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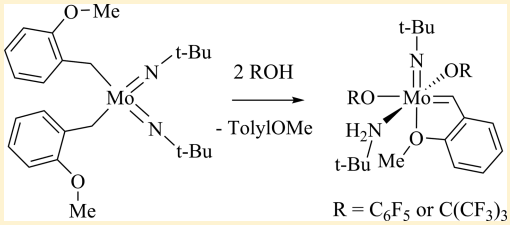
# Synthesis of Molybdenum and Tungsten Alkylidene Complexes that Contain a *tert*-Butylimido Ligand

Hyangsoo Jeong, Richard R. Schrock,* and Peter Müller

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

Supporting Information

**ABSTRACT:** A variety of molybdenum or tungsten complexes that contain a *tert*-butylimido ligand have been prepared. For example, the *o*-methoxybenzylidene complex W(N-*t*-Bu)(CH-*o*-MeOC$_6$H$_4$)(Cl)$_2$(py) was prepared through addition of pyridinium chloride to W(N-*t*-Bu)$_2$-(CH$_2$-*o*-MeOC$_6$H$_4$)$_2$, while Mo(N-*t*-Bu)(CH-*o*-MeOC$_6$H$_4$)(OR$_F$)$_2$(*t*-BuNH$_2$) complexes (OR$_F$ = OC$_6$F$_5$ or OC(CF$_3$)$_3$) were prepared through addition of two equivalents of R$_F$OH to Mo(N-*t*-Bu)$_2$(CH$_2$-*o*-MeOC$_6$H$_4$)$_2$. An X-ray crystallographic study of Mo(N-*t*-Bu)(CH-*o*-MeOC$_6$H$_4$)[OC-(CF$_3$)$_3$]$_2$(*t*-BuNH$_2$) showed that the methoxy oxygen is bound to the metal and that two protons on the *tert*-butylamine ligand are only a short distance away from one of the CF$_3$ groups on one of the perfluoro-*tert*-butoxide ligands (H···F = 2.456(17) and 2.467(17) Å). Other synthesized tungsten *tert*-butylimido complexes include W(N-*t*-Bu)(CH-*o*-MeOC$_6$H$_4$)(pyr)$_2$(2,2′-bipyridine) (pyr = pyrrolide), W(N-*t*-Bu)(CH-*o*-MeOC$_6$H$_4$)(pyr)(OHMT) (OHMT = O-2,6-(mesityl)$_2$C$_6$H$_3$), W(N-*t*-Bu)(CH-*t*-Bu)(OHMT)(Cl)(py) (py = pyridine), W(N-*t*-Bu)(CH-*t*-Bu)(OHMT)-(Cl), W(N-*t*-Bu)(CH-*t*-Bu)(pyr)(ODFT)(py), W(N-*t*-Bu)(CH-*t*-Bu)(OHMT)$_2$, and W(N-*t*-Bu)(CH-*t*-Bu)(ODFT)$_2$ (ODFT = O-2,6-(C$_6$F$_5$)$_2$C$_6$H$_3$). Interestingly, W(N-*t*-Bu)(CH-*t*-Bu)(OHMT)$_2$ does not react with ethylene or 2,3-dicarbomethoxynorbornadiene. Removal of pyridine from W(N-*t*-Bu)(CH-*t*-Bu)(Biphen$_{CF3}$)(pyridine) (Biphen$_{CF3}$ = 3,3′-di-*tert*-butyl-5,5′-bistrifluoromethyl-6,6′-dimethyl-1,1′-biphenyl-2,2′-diolate) with B(C$_6$F$_5$)$_3$ led to formation of a five-coordinate 14*e* neopentyl complex as a consequence of CH activation in one of the methyl groups in one *tert*-butyl group of the Biphen$_{CF3}$ ligand, as was proven in an X-ray study. An attempted synthesis of W(N-*t*-Bu)(CH-*t*-Bu)(Biphen$_{Me}$) (Biphen$_{Me}$ = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-1,1′-biphenyl-2,2′-diolate) led to formation of a 1:1 mixture of W(N-*t*-Bu)(CH-*t*-Bu)(Biphen$_{Me}$) and a neopentyl complex analogous to the one characterized through an X-ray study. The metallacyclobutane complexes W(N-*t*-Bu)(C$_3$H$_6$)(pyrrolide)(ODFT) and W(N-*t*-Bu)(C$_3$H$_6$)(ODFT)$_2$ were prepared in reactions involving W(N-*t*-Bu)(CH-*t*-Bu)(pyr)$_2$(bipy), ZnCl$_2$(dioxane), and one or two equivalents of DFTOH, respectively, under 1 atm of ethylene.




## INTRODUCTION

Imido alkylidene complexes of molybdenum and tungsten with the generic formula M(NR)(CHR′)(X)(Y) (M = Mo or W; X and Y can be a variety of monoanionic ligands, e.g., alkoxide, aryloxide, pyrrolide) have been the mainstay of the development of well-defined Mo or W catalysts for the metathesis of olefins.[1] The reactivity characteristics of these initiators depend strongly upon M and the steric and electronic nature of NR, X, and Y. In the majority of situations R is an aryl group. Analogues that contain a *tert*-butylimido ligand are rare. In 2012 we showed[2] that tungsten-based *tert*-butylimido alkylidene catalysts could be accessed through the chloro-bridged dimer [W(N-*t*-Bu)$_2$(*t*-BuNH$_2$)Cl$_2$]$_2$, which is prepared conveniently from *t*-BuNH-(TMS) and WCl$_6$.[3] The molybdenum *tert*-butylimido alkylidene complex Mo(N-*t*-Bu)(CH-*t*-Bu)[OCH(CF$_3$)$_2$]$_2$(*t*-BuNH$_2$) was prepared by Osborn (as an oil in 80% yield)[4] through the reaction between Mo(N-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ and hexafluoro-2-propanol, and several preliminary studies of metathesis reactions involving Mo(N-*t*-Bu)(CH-*t*-Bu)[OCH(CF$_3$)$_2$]$_2$(*t*-BuNH$_2$) as an initiator were explored. We confirmed that Mo(N-*t*-Bu)(CH-*t*-Bu)[OCH(CF$_3$)$_2$]$_2$(*t*-BuNH$_2$) could be prepared in this manner (and isolated as an off-white *solid* in 26% yield) and found that Mo(N-*t*-Bu)(CH-*t*-Bu)(OC$_6$F$_5$)$_2$(*t*-BuNH$_2$) similarly can be obtained in 84% yield upon treating Mo(N-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ with two equivalents of pentafluorophenol.[5] (Osborn noted that "various phenol derivatives" (not fluorinated) do not react with Mo(N-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ to yield phenoxide analogues of Mo(N-*t*-Bu)(CH-*t*-Bu)[OCH(CF$_3$)$_2$]$_2$(*t*-BuNH$_2$).[4]) These two syntheses of Mo(N-*t*-Bu)(CH-*t*-Bu)(OR$_F$)$_2$(*t*-BuNH$_2$) compounds are rare examples of formation of an alkylidene through addition of a relatively acidic alcohol, R$_F$OH, instead of triflic acid or HCl to a bisimido dialkyl complex. No analogous reactions for arylimido complexes have been reported, presumably because the arylimido ligand is less likely to be protonated for electronic reasons. Monoaryloxide pyrrolide (MAP) alkylidene complexes of molybdenum and tungsten that contain a *tert*-butylimido ligand have proven to be valuable catalysts for the *Z*-selective ring-opening metathesis polymerization (ROMP) of 3-substituted (Me, Hex, Ph) cyclooctenes[5] and for the stereospecific ROMP of norbornene,[6] *endo*-dicyclopentadiene,[7] and *endo,anti*-tetracyclododecene.[6]

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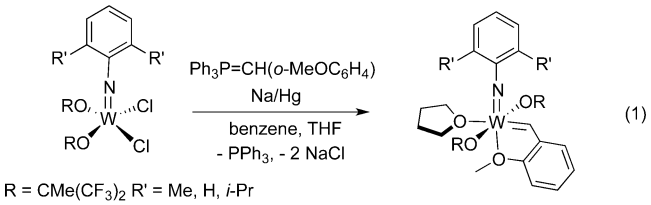
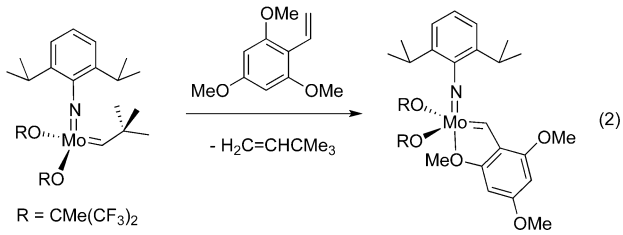
In this paper we employ *tert*-butylimido complexes of W (primarily) and Mo as a platform to explore new synthetic variations of imido alkylidene complexes, several of which are not known for arylimido analogues.

## RESULTS AND DISCUSSION

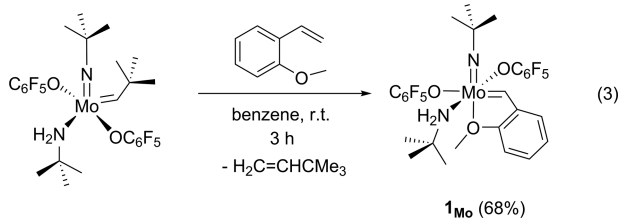
**Synthesis of *Ortho* Alkoxy Benzylidene Complexes.** *Ortho* alkoxy benzylidene complexes of tungsten were first prepared through addition of a Wittig reagent to a tungsten(IV) species (eq 1).[8] They also have been prepared through addition of



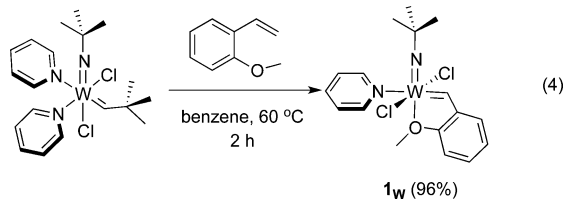




styrenes to neophylidene or neopentylidene complexes (eq 2).[9] In ruthenium alkylidene chemistry *ortho* alkoxy benzylidene complexes have allowed important phosphine-free catalysts to be synthesized, as first reported by Hoveyda.[10] For Mo and W we envisioned that five-coordinate complexes that contain an *ortho* alkoxy benzylidene ligand might be less soluble than related four-coordinate neopentylidene or neophylidene complexes and therefore isolated more readily.

Addition of 2-methoxystyrene to Mo(N-*t*-Bu)(CH-*t*-Bu)-$(OC_6F_5)_2$(*t*-BuNH$_2$) yields Mo(N-*t*-Bu)(CH-*o*-MeO$C_6H_4$)-$(OC_6F_5)_2$(*t*-BuNH$_2$) (**1$_{Mo}$**) in 68% yield (eq 3). A similar

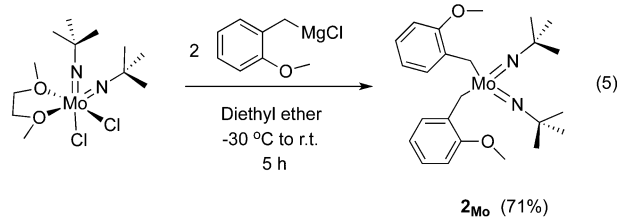


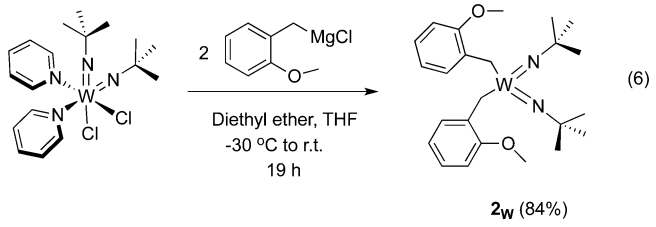

reaction between 2-methoxystyrene and W(N-*t*-Bu)(CH-*t*-Bu)$(Cl)_2(py)_2$ yields W(N-*t*-Bu)(CH-*o*-MeO$C_6H_4$)$(Cl)_2$(py) (**1$_W$**) in 96% yield (eq 4). We propose that heating is required in




the latter case in order for 18*e* W(N-*t*-Bu)(CH-*t*-Bu)$(Cl)_2(py)_2$ to lose a pyridine and form the more reactive intermediate 16*e* monopyridine derivative.

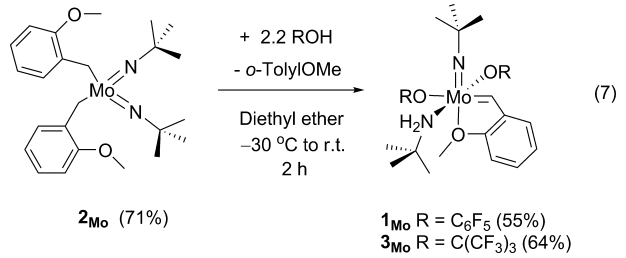
We wondered whether it might be possible to generate *o*-methoxybenzylidene complexes from bis-*o*-methoxybenzyl complexes directly through $\alpha$-hydrogen abstraction instead of preparing a neopentylidene or neophylidene complex first. M(N-*t*-Bu)$_2$(CH$_2$-*o*-MeO$C_6H_4$)$_2$ complexes (M = Mo (**2$_{Mo}$**, eq 5), W (**2$_W$**, eq 6)) can be prepared straightforwardly through




addition of two equivalents of 2-methoxybenzylmagnesium chloride to Mo(N-*t*-Bu)$_2$(Cl)$_2$(dme) or W(N-*t*-Bu)$_2$(Cl)$_2$(py)$_2$. We have no information as to whether the methoxy oxygens on **2$_{Mo}$** or **2$_W$** are bound strongly to Mo or W on the NMR time scale at room temperature in solution at 22 °C or not. Compound **2$_W$** also can be prepared from [W(N-*t*-Bu)$_2$($\mu$-Cl)(Cl)(*t*-BuNH$_2$)]$_2$. Compound **2$_{Mo}$** is a yellow solid, while **2$_W$** so far has been isolated only as a brown oil.

Addition of 2.2 equivalents of pentafluorophenol or perfluoro-*tert*-butanol to Mo(N-*t*-Bu)$_2$(CH$_2$-*o*-MeO$C_6H_4$)$_2$ leads to Mo(N-*t*-Bu)(CH-*o*-MeO$C_6H_4$)(OR$_F$)$_2$(*t*-BuNH$_2$) (OR$_F$ = $C_6F_5$ (**1$_{Mo}$**) or $C(CF_3)_3$ (**3$_{Mo}$**); eq 7). Although pentafluorophenol




reacts with Mo(N-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ to yield Mo(N-*t*-Bu)(CH-*t*-Bu)$(OC_6F_5)_2$(*t*-BuNH$_2$) (*vide supra*), we could not prepare the neopentylidene analogue of **3$_{Mo}$** by treating Mo(N-*t*-Bu)$_2$(CH$_2$-*t*-Bu)$_2$ with $(CF_3)_3$COH. Compounds **1$_{Mo}$** and **3$_{Mo}$** are believed to be the only examples of complexes that are not a neopentylidene or neophylidene complex formed through addition of a relatively acidic alcohol to a bisimido dialkyl complex, and the reaction to give **3$_{Mo}$** is the only one of this general type that employs perfluoro-*tert*-butanol.

Complexes **1$_{Mo}$** and **3$_{Mo}$** both have $^1J_{CH}$ values for the alkylidene protons characteristic of *anti* alkylidene isomers (145 Hz).[11] An X-ray crystallographic study of **3$_{Mo}$** (Figure 1) confirmed that the methoxy oxygen is bound to the metal (Mo(1)−O(1) = 2.3675 Å). One of perfluoro-*tert*-butoxide groups is disordered over three positions. The Mo(1)−N(2) distance in **3$_{Mo}$** (1.7039 Å) is comparable to the Mo═N bond distance in Mo(NAd)(CH-*t*-Bu)(pyr)(OHIPT) (1.707 Å).[12]



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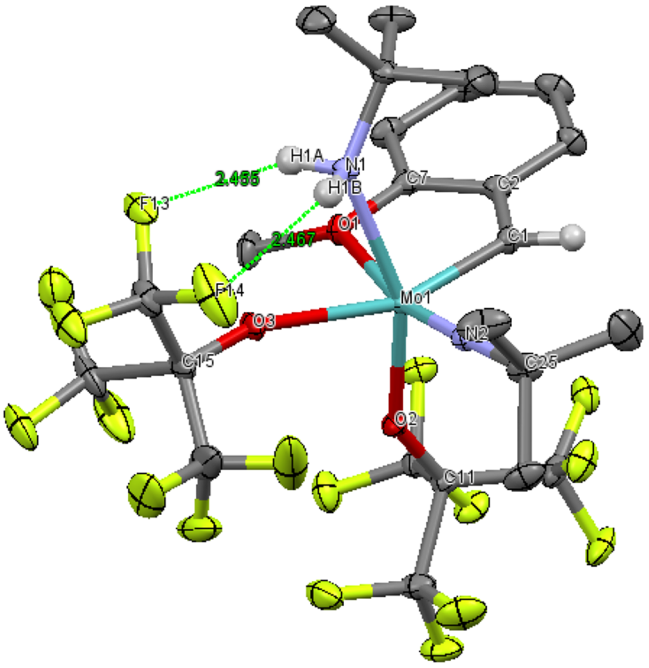
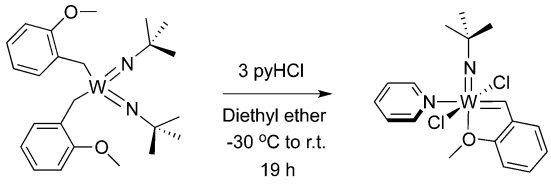



**Figure 1.** Thermal ellipsoid plots shown at the 50% probability level of $\mathbf{3_{Mo}}$. Minor components of disorder are omitted for clarity. Selected bond distances (Å) and angles (deg): Mo(1)−N(2) = 1.7039(11), Mo(1)−N(1) = 2.2551(10), Mo(1)−C(1) = 1.9611(12), Mo(1)−O(1) = 2.3675(9), Mo(1)−O(2) = 2.0452(9), Mo(1)−O(3) = 2.1421(9); C(2)−C(1)−Mo(1) = 122.00(9), C(11)−O(2)−Mo(1) = 144.01(8), C(15)−O(3)−Mo(1) = 148.07(9), C(21)−N(1)−Mo(1) = 134.48(8), C(25)−N(2)−Mo(1) = 177.20(10).

Two protons on the *tert*-butylamine ligand are a relatively short distance away from two fluorines in one of the $CF_3$ groups on one of the perfluoro-*tert*-butoxide ligands (H···F = 2.456(17) and 2.467(17) Å). (The sum of the van der Waals radii is ~2.55 Å).[13] The two inequivalent protons (H1A and H1B) on the *tert*-butylamine ligand in $\mathbf{3_{Mo}}$ are coupled to one another ($^2J_{HH}$ = 12.5 Hz) in the $^1$H NMR spectrum, but no coupling to are rare.fluorine could be observed. Two fluorine resonances are observed by $^{19}$F NMR spectroscopy at room temperature, which suggests that the two perfluoro-*tert*-butoxide ligands do not exchange readily on the NMR time scale, but the $C(CF_3)_3$ group that contains C15 must rotate readily on the time scale.

Addition of three equivalents of pyridinium chloride to $\mathbf{2_W}$ in diethyl ether yields $\mathbf{1_W}$ (eq 8). Compound $\mathbf{1_W}$ also showed a $^1J_{CH}$

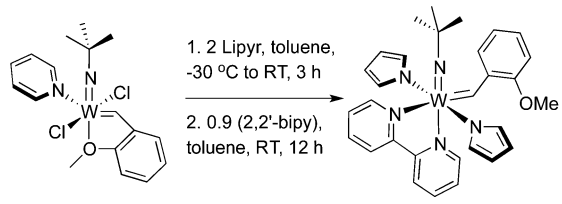



$\mathbf{2_W}$ $\mathbf{1_W}$ (79%) (8)

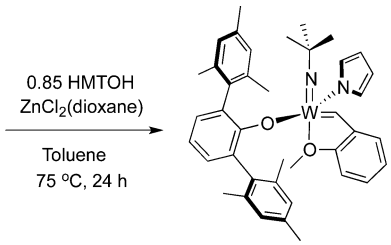
value of 145 Hz for the alkylidene proton, indicative of an *anti* alkylidene. We propose that $\mathbf{1_W}$ has a six-coordinate structure analogous to that of $\mathbf{1_{Mo}}$.

$Mo(NAr)_2(CH_2\text{-}o\text{-}MeOC_6H_4)_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$) is formed upon treatment of $Mo(NAr)_2Cl_2(dme)$ with two equivalents of the *o*-methoxybenzyl Grignard reagent. However, attempts to form alkylidene species from $Mo(NAr)_2(CH_2\text{-}o\text{-}MeOC_6H_4)_2$ using $C_6F_5OH$, TfOH, $CH_3SO_2H$, HCl, or pyHCl led only to apparent protonation of the benzyl group on the basis of the fact that 2-methoxytoluene was observed in $^1$H NMR spectra in all cases. Apparently the NAr ligand is not basic enough and is too sterically crowded to be protonated more readily than the benzyl ligand. The tendency for a *tert*-butylimido to be protonated preferentially in competition with a NAr ligand is illustrated dramatically in the reaction of Mo(NAr)(N-*t*-Bu)$(CH_2CMe_2Ph)_2$ with two equivalents of $C_6F_5OH$ in pentane at −35 °C to give Mo(NAr)$(CHCMe_2Ph)(OC_6F_5)_2$(*t*-$BuNH_2$) as a yellow, microcrystalline solid in high yield.[14] A *tert*-butylimido group is also protonated more readily than a $NC_6F_5$ ligand.[15] Finally, preferential protonation of a *tert*-butylimido ligand is the key to the synthesis of Mo and W complexes that contain a sterically demanding N-2,6-$(2,4,6\text{-}R_3C_6H_2)_2C_6H_3$ ligand (R = Me or *i*-Pr).[16] So far to our knowledge there are no reported examples of the use of fluorinated alcohols as acids for inducing $\alpha$-hydrogen abstraction to yield *arylimido* alkylidene Mo or W complexes.

We demonstrated that one tungsten MAP complex that contains an *o*-methoxybenzylidene ligand could be prepared through the reaction between $\mathbf{1_W}$ and two equivalents of lithium pyrrolide followed by addition of 2,2′-bipyridine to yield W(N-*t*-Bu)(CH-*o*-$MeOC_6H_4$)$(pyr)_2$(bipy) ($\mathbf{4_W}$), which is isolated readily (eq 9). In view of the six-coordinate metal center we




$\mathbf{1_W}$ $\mathbf{4_W}$ (81%)




$\mathbf{5_W}$ (97%) (9)

propose that the methoxy group in the alkylidene is not bound to the W center in $\mathbf{4_W}$. Treatment of $\mathbf{4_W}$ with $ZnCl_2$(dioxane) and HMTOH (2,6-dimesitylphenol) in toluene at 75 °C for 24 h then yields W(N-*t*-Bu)(CH-*o*-$MeOC_6H_4$)(pyr)(OHMT) ($\mathbf{5_W}$) in high yield (eq 9).

A comparison of $\mathbf{5_W}$ with its neopentylidene analogue W(N-*t*-Bu)(CH-*t*-Bu)(pyr)(OHMT) for the homocoupling of 1-octene (2 mol % catalysts in neat 1-octene) is shown in Table 1. The results are clearly approximately the same for the two initiators; neither is an efficient *Z*-selective homocoupling catalyst under the conditions employed. The formation of more *E* product with time is typical of isomerization of the product from *Z* to *E*, and there appears to be less isomerization when $\mathbf{5_w}$ is employed (Table 1).

**Synthesis of Tungsten *tert*-Butylimido Bisaryloxide Complexes.** Three complexes have prepared that contain two sterically demanding 2,6-terphenoxide ligands, W(O)-$(CHCMe_2Ph)(OHMT)_2$,[17] $Mo(NC_6F_5)(CHCMe_2Ph)$-$(ODFT)_2$ (ODFT = O-2,6-$(C_6F_5)_2C_6H_3$),[18] and Mo(N-2,6-$Me_2C_6H_3$)$(CHCMe_2Ph)(ODFT)_2$.[18] Analogous complexes



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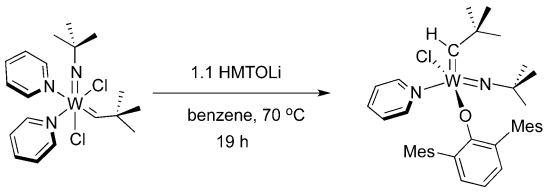
**Table 1. 1-Octene Homocoupling Catalyzed by W(N-*t*-Bu)(CH-*t*-Bu)(pyr)(OHMT) and $5_W$**

| | W(N-*t*-Bu)(CH-*t*-Bu)(pyr)(OHMT) | | W(N-*t*-Bu)(CH-*o*-MeOC$_6$H$_4$)(pyr)(OHMT) ($5_W$) | |
|---|---|---|---|---|
| time (h) | conv (%) | *cis* (%) | conv (%) | *cis* (%) |
| 1 | 42 | 80 | 32 | 90 |
| 4 | 68 | 72 | 63 | 88 |
| 8 | 81 | 60 | 73 | 84 |
| 24 | 81 | 48 | 75 | 76 |

that contain an NAr ligand could not be prepared employing analogous methods under the same conditions, presumably for steric reasons. BisOHMT complexes as ROMP initiators yield >90% *cis,syndiotactic* polymers, whereas >98% *cis,isotactic* polymers are formed from bisODFT species. Therefore, we became interested in attempting to synthesize W(N-*t*-Bu)(CH-*t*-Bu)(OHMT)$_2$ and W(N-*t*-Bu)(CH-*t*-Bu)(ODFT)$_2$ and compare them with W(O)(CHCMe$_2$Ph)(OHMT)$_2$ and Mo(NR)(CHCMe$_2$Ph)(ODFT)$_2$.

Addition of one equivalent of HMTOH to W(N-*t*-Bu)(CH-*t*-Bu)(pyr)(OHMT) in $C_6D_6$ (concentration = 73 mM) followed by heating the reaction mixture at 100 °C for 12 h led to no reaction to yield W(N-*t*-Bu)(CH-*t*-Bu)(OHMT)$_2$. However, addition of one equivalent of LiOHMT to a benzene solution of W(N-*t*-Bu)(CH-*t*-Bu)(Cl)$_2$(py)$_2$ followed by heating the mixture to 70 °C overnight led to formation of W(N-*t*-Bu)(CH-*t*-Bu)(Cl)(OHMT) (py) ($\mathbf{6_W}$) cleanly in 79% yield (eq 10).



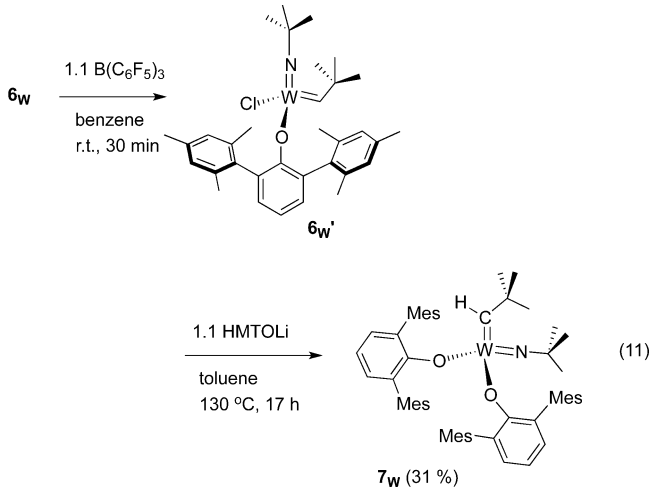

(10)

$\mathbf{6_W}$ (79 %)

Addition of another equivalent of LiOHMT to $\mathbf{6_W}$ followed by heating the reaction mixture to 100 °C for 48 h in toluene-$d_8$ led to no formation of a bisaryloxide complex. We propose that the pyridine ligand in $\mathbf{6_W}$ is not labile enough to form more reactive four-coordinate W(N-*t*-Bu)(CH-*t*-Bu)(Cl)(OHMT).

It has been reported that a mixture of W(O)(CH-*t*-Bu)(Cl)$_2$(PPh$_2$Me)$_2$ and 2.4 equivalents of LiOHMT in toluene at 100 °C for 48 h leads to formation of W(O)(CHCMe$_2$Ph)(OHMT)$_2$ in good yield.[19] Addition of 1.1 equivalents of B(C$_6$F$_5$)$_3$ to $\mathbf{6_W}$ led to formation of W(N-*t*-Bu)(CH-*t*-Bu)(Cl)(OHMT) ($\mathbf{6_W'}$) along with (py)B(C$_6$F$_5$)$_3$. Compound $\mathbf{6_W'}$ was separated from (py)B(C$_6$F$_5$)$_3$ through addition of pentane, in which $\mathbf{6_W'}$ is soluble, and that solution was treated with 1.1 equivalents of LiOHMT at 130 °C for 5 h in toluene to give $\mathbf{7_W}$ (eq 11). Compound $\mathbf{7_W}$ was isolated by adding acetonitrile, in which it is not soluble. Compound $\mathbf{6_W'}$, which could not be isolated in crystalline form, is a rare example of a monoaryloxide halide imido alkylidene complex. To our knowledge the only others that have been reported are adducts (like $\mathbf{6_W}$) with the formula Mo(N-2,6-Mes$_2$C$_6$H$_3$)(CHCMe$_2$Ph)(pyridine)(Cl)(OR) where OR is O-2,6-Mes$_2$C$_6$H$_3$, O-2,6-Me$_2$C$_6$H$_3$, O-*t*-Bu, or OCMe(CF$_3$)$_2$.[16a]

When two equivalents of B(C$_6$F$_5$)$_3$ were added to $\mathbf{6_W}$ along with one equivalent of LiOHMT, the starting materials were consumed and a mixture of $\mathbf{6_W'}$ and W(N-*t*-Bu)(CH-*t*-Bu)(OHMT)$_2$



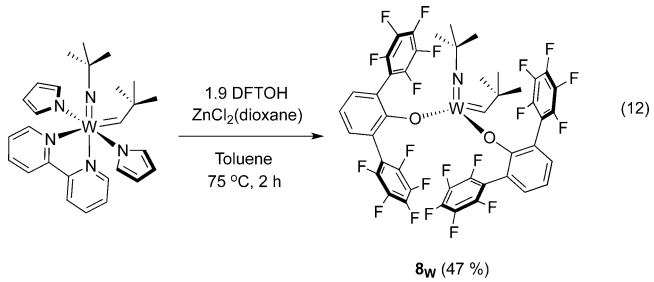

(11)

$\mathbf{7_W}$ (31 %)

($\mathbf{7_W}$) was observed by $^1$H NMR spectroscopy. Heating the reaction mixture at 60 °C led to formation of a new alkylidene complex with an alkylidene proton $^1$H NMR resonance at 9.77 ppm. This alkylidene resonance is a triplet ($J$ = 4.5 Hz) with tungsten satellites ($^2J_{WH}$ = 14.5 Hz). This side product could not be isolated and identified.

The metathesis reactivity of $\mathbf{7_W}$ for ROMP was tested using DCMNBD (2,3-dicarbomethoxynorbornadiene). Surprisingly, when $\mathbf{7_W}$ was treated with 50 equivalents of DCMNBD in CDCl$_3$ solution, *neither* $\mathbf{7_W}$ *nor DCMNBD was consumed, even at 60* °C. A degassed solution of $\mathbf{7_W}$ in $C_6D_6$ also did not react with ethylene (1 atm) either at room temperature or at 60 °C. Evidently, $\mathbf{7_W}$ is simply too crowded and the metal is not electrophilic enough to counteract what appears to be a significant steric problem. In contrast, W(O)(CH-*t*-Bu)(OHMT)$_2$ reacts with 1 atm of ethylene to form W(O)(C$_3$H$_6$)(OHMT)$_2$ and W(O)(CH$_2$)(OHMT)$_2$.[19] Another example of a 14*e* alkylidene complex that is relatively unreactive for steric reasons is Mo(NAd)(CHCMe$_2$Ph)(Silox)$_2$ (Ad = 1-adamantyl, Silox = OSi(*t*-Bu)$_3$), which does not react with ethylene (5 atm) at 120 °C in toluene-$d_8$.[20]

When a mixture of one equivalent of ZnCl$_2$(dioxane), 1.9 equivalents of DFTOH, and W(N-*t*-Bu)(CH-*t*-Bu)(pyr)$_2$(bipy) was heated in toluene at 75 °C, $\mathbf{8_W}$ was formed cleanly after 2 h and could be isolated in 47% yield (eq 12). Compound $\mathbf{8_W}$ was




(12)

$\mathbf{8_W}$ (47 %)

proposed to be formed as a major byproduct when the synthesis of W(N-*t*-Bu)(CH-*t*-Bu)(pyr)(ODFT) was attempted from W(N-*t*-Bu)(CH-*t*-Bu)(pyr)$_2$(bipy) and one equivalent of ZnCl$_2$(dioxane) in the presence of 0.9 equivalent of DFTOH.

When $\mathbf{8_W}$ was treated with 50 equivalents of DCMNBD in CDCl$_3$ solution, 33% of the DCMNBD was polymerized after 24 h. The isolated poly(DCMNBD) contained a *cis,syndiotactic*-biased microstructure (*cis* selectivity 88%; *syndiotactic* selectivity 67%). The metathesis activity of $\mathbf{8_W}$ versus $\mathbf{7_W}$ can be attributed to the electron-withdrawing nature of the smaller ODFT ligand versus the OHMT ligand.



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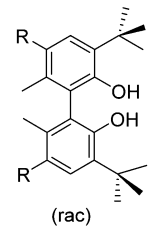
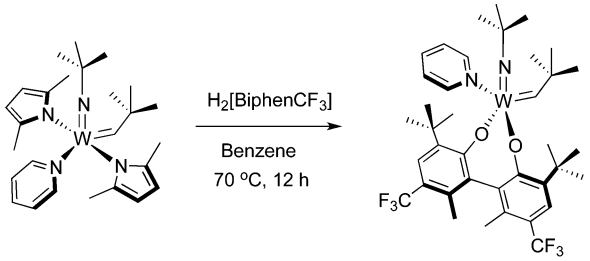
**Synthesis of Biphenoxide Complexes.** Molybdenum imido alkylidene complexes that contain a chelating biphenolate or binaphtholate ligand have been known for more than 20 years.[21] At present, biphenolate complexes of Mo and W are employed primarily to form *cis,isotactic* polymers through ROMP of various monomers.[1e,6,7,22] A typical successful biphenolate in stereoregular ROMP is one derived from the biphenols shown below. Because tungsten imido alkylidene complexes that contain biphenolate ligands of this type are especially rare,[23] we were curious as to whether *tert*-butylimido biphenolate complexes could be prepared. $Biphen_{CF3}$ and $Biphen_{Me}$ (shown below) were chosen as diolate ligands.[24]



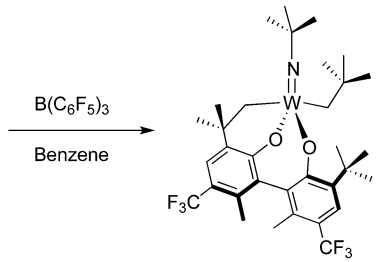

(rac)

R = Me = $[Biphen_{Me}]H_2$
R = $CF_3$ = $[Biphen_{CF3}]H_2$

The reaction between one equivalent of $[Biphen_{CF3}]H_2$ and W(N-*t*-Bu)(CH-*t*-Bu)($Me_2$pyr)$_2$(py) in benzene at 70 °C for 12 h yielded W(N-*t*-Bu)(CH-*t*-Bu)($Biphen_{CF3}$)(py) (**9**$_W$; eq 13).




**9**$_W$ (56 %)




(13)

**10**$_W$

The $^1$H NMR spectrum of **9**$_W$ (Figure 2, top) contains two alkylidene resonances in a 57:43 ratio, as would be expected if two diastereomers are formed. Both isomers of **9**$_W$ have the neopentylidene in a *syn* orientation on the basis of $^1J_{CH}$ values (112 Hz for both) compared to a typical value for $^1J_{CH}$ in an *anti* isomer (~135−155 Hz). One equivalent of $B(C_6F_5)_3$ was added to a benzene solution of **9**$_W$ at room temperature in order to remove the pyridine ligand. After 30 min (py)$B(C_6F_5)_3$ and a new complex were observed by $^1$H NMR spectroscopy. The new product did not contain any alkylidene resonances, but two doublets (at 3.53 and 2.24 ppm both with $^2J_{HH}$ = 16 Hz) were observed (Figure 2, bottom). The two alkyl protons that give rise to the 3.53 and 2.24 ppm resonances are not coupled to one another according to $^1$H−$^1$H gCOSY NMR spectra, which suggests that they arise from two distinct W-$CH_2$ groups. The two other $CH_2$ proton resonances were shown by $^1$H−$^1$H gCOSY NMR spectroscopy to be at 1.66 ppm (correlated with a resonance at 2.24 ppm) and 1.36 ppm (correlated with a resonance at 3.58 ppm).

The new compound, W(N-*t*-Bu)($CH_2$-*t*-Bu)($Biphen_{CF3}$-H) (**10**$_W$), crystallizes from a mixture of toluene and diethyl ether in the monoclinic space group $P2_{1/n}$ as a two-component nonmerohedral twin (Figure 3). The W atom is five-coordinate with $\tau$ = 0.81 (where $\tau$ = 0 for a square pyramid and $\tau$ = 1 for a trigonal bipyramid),[25] which indicates that it is close to a trigonal bipyramid in which the imido ligand and O1 occupy axial sites and O2, C1, and C18 occupy the equatorial sites. The W1−C18 bond results from addition of one of the methyl CH bonds in a Biphen *tert*-butyl group across the M═C bond. Bond lengths and angles are those expected for W imido alkyl species. Addition of a CH bond across a W═C bond was observed when the synthesis of W(NAr)(CH-*t*-Bu)[OC($CF_3$)$_2$(*p*-tolyl)]$_2$ was attempted; in this case an *ortho* CH bond in the tolyl group was cleaved.[26] Addition of CH bonds intramolecularly and intermolecularly across metal−carbon double bonds (as well as across metal−carbon single and metal−carbon triple bonds) in early transition metal chemistry is relatively well known.[27]

Addition of two equivalents of pyridine to a $C_6D_6$ solution of **10**$_W$ yielded no change in the proton NMR spectrum at room temperature after 2 h. However, upon heating the reaction mixture at 60 °C for 2.5 h, **9**$_W$ (43% conversion versus an internal standard) was re-formed, new alkylidene resonances (4% versus an internal standard) were observed at 11.13 and 9.59 ppm, and ~4% of **10**$_W$ remained. The new alkylidene resonances in **9**$_W$′ are postulated to result from $\alpha$-hydrogen abstraction in the methylene group (C18) to form an alkylidene in the biphen ligand (eq 14). Unfortunately, the low yield of the minor product and the likely formation of other side products does not allow us to confirm that neopentane is formed in the process of forming **9**$_W$′. However, we can at least conclude that **10**$_W$ is formed upon addition of $B(C_6F_5)_3$ to **9**$_W$, and addition of pyridine to **10**$_W$ yields **9**$_W$ in fair yield upon heating the reaction mixture to 60 °C.

W(N-*t*-Bu)(CH-*t*-Bu)(Cl)$_2$(py)$_2$ was added to a THF solution of $K_2(Biphen_{Me})$, which was generated *in situ* from benzyl potassium and $[Biphen_{Me}]H_2$, to yield **11**$_W$ (eq 15), which is analogous to **9**$_W$. For compound **11**$_W$ two alkylidene resonances at 10.56 and 9.27 ppm were observed in a ratio of 51:49 by $^1$H NMR spectroscopy in $C_6D_6$, which again we feel most likely can be assigned to two diastereomers. When one equivalent of $B(C_6F_5)_3$ was added to a $C_6D_6$ solution of **11**$_W$, a mixture of **11**$_W$′ (with an alkylidene peak at 7.59 ppm) and the C−H activation product (**11**$_W$″, eq 15) were observed in a ratio of about 1:1.

When W(N-*t*-Bu)(CH-*t*-Bu)(pyr)$_2$(bipy) was sonicated with one equivalent of $ZnCl_2$(dioxane) and 0.9 equivalent of $[Biphen_{Me}]H_2$ in toluene for 4.5 h, a mixture of **11**$_W$′ and what we propose is the C−H activated product (**11**$_W$″; ~1:1) again were observed by $^1$H NMR spectroscopy. We conclude that CH activation takes place in a biphenolate methyl group in **11**$_W$′. Because we could not isolate either **11**$_W$′ or **11**$_W$″ in pure form, we cannot say whether these two compounds interconvert readily, or not.

**Synthesis of Tungsten *tert*-Butylimido Metallacyclobutane Complexes.** The reaction between one equivalent of $ZnCl_2$(dioxane), 0.9 equivalent of DFTOH, and W(N-*t*-Bu)(CH-*t*-Bu)(pyr)(ODFT) in toluene under 1 atm of ethylene at room temperature for 30 min produced a pale yellow precipitate.



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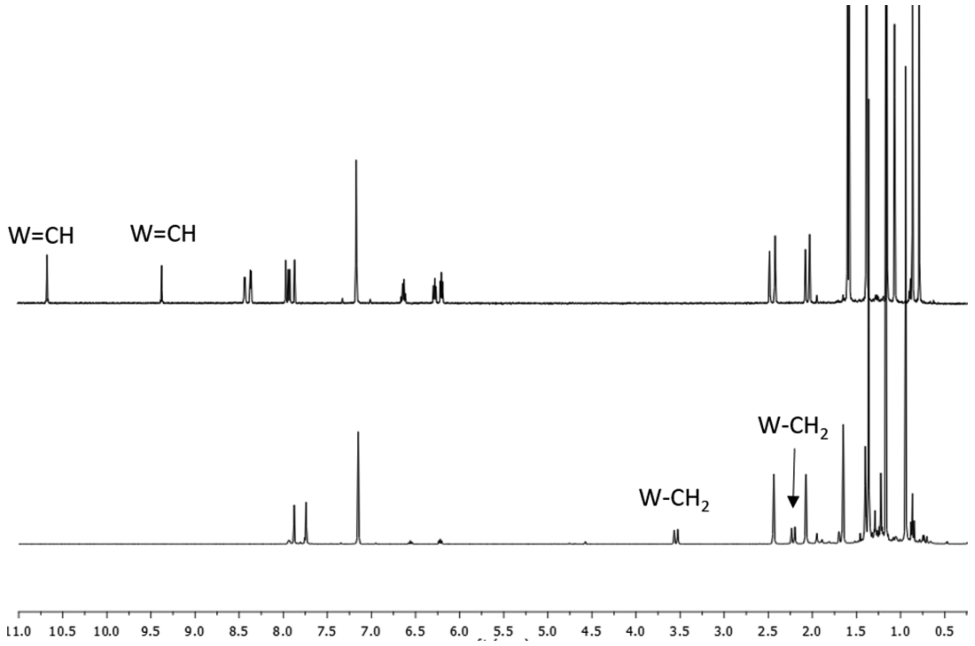



**Figure 2.** Top: $^1$H NMR spectrum of W(N-*t*-Bu)(CH-*t*-Bu)(Biphen$_{CF3}$)(py) (**9$_W$**) in $C_6D_6$. Bottom: $^1$H NMR spectrum of W(N-*t*-Bu)($CH_2$-*t*-Bu)(Biphen$_{CF3}$-H) (**10$_W$**) obtained *in situ* in $C_6D_6$.

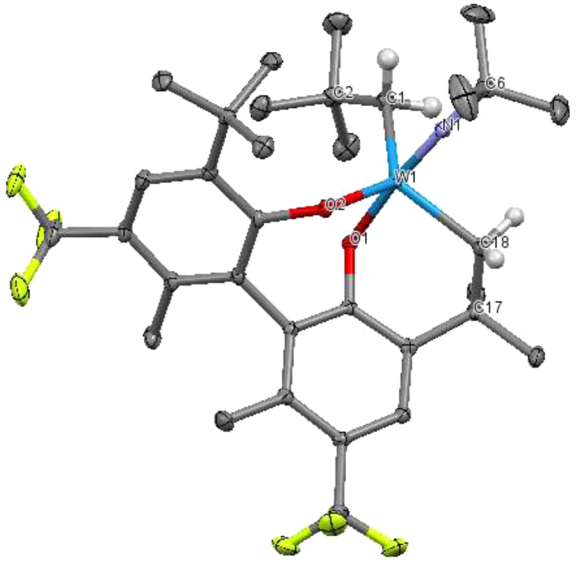
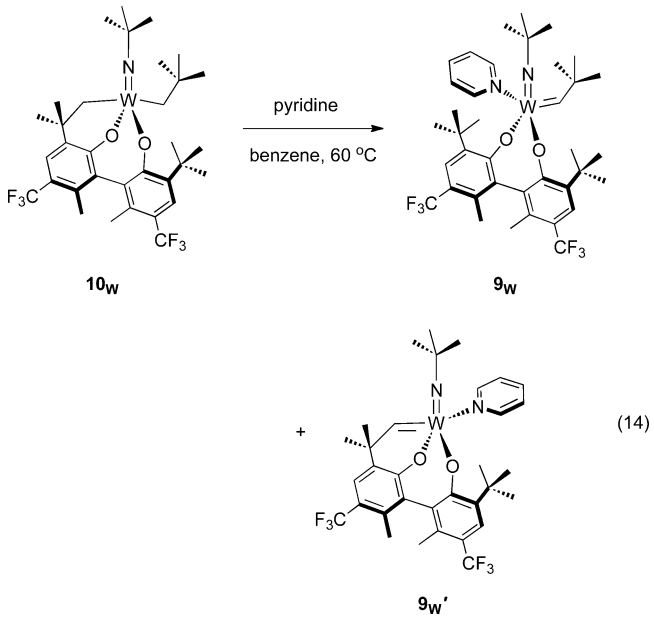



**Figure 3.** Thermal ellipsoid (50%) drawing of W(N-*t*-Bu)($CH_2$-*t*-Bu)(Biphen$_{CF3}$-H) (**10$_W$**). Selected bond lengths (Å) and angles (deg): W1−N1 = 1.7525(16), W1−C1 = 2.1239(20), W1−O1 = 2.0084(13), W1−O2 = 1.9315(13), W1−C18 = 2.1383(19); N1−W1−C1 = 92.18(8), C1−W1−O2 = 125.55(7), O2−W1−O1 = 85.92(5), W1−C18−C17 = 121.22, O1−W1−C18 = 83.39(6), C18−W1−N1 = 91.42(7), N1−W1−O1 = 174.32(6).




(14)

The mixture was filtered, and a white compound was isolated in 31% yield. Carbon and proton NMR data are consistent with the product being a TBP metallacyclobutane complex, W(N-*t*-Bu)($C_3H_6$)(pyr)(ODFT) (**12$_W$**; eq 16).[28] A similar reaction starting with W(N-*t*-Bu)(CH-*t*-Bu)(pyr)$_2$(bipy) yields W(N-*t*-Bu)($C_3H_6$)(ODFT)$_2$ (**13$_W$**; eq 17) in 29% yield. To our knowledge, **12$_W$** and **13$_W$** are the only reported Mo or W metallacyclobutane complexes of this general type that contain a *tert*-butylimido ligand. Reactions between a variety of molybdenum and tungsten NAr complexes and ethylene have been found to yield either unsubstituted metallacyclobutane complexes[12] or ethylene complexes.[29,30]

We were unable to isolate the proposed intermediate in eq 16, W(N-*t*-Bu)(CH-*t*-Bu)(pyr)(ODFT). However, addition of DFTOH to W(N-*t*-Bu)(CH-*t*-Bu)(pyr)$_2$(py) that had been generated *in situ* led to formation of a pyridine adduct, W(N-*t*-Bu)(CH-*t*-Bu)(pyr)(ODFT)(py), in 73% yield (**14$_W$**, eq 18). There was no immediate reaction of **14$_W$** (in $C_6D_6$) with ethylene (1 atm) in a J-Young tube. After 18 h, resonances for unreacted **14$_W$**, TBP metallacyclobutane resonances, and resonances assigned to olefin adducts were observed in $^1$H NMR spectra.

## CONCLUSIONS

In contrast to bis-arylimido dialkyl complexes, we have found that bis-*tert*-butylimido dialkyl complexes can be converted more



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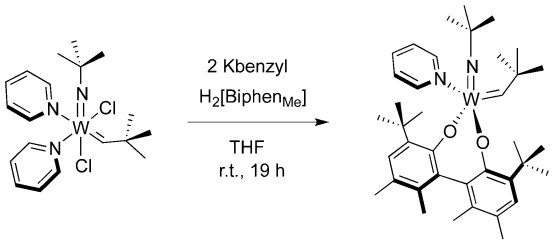
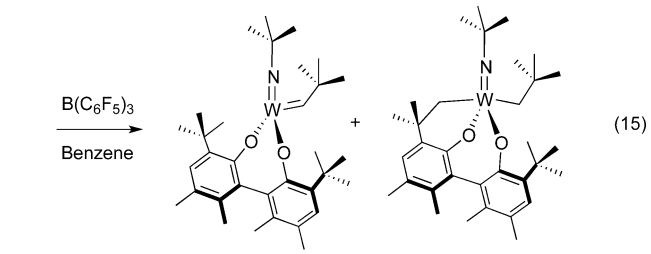
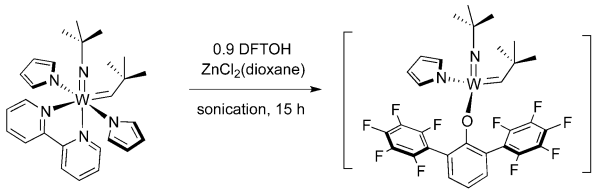


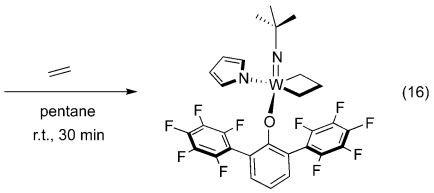

**11W** (76 %)




(15)

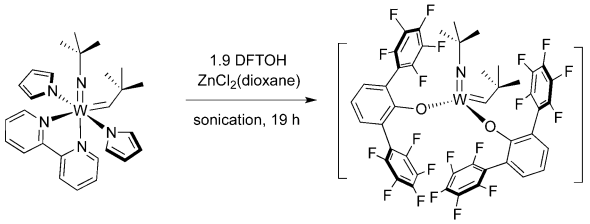
**11W'** **11W"**

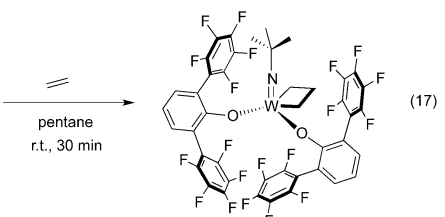



(16)

**12W** (31 %)

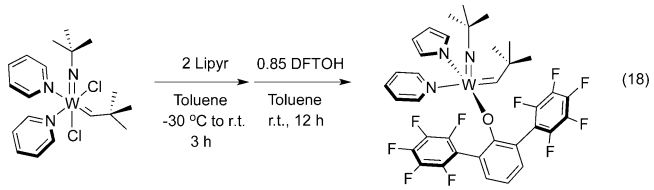



(17)

**13W** (29 %)

generally into imido alkylidene complexes with acids other than triflic acid, a reaction that was first reported by Osborn for $(CF_3)_2CHOH$,[4] as a consequence of the easier and controlled protonation of a *tert*-butylimido versus an arylimido ligand. Complexes that contain two *o*-methoxybenzyl ligands can be converted to *o*-methoxybenzylidene bisalkoxide complexes simply through addition of perfluoro-*tert*-butanol or $C_6F_5OH$,




(18)

**3W** **14W** (73 %)

and the resulting W=CH-*o*-$MeOC_6H_4$ complexes behave in metathesis reactions in a manner similar to the behavior of the analogous neopentyl complexes. W(N-*t*-Bu)(CH-*t*-Bu)-$(OHMT)_2$ and W(N-*t*-Bu)(CH-*t*-Bu)$(ODFT)_2$, the only examples of imido bisterphenoxide complexes at this time, could be prepared. W(N-*t*-Bu) (CH-*t*-Bu)$(OHMT)_2$ did not react readily with ethylene or DCMNBD, unlike W(O)(CH-*t*-Bu)$(OHMT)_2$ and W(N-*t*-Bu)(CH-*t*-Bu)$(ODFT)_2$. Attempts to prepare biphenolate complexes resulted in formation of a neopentyl complex through addition of a CH bond across the W=CH-*t*-Bu bond. One biphenolate complex could be observed in a mixture of it and the analogous product derived from CH addition across the W=C bond. Finally, the first examples of *tert*-butylimido tungsten metallacyclobutane complexes that contain one or two DFTO ligands were prepared and characterized. The synthetic approaches to *tert*-butylimido alkylidene complexes of Mo and W reported here are more direct and likely will be lower in cost in large-scale applications of Mo and W olefin metathesis chemistry.

## EXPERIMENTAL SECTION

**General Considerations.** All air- and moisture-sensitive materials were manipulated under a nitrogen atmosphere in a Vacuum Atmospheres glovebox or on a dual-manifold Schlenk line. All glassware, including NMR tubes, was dried in an oven prior to use. Diethyl ether, toluene, dichloromethane, 1,2-dimethoxyethane, and benzene were degassed, passed through activated alumina columns, and stored over 4 Å Linde-type molecular sieves prior to use. Pentane was washed with $H_2SO_4$, followed by water and saturated aqueous $NaHCO_3$, and dried over $CaCl_2$ pellets for at least 2 weeks prior to use in the solvent purification system. Deuterated solvents were dried over 4 Å Linde-type molecular sieves prior to use. Proton NMR spectra were obtained on 400 or 500 MHz spectrometers, $^{13}C$ NMR spectra on 100.61 or 125 MHz machines, and $^{19}F$ spectra on a 376.5 MHz machine. Chemical shifts for $^1H$ and $^{13}C$ spectra are reported as parts per million relative to tetramethylsilane and referenced to the residual $^1H$ or $^{13}C$ resonances of the deuterated solvent ($^1H$ ($\delta$): benzene 7.16, chloroform 7.26, methylene chloride 5.32; $^{19}F$ ($\delta$): external PhF standard −113.15; $^{13}C$ ($\delta$): benzene 128.06, chloroform 77.16, methylene chloride 53.84). $^1H-^1H$ gCOSY NMR experiments were conducted on a 500 MHz spectrometer. Sonications were performed on a Bransonic 1510R-MT ultrasonic cleaner purchased from Branson Ultrasonics Corporation. Benzaldehyde was distilled and stored under nitrogen. Pyridinium chloride was purchased from Sigma-Aldrich or Alfa Aesar and sublimed before use. Lipyr and LiOHMT were prepared by addition of one equivalent of *n*-butyllithium to a cold pentane or ether solution of pyrrole or HMTOH, and the solids were collected on a glass frit, washed with pentane, and dried *in vacuo*. *endo*-Dicyclopentadiene was purchased from Sigma-Aldrich and was distilled before use. 1-Octene was dried over $CaH_2$ and vacuum transferred. Ethereal solutions of HCl were prepared by bubbling HCl gas into diethyl ether and were titrated before use. Mo(N-*t*-Bu)(CH-*t*-Bu)$(OC_6F_5)_2(NH_2$-*t*-Bu),[5] $[W(N$-*t*-Bu$)_2(Cl)_2(t$-BuNH$_2)_2]_2$,[2] W(N-*t*-Bu)(CH-*t*-Bu)$(Cl)_2(py)_2$,[2] W(N-*t*-Bu)(CH-*t*-Bu)(pyr)(OHMT),[2] 2-methoxystyrene,[31] benzyl potassium,[32] DCMNBD,[33] $[Biphen_{Me}]H_2$,[24] $[Biphen_{CF3}]H_2$,[24] neopentyl Grignard,[34] HMTOH,[35] DFTOH,[36] and $ZnCl_2$(dioxane)[37] were prepared according to literature procedures. All other reagents were used as received. The CENTC Elemental Analysis Facility at the University of Rochester provided elemental analyses.



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*W(N-t-Bu)(CH-o-MeOC$_6$H$_4$)(Cl)$_2$(py) (**1$_W$**).* Pyridinium chloride (0.354 g, 3.06 mmol) was added portionwise to a cold (−30 °C) solution of W(N-*t*-Bu)$_2$(CH$_2$-*o*-MeOC$_6$H$_4$)$_2$ (**2$_W$**) (0.580 g, 1.02 mmol) in 20 mL of ether. The reaction mixture was stirred for 19 h at room temperature. The solvents were removed *in vacuo*. Dichloromethane was added, the mixture was filtered through a pad of Celite on a glass frit, and the solvents were removed from the filtrate *in vacuo*. Ether was added, and the yellow precipitate was collected by filtration (0.423 g, 79%): $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 11.96 (s, 1H, W=C*H*, $^1J_{CH}$ = 145 Hz), 8.65 (d, 2H, py), 6.96 (t, 1H, Ar), 6.59 (d, 1H, Ar), 6.45 (m, 3H, Ar and py), 6.10 (t, 2H, py), 4.35 (s, 3H, OMe), 1.44 (s, 9H, *t*-Bu); $^{13}$C NMR (125 MHz, C$_6$D$_6$) $\delta$ 260.87, 160.77, 156.67, 152.25, 138.45, 134.62, 129.48, 128.59, 125.88, 124.55, 122.42, 120.90, 110.31, 71.15, 59.55, 29.72. Anal. Calcd for C$_{17}$H$_{22}$Cl$_2$N$_2$OW: C, 38.88; H, 4.22; N, 5.33. Found: C, 39.20; H, 4.30; N, 5.42.

*Mo(N-t-Bu)(CH-o-MeOC$_6$H$_4$)(OC$_6$F$_5$)$_2$(t-BuNH$_2$) (**1$_{Mo}$**).* Pentafluorophenol (85.3 mg, 0.463 mmol) was added in portions to a cold (−30 °C) solution of Mo(N-*t*-Bu)$_2$(CH$_2$-*o*-MeOC$_6$H$_4$)$_2$ (**2$_{Mo}$**) (0.101 g, 0.211 mmol) in 6 mL of ether. The reaction mixture was stirred for 2 h at room temperature, and the solvents were then removed *in vacuo*. Pentane was added, and the yellow solid was isolated by filtration (0.084 g, 55%): $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 13.31 (s, 1H, Mo=CH), 6.60 (m, 2H, Ar), 6.48 (m, 1H, Ar), 6.09 (m, 1H, Ar), 4.10 (s, 3H, OMe), 3.06 (d, 1H, NH$_2$), 2.20 (d, 1H, NH$_2$), 1.51 (s, 9H, *t*-Bu), 0.45 (s, 9H, *t*-Bu); $^{19}$F NMR (300 MHz, C$_6$D$_6$) $\delta$ −166.23 (d, 2F), −161.92 (d, 2F), −188.69 (t, 2F), −169.62 (t, 2F), −176.41 (m, 2F); $^{13}$C NMR (125 MHz, C$_6$D$_6$) $\delta$ 281.31, 158.18, 146.19, 143.11, 141.74, 139.89, 138.90, 137.91, 136.99, 134.63, 134.03, 132.08, 130.09, 122.66, 122.07, 109.47, 75.19, 56.46, 51.72, 29.99, 28.57. Anal. Calcd for C$_{28}$H$_{28}$F$_{10}$N$_2$O$_3$Mo: C, 46.29; H, 3.88; N, 3.86. Found: C, 46.28; H, 3.91; N, 3.74.

*W(N-t-Bu)$_2$(CH$_2$-o-MeOC$_6$H$_4$)$_2$ (**2$_W$**).* 2-Methoxybenzylmagnesium chloride (9.76 mL, 0.25 M, 2.44 mmol) was added to a cold (−30 °C) solution of W(N-*t*-Bu)$_2$(Cl)$_2$(py)$_2$ (0.677 g, 1.22 mmol) in 50 mL of ether/THF. The reaction mixture was stirred for 19 h at room temperature. The mixture was filtered through a pad of Celite on a glass frit, and the solvents were removed from the filtrate *in vacuo*. Benzene was added, the mixture was filtered through a pad of Celite on a glass frit, and the solvents were removed from the filtrate *in vacuo*. Pentane was added, and the brown liquid product was separated by decantation (0.580 g, 84%): $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 7.20 (d, 2H, Ar), 6.86 (m, 4H, Ar), 6.30 (d, 2H, Ar), 3.43 (s, 6H, OMe), 2.76 (s, 4H, CH$_2$), 1.33 (s, 18H, CH$_3$); $^{13}$C NMR (125 MHz, C$_6$D$_6$) $\delta$ 160.63, 138.17, 131.75, 124.98, 122.18, 110.93, 67.41, 57.64, 39.34, 32.66. Anal. Calcd for C$_{24}$H$_{36}$N$_2$O$_2$W: C, 50.71; H, 6.38; N, 4.93. Found: C, 50.88; H, 6.43; N, 4.81.

*Mo(N-t-Bu)$_2$(CH$_2$-o-MeOC$_6$H$_4$)$_2$ (**2$_{Mo}$**).* 2-Methoxybenzylmagnesium chloride (21.9 mL, 0.25 M, 5.48 mmol) was added to a cold (−30 °C) solution of Mo(N-*t*-Bu)$_2$(Cl)$_2$(dme) (1.09 g, 2.74 mmol) in 50 mL of ether. The reaction mixture was stirred for 5 h at room temperature. The mixture was filtered through a pad of Celite on a glass frit, and the solvents were removed from the filtrate *in vacuo*. Pentane was added, the mixture was filtered through a pad of Celite on a glass frit, and the solvents were removed from the filtrate *in vacuo*. A minimum amount of pentane was added, and the yellow product was collected by filtration (0.934 g, 71%): $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 7.05 (d, 2H, Ar), 6.99 (t, 2H, Ar), 6.79 (t, 2H, Ar), 6.42 (d, 2H, Ar), 3.39 (s, 6H, OMe), 2.59 (s, 4H, CH$_2$), 1.28 (s, 18H, CH$_3$); $^{13}$C NMR (125 MHz, C$_6$D$_6$) $\delta$ 158.73, 131.93, 130.34, 125.74, 121.56, 110.88, 67.15, 55.45, 32.70, 31.93. Anal. Calcd for C$_{24}$H$_{36}$N$_2$O$_2$Mo: theory C, 59.99; H, 7.55; N, 5.83. Found: C, 60.04; H, 7.62; N, 5.70.

*Mo(N-t-Bu)(CH-o-MeOC$_6$H$_4$)[OC(CF$_3$)$_3$]$_2$(t-BuNH$_2$) (**3$_{Mo}$**).* Perfluoro-*tert*-butanol (150 $\mu$L, 1.08 mmol) was added to a cold (−30 °C) solution of Mo(N-*t*-Bu)$_2$(CH$_2$-*o*-MeOC$_6$H$_4$)$_2$ (**2$_{Mo}$**) (0.259 g, 0.540 mmol) in 20 mL of ether. The reaction mixture was stirred for 2 h at room temperature. The solvents were removed from the filtrate *in vacuo*. Pentane was added to precipitate, and the reaction mixture was chilled to −30 °C. The precipitated green solid was isolated by filtration (0.287 g, 64%): $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 13.28 (s, 1H, Mo=CH), 6.81 (t, 1H, Ar), 6.69 (t, 1H, Ar), 6.47 (d, 1H, Ar), 6.30 (d, 1H, Ar), 3.96 (s, 3H, OMe), 2.97 (d, 1H, NH$_2$), 2.550 (d, 1H, NH$_2$), 1.37 (s, 9H, *t*-Bu), 0.51 (s, 9H, *t*-Bu); $^{19}$F NMR (300 MHz, C$_6$D$_6$) $\delta$ −72.13 (s, 9F), −73.16 (s, 9F); $^{13}$C NMR (125 MHz, C$_6$D$_6$) $\delta$ 282.5, 159.04, 135.18, 130.00, 122.69, 121.10, 109.37, 84.66, 75.75, 56.56, 52.07, 30.13, 28.26. Anal. Calcd for C$_{24}$H$_{28}$F$_{18}$N$_2$O$_3$Mo: C, 34.71; H, 3.40; N, 3.37. Found: C, 34.95; H, 3.43; N, 3.26.

*Mo(NAr)$_2$(CH$_2$-o-MeOC$_6$H$_4$)$_2$.* 2-Methoxybenzylmagnesium chloride (5.64 mL, 0.25 M, 1.41 mmol) was added to a cold (−30 °C) solution of Mo(NAr)$_2$(Cl)$_2$(dme) (428 mg, 0.705 mmol) in 10 mL of ether. The reaction mixture was stirred for 12 h at room temperature. The mixture was filtered through a pad of Celite on a glass frit, and the solvent was removed from the filtrate *in vacuo*. Pentane was added, and an orange solid was filtered off. The orange solid was dissolved in benzene (10 mL), the mixture was filtered through a pad of Celite on a glass frit, and the solvent was removed from the filtrate *in vacuo*. Pentane was added, and the resulting orange solid was collected by filtration (380 mg, 78%): $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 7.17 (d, 2H, Ar), 7.01 (d, 4H, Ar), 6.93 (t, 2H, Ar), 6.84 (t, 2H, Ar), 6.78 (t, 2H, Ar), 6.22 (d, 2H, Ar), 3.87 (m, 4H, *i*-Pr), 3.36−3.34 (s, 10H, CH$_2$ and OMe), 1.17 (d, 24H, CH$_3$); $^{13}$C NMR (125 MHz, C$_6$D$_6$) $\delta$ 159.11, 153.94, 142.81, 134.46, 131.17, 125.85, 124.80, 122.74, 121.73, 110.45, 56.55, 39.94, 28.18, 24.10. Anal. Calcd for C$_{40}$H$_{52}$N$_2$O$_2$Mo: C, 69.75; H, 7.61; N, 4.07. Found: C, 69.42; H, 7.55; N, 3.93.

*W(N-t-Bu)(CH-o-MeOC$_6$H$_4$)(pyr)$_2$(bipy) (**4$_W$**).* W(N-*t*-Bu)(CH-*o*-MeOC$_6$H$_4$)(Cl)$_2$(py) (**1$_W$**, 0.626 g, 1.19 mmol) was suspended in toluene (50 mL), and the suspension was chilled at −30 °C for 1 h. Lipyr (0.183 g, 2.502 mmol) was added in one portion, and the mixture was allowed to stir at room temperature for 2 h. The precipitated salts were filtered off on a pad of Celite on a glass frit, and the pad was washed with toluene. 2,2′-Bipyidine (0.168 g, 1.072 mmol) was added to the solution, and the mixture was allowed to stir at room temperature overnight. The resulting precipitate was collected by filtration, and the solvents were removed from the filtrate *in vacuo* to give a red powder (0.574 g, 81%); at room temperature, two isomers were observed in the NMR spectra: $^1$H NMR (500 MHz, CD$_2$Cl$_2$) $\delta$ 11.87 (s, 1H, W=C*H*), 10.94 (s, 1H, W=CH), 9.91 (d, 1H, bipy), 9.61 (d, 1H, bipy), 9.50 (d, 1H, bipy), 8.63 (d, 1H, bipy), 8.18−7.55 (m, 18H, Ar), 7.01−6.50 (m, 10H, Ar), 6.31 (m, 4H, pyr), 6.17 (m, 2H, pyr), 5.97 (m, 2H, pyr), 5.75 (m, 2H, pyr), 5.67 (m, 4H, pyr), 5.32 (m, 4H, pyr), 3.93 (s, 3H, OMe), 3.66 (s, 3H, OMe), 1.37 (s, 9H, Me), 1.34 (s, 9H, Me); a $^{13}$C NMR spectrum could not be obtained readily at 22 °C due to the insolubility of the sample in CD$_2$Cl$_2$. Anal. Calcd for C$_{30}$H$_{33}$N$_5$OW: C, 54.31; H, 5.01; N, 10.56. Found: C, 54.50; H, 5.02; N, 10.16.

*W(N-t-Bu)(CH-o-MeOC$_6$H$_4$)(pyr)(OHMT) (**5$_W$**).* W(N-*t*-Bu)(CH-*o*-MeOC$_6$H$_4$)(pyr)$_2$(bipy) (**4$_W$**, 338.1 mg, 0.510 mmol), ZnCl$_2$(dioxane) (114.3 mg, 0.510 mmol), and HMTOH (143 mg, 0.433 mmol) were suspended in toluene (∼25 mL) in a 100 mL Schlenk bomb. The solution was stirred for 24 h at 75 °C and filtered through a pad of Celite on a glass frit, and the solvents were removed from the filtrate *in vacuo*. The compound was extracted with a minimum amount of pentane, the mixture was filtered through a pad of Celite on a glass frit, and the solvents were removed from the filtrate to yield an orange powder; 324 mg (97%): $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 10.83 (s, 1H, *anti*-W=C*H*, $^1J_{CH}$ = 152 Hz), 7.04−6.98 (m, 3H, Ar), 6.92 (t, 1H, Ar), 6.85 (s, 2H, Ar), 6.54 (t, 2H, Ar), 6.42−6.37 (m, 2H, Ar), 6.26 (m, 4H, pyr), 3.20 (s, 3H, OMe), 2.24−2.07 (br, 18H, Me), 1.25 (s, 9H, Me); $^{13}$C NMR (100.61 MHz, C$_6$D$_6$) 232.19, 159.32, 156.04, 136.50, 136.26, 135.51, 135.45, 134.76, 130.89, 129.84, 129.07, 128.60, 128.47, 125.11, 123.67, 122.00, 121.04, 109.70, 107.67, 70.12, 56.03, 32.83, 30.44, 21.65, 21.34, 21.17. Anal. Calcd for C$_{40}$H$_{46}$N$_2$O$_2$W: C, 62.34; H, 6.02; N, 3.64. Found: C, 62.07; H, 5.90; N, 3.49.

*W(N-t-Bu)(CH-t-Bu)(OHMT)(Cl)(py) (**6$_W$**).* Solid LiOHMT·THF (398.4 mg, 0.975 mmol) was added portionwise to a solution of W(N-*t*-Bu)(CH-*t*-Bu)(Cl)$_2$(py)$_2$ (491.3 mg, 0.887 mmol) in benzene (20 mL). The reaction mixture was stirred for 19 h at 70 °C. The mixture was filtered through a pad of Celite on a glass frit, and the filtrate was dried *in vacuo*. Pentane was added and removed *in vacuo* a couple of times to remove excess benzene. The resulting precipitate was collected by filtration in pentane, and the solvents were removed from the filtrate to yield an ivory-colored powder (541 mg, 79%): $^1$H NMR (500 MHz, C$_6$D$_6$) $\delta$ 9.67 (s, 1H, W=CH), 8.05 (m, 2H, py), 7.24 (d, 1H, Ar),


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7.17 (d, 1H, Ar), 7.08 (s, 1H, Ar), 7.01 (m, 2H, Ar), 6.92 (s, 1H, Ar), 6.74 (m, 2H, py and Ar), 6.41 (m, 2H, py), 2.76 (s, 3H, Me), 2.74 (s, 3H, Me), 2.31 (s, 3H, Me), 2.27 (s, 3H, Me), 1.95 (s, 3H, Me), 1.65 (s, 3H, Me), 1.22 (s, 9H, *t*-Bu), 1.14 (s, 9H, *t*-Bu); $^{13}$C NMR (125 MHz, $C_6D_6$) $\delta$ 278.23, 160.82, 153.75, 139.13, 138.99, 138.12, 138.02, 137.54, 137.07, 135.81, 135.50, 132.04, 131.47, 130.01, 129.90, 129.47, 129.24, 127.49, 127.23, 124.44, 119.81, 67.85, 43.11, 32.68, 31.88, 31.10, 22.41, 22.23, 21.44, 21.24, 20.91, 20.86. Anal. Calcd for $C_{38}H_{49}ClN_2OW$: C, 59.34; H, 6.42; N, 3.64. Found: C, 58.27; H, 6.17; N, 3.75. Several other attempts at elemental analysis produced similar and variable results. However, W(N-*t*-Bu)(CH-*t*-Bu)(OHMT)(Cl)(py) could be employed in the next step without further purification.

*Observation of W(N-t-Bu)(CH-t-Bu)(OHMT)(Cl) (**6$_W$'**).* $B(C_6F_5)_3$ (66 mg, 0.129 mmol) was added portionwise to a solution of W(N-*t*-Bu)(CH-*t*-Bu)(OHMT)(Cl)(py) (99 mg, 0.129 mmol) in benzene (5 mL). The reaction mixture was stirred for 30 min at room temperature, and the solvents were removed from the filtrate *in vacuo*. Pentane was added and removed *in vacuo* a couple of times to remove benzene. Pentane was added, and the mixture was filtered through a pad of Celite on a glass frit. The solvents were removed from the filtrate *in vacuo*, leaving a sticky orange solid: $^1$H NMR (500 MHz, $C_6D_6$) $\delta$ 8.21 (s, 1H, W=CH), 6.98−6.90 (m, 7H, Ar), 2.22 (s, 6H, Me), 2.19 (s, 6H, Me), 2.17 (s, 6H, Me), 1.16 (s, 9H, *t*-Bu), 1.05 (s, 9H, *t*-Bu).

*W(N-t-Bu)(CH-t-Bu)(OHMT)$_2$ (**7$_W$**).* $B(C_6F_5)_3$ (96.4 mg, 0.19 mmol) was added in portions to a solution of W(N-*t*-Bu)(CH-*t*-Bu)(OHMT)-(Cl)(py) (132 mg, 0.17 mmol) in benzene (6 mL). The reaction mixture was stirred for 30 min at room temperature, and the solvents were removed from the mixture *in vacuo*. Pentane was added and removed *in vacuo* a couple of times to remove benzene. Pentane was added, and the mixture was filtered through a pad of Celite on a glass frit. The solvents were removed from the filtrate *in vacuo*, the residue was dissolved in toluene-$d_8$, and the mixture was transferred into a J-Young tube along with LiOHMT (69 mg, 0.21 mmol). The mixture was placed in a 130 °C oil bath for 17 h and then filtered through a pad of Celite on a glass frit. The mixture was washed with benzene, and the solvents were removed from the filtrate *in vacuo*. A small quantity of acetonitrile was added, and a light yellow powder was filtered off after 30 min; yield 52.6 mg (31%): $^1$H NMR (500 MHz, $C_6D_6$) $\delta$ 7.64 (s, 1H, W=CH), 6.92 (s, 4H, Ar), 6.89 (s, 4H, Ar), 6.86−6.79 (m, 6H, Ar), 2.27 (s, 12H, Me), 2.18 (s, 12H, Me), 2.05 (s, 12H, Me), 0.94 (s, 9H, *t*-Bu), 0.92 (s, 9H, *t*-Bu); $^{13}$C NMR (125 MHz, $C_6D_6$) $\delta$ 241.61 ($^1J_{CW}$ = 192.5 Hz), 160.33, 137.00, 136.82, 136.34, 136.29, 131.88, 131.24, 128.91, 128.80, 121.63, 70.44, 41.63, 34.72, 32.78, 32.04, 22.12, 21.55, 21.36. Anal. Calcd for $C_{57}H_{69}NO_2W$: C, 69.57; H, 7.07; N, 1.42. Found: C, 69.77; H, 6.99; N, 1.29.

*W(N-t-Bu)(CH-t-Bu)(ODFT)$_2$ (**8$_W$**).* W(N-*t*-Bu)(CH-*t*-Bu)-(pyr)$_2$(bipy) (197.3 mg, 0.322 mmol), $ZnCl_2$(dioxane) (72.2 mg, 0.322 mmol), and DFTOH (260.5 mg, 0.611 mmol) were dissolved in toluene (20 mL) in a 100 mL Schlenk bomb. The mixture was heated for 2 h at 75 °C. The solution was filtered through a pad of Celite on a glass frit, and the filtrate was dried *in vacuo*. The compound was triturated with a minimum amount of pentane and isolated by filtration; yield of yellow solid = 179.2 mg (47%): $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.86 (s, 1H, W=CH), 6.97 (d, 4H, Ar), 6.73 (t, 2H, Ar), 0.84 (s, 9H, *t*-Bu), 0.73 (s, 9H, *t*-Bu); $^{19}$F NMR (300 MHz, $C_6D_6$) $\delta$ −130.37 (m, 4F), −144.38 (t, 2F), −151.46 (m, 4F); $^{13}$C NMR (100.62 MHz, $C_6D_6$) $\delta$ 248.95, 161.99, 145.75, 143.22, 142.70, 139.74, 138.19, 133.62, 122.23, 117.82, 112.16, 71.96, 42.56, 33.45, 31.61. Anal. Calcd for $C_{45}H_{25}F_{20}NO_2W$: C, 45.98; H, 2.14; N, 1.19. Found: C, 45.69; H, 1.81; N, 1.41.

*W(N-t-Bu)(CH-t-Bu)(Biphen$_{CF3}$)(py) (**9$_W$**).* W(N-*t*-Bu)(CH-*t*-Bu)-(Me$_2$pyr)$_2$(py) (173.5 mg, 0.314 mmol) and [Biphen$_{CF3}$]H$_2$ (145 mg, 0.314 mmol) were dissolved in benzene (10 mL) in a 20 mL Schlenk bomb. The mixture was heated at 70 °C for 12 h, and the solvent was removed *in vacuo*. The mixture was triturated with pentane, and the resulting suspension was filtered off to give an off-white solid. The filtrate contained some product, W(N-*t*-Bu)(CH-*t*-Bu)(Me$_2$pyr)$_2$(py), and some free [Biphen$_{CF3}$]H$_2$, so the mixture was dissolved in benzene (5 mL) in a 20 mL Schlenk bomb and heated at 70 °C for 12 h. After the same workup, two crops were combined (153.2 mg, 56%). Two isomers were present in a 56:44 ratio, according to NMR spectra: $^1$H NMR (500 MHz, $C_6D_6$) $\delta$ 10.66 (s, 1H, W=C*H*, $^1J_{CH}$ = 112 Hz, $^2J_{HW}$ = 15 Hz, major), 9.37 (s, 1H, W=CH, $^1J_{CH}$ = 112 Hz, $^2J_{HW}$ = 15 Hz, minor), 8.36−8.44 (dd, 4H, Ar), 7.85−7.95 (m, 4H, Ar), 6.66 (m, 2H, Ar), 6.31 (t, 2H, Ar), 6.24 (t, 2H, Ar), 2.47 (s, 3H, Me), 2.41 (s, 3H, Me), 2.06 (s, 3H, Me), 2.01 (s, 3H, Me), 1.59 (d, 18H, *t*-Bu), 1.38 (s, 18H, *t*-Bu), 1.15 (s, 9H, *t*-Bu), 1.06 (s, 9H, *t*-Bu), 0.85 (s, 9H, *t*-Bu), 0.78 (s, 9H, *t*-Bu); $^{19}$F NMR (300 MHz, $C_6D_6$) $\delta$ − 58.41 (m, 3F), − 58.45 (m, 6F), − 58.62 (m, 3F); $^{13}$C NMR (125 MHz, $C_6D_6$) $\delta$ 276.84, 271.98, 170.78, 167.59, 164.66, 164.30, 154.64, 153.84, 138.61, 137.81, 135.88, 135.86, 135.79, 135.42, 134.74, 134.61, 133.72, 131.87, 131.18, 130.44, 130.27, 128.60, 125.97, 125.90, 125.62, 125.50, 125.21, 124.58, 124.51, 124.39, 123.98, 123.58, 121.05, 120.82, 120.66, 120.43, 119.70, 119.47, 119.36, 119.13, 69.61, 69.12, 44.06, 43.75, 35.92, 35.50, 34.56, 34.13, 33.52, 32.34, 32.31, 31.58, 31.54, 31.53, 30.09, 30.00, 16.47, 16.25, 16.19, 16.02. Anal. Calcd for $C_{38}H_{50}F_6N_2O_2W$: C, 52.79; H, 5.83; N, 3.24. Found: C, 52.46; H, 5.64; N, 3.02.

*W(N-t-Bu)(CH$_2$-t-Bu)(Biphen$_{CF3}$-H) (**10$_W$**).* In a 20 mL vial, W(N-*t*-Bu)(CH-*t*-Bu)(Biphen$_{CF3}$)(py) (35.5 mg, 0.041 mmol) was dissolved in benzene (3 mL). $B(C_6F_5)_3$ (21.0 mg, 0.041 mmol) was added in portions, and the mixture was stirred at room temperature for 30 min before the solvent was removed *in vacuo*. The product was extracted into pentane, and the mixture was filtered through a bed of Celite to remove py·$B(C_6F_5)_3$. The pentane was removed from the filtrate *in vacuo* to yield an orange solid, which was recrystallized from a mixture of toluene and diethyl ether. A small quantity of residual py·$B(C_6F_5)_3$ was observed in the $^1$H NMR spectrum, and the product could not be completely freed of py·$B(C_6F_5)_3$: $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 7.95 (br, py·$B(C_6F_5)_3$), 7.89 (s, 1H, Ar), 7.75 (s, 1H, Ar), 6.57 (t, py·$B(C_6F_5)_3$), 6.23 (t, py·$B(C_6F_5)_3$), 3.58 (d, 1H, $WCH_2$, $^2J_{HW}$ = 16 Hz, other $WCH_2$ signal is at 1.36 ppm), 2.45 (d, 3H, Me), 2.25 (d, 1H, $WCH_2$, $^2J_{HW}$ = 15.2 Hz, other $WCH_2$ signal is at 1.66 ppm), 2.08 (d, 3H, Me), 1.66 (s, 3H, Me), 1.41 (s, 3H, Me), 1.37 (s, 9H, *t*-Bu), 1.18 (s, 9H, *t*-Bu), 0.95 (s, 9H, *t*-Bu).

*W(N-t-Bu)(CH-t-Bu)(Biphen$_{Me}$)(py) (**11$_W$**).* Benzyl potassium (145 mg, 1.114 mmol) was added to a solution of [Biphen$_{Me}$]H$_2$ (197.4 mg, 0.557) in THF (20 mL), and the mixture was stirred for 20 min at room temperature. A solution of W(N-*t*-Bu)(CH-*t*-Bu)(py)$_2$(Cl)$_2$ (308.5 mg, 0.557 mmol) in THF was added to this reaction mixture, and the mixture was stirred for 19 h at room temperature. The solvents were removed from the reaction mixture *in vacuo*. Pentane was added and then removed *in vacuo* in order to remove THF. The solid was extracted with benzene, and the mixture was filtered through a bed of Celite to remove KCl. The solvent was removed *in vacuo*, the product was triturated with pentane, and the resulting suspension was filtered off to give an off-white solid; yield 318.9 mg (76%). Two isomers were present in a 51:49 ratio, according to NMR data: $^1$H NMR (500 MHz, $C_6D_6$) $\delta$ 10.56 (s, 1H, W=CH, $^2J_{HW}$ = 11.2 Hz, major), 9.27 (s, 1H, W=CH, $^2J_{HW}$ = 12.8 Hz, minor), 8.61−8.55 (dd, 4H, Ar), 7.38 (s, 1H, Ar), 7.36 (s, 1H, Ar), 7.30 (d, 2H, Ar), 6.66 (m, 2H, Ar), 6.32 (t, 2H, Ar), 6.25 (t, 2H, Ar), 2.41 (s, 3H, Me), 2.35 (s, 3H, Me), 2.30 (s, 3H, Me), 2.24 (s, 3H, Me), 2.22 (s, 3H, Me), 2.18 (s, 3H, Me), 1.79 (d, 21H, Me and *t*-Bu), 1.75 (s, 3H, Me), 1.45 (s, 18H, *t*-Bu), 1.35 (s, 9H, *t*-Bu), 1.26 (s, 9H, *t*-Bu), 0.94 (s, 9H, *t*-Bu), 0.90 (s, 9H, *t*-Bu); $^{13}$C NMR (100.61 MHz, $C_6D_6$) $\delta$ 273.50, 268.81, 164.80, 160.96, 160.45, 160.01, 154.76, 153.88, 138.01, 137.19, 135.15, 134.87, 134.81, 134.63, 134.54, 133.79, 133.66, 133.06, 131.17, 130.92, 130.31, 129.76, 127.57, 127.46, 126.86, 126.74, 126.30, 126.10, 125.77, 124.17, 124.12, 69.05, 68.32, 43.66, 43.33, 35.88, 35.47, 34.44, 34.00, 33.81, 32.77, 32.51, 32.41, 32.35, 31.79, 30.89, 30.84, 29.87, 22.73, 20.76, 20.67, 20.33, 20.24, 17.48, 17.26, 17.05, 16.81, 14.28. Anal. Calcd for $C_{38}H_{56}N_2O_2W$: C, 60.32; H, 7.46; N, 3.79. Found: C, 60.68; H, 7.80; N, 3.40.

*W(N-t-Bu)($C_3H_6$)(pyr)(ODFT) (**12$_W$**).* W(N-*t*-Bu)(CH-*t*-Bu)-(pyr)$_2$(bipy) (270 mg, 0.440 mmol), $ZnCl_2$(dioxane) (98.7 mg, 0.440 mmol), and DFTOH (169 mg, 0.396 mmol) were dissolved in toluene (20 mL) in a 100 mL Schlenk bomb. The mixture was sonicated for 15 h and filtered through a pad of Celite on a glass frit, and the filtrate was dried *in vacuo*. The compound was extracted with pentane (20 mL) and filtered through a pad of Celite on a glass frit, and the solvent was removed from the filtrate *in vacuo* to a volume of about 2 mL. The mixture was transferred to a Schlenk bomb. The solution was degassed


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via three freeze−pump−thaw cycles, and it was exposed to 1 atm of ethylene for 30 min. An off-white solid precipitated out and was filtered off; yield 98.1 mg (31%): $^1$H NMR (500 MHz, $C_6D_6$) $\delta$ 7.36 (m, 2H, pyr), 7.08 (d, 2H, Ar), 6.79 (t, 1H, Ar), 6.47 (m, 2H, pyr), 4.00 (m, 2H, $WCH_\alpha$), 3.10 (m, 2H, $WCH_\alpha$), 0.66 (s, 9H, *t*-Bu), −1.55 (m, 1H, $WCH_\beta$), −1.84 (m, 1H, $WCH_\beta$); $^{19}$F NMR (300 MHz, $C_6D_6$) $\delta$ −137.61 (m, 4F), −156.06 (t, 2F), −161.57 (m, 4F); $^{13}$C NMR (125 MHz, $C_6D_6$) $\delta$ 159.17, 145.72, 143.76, 142.00, 139.99, 138.74, 136.76, 133.16, 132.52, 119.68, 118.65, 113.98, 110.32, 96.12, 65.96, 29.00, −6.47. Anal. Calcd for $C_{29}H_{22}F_{10}N_2OW$: C, 44.18; H, 2.81; N, 3.55. Found: C, 44.29; H, 2.87; N, 3.42.

*W(N-t-Bu)(C$_3$H$_6$)(ODFT)$_2$ (**13$_W$**).* W(N-*t*-Bu)(CH-*t*-Bu)(pyr)$_2$(bipy) (160 mg, 0.260 mmol), $ZnCl_2$(dioxane) (58.5 mg, 0.260 mmol), and DFTOH (211 mg, 0.495 mmol) were dissolved in toluene (10 mL) in a 100 mL Schlenk bomb. The mixture was sonicated for 19 h and filtered through a pad of Celite on a glass frit, and the solvent was removed from the filtrate *in vacuo*. The compound was extracted with pentane (20 mL), the mixture was filtered through a pad of Celite on a glass frit, and the solvent was removed from the filtrate until the volume was about 2 mL. The mixture was transferred to a Schlenk bomb. The solution was degassed via three freeze−pump−thaw cycles, and it was exposed to 1 atm of ethylene for 30 min. Off-white solids precipitated out and were filtered off; yield 85.5 mg (29%): $^1$H NMR (500 MHz, $C_6D_6$) $\delta$ 6.98 (d, 4H, Ar), 6.74 (t, 2H, Ar), 2.72 (m, 2H, $WCH_\alpha$), 1.87 (m, 2H, $WCH_\alpha$), 0.53 (s, 10H, *t*-Bu and $WCH_\beta$), −0.20 (m, 1H, $WCH_\beta$); $^{19}$F NMR (300 MHz, $C_6D_6$) $\delta$ −138.72 (m, 4F), −154.76 (m, 2F), −162.22 (m, 4F); $^{13}$C NMR (125 MHz, $C_6D_6$) $\delta$ 161.04, 145.71, 143.74, 142.11, 140.10, 139.13, 137.13, 133.88, 121.27, 118.59, 113.65, 70.48, 68.85, 28.50, 5.99. Anal. Calcd for $C_{43}H_{21}F_{20}NO_2W$: C, 45.01; H, 1.84; N, 1.22. Found: C, 45.13; H, 1.92; N, 1.10.

*W(N-t-Bu)(CH-t-Bu)(pyr)(ODFT)(py) (**14$_W$**).* W(N-*t*-Bu)(CH-*t*-Bu)-$(Cl)_2(py)_2$ (158.8 g, 0.287 mmol) was suspended in toluene (20 mL). Lipyr (0.043 g, 0.587 mmol) was added in one portion, and the mixture was stirred at room temperature for 2 h, during which time salts precipitated out. The precipitate was filtered off on a pad of Celite on a glass frit, and the pad was washed with toluene. DFTOH (0.104 g, 0.244 mmol) was added to the solution, and the mixture was allowed to stir at room temperature overnight. All solvents were removed from the filtrate *in vacuo*. Pentane was added and removed *in vacuo* a couple of times to remove excess toluene. The resulting precipitate was collected by filtration in pentane and dried *in vacuo* to yield a gray powder; yield 159 mg (73%): $^1$H NMR (400 MHz, $C_6D_6$) $\delta$ 10.79 (s, 1H, *anti*-W=*CH*, $^1J_{CH}$ = 178.3 Hz, $^2J_{WH}$ = 9.6 Hz), 8.47 (d, 2H, Ar), 6.81 (t, 1H, Ar), 6.89 (t, 1H, Ar), 6.43 (m, 4H, pyr), 6.32 (m, 2H, Ar), 1.08 (s, 9H, Me), 1.06 (s, 9H, Me); $^{19}$F NMR (400 MHz, $C_6D_6$) $\delta$ −137.81, −138.83, −157.77, −161.48, −162.92; $^{13}$C NMR (100.61 MHz, $C_6D_6$) $\delta$ 281.31 ($WCHCMe_3$, $^1J_{CW}$ = 178 Hz), 160.02, 152.02, 146.07, 143.29, 141.54, 139.04, 138.42, 133.29, 131.29, 124.67, 119.72, 118.18, 114.30, 108.81, 69.61, 43.92, 32.53, 31.43. Anal. Calcd for $C_{36}H_{31}F_{10}N_3OW$: C, 48.29; H, 3.49; N, 4.69. Found: C, 48.03; H, 3.66; N, 4.96.

**General Procedure for Polymerization Reactions.** In a 20 mL vial in the glovebox were placed 50 equivalents of monomer with a stir bar and solvents ($C_6D_6$, dichloromethane, or $CDCl_3$). In a small vial, 1 equiv of catalyst was dissolved in appropriate solvents, and catalyst solution was added dropwise to the monomer solution. The reaction progress was monitored by $^1$H NMR spectroscopy by taking aliquots in wet $CDCl_3$ outside the box.

**General Procedure for 1-Octene Homocoupling Experiments.** In a 0.5 dram vial in the glovebox was placed 5 $\mu$mol of solid catalyst (2 mol %), and 43 $\mu$L of 1-octene (0.272 mmol, 50 equiv) was injected. The vial was capped with a septum, a needle was added through the septum to allow ethylene to excape, and the mixture was stirred at room temperature. The aliquots were taken after 1, 2, 8, and 24 h, and wet chloroform-*d* was added outside the box. The conversion of 1-octene to 7-tetradecene was measured with $^1$H NMR spectroscopy.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00633.

Crystallographic data (CIF)

Experimental details for X-ray structural studies and proton NMR spectra for **1$_{Mo}$**, **2$_W$**, **2$_{Mo}$**, **4$_{Mo}$**, **5$_W$**, **6$_W$**, **7$_W$**, **8$_W$**, **9$_W$**, **10$_W$**, **11$_W$**, **12$_W$**, **13$_W$**, and **14$_W$** (PDF)

## ■ AUTHOR INFORMATION


### Corresponding Author

*E-mail: rrs@mit.edu.


### Notes

The authors declare no competing financial interest.

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## ■ NOTE ADDED AFTER ASAP PUBLICATION

This paper was published on the Web on September 1, 2015, with errors in the Table of Contents graphic, the Abstract graphic, and Equation 3. The corrected version was reposted on September 3, 2015.



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