidly with W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$ to yield yellow, crystalline W(C_3-*t*-Bu$_2$)(DIPP)$_2$(py). Note that the bis(pyridine) complex (cf. W(C_3-*t*-Bu$_2$)(HFIP)$_2$(py)$_2$ above) is not formed, presumably for steric reasons. It is worth discussing the NMR spectral data for W(C_3-*t*-Bu$_2$)(DIPP)$_2$(py), as they serve to illustrate how crowded even the mono(pyridine) adduct is. At 340 K the coordinated pyridine is exchanging rapidly with free pyridine, and only one type of DIPP ligand is observed. At 230 K, where pyridine exchange is slow, the ^{1}H NMR spectrum shows two *tert*-butyl proton resonances, four

isopropyl methyl proton resonances, and one isopropyl methine proton resonance of area two at 3.94 ppm. We believe the other methine proton resonance of area two occurs at ~0.7 ppm, since two isopropyl methyl resonances at 0.71 and 0.66 ppm are roughly singlets, instead of the normal doublets, due to what we presume to be non-first-order coupling of the methyl protons to the methine proton. We see five phenyl carbon resonances. therefore we propose that the phenoxide ligands are equivalent but not freely rotating and that we observe only five of the possible six inequivalent ring carbon atom resonances. The structure of W(C_3-*t*-Bu_2)(DIPP)$_2$(py) cannot be a TBP-containing nonrotating axial DIPP groups and a symmetrically disposed equatorial py ligand, since the ring's *tert*-butyl groups would then be equivalent (not observed). We feel the most likely alternative is a roughly square-pyramidal species (essentially a distorted trigonal bipyramid in which the pyridine is not symmetrically disposed), viz. Such a structure is related to that of distorted TBP

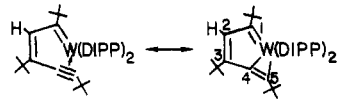


tungstenacyclobutadiene complexes in which the equatorial alkoxide ligand is not located in a symmetrical position in the trigonal plane.[2b,c]

A route to W(C_3-*t*-Bu_2)(DIPP)$_2$ free of DIPPH was devised. "W(C-*t*-Bu)(DIPP)$_2$Cl" was prepared in situ by adding 2 equiv of LiDIPP to W(C-*t*-Bu)(dme)Cl_3 in ether. Addition of *tert*-butylacetylene yielded an orange-red tungstenacyclobutadiene complex whose NMR spectra are consistent with it being W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_2$Cl containing one axial chloride and one axial DIPP ligand. In contrast to W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$, which decomposes extensively in the solid state after 1 day at room temperature, W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_2$Cl is stable as a solid. In solution, however, it decomposes to a mixture of products, among which free DIPPH and W(C_3-*t*-Bu_2)(DIPP)$_2$ (in poor yield) can be identified by NMR. Upon addition of triethylamine to a solution of W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_2$Cl in ether, Et_3NHCl precipitates immediately and W(C_3-*t*-Bu_2)(DIPP)$_2$ can be isolated as a pure yellow oil from the supernatant by removing the ether in vacuo (eq 10). We presume that this reaction is another example of the direct deprotonation (here a dehydrohalogenation) of a protiometallacycle by an external base.

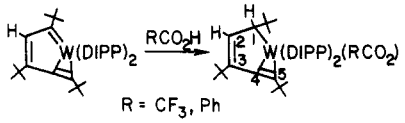
$$\text{W(C-}t\text{-BuCHC-}t\text{-Bu)(DIPP)}_2\text{Cl} \xrightarrow[-Et_3NHCl]{+Et_3N} \text{W(}C_3\text{-}t\text{-Bu}_2\text{)(DIPP)}_2 \quad (10)$$

Further Reaction of W(C_3-*t*-Bu_2)(DIPP)$_2$ with *tert*-Butylacetylene. W(C_3-*t*-Bu_2)(DIPP)$_2$ reacts further with excess *tert*-butylacetylene over a period of 1 day to give a blue, pentane-soluble, diamagnetic product with the empirical composition W(C_3-*t*-Bu_2)(DIPP)$_2$(*t*-BuC≡CH). The main features of its ^{13}C NMR spectrum are virtually identical with those in the spectrum of Mo(C_5H-*t*-Bu_3)(HFIP)$_2$(py), a structurally characterized species.[7] Therefore, we propose that the tungsten complex is W(C_5H-*t*-Bu_3)(DIPP)$_2$ with a planar metallacyclic ring structure similar to that in Mo(C_5H-*t*-Bu_3)[OCH(CF_3)$_2$]$_2$(py) (eq 11). At low temperatures four doublets for the isopropyl methyl groups and two septets for the methine protons are found, indicative of equivalent phenoxide ligands which rotate about the W–O bond slowly on the NMR time scale. The five ring carbon resonances are found at 266.2 (s), 193.9 (s), 187.7 (d, J = 15.9 Hz), 158.4 (or 158.1, s), and 156.1 ppm (d, J = 150 Hz). the resonance at 266.2 ppm can be ascribed to C(1), that at 156.1 ppm to C(2), and that at 187.7 ppm to C(3). Addition of pyridine yields a fully characterized complex with the formula W(C_5H-*t*-Bu_3)(DIPP)$_2$(py), one whose structure we presume is analogous to that of Mo(C_5H-*t*-Bu_3)[OCH(CF_3)$_2$]$_2$(py), i.e., a TBP species containing axial DIPP ligands. At low temperatures rotation of the DIPP ligands in W(C_5H-*t*-Bu_3)(DIPP)$_2$(py) is slow on the NMR time scale.



(11)

We attempted to cleave off the organic fragment in W(C_5H-*t*-Bu_3)(DIPP)$_2$ with trifluoroacetic or benzoic acid. Red (with CH_3CO_2H) or orange (with $PhCO_2H$) products were obtained in good yield that we propose result from protonation of the alkylidene-like α-carbon atom in the ring system of W(C_5H-*t*-Bu_3)(DIPP)$_2$ (eq 12). In the



(12)

CF_3CO_2H product, for example, ^{13}C NMR resonances for the ring carbon atoms are found at 194.8 (s), 188.0 (J_{CH} = 15.9 Hz), 162.2 (J_{CH} = 151, 7.9 Hz), 151.1 (s), and 90.2 ppm (J_{CH} = 119, J_{CW} = 77 Hz). The characteristic alkylidene carbon atom signal for C(1) at 266.2 ppm in W(C_5H-*t*-Bu_3)(DIPP)$_2$ appears to have been replaced by a signal at 90.2 ppm; the chemical shifts of the four other ring carbon atoms change comparatively little. We suggest that the basic structure of W(C_5H_2-*t*-Bu_3)(DIPP)$_2$(RCO_2) is a TBP with the DIPP ligands occupying axial positions. The DIPP ligands again apparently do not rotate rapidly on the NMR time scale, thereby resulting in relatively complex NMR spectra.

Studies Involving 2,6-Dimethylphenoxide (DMP) Complexes. In studies focused on metathesis of internal acetylenes we had found that substituting the sterically less demanding 2,6-dimethylphenoxide ligand for the 2,6-diisopropylphenoxide ligand led to significantly different chemistry. For example, while W(C-*t*-Bu)(DIPP)$_3$ reacts cleanly to give tungstenacyclobutadiene complexes, W(C-*t*-Bu)(DMP)$_3$(THF) extensively polymerizes internal acetylenes, and no tungstenacyclobutadiene complexes were observed.[2b] Consequently, metathesis of internal acetylenes is prolonged with W(C-*t*-Bu)(DIPP)$_3$ as the catalyst, while metathesis with W(C-*t*-Bu)(DMP)$_3$(THF) is short-lived. Therefore, we expected the reactions between W(C-*t*-Bu)(DMP)$_3$(THF) and terminal acetylenes to differ significantly from those involving W(C-*t*-Bu)(DIPP)$_3$. In fact, the differences turn out to be negligible.

W(C-*t*-Bu)(DMP)$_3$(THF) reacts cleanly with 1 equiv of *tert*-butylacetylene to give W(C-*t*-BuCHC-*t*-Bu)(DMP)$_3$ in high yield. W(C-*t*-BuCHC-*t*-Bu)(DMP)$_3$ subsequently decomposes to W(C_3-*t*-Bu_2)(DMP)$_2$ and free DMPH with a $t_{1/2} \approx$ 12 h at 25 °C. The yield of W(C_3-*t*-Bu_2)(DMP)$_2$ is >90% by ^1H NMR at 25 °C, but the yield drops dramatically at higher temperatures. Addition of pyridine yields W(C_3-*t*-Bu_2)(DMP)$_2$(py). Pure W(C_3-*t*-Bu_2)(DMP)$_2$ can be prepared by treating W(C-*t*-BuCHC-*t*-Bu)(DMP)$_2$Cl with triethylamine. In both W(C_3-*t*-Bu_2)(DMP)$_2$ and W(C_3-*t*-Bu_2)(DMP)$_2$(py) the DMP ligands

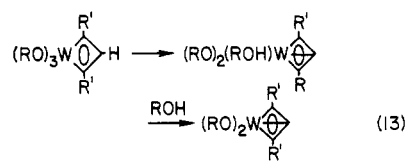
(7) Strutz, H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5999.

rotate more rapidly than the DIPP ligands in the analogous DIPP complexes.

$W(C_3\text{-}t\text{-}Bu_2)(DMP)_2$ reacts with excess *tert*-butylacetylene over a period of ~3 h to give an impure waxy blue solid. This reaction is faster than that between $W(C_3\text{-}t\text{-}Bu_2)(DIPP)_2$ and *tert*-butylacetylene, but it is not as clean. Addition of pyridine yields pure, crystalline $W(C_5H\text{-}t\text{-}Bu_3)(DMP)_2(py)$ in good yield. $W(C_5H\text{-}t\text{-}Bu_3)(DMP)_2(py)$ is virtually identical with its DIPP analogue, except that the DMP ligands again apparently rotate more rapidly than the DIPP ligands about the W–O axes at room temperature.

Discussion

The chemistry disclosed here convincingly demonstrates that a metallacyclobutadiene complex containing a proton in the ring system is readily converted into a "deprotiometallacyclobutadiene" complex by loss of 1 equiv of alcohol. Although much of the evidence is qualitative, we feel comfortable proposing that the proton can be lost directly from the β-carbon atom in the ring to a noncoordinating external base to give an intermediate anion (eq 9). We feel considerably less comfortable proposing that the alcohol can be lost intramolecularly as shown in eq 13



(13)

but cannot offer any more satisfactory alternative. The proposed intermediate alcohol complex seems resonable. It is also a plausible intermediate in a reaction in which a deprotiocycle is reprotonated by $(CF_3)_2CHOH$. The fact that DIPPH does not add to $W(C_3R_2)(DIPP)_2$ to give $W(C_3R_2H)(DIPP)_3$ therefore might be ascribed to severe steric problems in forming intermediate $W(C_3R_2)(DIPP)_2(DIPPH)$ that apparently are not as severe in intermediate $W(C_3R_2)(HFIP)_2(HFIPH)$.

An important question is how the proton transfers from a β-carbon atom to an alkoxide ligand (and back again in the HFIP system). Such a proton migration might seem more reasonable if the proton were lost from an α-carbon atom in an α,β-disubstituted metallacycle or a carbon atom in an η^3-cyclopropenyl complex,[8] by analogy with α-hydrogen atom abstraction reactions. But the β-carbon atom in a metallacyclobutadiene complex *is* within a M–C single bond distance of the metal. Therefore what appears to be migration of a proton across the electron-rich face of an MC_3 ring system to (most likely) an axial alkoxide oxygen atom should be no less plausible than what is likely to be a related proton transfer from an α-carbon atom in an alkyl or an alkylidene complex to a neighboring alkyl ligand.

What we feel is a justifiable conclusion on the basis of what we have found here is that metathesis of unprotected terminal acetylenes is an exceedingly ambitious goal. If an α,α'-disubstituted deprotiocycle were to form it would have to back react with ROH to yield an as yet unobserved α,β-disubstituted protiocycle. What we believe is likely to be an unstable methylidyne complex[2e,6] formed by loss of the disubstituted acetylene would have to be stable long enough to react with more terminal acetylene to give an α-substituted metallacycle. And finally, acetylene itself would have to be lost from the α-substituted metallacycle and removed from the system before it could (inter alia) react with W–C bonds in metallacyclobutadiene rings to give (e.g.) expanded ring systems. Our opinion is that such a combination of circumstances will be extremely rare, if it can be found at all.

Experimental Section

General procedures can be found elsewhere.[6] $W(C\text{-}t\text{-}Bu)(HFIP)_3(dme)$,[2c] $W(C\text{-}t\text{-}Bu)(DIPP)_3$,[2b] and $W(C\text{-}t\text{-}Bu)(DMP)_3(THF)$[2b] were prepared as described in the literature. $t\text{-}BuC{\equiv}CD$ was prepared by hydrolysis of $t\text{-}BuC{\equiv}CLi$ with excess of D_2O in ether and isolated by distillation.

NMR spectra were obtained at relatively high field (250-MHz ^1H). Chemical shifts are quoted in parts per million relative to Me_4Si and coupling constants in hertz. Routine multiplicities, intensities, and coupling constants are omitted. (For example, all aliphatic CH coupling constants lie in the range 125–130 Hz and all aromatic in the range 160–180 Hz.) Patterns that change little (e.g., for the $OCH(CF_3)_2$ ligand system) are described in detail only in the preparation of the first compound containing that ligand. In special circumstances (e.g., a fluxional molecule between slow- and fast-exchange limits) more details are again provided.

Preparation of Compounds. $W(C\text{-}t\text{-}BuCHC\text{-}t\text{-}Bu)[OCH(CF_3)_2]_3$. *tert*-Butylacetylene (230 μL, 1.93 mmol) was added to a suspension of $W(C\text{-}t\text{-}Bu)[OCH(CF_3)_2]_3(dme)$ (1.50 g, 1.78 mmol) in pentane (25 mL). The solution turned red as the starting material began to dissolve. After several minutes all starting material had dissolved. The solution was then concentrated in vacuo to approximately 10 mL. Fine dark red crystals formed and were collected via filtration (yield 1.19 g, 80%): ^1H NMR (C_6D_6) δ 10.01 (s, 1, J_{HW} = 15.3, H_β), 5.88 (sept, 1, J_{HF} = 6.1, eq $OCH(CF_3)_2$), 4.61 (sept, 2, J_{HF} = 6.1, ax $OCH(CF_3)_2$), 1.13 (CMe_3); ^{13}C NMR (CD_2Cl_2) δ 252.7 (s, J_{CW} = 122, C_α), 128.3 (d, J_{CH} = 202, C_β), 122.7 (q, J_{CF} = 284, $OCH(CF_3)_2$), 79.7 (d sept, J_{CF} = 32, J_{CH} = 149, ax $OCH(CF_3)_2$), 77.4 (d sept, J_{CF} = 32, J_{CH} = 151, eq $OCH(CF_3)_2$), 44.0 ($CCMe_3$), 32.4 (CMe_3). Anal. Calcd for $WC_{20}H_{22}F_{18}O_3$: C, 28.73; H, 2.65. Found: C, 28.94; H, 2.74.

Observation of $W(C_3\text{-}t\text{-}Bu_2)[OCH(CF_3)_2]_2(dme)$. Approximately 1 equiv of dimethoxyethane (3.7 μL, 0.036 mmol) was added to a solution of $W(C\text{-}t\text{-}BuCHC\text{-}t\text{-}Bu)[OCH(CF_3)_2]_3$ (30 mg, 0.036 mmol) in C_6D_6 (~0.5 mL). After 2 h a mixture of the deprotiometallacycle, protiometallacycle, dme, and $HOCH(CF_3)_2$ was observed by ^1H NMR. The ratio of protio- to deprotiometallacycles (7:1) did not change with time. The characteristic peaks of $W(C_3\text{-}t\text{-}Bu_2)[OCH(CF_3)_2]_2(dme)$ in the ^1H NMR spectrum are found at δ 3.55 (sept, 2, J_{HF} = 6.1, $OCH(CF_3)_2$) and 1.65 (CMe_3).

$W(C_3\text{-}t\text{-}Bu_2)[OCH(CF_3)_2]_2(py)_2$. *tert*-Butylacetylene (145 μL, 1.18 mmol) was added to a solution of $W(C\text{-}t\text{-}Bu)[OCH(CF_3)_2]_3(dme)$ (1.00 g, 1.18 mmol) in ether (25 mL). The solution turned dark red immediately, indicating that $W(C\text{-}t\text{-}BuCHC\text{-}t\text{-}Bu)[OCH(CF_3)_2]_3$ had formed. A slight excess of pyridine (210 μL, 2.60 mmol) was then added. The color of the solution changed to a lighter shade of red. The solvent was removed in vacuo and the residue recrystallized from ether at −40 °C to give large red prisms (2 crops, 0.79 g, 81% yield): ^1H NMR (C_6D_6) δ 8.91 (d, 4, H_o), 6.91 (t, 2, H_p), 6.62 (t, 4, H_m), 3.28 (sept, 2, $OCH(CF_3)_2$), 1.67 (s, 18, CMe_3); ^{13}C NMR (C_6D_6) δ 219.2 (s, C_α), 206.7 (s, C_β), 151.2 (d, J_{CH} = 183, C_o), 138.1 (d, J_{CH} = 167, C_p), 123.8 (d, J_{CH} = 167, C_m), 123.5 (q, $OCH(CF_3)_2$), 83.0 (d sept, $OCH(CF_3)_2$), 45.1 (CMe_3), 33.4 (CMe_3). Anal. Calcd for $WC_{27}H_{30}F_{12}N_2O_2$: C, 39.24; H, 3.66. Found: C, 39.58; H, 3.55.

$W(C\text{-}t\text{-}BuCHCPh)[OCH(CF_3)_2]_3$. *tert*-Butylacetylene (145 μL, 1.18 mmol) was added to a solution of $W(CPh)[OCH(CF_3)_2]_3(dme)$ (1.00 g, 1.16 mmol) in ether (25 mL) at −40 °C. The solution turned red-purple immediately. The volume of the solution was reduced in vacuo to ~5 mL, and then ~20 mL of pentane was added. Concentrating this solution in vacuo resulted in the formation of small red-purple crystals that were collected by filtration and washed with pentane (0.69 g, 70% yield): ^1H NMR (C_6D_6) δ 10.17 (J_{HW} = 14, H_β), 7.06 (H_o and H_m), 6.69 (H_p), 6.03 (sept, 1, eq $OCH(CF_3)_2$), 4.66 (sept, 2, ax $OCH(CF_3)_2$), 1.22 (CMe_3); ^{13}C NMR (C_6D_6) δ 248.9 (C_α), 239.4 ($C_{\alpha'}$), 134.0 (C_{ipso}), 132.8 (C_o or C_m), 132.3 (C_p), 129.0 (C_o or C_m), 124.7 (d, J_{CH} = 204,

(8) (a) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574. (b) Schrock, R. R.; Murdzek, J. S.; Freudenberger, J. H.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1986**, *5*, 25.

C_β), 122.9 (q, ax $OCH(CF_3)_2$), 122.6 (q, eq $OCH(CF_3)_2$), 79.1 (d sept, ax $OCH(CF_3)_2$), 77.9 (d sept, eq $OCH(CF_3)_2$), 43.0 (CMe_3), 32.1 (CMe_3). Anal. Calcd for $WC_{22}H_{18}F_{18}O_3$: C, 30.86; H, 2.12. Found: C, 31.33; H, 2.25.

W(C$_3$-*t*-BuPh)[OCH(CF$_3$)$_2$]$_2$(dme). An excess of triethylamine (1.0 mL, 7.2 mmol) and dimethoxyethane (0.75 mL, 7.2 mmol) were added to a solution of W(C-*t*-BuCHCPh)[OCH(CF$_3$)$_2$]$_3$ (0.62 g, 0.72 mmol) in ether (50 mL). The solvent was removed in vacuo leaving an orange oil. The oil was dissolved in ~5 mL of ether,and the solution was cooled to −40 °C to give the product as orange needles (2 crops, 0.22 g, 39% yield): ^{1}H NMR (C_6D_6) δ 8.13 (H_o), 7.41 (H_m), 6.96 (H_p), 3.69 (CH_3O), 3.46 ($OCH(CF_3)_2$), 3.17 (OCH_2), 1.70 (CMe_3); ^{13}C NMR (C_6D_6) δ 216.8, 204.3, 200.4 (C_α, $C_{\alpha'}$, C_β), 141.8 (C_{ipso}), 132.0, 128.8, 128.2 (C_o, C_m, and C_p), 123.1 ($OCH(CF_3)_2$), 80.8 ($OCH(CF_3)_2$), 72.6 (t, J_{CH} = 148, OCH_2), 64.7 (q, J_{CH} = 146, CH_3O), 44.3 (CMe_3), 33.4 (CMe_3). Anal. Calcd for $WC_{23}H_{26}O_4F_{12}$: C, 35.49; H, 3.37. Found: C, 35.22; H, 3.45.

W(C$_3$-*t*-BuPh)[OCH(CF$_3$)$_2$]$_2$(py)$_2$. A solution of W(C-*t*-BuCHCPh)[OCH(CF$_3$)$_2$]$_3$ in ether (25 mL) was prepared by treating W(C-*t*-Bu)[OCH(CF$_3$)$_2$]$_3$(dme) (1.00 g, 1.18 mmol) with phenylacetylene (130 μL, 1.18 mmol) at −40 °C. Slightly more than 2 equiv of pyridine (200 μL, 2.47 mmol) were then added. the solvent was removed in vacuo, and the residue was recrystallized from ether at −40 °C. The product was obtained as small red-purple crystals (2 crops, 0.85 g, 85% yield): ^{1}H NMR (C_6D_6) δ 8.95 (br, 4, py-H_o), 8.20 (Ph-H_o), 7.41 (Ph-H_m), 6.94 (py-H_p), 6.91 (Ph-H_p), 6.64 (py-H_m), 3.19 ($OCH(CF_3)_2$), 1.70 (CMe_3); ^{13}C NMR (C_6D_6 δ 217.0, 206.8, 204.1 (C_α, $C_{\alpha'}$, C_β), 151.3 (py-C_o), 141.9 (Ph-C_{ipso}), 138.6 (py-C_p), 133.5, 128.5, 128.0 (Ph-C_o, -C_m, and -C_p), 124.7 (py-C_m), 123.4 ($OCH(CF_3)(CF_3)'$), 122.9 ($OCH(CF_3)(CF_3)'$), 82.4 ($OCH(CF_3)_2$), 45.1 (CMe_3), 33.4 (CMe_3). Anal. calcd for $WC_{29}H_{26}F_{12}N_2O_2$: C, 41.15; H, 3.10. Found: C, 41.25; H, 3.05.

W(CPh)[OCH(CF$_3$)$_2$]$_3$(dme). A slight excess of diphenylacetylene (0.64 g, 3.6 mmol) was added to a solution of W(C-*t*-Bu)[OCH(CF$_3$)$_2$]$_3$(dme) (2.75 g, 3.26 mmol) in ether (25 mL). The solution was stirred overnight. The solvent was then removed in vacuo. The residue was recrystallized from ether/pentane at −40 °C to give large orange crystals (2 crops, 2.30 g, 82% yield): ^{1}H NMR (C_6D_6) δ 7.11 (H_m), 6.78 (H_o), 6.59 (H_p), 5.83 (br, 3, $OCH(CF_3)_2$), 3.61 (br, 3, CH_3O), 2.94 (br, 5, CH_3O and OCH_2), 2.67 (br, 2, OCH_2); ^{13}C NMR (C_6D_6) δ 281.0 (s, C_α), 142.8 (C_{ipso}), 133.8, 129.3, 127.5 (C_o, C_m, C_p), 123.6 ($OCH(CF_3)_2$), 84.9 ($OCH(CF_3)_2$), 74.6 (br t, J_{CH} = 139, OCH_2), 71.7 (br q, J_{CH} = 150, CH_3O), 70.0 (br t, J_{CH} = 145, OCH_2), 59.5 (br q, J_{CH} = 145, CH_3O). Anal. Calcd for $WC_{20}H_{18}F_{18}O_5$: C, 27.80; H, 2.10. Found: C, 28.18; H, 2.33.

W(C$_3$Ph$_2$)[OCH(CF$_3$)$_2$]$_2$(dme). Phenylacetylene (130 μL, 1.18 mmol) was added dropwise to a solution of W(CPh)[OCH(CF$_3$)$_2$]$_3$(dme) (1.00 g, 1.16 mmol) in ether (20 mL) at −40 °C. The solution was allowed to warm to room temperature, and the solvent was then removed in vacuo. Recrystallization of the residue from ether/pentane at −40 °C gave fine dark red crystals (2 crops, 0.55 g, 60% yield): ^{1}H NMR (C_6D_6) δ 8.23 (H_o), 7.45 (H_m), 7.00 (H_p), 3.73 (CH_3O), 3.42 ($OCH(CF_3)_2$), 3.16 (OCH_2); ^{13}C NMR (C_6D_6) δ 202.0 (C_α), 201.9 (C_β), 141.8 (C_{ipso}), 132.3, 128.9, 128.4 (C_o, C_m, C_p), 122.9 ($OCH(CF_3)_2$), 80.4 ($OCH(CF_3)_2$), 73.0 (OCH_2), 65.1 (CH_3O).

Observation of W(CPhCHCPh)[OCH(CF$_3$)$_2$]$_3$. An adequate ^{1}H NMR spectrum of this compound was obtained in the presence of ~5 equiv of $(CF_3)_2CHOH$ as explained in the text: ^{1}H NMR (C_6D_6) δ 10.28 (J_{HW} = 13.2, H_β), 7.13 (H_o and H_m), 6.75 (H_p), 6.17 (eq $OCH(CF_3)_2$), 4.67 (ax $OCH(CF_3)_2$).

W(C-*t*-BuCHC-*t*-Bu)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_3$. One equivalent of *tert*-butylacetylene (78 μL, 0.64 mmol) was added to a solution of W(C-*t*-Bu)(DIPP)$_3$ (0.50 g, 0.64 mmol) in pentane (5 mL). The solution turned dark red immediately. Upon cooling the solution to −40 °C small red crystals formed (0.33 g, 60% yield): ^{1}H NMR (C_6D_6) δ 9.34 (J_{HW} = 12.8, H_β), 7.11 (d, 2, eq H_m), 6.96 (d, 4, ax H_m), 6.91 (t, 1, eq H_p), 6.78 (t, 2, ax H_p), 3.81 (sept, 2, eq C*H*Me$_2$), 3.09 (sept, 4, ax C*H*Me$_2$), 1.29 (s, 18, CMe_3), 1.28 (d, 12, eq CH*Me*$_2$), 1.04 (d, 24, ax CH*Me*$_2$); ^{13}C NMR (C_6D_6) δ 248.6 (C_α), 160.3 (ax C_{ipso}), 159.7 (eq C_{ipso}), 138.0 (ax C_o), 137.4 (eq C_o), 123.9 (eq C_m), 123.4 (ax C_m), 122.8 (eq C_p), 121.0 (ax C_p), 114.6 (d, J_{CH} = 197, C_β), 43.3 (CMe_3), 33.5 (CMe_3), 28.2 (eq, $CHMe_2$), 26.6 (ax $CHMe_2$), 24.5 (eq CH*Me*$_2$), 24.4 (ax CH*Me*$_2$).

W(C$_3$-*t*-Bu$_2$)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_2$(py). A solution of W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$ was prepared by adding *tert*-butylacetylene (155 μL, 1.26 mmol) to a solution of W(C-*t*-Bu)(DIPP)$_3$ (1.00 g, 1.27 mmol) in pentane (20 mL). An excess of pyridine (250 μL, 3.09 mmol) was added. The solution turned from dark red to yellow immediately and was left undisturbed. After several minutes large yellow-orange needles began to form. After ~30 min the solution was cooled to −40 °C to ensure more complete crystallization (0.86 g, 88% yield): ^{1}H NMR (C_6D_6, 300 K) δ 9.39 (d, 2, py-H_o), 6.99 (br, m, 5, Ph-H_m and py-H_p), 6.85 (t, 2, Ph-H_p), 6.78 (t, 2, py-H_m), 1.32 (br s, 18, CMe_3), 1.14 (br d, 24, CH*Me*$_2$); ^{1}H NMR (CD_2Cl_2, 330 K) δ 9.29 (py-H_o), 8.00 (py-H_p), 7.57 (py-H_m), 6.89 (Ph-H_m), 6.74 (Ph-H_p), 2.3–2.7 (br, 4, C*H*Me$_2$), 1.16 (CMe_3), 1.03 (CH*Me*$_2$); ^{1}H NMR (CD_2Cl_2, 235 K) δ 9.35 (py-H_o), 8.05 (py-H_p), 7.61 (py-H_m), 6.97 (dd, 2, $^3J_{HH}$ = 6.0, $^4J_{HH}$ = 3.0, Ph), 6.71 (m, 4, Ph), 3.94 (br sept, 2, OC*H*Me$_2$), 1.43 (d, 6, CH*Me*$_2$), 1.35 (s, 9, CMe_3), 1.02 (d, 6, CH*Me*$_2$), 0.71 (s, 6, CH*Me*$_2$), 0.66 (s, 6, CH*Me*$_2$), 0.62 (s, 9, CMe_3), ~0.7 (C*H*Me$_2$, presence implied by 0.71 singlet and 0.66 singlet); ^{13}C NMR (CD_2Cl_2, 230 K) δ 223.2, 208.1, 181.4 (C_α, $C_{\alpha'}$, C_β), 161.3 (C_{ipso}), 149.5 (py-C_o), 139.1 (py-C_p), 135.5 (Ph-C_o), 124.8 (py-H_m), 122.7, 121.3, 120.2 (C_p, C_m, $C_{m'}$), 42.3 (CMe_3), 42.1 (CMe_3), 32.7 (CMe_3), 30.7 (CMe_3), 28.7, 24.8, 23.9, 23.6, 21.1, 19.9 (complex, $CHMe_2$ and CH*Me*$_2$). Anal. Calcd for $WC_{40}H_{57}O_2N$: C, 62.57; H, 7.48. Found: C, 62.70; H, 7.48.

W(C-*t*-BuCHC-*t*-Bu)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_2$Cl. Two equivalents of LiDIPP·ether (1.72 g, 6.67 mmol) were added to a solution of W(C-*t*-Bu)(dme)Cl_3 (1.50 g, 3.34 mmol) in ether (50 mL). The solution turned orange and LiCl precipitated. The solution was filtered through Celite and the solvent removed from the filtrate in vacuo. The residue was redissolved in ~150 mL of pentane, and *tert*-butylacetylene (410 μL, 3.34 mmol) was added. Orange needles of the product formed and were collected via filtration (1.75 g, 72% yield): ^{1}H NMR (C_6D_6) δ 8.99 (J_{HW} = 11.6, H_β), 7.22 (eq H_m), 6.99 (eq H_p), 6.98 (ax H_m), 6.83 (ax H_p), 4.06 (eq C*H*Me$_2$), 3.11 (ax C*H*Me$_2$), 1.55 (br d, 12, eq CH*Me*$_2$), 1.32 (s, 18, CMe_3), 1.13 (d, 12, ax CH*Me*$_2$); ^{13}C NMR (C_6D_6) δ 259.1 (C_α), 163.3 (C_{ipso}), 161.0 (C_{ipso}), 137.1 (C_o), 136.8 (C_o), 123.9 (C_p), 123.3 (C_m), 123.1 (C_m), 121.9 (C_p), 113.5 (d, J_{CH} = 200, C_β), 43.5 (CMe_3), 31.8 (CMe_3), 29.6 ($CHMe_2$), 27.8 ($CHMe_2$), 24.2 (CH*Me*$_2$), 23.4 (CH*Me*$_2$). Anal. Calcd for $WC_{35}H_{53}O_2Cl$: C, 57.97; H, 7.37. Found: C, 57.56; H, 7.58.

W(C$_3$-*t*-Bu$_2$)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_2$. Triethylamine (20 mL, 0.14 mmol) was added to a solution of W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_2$Cl (0.10 g, 0.14 mmol) in ether (15 mL). The solution turned from orange to colorless and Et_3N·HCl precipitated immediately. The solution was filtered through Celite. The solvent was removed from the filtrate in vacuo leaving a pale yellow oil which by ^{1}H NMR was found to be pure W(C$_3$-*t*-Bu$_2$)(DIPP)$_2$: ^{1}H NMR (C_6D_6) δ 7.0–6.8 (H_m and H_p), 2.87 (C*H*Me$_2$), 1.48 (CMe_3), 1.16 (CH*Me*$_2$); ^{13}C NMR (C_6D_6) δ 227.0 (C_α), 168.5 (C_β), 155.6 (C_{ipso}), 136.8 (C_o), 123.2 (C_p and C_m), 42.8 (CMe_3), 32.6 (CMe_3), 27.3 ($CHMe_2$), 23.2 (CH*Me*$_2$).

W(C$_5$H-*t*-Bu$_3$)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_2$ W(C$_3$-*t*-Bu$_2$)(DIPP)$_2$ was prepared as described above starting with W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_2$Cl (2.00 g, 2.76 mmol). The yellow oil was dissolved in pentane (25 mL), and excess *tert*-butylacetylene (1.00 mL, 8.16 mmol) was added. The solution turned dark blue overnight. The solution was filtered through Celite to remove some polymer. The solvent was removed from the filtrate in vacuo to give a blue oil which slowly crystallized to a blue solid. This solid could not be recrystallized successfully but was essentially pure by NMR (1.9 g, ~89% yield): ^{1}H NMR (C_6D_6, 295 K) δ 7.65 (J_{HW} = 15.3, H_β), 7.14 (H_m), 7.00 (H_p), 3.8–3.5 (br, 4, C*H*Me$_2$), 1.51 (s, 9, CMe_3), 1.43 (s, 9, CMe_3), 1.33 (d, 12, CH*Me*$_A$Me$_B$), 1.5–0.9 (br, 12, CHMe$_A$*Me*$_B$), 0.77 (s, 9, CMe_3); ^{1}H NMR (CD_2Cl_2, 230 K) δ 7.51 ($J_{HW} \approx$ 15, H_β), 7.09 (d, 2, H_m), 7.06 (d, 2, $H_{m'}$), 6.94 (t, 2, H_p), 3.63 (br, 2, C*H*Me$_2$), 3.45 (br, 2, C*H*Me$_2$), 1.42 (s, 9, CMe_3), 1.34 (d, 6, CHMe$_A$*Me*$_B$), 1.33 (s, 9, CMe_3), 1.25 (d, 6, CH*Me*$_A$Me$_B$), 1.22 (d, 6, CH*Me*$'_A$Me$_B$), 0.88 (d, 6, CHMe$_A$*Me*$'_B$), 0.63 (s, 9, CMe_3); ^{13}C NMR (CD_2Cl_2, 240 K) δ 266.2 (C_α), 193.9 (C_{ring}), 187.7 (d, J_{CH} = 15.9, C_{ring}), 158.4, 158.1 (each a s, C_{ipso} and C_{ring}), 156.1 (d, J_{CH} = 150, J_{CW} = 23.8 C_β in ring), 137.3 (C_o), 123.7 (br d, C_m), 122.7 (br d, C_m), 122.1 (C_p), 40.5, 37.5, 32.7 (CMe_3), 31.9, 31.7, 31.5 (CMe_3), 26.1, 22.8 ($CHMe_2$), 25.5, 24.2, 22.3, 21.6 (CH*Me*$_2$).

W(C$_5$H-*t*-Bu$_3$)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_2$(py). A solution of W(C$_5$H-*t*-Bu$_3$)(DIPP)$_2$ in pentane (25 mL) was prepared as described

above beginning with W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_2$Cl (1.00 g, 1.38 mmol). Excess pyridine (200 μL, 2.47 mmol) was then added, and the solvent was removed *in vacuo*. Recrystallization from ether/pentane at −40 °C gave large, black prisms (0.62 g, 53% yield): ^{1}H NMR (C_6D_6, 295 K) δ 8.61 (py-H_o), 7.68 (J_{HW} = 15.3, H_β), 7.14 (Ph-H_m), 7.00 (Ph-H_p), 6.97 (py-H_p), 6.66 (py-H_m), 3.9–3.6 (br, 4, C*H*Me$_2$), 1.36 (s, 9, CMe$_3$), 1.35 (br d, 12, CH*Me*$_A$Me$_B$), 1.33 (s, 9, CMe$_3$), 1.5–1.0 (br, 12, CHMe$_A$*Me*$_B$), 0.83 (s, 9, CMe$_3$); ^{13}C NMR (CD_2Cl_2, 240 K) δ 277.9 (C_α), 194.4 (C_{ring}), 185.8 (d, J_{CH} = 15.5, C_{ring}), 161.5, 159.8 (each a s, C_{ipso} and C_{ring}), 155.1 (d, J_{CH} = 148, J_{CW} = 28, C_β), 150.3 (py-C_o), 137.5 (py-C_p), 137.1 (Ph-C_o), 123.9 (py-C_m), 123.3, 122.6, 121.2 (Ph-C_p, Ph-C_m, and Ph-$C_{m'}$), 40.4, 38.7, 32.4 (*C*Me$_3$), 32.4, 32.1, 31.7 (C*Me*$_3$), 26.9, 25.2 (*C*HMe$_2$), 25.7, 21.9, 21.7 (CH*Me*$_2$). Anal. Calcd for $WC_{46}H_{67}O_2N$: C, 65.01; H, 7.95. Found: C, 64.83; H, 7.83.

W(C$_5$H$_2$-*t*-Bu$_3$)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)$_2$(O$_2$CR). [R = CF$_3$]. One equivalent of CF_3CO_2H (50 μL, 0.65 mmol) was added to a solution of W(C$_5$H-*t*-Bu$_3$)(DIPP)$_2$ (0.50 g, 0.65 mmol) in ether (20 mL). The solution turned from blue to red. After 1 h the solvent was removed from the solution in vacuo. The residue was recrystallized from ether/pentane at −40 °C as small red crystals (0.35 g, 61% yield): ^{1}H NMR (C_6D_6) δ 8.25 (d, 1, $^3J_{HH}$ = 1.7, J_{HW} = 18.3, H_β), 6.94 (m, 3, phenyl), 6.90 (m, 3, phenyl), 3.46 (br, 1, H_α), 3.0–3.3 (br, 4, C*H*Me$_2$), 1.48 (CMe$_3$), 1.35 (CMe$_3$), 1.24 (d, 12, CH*Me*$_2$), 1.21 (d, 6, CH*Me*$_2$), 1.14 (d, 6, CH*Me*$_2$), 0.96 (CMe$_3$); ^{13}C NMR (C_6D_6) δ 194.8 (C_{ring}), 188.0 (d, J_{CH} = 15.9, C_{ring}), 162.2 (dd, J_{CH} = 151, 7.9, C_β), 161.0 (q, $^2J_{CF}$ = 37.2, CF_3CO_2), 159.1 (C_{ipso}), 158.6 (C_{ipso}), 139.1 (C_o), 138.9 (C_o), 126.2 (C_p), 125.7 (C_p), 124.3 (C_m), 124.1 (C_m), 117.7 (q, J_{CF} = 292, CF_3CO_2), 90.2 (d, J_{CH} = 119, J_{CW} = 77, C_α), 41.4, 39.1, 35.2 (*C*Me$_3$), 31.6, 31.2, 30.4 (C*Me*$_3$), 26.6 (*C*HMe$_2$), 25.2, 24.8, 24.3, 23.9 (CH*Me*$_2$). Anal. Calcd for $WC_{43}H_{63}O_4F_3$: C, 58.37; H, 7.18. Found: C, 58.43; H, 7.10.

[R = Ph]. This compound was prepared in the same manner as W(C$_5$H$_2$-*t*-Bu$_3$)(DIPP)$_2$(O$_2$CCF$_3$) starting from W(C$_5$H-*t*-Bu$_3$)(DIPP)$_2$ (0.90 g, 1.2 mmol) and benzoic acid (0.14 g, 1.1 mmol). The product was obtained as an orange powder from ether/pentane at −40 °C (2 crops, 0.74 g, 71% yield): ^{1}H NMR (C_6D_6) δ 8.62 (d, 1, $^3J_{HH}$ = 1.9, J_{HW} = 17.7, H_β), 8.26 (PhCO$_2$-H_o), 7.04 (m, 3, PhCO$_2$-H_m and -H_p), 6.87 (m, 5, DIPP-H's), 6.72 (t, 1, DIPP-H_p), 4.4–4.6 (br, 1, H_α), 3.66 (C*H*Me$_2$), 3.43 (C*H*Me$_2$), 1.78 (CMe$_3$), 1.45 (CMe$_3$), 1.38 (CMe$_3$), 1.15 (m, 18, CH*Me*$_2$), 0.96 (d, 6, CH*Me*$_2$); ^{13}C NMR (CD_2Cl_2, 240 K) δ 186.6, 184.9 (each a s, C_{ring} and PhCO$_2$), 182.0 (d, J_{CH} = 14.7, C_{ring}), 165.3 (dd, J_{CH} = 149, 7.1, C_β), 158.3 (DIPP-C_{ipso}), 156.9 (DIPP-C_{ipso}), 149.5 (C_{ring}), 140.7 (DIPP-C_o), 139.1 (DIPP-C_o), 134.4 (PhCO$_2$-C_{ipso}), 132.8 (PhCO$_2$-C_p), 129.6, 128.0 (PhCO$_2$-C_m and -C_o), 124.6, 123.6, 123.3 (DIPP-C_p and -C_m), 83.1 (d, J_{CH} = 120, C_α), 43.1, 39.6, 35.4 (*C*Me$_3$), 32.3, 31.9, 30.7 (C*Me*$_3$), 25.4, 24.8 (*C*HMe$_2$), 25.9, 25.4, 25.0, 24.8 (CH*Me*$_2$).

W(C-*t*-BuCHC-*t*-Bu)(O-2,6-C$_6$H$_3$Me$_2$)$_3$. A sample of W(C-*t*-Bu)(DMP)$_3$(THF) (1.00 g, 1.45 mmol) was dissolved in ether (20 mL), and *tert*-butylacetylene (180 μL, 1.47 mmol) was added. The solution turned dark red immediately. The solvent was removed in vacuo leaving a viscous red oil. The oil was dissolved in ~15 mL of pentane, and the solution was cooled to −40 °C to give small dark red prisms (0.70 g, 69% yield): ^{1}H NMR (C_6D_6) δ 9.58 (J_{HW} = 14.0, H_β), 6.98 (eq H_m), 6.83 (ax H_m), 6.71 (eq H_p), 6.61 (ax H_p), 2.49 (eq OC$_6$H$_3$*Me*$_2$), 2.09 (ax OC$_6$H$_3$*Me*$_2$), 1.22 (CMe$_3$); ^{13}C NMR (CD_2Cl_2) δ 244.7 (C_α), 163.7 (ax C_{ipso}), 162.2 (eq C_{ipso}), 128.1 (ax and eq C_m), 128.0 (C_o), 127.3 (C_o), 122.6 (d, J_{CH} = 199, C_β), 121.3 (eq C_p), 120.3 (ax C_p), 43.5 (*C*Me$_3$), 33.2 (C*Me*$_3$), 18.6 (ax OC$_6$H$_3$*Me*$_2$), 18.4 (eq OC$_6$H$_3$*Me*$_2$).

W(C-*t*-BuCHC-*t*-Bu)(O-2,6-C$_6$H$_3$Me$_2$)$_2$Cl. A sample of W(CCMe$_3$)(dme)Cl$_3$ (0.65 g, 1.45 mmol) and 2 equiv of W(CCMe$_3$)(DMP)$_3$(THF) (2.00 g, 2.90 mmol) were dissolved in ether (100 mL). After 1 h the solution had turned orange. *tert*-Butylacetylene (540 μL, 4.40 mmol) was then added. The resulting deep red solution was concentrated in vacuo to ~10 mL, and 50 mL of pentane was added. Orange-red crystals began to form. The solution was cooled to −40 °C in order to complete the crystallization (1.43 g, 54% yield): ^{1}H NMR (C_6D_6) δ 9.11 (J_{HW} = 11.6, H_β), 7.10 (eq H_m), 6.81 (ax H_m), 6.81 (eq H_p), 6.65 (ax H_p), 2.77 (eq Me), 1.98 (ax Me), 1.27 (CMe$_3$); ^{13}C NMR (C_6D_6) δ 259.6 (C_α), 128.3 (C_m), 126.8 (C_o), 126.5 (C_o), 123.0 (C_p), 121.3 (C_p), 114.5 (d, J_{CH} = 200, C_β), 43.3 (*C*Me$_3$), 31.8 (C*Me*$_3$), 18.7 (Me), 18.4 (Me). Anal. Calcd for $WC_{27}H_{37}O_2Cl$: C, 52.91; H, 6.09. Found: C, 52.95; H, 6.03.

W(C$_3$-*t*-Bu$_2$)(O-2,6-C$_6$H$_3$Me$_2$)$_2$. One equivalent of triethylamine (23 μL, 0.17 mmol) was added to a solution of W(C-*t*-BuCHC-*t*-Bu)(DMP)$_2$Cl (0.10 g, 0.16 mmol) in ether (5 mL). The solution turned yellow and NEt$_3$·HCl immediately precipitated. The solution was filtered and the solvent removed from the filtrate in vacuo to give a yellow oil that was pure by NMR: ^{1}H NMR (C_6D_6) δ 6.80 (H_m), 6.69 (H_p), 1.93 (Me), 1.42 (CMe$_3$); ^{13}C NMR (C_6D_6) δ 224.1 (C_α), 171.6 (C_β), 159.0 (C_{ipso}), 128.2 (C_m), 126.2 (C_o), 121.9 (C_p), 42.6 (*C*Me$_3$), 32.3 (C*Me*$_3$), 17.1 (Me).

W(C$_3$-*t*-Bu$_2$)(O-2,6-C$_6$H$_3$Me$_2$)$_2$(py). A solution of W(C$_3$-*t*-Bu$_2$)(DMP)$_2$ was prepared by adding NEt$_3$ (350 μL, 2.51 mmol) to a solution of W(C-*t*-BuCHC-*t*-Bu)(DMP)$_2$Cl (1.50 g, 2.45 mmol) in ether (75 mL). The solution was filtered to remove NEt$_3$·HCl. One equivalent of pyridine (200 μL, 2.47 mmol) was then added, and the solvent was removed from the solution in vacuo. The residue was recyrstallized from ether/pentane at −40 °C to give large yellow crystals (2 crops, 1.26 g, 79% yield): ^{1}H NMR (CD_2Cl_2, 300 K) δ 9.47 (py-H_o), 8.05 (py-H_p), 7.65 (py-H_m), 6.79 (br d, Ph-H_m), 6.58 (Ph-H_p), 2.5–1.0 (br s, 12, Me), 1.07 (br, 18, CMe$_3$); ^{1}H NMR (CD_2Cl_2, 230 K, alkyl resonances only) δ 2.58 (s, 6, Me), 1.34 (s, 9, CMe$_3$), 0.80 (s, 6, Me), 0.66 (s, 9, CMe$_3$); ^{13}C NMR (CD_2Cl_2, 340 K) δ 218.5 (C_α), 180.1 (C_β), 162.8 (C_{ipso}), 151.0 (py-C_o), 139.2 (py-C_p), 128.2 (Ph-C_m), 126.6 (Ph-C_o), 125.1 (py-C_m), 120.9 (Ph-C_p), 43.2 (*C*Me$_3$), 32.5 (C*Me*$_3$), 17.4 (Me); ^{13}C NMR (CD_2Cl_2, 230 K) δ 222.9 (C_α), 209.1 ($C_{\alpha'}$), 179.0 (C_β), 162.3 (C_{ipso}), 149.8 (py-C_o), 138.9 (py-C_p), 127.4 (Ph-C_m), 126.8 (Ph-C_m), 125.7 (Ph-C_o), 124.6 (py-C_m), 119.9 (Ph-C_p), 42.3 (*C*Me$_3$), 42.2 (*C*Me$_3$), 32.7 (C*Me*$_3$), 30.1 (C*Me*$_3$), 18.0 (Me), 16.0 (Me).

W(C$_5$H-*t*-Bu$_3$)(O-2,6-C$_6$H$_3$Me$_2$)$_2$(py). W(C$_3$-*t*-Bu$_2$)(DMP)$_2$ was prepared as above from W(C-*t*-BuCHC-*t*-Bu)(DMP)$_2$Cl (1.00 g, 1.63 mmol) and dissolved in pentane (25 mL). Excess *tert*-butylacetylene (600 μL, 4.89 mmol) was added. Over a period of 3 h the solution changed from yellow to dark blue. Excess pyridine (200 μL, 2.47 mmol) was then added, and the solution was filtered through Celite to remove some polymer. The solvent was then removed from the filtrate in vacuo, and the residue was recyrstallized from ether/pentane at −40 °C to give small black prisms (2 crops, 0.75 g, 63% yield): ^{1}H NMR (C_6D_6) δ 8.88 (py-H_o), 7.90 (J_{HW} = 14.7, H_β), 7.01 (Ph-H_m), 6.96 (py-H_p), 6.84 (Ph-H_p), 6.63 (py-H_m), 2.40 (OC$_6$H$_3$*Me*$_2$), 1.41 (CMe$_3$), 1.45 (CMe$_3$), 0.80 (CMe$_3$); ^{13}C NMR (C_6D_6) δ 275.9 (C_α), 193.4 (C_{ring}), 187.0 (d, J_{CH} = 6.3, C_{ring}), 163.0, 162.5 (each a s, C_{ring} and C_{ipso}), 156.0 (d, J_{CH} = 148, J_{CW} = 27, C_β), 150.8 (py-C_o), 136.8 (py-C_p), 129.1 (Ph-C_m), 126.7 (Ph-C_o), 123.5 (py-C_m), 121.6 (Ph-C_p), 40.8, 38.2, 32.8 (*C*Me$_3$), 32.5, 32.4, 31.5 (C*Me*$_3$), 17.6 (OC$_6$H$_3$*Me*$_2$). Anal. Calcd for $WC_{38}H_{51}O_2N$: C, 61.87; H, 6.97. Found: C, 62.14; H, 7.23.

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Registry No. LiDIPP, 72727-49-2; W(C-*t*-BuCHC-*t*-Bu)[OCH(CF$_3$)$_2$]$_3$, 99342-25-3; W(C-*t*-Bu)[OCH(CF$_3$)$_2$]$_3$(dme), 91202-86-7; W(C$_3$-*t*-Bu$_2$)[OCH(CF$_3$)$_2$]$_2$(dme), 101420-52-4; W(C$_3$-*t*-Bu$_2$)[OCH(CF$_3$)$_2$](py)$_2$, 101420-57-9; W(C-*t*-BuCHCPh)[OCH(CF$_3$)$_2$]$_3$, 101471-29-8; W(CPh)[OCH(CF$_3$)$_2$]$_3$(dme), 101420-58-0; W(C$_3$-*t*-BuPh)[OCH(CF$_3$)$_2$]$_2$(dme), 101420-53-5; W(C$_3$-*t*-BuPh)[OCH(CF$_3$)$_2$]$_2$(py)$_2$, 101420-48-8; W(C$_3$Ph$_2$)[OCH(CF$_3$)$_2$]$_2$(dme), 101420-49-9; W(CPhCHCPh)[OCH(CF$_3$)$_2$]$_3$, 101471-30-1; W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_3$, 101471-31-2; W(C-*t*-Bu)(DIPP)$_3$, 91229-76-4; W(C$_3$-*t*-Bu$_2$)(DIPP)$_2$(py), 101420-51-3; W(C-*t*-BuCHC-*t*-Bu)(DIPP)$_2$Cl, 101471-32-3; W(C-*t*-Bu)(dme)Cl$_3$, 83542-12-5; W(C$_3$-*t*-Bu$_2$)(DIPP), 101420-50-2; W(C$_5$H-*t*-Bu$_3$)(DIPP)$_2$, 101420-56-8; W(C$_5$-*t*-Bu$_3$)(DIPP)$_2$(py), 101420-55-7; W(C$_5$H$_2$-*t*-Bu$_3$)(DIPP)$_2$(O$_2$CCF$_3$), 101471-27-6; W(C$_5$H$_2$-*t*-Bu$_3$)(DIPP)$_2$(O$_2$CPh), 101471-28-7; W(C-*t*-BuCHC-*t*-Bu)(O-2,6-C$_6$H$_3$Me$_2$)$_3$, 101471-33-4; W(C-*t*-BuCHC-*t*-Bu)(O-2,6-C$_6$H$_3$Me$_2$)$_2$Cl, 101492-12-0; W(C$_3$-*t*-Bu$_2$)(O-2,6-C$_6$H$_3$Me$_2$)$_2$, 101420-54-6; W(C$_3$-*t*-Bu$_2$)(O-2,6-C$_6$H$_3$Me$_2$)$_2$(py), 101471-26-5; W(C$_5$H-*t*-Bu$_3$)(O-2,6-C$_6$H$_3$Me$_2$)$_2$(py), 101420-59-1; W(C-*t*-Bu)(DMP)$_3$(THF), 91229-83-3; W(CCMe$_3$)(dme)Cl$_3$, 83542-12-5; *tert*-butylacetylene, 917-92-0; phenylacetylene, 536-74-3; diphenylacetylene, 501-65-5.