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Tungsten Oxo Alkylidene Complexes as Initiators for the Stereoregular Polymerization of 2,3-Dicarbomethoxynorbornadiene

by

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Abstract

We have employed 2,3-dicarbomethoxynorbornadiene (DCMNBD) as a monomer to explore new tungsten oxo alkylidene complexes as initiators for stereoregular ROMP (Ring-Opening Metathesis Polymerization). The initiators include MAP (MonoAryloxide Pyrrolide) oxo alkylidene complexes with the general formula $W(O)(CHCMe_2Ph)(Me_2Pyr)(OAr)$ (Me_2Pyr = 2,5-dimethylpyrrolide, OAr = an aryloxide) and $W(O)(CHCMe_2Ph)(OR)_2$ (OR = an aryloxide or $OC(CF_3)_3$), or PPh_2Me or CH_3CN adducts thereof. We have found that MAP initiators yield *cis,syndiotactic*-poly(DCMNBD) as a consequence of stereogenic metal control. In contrast, $W(O)(CHCMe_2Ph)(OR)_2(L)$ initiators (where L = PPh_2Me or acetonitrile) are strongly biased toward formation of *cis,isotactic* structures, while $W(O)(CHCMe_2Ph)(OR)_2$ initiators are strongly biased toward formation of *cis,syndiotactic* structures. Addition of $B(C_6F_5)_3$ to $W(O)(CHCMe_2Ph)(Me_2Pyr)(OR)$ species leads to a dramatic increase in the rate of polymerization, and to an increase in the *cis,syndiotacticity* of the polymer (if not already high), while addition of $B(C_6F_5)_3$ to $W(O)(CHCMe_2Ph)(OR)_2$ initiators leads to a dramatic increase in the rate of polymerization and to the formation of highly *cis,syndiotactic* polymers. All evidence supports the proposal that 16e $W(O)(CHCMe_2Ph)(OR)_2(L)$ complexes can operate either through loss of L to yield 14e $W(O)(CHCMe_2Ph)(OR)_2$ species (which yield largely *cis,syndiotactic*-poly(DCMNBD)) or by directly reacting with DCMNBD to yield an 18e intermediate and largely *cis,isotactic*-poly(DCMNBD). All polymerizations by $W(O)(CHCMe_2Ph)(OR)_2(L)$ and $W(O)(CHCMe_2Ph)(OR)_2$ initiators must operate through some version of chain end control.

INTRODUCTION

The synthesis of polymers from strained cyclic olefins (ring-opening metathesis polymerization or ROMP)^{1,2} was an important application of olefin metathesis well before "well-defined" high oxidation state alkylidene complexes, isolable compounds that are essentially the same as the active alkylidene species, were discovered.³ Well-defined alkylidene initiators offer the possibility of controlling the formation of *cis* or *trans* double bonds, tacticity, molecular weight, and polydispersity in the resulting ROMP polymer through a careful design of the catalyst at a molecular level. Early examples of well-defined alkylidene complexes that were employed for ROMP, typically ROMP of highly reactive monomers such as norbornene(s) and disubstituted norbornadienes, were based on Ti,⁴ Ta,⁵ or W.⁶ In the last 25 years the well-defined olefin metathesis catalysts that have been employed for ROMP include largely either imido alkylidene complexes that contain Mo or W⁷ or alkylidene complexes that contain Ru.⁸

Synthesis of highly stereoregular ROMP polymers from achiral monomers requires that only *cis* or *trans* C=C bonds be formed and that only an *isotactic* (*meso*) or a *syndiotactic* (*rac*) relationship between monomer units be present. Using norbornene as the example (Figure 1) the two possible *cis* polymers that have a repeating regular structure are *cis, isotactic* (...mmmm...) and *cis, syndiotactic* (...rrrrr...). (Other repeating structures can be imagined, e.g., ...mrmrmr..., although the mechanisms required to form them are not known.) *Isotactic* sequences are formed through repeated addition of norbornene through the *exo* face of its C=C bond to one side of the M=C bonds in propagating intermediates, while *syndiotactic* sequences are formed through alternating addition of the monomer to one side of a M=C bond in a propagating species and then the other. Relatively air-stable, saturated hydrocarbon polymers are formed upon hydrogenation of the C=C bonds that connect each former monomer unit, but the stereochemical relationship between the five-membered rings in

Figure 1. The two regular *cis* structures for polynorbornene.

not known.) *Isotactic* sequences are formed through repeated addition of norbornene through the *exo* face of its C=C bond to one side of the M=C bonds in propagating intermediates, while *syndiotactic* sequences are formed through alternating addition of the monomer to one side of a M=C bond in a propagating species and then the other. Relatively air-stable, saturated hydrocarbon polymers are formed upon hydrogenation of the C=C bonds that connect each former monomer unit, but the stereochemical relationship between the five-membered rings in

the saturated polymer remains. An unanswered question in ROMP polymer chemistry is to what extent the polymer properties (melting point, crystallinity, recrystallization rate, etc.) will differ in isotactic *versus* syndiotactic saturated polymers. An example of a polymer today where an answer to that question is being sought is high-melting, crystalline hydrogenated poly(*endo*-dicyclopentadiene).⁹ Although a hydrogenated polymer with a single tacticity would result from hydrogenation of a mixture of *cis* and *trans* polymers with the same tacticity, it seems most promising in terms of forming a hydrogenated polymer with a single tacticity that the precursor should be highly tactic and all *cis* or all *trans*. At this point all *cis* polymers appear to be the more likely option, as outlined below.

For some time we have employed various norbornenes or substituted norbornadienes, such as 2,3-dicarbomethoxynorbornadiene (DCMNBD), to probe how to prepare stereoregular ROMP polymers. Formation of highly stereoregular ROMP polymers from DCMNBD employing $\text{Mo}(\text{NR})(\text{CHR}')(\text{OR}'')_2$ initiators has enjoyed limited success.⁷ While *cis* ROMP polymers often can be formed, especially at low temperatures,¹⁰ high tacticity (>95%) has rarely been achieved with $\text{Mo}(\text{NR})(\text{CHR}')(\text{OR}'')_2$ initiators, perhaps in part because tacticity can arise only through *chain end control* if the initiator is not chiral.

When "second generation" initiators that contain a biphenolate or binaphtholate ligand are employed instead of $\text{Mo}(\text{NR})(\text{CHR}')(\text{OR}'')_2$ initiators,¹¹ exclusively *cis* double bonds and a single tacticity can be obtained relatively easily. When the ester in the 2,3-dicarboalkoxynorbornene is enantiomerically pure (mentholate), the resulting polymer was proven to be isotactic.¹¹ Isotacticity is what would be expected from *enantiomorphic site control*, i.e., addition of monomer repeatedly to one side of the $\text{M}=\text{C}$ bond in the propagating species as a consequence of the fixed chirality in the biphenolate or binaphtholate ligand.

"Third generation" MAP (MonoAryloxy Pyrrolide) imido alkylidene catalysts,^{3d} i.e. $\text{M}(\text{NR})(\text{CHR}')(\text{Pyrrolide})(\text{OR}'')$ complexes ($\text{M} = \text{Mo}$ or W), have been found to promote formation of *Z* double bonds in metathesis reactions of acyclic olefins¹² and to yield stereoregular *cis*-poly(DCMNBD).^{13a,15} When the ester in the 2,3-dicarboalkoxynorbornene is

enantiomerically pure (mentholate), the *cis* polymer was proven to be *syndiotactic*.^{13a} Formation of only *cis* C=C bonds is encouraged through the presence of a large OR" group in MAP species that limits formation of trigonal bipyramidal metallacyclobutane intermediates (in which the metallacycle and pyrrolide occupy equatorial positions) to only those in which the metallacyclobutane substituents point away from the bulky axial OR" group; we have had most success with OR" groups in MAP initiators that are 2,6-disubstituted phenoxides, especially 2,6-diarylsubstituted ("2,6-terphenoxides"). *Inversion of configuration at the metal center* in MAP species with each monomer insertion (see later) is proposed to be why the monomer adds alternatively to one and then the other face of M=C bonds in the propagating species.¹³ Alternating chirality at the stereogenic metal center with each insertion has been dubbed "*stereogenic metal control*." It is essentially an unknown means of controlling polymer structure in polymer chemistry in general. Stereogenic metal control seems most closely related to formation of *cis,syndiotactic* polypropylene.¹⁴

When *stereogenic metal control* determines the polymer structure, ROMP polymers formed from *racemic* monomers and molybdenum imido alkylidene initiators can have a basic *cis,syndiotactic* structure, and enantiomers can be incorporated into the polymer chain in a perfectly alternating fashion to give a "*cis,syndiotactic,alt*" ROMP structure.¹⁵ What may be the only example of formation of a structure of this type in the literature employing a "classical" metathesis catalyst is the polymer prepared through ROMP of *rac*-1-methylnorbornene with ReCl₅.¹⁶

Well-defined tungsten oxo alkylidene complexes have been synthesized recently.¹⁷ Oxo alkylidene complexes are of special interest because (*inter alia*) they are likely to be found in many classical metathesis catalyst systems, because a Lewis acid (B(C₆F₅)₃) has been shown in preliminary studies to add to the relatively nucleophilic oxo ligand¹⁸ (reversibly) to give highly active catalysts, and because oxo alkylidene complexes are more natural components of catalysts supported on silica.¹⁹ A dramatic increase in the rate of processes relevant to olefin metathesis has been ascribed to binding of B(C₆F₅)₃ to the oxo ligand.²⁰ Oxo alkylidene complexes appear

to be especially *Z*-selective when the OR" ligand is an appropriately sterically tuned 2,6-terphenoxide. A recent example of a virtually exclusive *Z* coupling of terminal olefins is the synthesis of a macrocyclic triethylenetetramine ligand in which the aryl substituents are part of a 45 atom macrocycle that contains three *cis* C=C bonds and which is formed in ~75% yield;²¹ the only successful catalyst out of approximately a dozen tested (Mo, W, or Ru catalysts) was W(O)(CH-*t*-Bu)(Me₂Pyr)(OHMT)(PMe₂Ph) (Me₂Pyr = 2,5-dimethylpyrrolide; OHMT = O-2,6-(Mesityl)₂C₆H₃).¹⁷ The relevant initiating and propagating species were proposed to be 14 electron W(O)(CHR)(Me₂Pyr)(OHMT) complexes in these reactions.

This paper is the first in which well-defined oxo alkylidene complexes as ROMP initiators are explored in some depth. We chose DCMNBD as the test monomer because more is known about the stereoregular structures of poly(DCMNBD) than any other ROMP polymer in our hands, and because tolerance of ester functionalities is tested in the process. Since stereoselectivities may depend on the monomer, it is important to employ a single achiral monomer in initial studies. We first focus on W(O)(CHR)(OR')(Pyr) (MAP) complexes (or adducts thereof) as initiators, and then on W(O)(CHR)(OR')₂ complexes (or adducts thereof), in each case especially those in which OR' is a 2,6-terphenoxide ligand. We chose to explore W(O)(CHR)(terphenoxide)₂ complexes as a consequence of the observation that M(NC₆F₅)(CHR)(ODFT)₂ (M = Mo or W, R = *t*-Bu or CMe₂Ph, ODFT = O-2,6-(C₆F₅)₂C₆H₃)²² was found to yield highly *cis, isotactic*-poly(DCMNBD),²⁷ a result that has been restricted essentially to initiators that contain a chiral biphenolate or binaphtholate ligand.⁷

RESULTS

Synthesis of Tungsten(VI) Oxo Alkylidene Monoaryloxide Pyrrolide (MAP) Compounds.

Three MAP oxo alkylidene complexes are known in the literature.¹⁷ The reaction between W(O)(CH-*t*-Bu)Cl₂(PMe₂Ph)₂ and LiOHPT (OHPT = O-2,6-(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃) yields off-white W(O)(CH-*t*-Bu)(OHPT)Cl(PMe₂Ph), which upon treatment with Li(Me₂Pyr) in benzene yields yellow W(O)(CH-*t*-Bu)(Me₂Pyr)(OHPT).^{17a} W(O)(CH-*t*-

Bu)(OHMT)Cl(PMe₂Ph) and W(O)(CH-*t*-Bu)(Me₂Pyr)(OHMT)(PMe₂Ph) were prepared in a similar fashion. Retention of one phosphine in W(O)(CH-*t*-Bu)(Me₂Pyr)(OHMT)(PMe₂Ph) is ascribed to reduced steric crowding in the OHMT complex compared to the OHPT complex, although the phosphine is relatively labile and dissociated to a significant degree in solution. The third MAP species, W(O)(CH-*t*-Bu)(Ph₂Pyr)(OHMT) (Ph₂Pyr = 2,5-diphenylpyrrolide), is the product of addition of Li(Ph₂Pyr) to W(O)(CH-*t*-Bu)(OHMT)Cl(PMe₂Ph).^{17b} The phosphine is not present in W(O)(CH-*t*-Bu)(Ph₂Pyr)(OHMT) as a consequence of an increase in steric crowding ascribable to the Ph₂Pyr ligand, which may include it binding in an η⁵-fashion to give an 18e species.²³ Addition of two equivalents of B(C₆F₅)₃ to W(O)(CH-*t*-Bu)(Me₂Pyr)(OHMT)(PMe₂Ph) led to the formation of (Me₂PhP)[B(C₆F₅)₃] and W[OB(C₆F₅)₃](CH-*t*-Bu)(Me₂Pyr)(OHMT), which was characterized structurally in an X-ray study. W[OB(C₆F₅)₃](CH-*t*-Bu)(Me₂Pyr)(OHMT) is in equilibrium with W(O)(CH-*t*-Bu)(Me₂Pyr)(OHMT) and B(C₆F₅)₃ in solution.

We first turned to the syntheses of oxo complexes that contain a neophylidene ligand in combination with PPh₂Me instead of PMe₂Ph. The reason for making neophylidenes is that neophyl starting materials (*e.g.*, neophyl chloride) are inexpensive relative to neopentyl starting materials. The reason to use PPh₂Me is that a larger, more sterically-hindered phosphine could lead to more phosphine-free MAP species, or at least to complexes in which the phosphine is dissociated to a greater extent.

W(O)(CHCMe₂Ph)Cl₂(PPh₂Me)₂ (**1**) was prepared in a manner analogous to that reported for W(O)(CH-*t*-Bu)Cl₂(PMe₂Ph)₂ and W(O)(CHCMe₂Ph)Cl₂(PMe₂Ph)₂.^{17b} A toluene solution of W(O)₂(CH₂CMe₂Ph)₂(bipy) (1 equiv), ZnCl₂(dioxane) (1.05 equiv), TMSCl (2.3 equiv), and PPh₂Me (1.8 equiv) was heated to 100 °C for 2 h. Compound **1** was isolated from this mixture in 55% yield. As expected by analogy with W(O)(CH-*t*-Bu)Cl₂(PMe₂Ph)₂ and W(O)(CHCMe₂Ph)Cl₂(PMe₂Ph)₂, the alkylidene ligand in **1** was found to be in the *syn* orientation according to the value for *J*_{CαH} (127 Hz); the two PPh₂Me ligands are equivalent and bound to tungsten (*J*_{PW} = 330 Hz) on the ³¹P NMR time scale at 22 °C.

The reaction between **1** and LiOAr reagents (OAr = OHMT, ODFT, OTTP, OdAdP, and ODBMP; equation 1) led to the formation of off-white $W(O)(CHCMe_2Ph)(OAr)Cl(PPh_2Me)$ complexes **2a-2e** in 52 – 86% yields. (The OHIPT ligand and related ligands such as O-2,6-(2,6-*i*-Pr₂C₆H₃)₂C₆H₃ have been found to be "too large" in *some* circumstances that we have explored, and so was avoided in this study.) As found for $W(O)(CH-*t*-Bu)(OHMT)Cl(PMe_2Ph)$, the ¹H NMR spectrum of **2a** contains two alkylidene doublet resonances in a 88:12 ratio (see Figure S1). Both isomers of **2a** were found to have the neophylidene in a *syn* orientation on the basis of relatively low J_{CaH} values (122 Hz for the major isomer, 118 Hz for the minor isomer) compared to a typical value for J_{CaH} in an *anti* alkylidene (~135-145 Hz). The PPh₂Me ligand remains

bound to tungsten on the NMR time scale at 22 °C in each isomer. The alkylidene has been found to be in an axial position in all square pyramidal base adducts of imido or oxo alkylidene complexes whose structures have been determined;²⁴ we suggest that one isomer of **2a** is that shown in equation 1, while the other is the one in which the OAr and Cl ligands have switched positions. For **2b-2e**, the alkylidene H_α resonances are all doublets and the alkylidenes are in *syn* orientations (see Figure S1). The PPh₂Me ligands are also all bound on the NMR time scale at 22 °C. For **2c**, the ¹H NMR spectrum showed one alkylidene doublet (³J_{HP} = 3 Hz) that was similar to other type **2** compounds reported herein (¹J_{CH} = 125 Hz for *syn* alkylidene). However, the other alkylidene resonance was broadened (³J_{HP} = 7 Hz) and the alkylidene was shown to be

in the *anti* orientation on the basis of the higher value for $^1J_{\text{CH}}$ (146 Hz; see Figure S1).

Treatment of **2a** with 1.1 equiv of Li(Me₂Pyr) in toluene at 22 °C for 16 h led to formation of yellow W(O)(CHCMe₂Ph)(Me₂Pyr)(OHMT)(PPh₂Me) (**3a(P)**) in 85% isolated yield (equation 2). In contrast to W(O)(CH-*t*-Bu)(Me₂Pyr)(OHMT)(PMe₂Ph), where the alkylidene α proton resonance is broadened and its position concentration dependent, the single alkylidene resonance in **3a(P)** is sharp and not strongly concentration dependent (see Figure S2).

On the basis of the position of the resonance for PPh₂Me in the ^{31}P NMR spectrum of a 48 mM C₆D₆ solution of **3a(P)**, ~10% of the PPh₂Me is bound (resonance at 23.0 ppm) and ~90% dissociated (resonance at -26.5 ppm) at room temperature. We ascribe the greater extent and rate of dissociation of PPh₂Me (*vs.* PMe₂Ph) to the larger size and lower basicity of PPh₂Me. We propose that the structure of **3a(P)** is that shown in equation 2, which is analogous to the structure found for W(O)(CH-*t*-Bu)(Me₂Pyr)(OHMT)(PMe₂Ph).^{17a} Treatment of **2b**, **2c**, or **2e** with 1.1 equiv of Li(Me₂Pyr) led to **3b(P)**, **3c(P)**, and **3e(P)** in 71, 88, and 63% isolated yields. The alkylidene resonances in **3b(P)**, **3c(P)**, and **3e(P)** (see Figure S2) are broad as a consequence of the PPh₂Me ligand being partially dissociated and rapidly exchanging on and off of the metal at 22 °C. Phosphorus NMR spectra of each compound in C₆D₆ at 22 °C showed a broad average phosphorus resonance at ~20 ppm. Only when OAr = OdAd is a phosphine-free complex (**3d**) obtained. It is possible that formation of **3d** is a consequence of η^5 binding of the dimethylpyrrolide ligand to give an 18e species.²³

When crude **3a(P)** was triturated overnight with acetonitrile, a suspension was obtained from which pale yellow $\text{W(O)(CHCMe}_2\text{Ph)(Me}_2\text{Pyr)(OHMT)(MeCN)}$ (**3a(N)**) could be filtered off and isolated in 68% yield (equation 3). The neophylidene ligand was found to be in the *syn* orientation on the basis of the value for $J_{\text{C}\alpha\text{H}}$ (122 Hz). The acetonitrile was still present

after several cycles of dissolving **3a(N)** in toluene and removing all volatiles *in vacuo*. However, addition of 0.98 equiv of $\text{B(C}_6\text{F}_5)_3$ to **3a(N)** in toluene resulted in the formation of relatively insoluble $(\text{MeCN})[\text{B(C}_6\text{F}_5)_3]$ and soluble **3a**. Compound **3a** could be isolated in pure form in 80% yield. All 16e and 14e MAP complexes that have been isolated or generated *in situ* through addition of $\text{B(C}_6\text{F}_5)_3$ are listed in Table 1.

Synthesis of Tungsten(VI) Oxo Alkylidene Bisaryloxyde and Bisalkoxyde Complexes.

Bis(terphenoxide) imido alkylidene complexes are relatively rare, in part as a consequence of the steric demand of an imido ligand *versus* an oxo ligand, and possibly also the greater electron donor ability of an imido *versus* an oxo ligand, which could result in slower nucleophilic attack at the metal. The known oxo bisaryloxyde complexes are W(O)(CHR)(OHMT)_2 ($\text{R} = t\text{-Bu}$ or H), $\text{W(O)(CH-}t\text{-Bu)(OdAdP)}_2$,²⁰ and $\text{W(O)(CH-}t\text{-Bu)(O-2,6-Ph}_2\text{C}_6\text{H}_3)_2(\text{L})$ ($\text{L} = \text{PPh}_2\text{Me}$, PMe_2Ph).²⁵

Compound **4a** (equation 4) was prepared and isolated in 74% yield by the same method as that employed for the synthesis of $\text{W(O)(CH-}t\text{-Bu)(OHMT)}_2$, namely by treating $\text{W(O)(CHCMe}_2\text{Ph)Cl}_2(\text{PPh}_2\text{Me})_2$ (**1**) with 2.2 equivalents of LiOHMT at 100°C in toluene for two days. Compounds **4c(P)**, **4d**, and **4e(P)** were prepared in an analogous fashion in 72%, 75%, and 45% yields, while **4d** and **4e(P)** were prepared at a lower temperature. (Crude **4e(P)** was

isolated through a procedure that included acetonitrile in the workup, so **4e(N)** was the compound actually isolated; see equation 3 for **3a(P)**.) In all bisaryloxides the alkylidenes are in the *syn* orientation according to the relatively low values for J_{CH} (117 to 126 Hz). In all compounds the OR ligands are equivalent on the 1H NMR time scale at room temperature.

A temperature-dependent proton NMR spectrum of **4a** in CD_2Cl_2 (see Figure S4) shows resonances for three types of methyl groups in the OHMT ligands at 22 °C (with the *ortho* methyl resonances differing by 4 Hz at 500 MHz), consistent with no rotation of the mesityl rings with respect to the central OHMT phenyl ring, ready rotation about the OC_{ipso} bond, and the presence of only one molecular mirror plane that contains the oxo and alkylidene C_α atoms. Each *ortho* methyl resonance is the average of *ortho* methyl resonances on *separate* mesityl rings in a single OHMT ligand. Although only one resonance for *ortho* methyl groups is observed at -80 °C at ~1.80 ppm, we ascribe the apparent "equilibration" of *ortho* methyl groups to a simple inequivalent temperature-dependent chemical shift of the two types of *ortho* methyl resonances as the temperature is lowered. There is no evidence for any atropisomeric form of **4a** on the NMR time scale in the proton NMR spectra at -80 °C, as has been observed in $Mo(NC_6F_5)(CHCMe_2Ph)(ODFT)_2$ in ^{19}F NMR spectra at low temperatures.²⁷

We have been able to prepare and isolate $W(O)(CHCMe_2Ph)(ODFT)_2(PPh_2Me)$ (**4b(P)**) in 40% yield as a light yellow solid only from isolated $W(O)(CHCMe_2Ph)(ODFT)Cl(PPh_2Me)$ (**2b**) and 1.1 equivalents of LiODFT in toluene at 80 °C overnight (equation 5). We do not know at this time why we have not been able to prepare **4b(P)** directly from **1** and two equivalents of

LiODFT. Two alkylidene singlets in a 40:60 ratio at 11.85 ($J_{\text{CH}} = 141$ Hz) and 10.91 ppm ($J_{\text{CH}} = 122$ Hz) in the alkylidene region of the ^1H NMR of **4b(P)** suggest that both *syn* ($J_{\text{CH}} = 122$ Hz) and *anti* ($J_{\text{CH}} = 141$ Hz) isomers are present. The room temperature ^{31}P NMR spectrum of **4b(P)** in C_6D_6 showed two broad resonances at 19.14 and 16.24 ppm in a 40:60 ratio, consistent with the presence of two isomers in which the phosphine is relatively labile. We propose that the phosphine is retained in **4b(P)**, in spite of the presence of two sterically demanding ODFT ligands, as a consequence of the enhanced electrophilicity of the metal center.

The bisalkoxide complex, $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})[\text{OC}(\text{CF}_3)_3]_2(\text{PPh}_2\text{Me})$ (**5(P)**) was prepared in 52% yield from **1** in a manner similar to what has been described for the bisaryloxides **4** in order to test whether the phenomena described for bisaryloxide initiators are also found for bisalkoxides.

All 14e $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{OR})_2$ and 16e $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{OR})_2(\text{L})$ species are listed in Table 2. Compound **4c** was prepared and isolated by treating **4c(P)** with $\text{B}(\text{C}_6\text{F}_5)_3$ (1 equiv) in cold (-30°C) toluene. Confirmation that the PPh_2Me ligand had been removed was provided through a single-crystal X-ray diffraction study of **4c** (Figure S5). Compound **4e** could be generated from **4e(N)** through repeated removal of all solvent from toluene solutions of **4e(N)** *in vacuo*.

Polymerization of DCMNBD Initiated by MAP Species.

The structure of *cis*-poly(DCMNBD) is most readily analyzed through a combination of proton and carbon NMR spectra. In the proton NMR spectra of stereoregular *cis*-

poly(DCMNBD) in CDCl_3 (Figure 2) the olefinic proton resonance (H_a) and the methine resonance (H_b) show the most variation in chemical shift; the H_a and the H_b resonances differ by 0.08 ppm in *cis, isotactic*¹¹ and *cis, syndiotactic*¹³ structures with the H_a resonance being slightly sharper. In carbon NMR spectra the methylene carbon resonance (C7, Figure 3) is found at 38.83 ppm in *cis, isotactic* and 38.08 ppm in *cis, syndiotactic* structures. Therefore expanded proton NMR spectra in the 5.3-5.5 ppm region and/or carbon NMR spectra in the 38-39 ppm region provide an accurate snapshot of the stereoregularity of *cis*-poly(DCMNBD). In carbon NMR spectra the carbon atom being detected (C7, Figure 3) lies on the mirror plane through one polymer unit, so the mm, rr, and mr/rm nomenclature refers to the orientation of the five-membered rings on each side of the central unit in a triad.

Addition of 50 equivalents of DCMNBD to all MAP complexes in CDCl_3 led to the total consumption of monomer and formation of *cis, syndiotactic*-poly(DCMNBD), whether PPh_2Me or acetonitrile was present as a ligand in the initiator or not (Table 1 and Figure 4).¹³ *Cis, syndiotactic*-poly(DCMNBD) shows a second-order pattern for the olefinic protons at 5.33 ppm in CDCl_3 in the proton NMR spectrum and a singlet at 38.08 ppm for the C(7) resonance (rr) in the ^{13}C NMR spectrum, as shown in Figure 4. When one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ was added to **3a** or **3d**, or two equivalents to **3a(P)**, **3a(N)**, **3b(P)**, **3c(P)**, and **3e(P)**, **3a(P)**, the resulting poly(DCMNBD) was again rigorously *cis, syndiotactic* in all cases except when **3d** was employed, where little change was observed in the NMR spectrum of the polymer. These results prove that the presence of the phosphine or acetonitrile has little to no effect on the stereoregularity of the resulting polymer and the propagating species are four-coordinate 14e species in all cases. We propose that *cis, syndiotactic*-poly(DCMNBD) is formed as a consequence of stereogenic metal control. Unfortunately, the rates of the ROMP of DCMNBD in CDCl_3 upon addition of one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ to 14e MAP initiators or two equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ (one to sequester L) to 16e MAP initiators were too fast (<5 min) to measure readily at room temperature by proton NMR. However, qualitatively the rates of polymerization in the

presence of one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ per $\text{W}=\text{O}$ group are much faster than in the absence of $\text{B}(\text{C}_6\text{F}_5)_3$.

Polymerization of DCMNBD Initiated by Bisaryl- and Bisalkoxide Species.

Bisaryloxide and bisalkoxide compounds **4** and **4(L)**, with the exception of **4d**, all polymerize DCMNBD readily; the proton and carbon NMR spectra of the resulting poly(DCMNBD) are shown in Figure 5 and the results are summarized in Table 2. The ROMP of 50 equivalents of DCMNBD using initiators **4a** and **4d** (which was extremely slow with only 60% conversion at 5 h) yield poly(DCMNBD) with a strong *cis,syndiotactic* bias, while all adducts yield poly(DCMNBD) with a strong *cis,isotactic* bias.

Initiator **4a** alone was found to polymerize DCMNBD (3.43 mM in CDCl_3) in a pseudo first order manner with $k_{\text{obs}} = 0.01 \text{ (M s)}^{-1}$ (Figure 6). In the presence of 1.05 equivalents of BPh_3 , $k_{\text{obs}} = 0.30 \text{ (M s)}^{-1}$, while in the presence of 1.05 equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$, $k_{\text{obs}} = 0.52 \text{ (M s)}^{-1}$. The degree of acceleration in the presence of one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ is approximately a factor of 50. The poly(DCMNBD) formed from **4a** alone was found to be 96% *cis*, 90% *syndiotactic* (Figure 5). Upon addition of BPh_3 to **4a** the stereoregularity improved (96% *cis,syndiotactic*), and with $\text{B}(\text{C}_6\text{F}_5)_3$ it improved again (to >99% *cis,syndiotactic*; Figure 7). The formation of >99% *cis,syndiotactic* poly(DCMNBD) from **4a** in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ can be taken essentially as proof that the nature of the catalyst is retained, i.e., $\text{B}(\text{C}_6\text{F}_5)_3$ has added to the oxo ligand to give $\text{W}[\text{OB}(\text{C}_6\text{F}_5)_3](\text{CHR})(\text{OHMT})_2$ complexes as the propagating species. (Low temperature NMR studies clearly show that $\text{W}[\text{OB}(\text{C}_6\text{F}_5)_3](\text{CH}_2)(\text{OHMT})_2$ is formed upon addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to $\text{W}(\text{O})(\text{CH}_2)(\text{OHMT})_2$,²⁰ although analogous studies have not yet been carried out with **4a**.) The spectra shown in Figure 5 raise the question as to whether L can be removed from **4(L)** initiators and whether the resulting ligand-free species yield poly(DCMNBD) with a strong *cis,syndiotactic* bias, as observed for **4a** and **4d**.

Addition of one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$ to **4c** and **4e** led to formation of a greater percentage of *cis,syndiotactic* poly(DCMNBD) (and some *trans** poly(DCMNBD)). Addition of

two equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ to **5(P)** led to acceleration of the rate of polymerization of DCMNBD and to formation of poly(DCMNBD) with a *cis,syndiotactic* bias (Figure 8). The dramatic results obtained employing **5(P)** suggest that the switching of the tacticity from *iso* to *syndio* can be observed in complexes other than bisaryloxides or bisterphenoxides. In contrast, PPh_2Me in **4b(P)** apparently is bound too strongly to dissociate to any significant degree under the experimental conditions to be captured by one equivalent of added $\text{B}(\text{C}_6\text{F}_5)_3$; therefore the poly(DCMNBD) obtained in the presence of **4b(P)** and $\text{B}(\text{C}_6\text{F}_5)_3$ is largely *isotactic*. Although $\text{B}(\text{C}_6\text{F}_5)_3$ could bind to the oxo ligand in **4b(P)**, if that is happening it does not alter the structure of the *cis,isotactic*-poly(DCMNBD). Addition of one equivalent of PPh_2Me to **5(P)** led to a dramatically slower polymerization but still formation of *cis,isotactic*-poly(DCMNBD). We propose that the polymerization is retarded through formation of 18e $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{ODFT})_2(\text{PPh}_2\text{Me})_2$ and that $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{ODFT})_2(\text{PPh}_2\text{Me})$ is still the active species.

On the basis of these data we are forced to conclude that poly(DCMNBD) with a strong *cis,isotactic* bias is formed upon reaction of a 16e adduct with DCMNBD (Figure 5). In contrast, ligand-free 14e initiators, especially in the presence of one equivalent of $\text{B}(\text{C}_6\text{F}_5)_3$, yield poly(DCMNBD) whose structure is strongly biased toward a *cis,syndiotactic* structure (Figures 5 and 8). We propose that all polymerizations initiated by $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{OR})_2(\text{L})$ and $\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{OR})_2$ initiators operate through some version of chain end control.

DISCUSSION

We have found that tungsten oxo MAP initiators that contain a relatively large terphenoxide ligand produce highly *cis* and highly *syndiotactic* poly(DCMNBD). These results are analogous to the ring-opening metathesis polymerization of DCMNBD employing imido alkylidene initiators of the general type $\text{M}(\text{NR})(\text{CHCMe}_2\text{Ph})(\text{Pyrrolide})(\text{OR}''')$ (where $\text{M} = \text{Mo}$ or W ; $\text{R} =$ various carbon-based groups; $\text{OR}''' =$ alkoxide or aryloxide, Pyrrolide = pyrrolide itself or 2,5-dimethylpyrrolide).^{13,15,26} *Syndiotacticity* is proposed to arise employing MAP initiators as a

consequence of the monomer arriving at the metal center *trans* to the pyrrolide ligand (*cis* to the oxo and alkylidene ligands) and the stereochemistry *inverting* at the metal center with each productive metathesis step (*stereogenic metal control*; Scheme 1).^{7,13,15,26} It should be noted that for Mo imido alkylidene initiators in which R in the M=NR group is "small" (e.g., 1-adamantyl or *t*-butyl), highly *cis,syndiotactic*-poly(DCMNBD) is formed only when a sufficiently bulky terphenoxide ligand is present.¹³ Although many more comparisons of W oxo and Mo imido initiators and examination of many more monomers will be necessary, our tentative conclusion is that W oxo MAP initiators and Mo imido MAP initiators that contain terphenoxides behave similarly and the principles of forming *cis,syndiotactic* poly(DCMNBD) through stereogenic metal control (Scheme 1) hold for both. We hope that stereogenic metal control will become a relatively robust way to form *cis,syndiotactic* ROMP polymers from a variety of monomers.

Scheme 1. Proposed mechanism for the formation of *cis,syndiotactic*-poly(DCMNBD) using molybdenum-based or tungsten-based MAP initiators.

There are two exceptions to formation of *cis,syndiotactic* polymers with MAP species known so far. One is a reaction of (+)-5,6-dicarbomethoxynorbornene with Mo(NAd)(CHCMe₂Ph)(Pyr)(OHIPT) (Ad = 1-adamantyl; Pyr = pyrrolide = NC₄H₄; OHIPT =

O-2,6-(2,4,6-*i*-Pr₃)₂C₆H₃) in which largely *trans, isotactic*-poly((+)-5,6-dicarbomethoxynorbornene) (~92%) sequences are formed with *cis, syndiotactic* dyads amounting to only ~8%.²⁶ The mechanism of forming *trans, isotactic* sequences is proposed to be one in which an intermediate *trans* metallacyclobutane undergoes a five-coordinate rearrangement before opening to give the *syn* form of the intermediate propagating alkylidene. The second exception is formation of 95% *cis*, 91% *isotactic*-poly(DCMNBD) employing Mo(NC₆F₅)(CHCMe₂Ph)(Me₂Pyr)(ODFT) (ODFT = O-2,6-(C₆F₅)₂C₆H₃) as an initiator.²⁷ Competition between chain end control (to give *isotactic* polymer) and stereogenic metal control (to give *syndiotactic* polymer) is suggested by the finding that when Mo(NC₆F₅)(CHCMe₂Ph)(Me₂Pyr)(ODFT)(CH₃CN) is employed as an initiator, the resulting poly(DCMNBD) was 95% *cis*, but relatively *atactic*. It was also found that Mo(NC₆F₅)(CHCMe₂Ph)(Me₂Pyr)(OHMT) yielded >98% *cis, syndiotactic*-poly(DCMNBD). We recognize that differences between imido alkylidene and oxo alkylidene complexes, and between Mo and W, ultimately could prove to be significant, but differences have not been explored in detail.

Perhaps the biggest surprises to come out of this study are (i) 16e donor ligand adducts of bisalkoxides or bisaryloxides can yield quite high *cis, isotactic*-polyDCMNBD, (ii) 14e bisaryloxides (and a bisalkoxide) can yield high *cis, syndiotactic*-polyDCMNBD, and (iii) upon addition of B(C₆F₅)₃ the rate and *cis, syndiotacticity* can *both* increase to a significant degree. Formation of each stereochemistry must be the consequence of some variation of chain end control. However, it should be noted that a complicating feature of W(O)(CHR')(OR)₂(L) complexes if R' is a chiral chain end is that diastereomers could be present that may or may not interconvert readily through Berry processes. Formation of an 18e W(O)(CHR')(OR)₂(L)(olefin) intermediate instead of a 16e W(O)(CHR')(OR)₂(olefin) intermediate will depend strongly upon the metal center being electrophilic enough to retain L in the coordination sphere and upon the olefin in question being highly reactive (norbornene, cyclopropene, cyclobutene, etc.). We cannot say that metallacyclobutane intermediates are necessarily six-coordinate, i.e., L may not

be retained in all intermediates that lead to formation of the insertion product, $W(O)(CHR')(OR)_2(L)$. Formation of a six-coordinate intermediate could also be less likely for olefins that are significantly less reactive than strained cyclic olefins, for imido complexes instead of oxo complexes, or for Mo instead of W complexes. It should be noted that polymerization of cyclobutene initiated by $W(NAr)(CH-t-Bu)(O-t-Bu)_2(PMe_3)$ ($Ar = 2,6$ -diisopropylphenyl) has been shown to proceed via a 14e $W(NAr)(CHR)(O-t-Bu)_2$ intermediate,²⁸ and that ROMP of DCMNBD using $W(O)(CH-t-Bu)(2,6-Ph_2C_6H_3)_2(L)$ ($L = PMe_2Ph$ or PPh_2Me) initiators²⁵ gave *cis, isotactic*-poly(DCMNBD), as found here for the "six-coordinate pathway." It is still impressive to us that what would appear to be an extremely crowded $W(O)(CHR)(OR')_2(L)(olefin)$ and (*perhaps*) $W(O)(OR')_2(L)(metallacycle)$ intermediates can be on the kinetically favored pathway for polymerization in some circumstances. To our knowledge these results are the first that show that an 18e ROMP intermediate can be formed from a 16e alkylidene complex. However, exactly why the "six-coordinate pathway" yields *cis, isotactic*-poly(DCMNBD) and why the "five-coordinate pathway" yields *cis, syndiotactic*-poly(DCMNBD) are unclear.

An indication that tungsten oxo MAP initiators can behave quite differently in ROMP than Mo-based imido MAP initiators is formation of ~99% *cis, syndiotactic*-poly((+)-5,6-dicarbomethoxynorbornene) with $W(O)(CH-t-Bu)(Me_2Pyr)(OHMT)(PMe_2Ph)$ as the initiator vs. ~92% *trans, isotactic*-poly((+)-5,6-dicarbomethoxynorbornene) with $Mo(NAd)(CHCMe_2Ph)(Pyr)(OHIPT)$ as the initiator (*vide supra*).²⁶ The tungsten oxo complex accepts (+)-5,6-dicarbomethoxynorbornene in each step in spite of the formation of diastereomers (assuming that the configuration of the metal inverts with each step; Scheme 1). Consistent with this conclusion is the finding that the rates of polymerization of (+)-DCMNBD and *rac*-DCMNBD by $W(O)(CH-t-Bu)(Me_2Pyr)(OHMT)(PMe_2Ph)$ are similar, with the rate for polymerization of *rac*-DCMNBD being only slightly slower.

$W(O)(CHR')(OR'')_2$ initiators that are activated with $B(C_6F_5)_3$, tend to form *cis, syndiotactic*-poly(DCMNBD) with the highest degree of regularity and at the highest rate.

The same type of chain end control must be responsible when boron is bound to the oxo as when it is not. These results differ from the results observed with $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{Ph})(\text{ODFT})_2$ ($\text{R} = \text{C}_6\text{F}_5$ and 2,6- $\text{Me}_2\text{C}_6\text{H}_3$) complexes as initiators,²² which yielded essentially pure (99%) *cis, isotactic*-poly(DCMNBD).²⁷ Again, at this stage we do not have enough data to understand why *cis, syndiotactic*-poly(DCMNBD) is not formed when $\text{Mo}(\text{NR})(\text{CHCMe}_2\text{Ph})(\text{ODFT})_2$ is employed as an initiator. In any case, chain end control, which is relatively unpredictable, is responsible for the result in any bisaryloxide initiator.

The results obtained here resemble those found in earlier studies of imido bisalkoxides and bisaryloxides, although the "six-coordinate pathway" is new.¹⁰ If an electron poor metal gives rise to highly stereoregular poly(DCMNBD) in some circumstances, it would help explain why the stereoregularity of poly(DCMNBD) *improves* upon addition of $\text{B}(\text{C}_6\text{F}_5)_3$. However, the *root cause* of high stereoregularity with a more electrophilic metal remains elusive.

Understanding ROMP polymerization in mechanistic detail continues to be challenging. Among the issues that are likely to continue to be important for understanding stereoregular ROMP include (i) rates of interconversion of *syn* and *anti* isomers of intermediate alkylidenes, (ii) relative reactivities of intermediate alkylidenes, (iii) fluxionality of intermediate metallacyclobutanes, (iv) fluxionality of five-coordinate donor ligand adducts, (v) the role of functionalities within monomers that can coordinate to the metal, and (vi) "alternate" pathways of ROMP polymerization that now include formation of six-coordinate intermediates when the metal center is highly electrophilic and the olefin highly reactive. It is also possible that the principles being uncovered in studies of tungsten oxo alkylidene complexes will turn out not to be analogous to those obtained with molybdenum imido alkylidene initiators in at least some circumstances. Nevertheless, progress is accelerating now that we have a good basis for understanding how *cis, isotactic* and *cis, syndiotactic* structures can be formed in ROMP reactions. Formation through enantiomorphic site control for *cis, isotactic* and stereogenic metal control for *cis, syndiotactic* are emerging as the most reliable methods of controlling structure at

this time. The next step is to determine how general these methods are for a larger variety of monomers than have been employed so far.

EXPERIMENTAL

General All manipulations of air- and moisture-sensitive materials were performed either in a Vacuum Atmospheres glovebox (N_2 atmosphere) or on an air-free dual-manifold Schlenk line. All solvents were sparged with nitrogen, passed through activated alumina, and stored over activated 4 Å molecular sieves. $W(O)_2(CHCMe_2Ph)_2(bipy)$ was prepared according to the literature procedure.^{17b} $LiOAr$ ligands were prepared from the corresponding $ArOH$ (1 equiv) through reaction with 1.2 equivalents of $n-BuLi$ (1.6 M in hexanes) in pentane ($ArOH$ = HMTOH (O-2,6-Mesityl $_2C_6H_3$)^{17b}, DFTOH (O-2,6-(C_6F_5) $_2C_6H_3$)²² and (CF_3) $_3COH$ ²⁹), THF ($ArOH$ = dAdPOH (O-2,6-Ad $_2$ -4-Me C_6H_3)³⁰) or Et $_2O$ ($ArOH$ = TPPOH (O-2,3,5,6-Ph $_4C_6H$)³¹ and DBMPOH (O-2,6-(CHPh $_2$) $_2C_6H_3$)³²). All other reagents were used as received unless noted otherwise. Methylene chloride- d_2 , benzene- d_6 , and toluene- d_8 were distilled from calcium hydride (CD_2Cl_2) or sodium ketyl (C_6D_6 , C_7D_8), and stored over activated 4 Å molecular sieves. NMR measurements of air- and moisture-sensitive materials were carried out in Teflon-valve-sealed J. Young-type NMR tubes. NMR spectra were recorded using Varian spectrometers at 500 (1H), 125 (^{13}C) and 121 (^{31}P) MHz, reported in δ (parts per million) relative to tetramethylsilane (1H , ^{13}C) or 85% phosphoric acid (^{31}P), and referenced to the residual $^1H/^{13}C$ signals of the deuterated solvent (1H (δ): benzene 7.16; methylene chloride 5.32, chloroform 7.26, toluene 7.09, 7.01, 6.97, 2.08; ^{13}C (δ): benzene 128.06; methylene chloride 53.84, chloroform 77.16, toluene 137.48, 128.87, 127.96, 125.13, 20.43) or external 85% phosphoric acid standard (^{31}P (δ): 0). The CENTC Elemental Analysis Facility at the University of Rochester provided the elemental analysis results.

$W(O)(CHCMe_2Ph)Cl_2(PPh_2Me)_2$ (1). Compound **1** was prepared in a manner analogous to that for $W(O)(CHCMe_2Ph)Cl_2(PMe_2Ph)_2$.^{17b} $W(O)_2(CH_2CMe_2Ph)_2(bipy)$ (4.45 g, 6.97 mmol) was

mixed with ZnCl_2 (dioxane) (1.67 g, 7.32 mmol, 1.05 equiv) and PPh_2Me (2.33 mL, 12.6 mmol, 1.8 equiv) in toluene (80 mL). The mixture was cooled to $-30\text{ }^\circ\text{C}$ for 1 h then TMSCl (2.05 mL, 16.0 mmol, 2.3 equiv) was added dropwise while stirring. The reaction mixture was stirred at room temperature for ~ 30 min and then was heated at $100\text{ }^\circ\text{C}$ for 2 h during which time the solution darkened and a precipitate formed. Pentane (12 mL) was added and the reaction mixture was filtered through a bed of Celite. The volatiles were removed *in vacuo*. Trituration of the resulting brown residue with MeCN (20 mL) overnight resulted in a yellow solid which was washed with cold ($-30\text{ }^\circ\text{C}$) MeCN (3x10mL) then vacuum dried to yield a yellow solid (3.08 g, 3.83 mmol, 55%). ^1H NMR (C_6D_6 , $20\text{ }^\circ\text{C}$): δ [ppm] 12.28 (t, 1H, WCHCMe_2Ph , $^1J_{\text{CH}} = 127\text{ Hz}$, $^3J_{\text{HP}} = 7\text{ Hz}$), 7.81 (m, 4H, ArH), 7.64 (m, 4H, ArH), 7.04-6.94 (m, 17H, ArH) 2.28 (t, 6H, PMePh_2 , $^2J_{\text{HP}} = 10\text{ Hz}$), 1.32 (s, 6H, WCHCMe_2Ph). ^{13}C NMR (C_6D_6 , $20\text{ }^\circ\text{C}$): δ [ppm] 319.1 (t, WCHCMe_2Ph , $^2J_{\text{CP}} = 21\text{ Hz}$), 151.2, 134.8, 134.0, 133.1, 130.8, 130.6, 128.6, 128.5, 52.5, 31.6, 22.7, 16.0, 14.3. ^{31}P NMR (C_6D_6 , $20\text{ }^\circ\text{C}$): δ [ppm] 15.29 (s, $^1J_{\text{PW}} = 330\text{ Hz}$). Anal. Calcd for $\text{C}_{36}\text{H}_{38}\text{Cl}_2\text{OP}_2\text{W}$: C, 53.82; H, 4.77. Found: C, 53.80; H, 4.78.

$\text{W(O)(CHCMe}_2\text{Ph)(OHMT)Cl(PPh}_2\text{Me)}$ (2a). A solution of **1** (0.645 g, 0.803 mmol) in 12 mL of benzene was added to a solid portion of LiOHMT (0.284 g, 0.843 mmol, 1.05 equiv). The cloudy, yellow reaction mixture was stirred for 3 h and then the solvent was removed *in vacuo* to give a yellow residue. The product was extracted into toluene (5 mL) and the mixture was filtered through a bed of Celite to remove LiCl . Toluene was removed *in vacuo* to yield a yellow residue. Following trituration with pentane (5 mL) overnight and then filtering the resulting suspension, the product was isolated as an off-white solid (0.620 g, 0.691 mmol, 86% yield). Two isomers in an 88:12 ratio formed according to NMR spectra; only non-overlapping alkylidene signals are listed: Major isomer ^1H NMR (C_6D_6 , $20\text{ }^\circ\text{C}$): δ [ppm] 9.60 (d, 1H, WCHCMe_2Ph , $^1J_{\text{CH}} = 122\text{ Hz}$, $^3J_{\text{HP}} = 3\text{ Hz}$, $^2J_{\text{HW}} = 7\text{ Hz}$); ^{13}C NMR (C_6D_6 , $20\text{ }^\circ\text{C}$): δ [ppm] 295.4 (d, WCHCMe_2Ph , $^2J_{\text{CP}} = 11\text{ Hz}$); ^{31}P NMR (C_6D_6 , $20\text{ }^\circ\text{C}$): δ [ppm] 23.04 (s, $^1J_{\text{WP}} = 402\text{ Hz}$). Minor isomer ^1H NMR (C_6D_6 , $20\text{ }^\circ\text{C}$): δ [ppm] 9.26 (d, 1H, WCHCMe_2Ph , $^1J_{\text{CH}} = 118\text{ Hz}$, $^3J_{\text{HP}} =$

3 Hz, $^2J_{\text{HW}} = 14$ Hz); ^{13}C NMR (C_6D_6 , 20 °C): δ [ppm] 279.2 (d, WCHCMe_2Ph , $^2J_{\text{CP}} = 16$ Hz); ^{31}P NMR (C_6D_6 , 20 °C): δ [ppm] 26.67 (s, $^1J_{\text{WP}} = 370$ Hz). Anal. Calcd for $\text{C}_{47}\text{H}_{50}\text{ClO}_2\text{PW}$: C, 62.92; H, 5.62. Found: C, 63.15; H, 5.58.

W(O)(CHCMe₂Ph)(ODFT)Cl(PPh₂Me) (2b). A solution of **1** (0.187 g, 0.233 mmol) in 8 mL of benzene was added to a solid portion of LiODFT (0.106 g, 0.244 mmol, 1.05 equiv). The cloudy, yellow-orange reaction mixture was stirred for 3 h and then the solvent was removed *in vacuo* to give a yellow solid. The product was extracted into toluene (5 mL) and the mixture was filtered through a bed of Celite to remove LiCl. Toluene was removed *in vacuo* to yield a yellow solid. The product was triturated with pentane (5 mL) overnight and then the resulting suspension was filtered to yield an off-white solid (0.154 g, 0.155 mmol, 67% yield). Two isomers in a 50:50 ratio formed according to NMR spectra; only non-overlapping alkylidene signals are listed: Isomer 1 ^1H NMR (C_6D_6 , 20 °C): δ [ppm] 9.65 (d, 1H, WCHCMe_2Ph , $^3J_{\text{HP}} = 3$ Hz, $^2J_{\text{HW}} = 8$ Hz); ^{13}C NMR (C_6D_6 , 20 °C): δ [ppm] 294.5 (d, WCHCMe_2Ph , $^2J_{\text{CP}} = 13$ Hz); ^{31}P NMR (C_6D_6 , 20 °C): δ [ppm] 27.2 (s, $^1J_{\text{WP}} = 348$ Hz); ^{19}F NMR (C_6D_6 , 20 °C) δ [ppm] -134.6 (m, 1F), -137.4 (m, 2F), -154.5 (t, 1F), -157.4 (t, 2F), -160.0 (m, 1F), -162.0 (m, 1H), -163.7 (m, 2F). Isomer 2 ^1H NMR (C_6D_6 , 20 °C): δ [ppm] 9.58 (d, 1H, WCHCMe_2Ph , $^3J_{\text{HP}} = 4$ Hz, $^2J_{\text{HW}} = 9$ Hz); ^{13}C NMR (C_6D_6 , 20 °C): δ [ppm] 286.2 (d, WCHCMe_2Ph , $^2J_{\text{CP}} = 14$ Hz); ^{31}P NMR (C_6D_6 , 20 °C): δ [ppm] 20.0 (s, $^1J_{\text{WP}} = 395$ Hz); ^{19}F NMR (C_6D_6 , 20 °C) δ [ppm] -135.5 (m, 1F), -139.3 (m, 2F), -155.2 (t, 1F), -157.4 (t, 2H), -161.7 (m, 1F), -164.1 (m, 2F), -165.6 (m, 1F). Anal. Calcd for $\text{C}_{41}\text{H}_{28}\text{ClF}_{10}\text{O}_2\text{PW}$: C, 49.60; H, 2.84. Found: C, 49.38; H, 2.83.

W(O)(CHCMe₂Ph)(OTPP)Cl(PPh₂Me) (2c). A solution of **1** (0.198 g, 0.246 mmol) in 10 mL of benzene was added to a solid portion of LiOTPP (0.105 g, 0.259 mmol, 1.05 equiv). The cloudy, yellow reaction mixture was stirred for 3 h and then the solvent was removed *in vacuo* to give a yellow residue. The reaction mixture was filtered directly through Celite then the solvent was removed from the filtrate *in vacuo* to give a yellow solid. The product was triturated with pentane (12 mL) overnight and the resulting suspension was filtered to yield an off-white solid,

which was washed with pentane (3x4 mL) and vacuum dried (0.156 g, 0.204 mmol, 83% yield). Two isomers (*syn/anti*) present in a 52:48 ratio: ^1H NMR (C_6D_6 , 20 $^\circ\text{C}$): δ [ppm] 9.36 (d, 1H, WCHCMe_2Ph , $^1J_{\text{CH}} = 125$ Hz, $^3J_{\text{HP}} = 3$ Hz, $^2J_{\text{HW}} = 10$ Hz, *syn* isomer), 8.96 (broadened d, 1H, WCHCMe_2Ph , $^1J_{\text{CH}} = 146$ Hz, $^3J_{\text{HP}} = 7$ Hz, *anti* isomer), 7.33-6.74 (multiplets, 36H, *ArH*), 1.60 (s, 3H, WCHCMe_2Ph), 1.55 (s, 3H, WCHCMe_2Ph), 0.91 (d, 3H, PPh_2Me); ^{13}C NMR (CDCl_3 , 20 $^\circ\text{C}$): δ [ppm] 299.2 (d, WCHCMe_2Ph , $^2J_{\text{CP}} = 12$ Hz), 160.6, 149.0, 141.9 (d, $^2J_{\text{CP}} = 12$ Hz), 139.2, 138.5, 133.1 (d, $^2J_{\text{CP}} = 10$ Hz), 132.5 (d, $^2J_{\text{CP}} = 10$ Hz), 132.3, 130.1, 129.9, 129.4, 129.0 (d, $^2J_{\text{CP}} = 9$ Hz), 128.7 (d, $^2J_{\text{CP}} = 10$ Hz), 128.5, 128.3, 128.1, 127.8, 127.6, 127.4, 127.1, 127.0, 126.4, 126.2, 126.1, 125.7, 124.6, 50.4, 30.9, 28.7, 11.2 (d, $^1J_{\text{CP}} = 28$ Hz). ^{31}P NMR (C_6D_6 , 20 $^\circ\text{C}$): δ [ppm] 24.5 (s, $^1J_{\text{WP}} = 405$ Hz). Anal. Calcd for $\text{C}_{53}\text{H}_{46}\text{ClO}_2\text{PW}$: C, 65.95; H, 4.80. Found: C, 65.60; H, 4.85.

W(O)(CHCMe₂Ph)(OdAdP)Cl(PPh₂Me) (2d). A solution of **1** (0.200 g, 0.245 mmol) in 10 mL of benzene was added to a solid portion of $\text{LiOdAdP}(\text{THF})_2$ (0.138 g, 0.262 mmol, 1.05 equiv). The cloudy orange reaction mixture was stirred overnight. Removal of the solvent *in vacuo* gave an orange-brown residue which was dissolved in toluene (5 mL) and was filtered through a bed of Celite to remove LiCl. Toluene was removed *in vacuo* to yield a brown residue. The product was triturated with pentane (8 mL) overnight and then the resulting suspension was filtered off to give a light-yellow solid (0.120 g, 0.127 mmol, 52%). Two isomers in an 87:13 ratio formed according to NMR spectra; only non-overlapping alkylidene signals are listed: Major isomer ^1H NMR (C_6D_6 , 20 $^\circ\text{C}$): δ [ppm] 12.04 (broad d, 1H, WCHCMe_2Ph , $^1J_{\text{CH}} = 125$ Hz, $^3J_{\text{HP}} = 3$ Hz); ^{31}P NMR (C_6D_6 , 20 $^\circ\text{C}$): δ [ppm] 23.03 (s, $^1J_{\text{WP}} = 402$ Hz); ^{13}C NMR (C_6D_6 , 20 $^\circ\text{C}$): δ [ppm] 302.8 (d, WCHCMe_2Ph , $^2J_{\text{CP}} = 13$ Hz). Minor isomer ^1H NMR (C_6D_6 , 20 $^\circ\text{C}$): δ [ppm] 10.47 (d, 1H, WCHCMe_2Ph , $^3J_{\text{HP}} = 3$ Hz, $^2J_{\text{HW}} = 13$ Hz); ^{31}P NMR (C_6D_6 , 20 $^\circ\text{C}$): δ [ppm] 26.66. ^{13}C NMR (C_6D_6 , 20 $^\circ\text{C}$): δ [ppm] 283.4 (d, WCHCMe_2Ph , $^2J_{\text{CP}} = 14$ Hz). Anal. Calcd for $\text{C}_{50}\text{H}_{60}\text{ClO}_2\text{PW}$: C, 63.67; H, 6.41. Found: C, 63.55; H, 6.48.

W(O)(CHCMe₂Ph)(ODBMP)Cl(PPh₂Me) (2e). A solution of **1** (0.160 g, 0.199 mmol) in 10 mL of benzene was added to a solid portion of LiODBMP(Et₂O) (0.110 g, 0.211 mmol, 1.05 equiv). The cloudy light-orange reaction mixture was stirred for 3 h the mixture was filtered through a bed of Celite to remove LiCl. Toluene was removed *in vacuo* to yield an orange residue. The product was triturated with pentane (10 mL) overnight and the solid was filtered off to give an off-white product (0.112 g, 0.111 mmol, 56%). ¹H NMR (C₆D₆, 20 °C): δ [ppm] 10.46 (d, 1H, WCHCMe₂Ph, ¹J_{CH} = 119 Hz, ³J_{HP} = 3 Hz, ²J_{HW} = 7 Hz), 7.32-7.03 (overlapping multiplets, 31H, ArH), 6.87 (m, 4H, ArH), 6.74 (m, 2H, ArH), 6.53 (d, 1H, 2,6-(Ph₂CH)₂-4-Me-C₆H₂), 6.32 (d, 1H, 2,6-(Ph₂CH)₂-4-Me-C₆H₂), 5.68 (s, 1H, 2,6-(Ph₂CH)₂-4-Me-C₆H₂), 5.30 (s, 1H, 2,6-(Ph₂CH)₂-4-Me-C₆H₂), 2.03 (s, 3H, 2,6-(Ph₂CH)₂-4-Me-C₆H₂) 1.48 (s, 3H, WCHCMe₂Ph), 1.30 (s, 3H, WCHCMe₂Ph), 0.99 (d, 3H, PPh₂Me). ³¹P NMR (CDCl₃, 20 °C): δ [ppm] 21.65 (s, ¹J_{PW} = 404 Hz). ¹³C NMR (CDCl₃, 20 °C): δ [ppm] 299.2 (d, WCHCMe₂Ph, ²J_{CP} = 13 Hz), 159.6, 149.7, 145.5, 144.9, 143.7, 143.5, 132.5 (d, ²J_{CP} = 10 Hz), 132.1 (d, ²J_{CP} = 10 Hz), 131.8, 131.7, 131.5, 131.2, 130.5, 130.3, 130.0, 129.9, 129.7, 129.4, 129.3, 129.2, 129.1, 128.5, 128.3, 128.1, 126.4, 126.2, 50.7, 50.6, 49.8, 31.3, 28.4, 21.2, 10.0 (d, ¹J_{CP} = 30 Hz). Anal. Calcd for C₅₆H₅₂ClO₂PW: C, 66.77; H, 5.20. Found: C, 67.07; H, 5.32.

W(O)(CHCMe₂Ph)(Me₂Pyr)(OHMT)(PPh₂Me) (3a(P)). A portion of Li(Me₂Pyr) (0.062 g, 0.613 mmol, 1.1 equiv) was added as a solid to a cold (-30 °C) solution of **2a** (0.500 g, 0.557 mmol) in toluene (15 mL). The reaction mixture was allowed to stir at room temperature for a minimum of 10 h before the solvent was decreased to 5 mL *in vacuo*. Filtration through a bed of Celite to remove LiCl followed by trituration with minimal pentane (3-5 mL) yielded a yellow solid (0.452 g, 0.473 mmol, 85%). ¹H NMR (C₆D₆, 20 °C): δ [ppm] 8.48 (s, 1H, WCHCMe₂Ph, ¹J_{CH} = 122 Hz, ²J_{HW} = 12 Hz), 7.38 (m, 4H, ArH), 7.18-6.81 (overlapping multiplets, 18H, Ar-H), 5.99 (s, 2H, Me₂Pyr-H), 2.18 (s, 6H, Me₂Pyr), 1.99-1.91 (overlapping singlets, 18H, Ar-Me) 1.75 (s, 3H, WCHCMe₂Ph), 1.52 (s, 3H, WCHCMe₂Ph), 1.38 (d, 3H, PPh₂Me, ²J_{HP} = 4Hz) ; ³¹P NMR (45 mM in C₆D₆, 20 °C): δ [ppm] 23.0 (s, 10%), -26.5 (s, 90%, unbound PPh₂Me). ¹³C

NMR (45 mM in C₆D₆, 20 °C): δ [ppm] 272.7 (WCHCMe₂Ph), 156.8, 150.7, 141.6 (d, $^1J_{CP}$ = 55 Hz), 137.5, 136.7, 136.6, 135.8, 134.2, 133.5 (d, $^2J_{CP}$ = 12 Hz), 132.0, 130.0, 129.4, 129.0 (d, $^3J_{CP}$ = 8 Hz), 128.6, 128.4, 126.6, 126.4, 124.2, 49.5 (WCHCMe₂Ph, $^3J_{CW}$ = 11 Hz), 33.0, 30.5, 21.5, 21.3, 19.3 (WCHCMe₂Ph), 16.6, 12.9 (d, $^1J_{CP}$ = 20 Hz). Anal. Calcd for C₅₃H₅₈NO₂PW: C, 66.60; H, 6.12; N, 1.47. Found: C, 66.71; H, 6.24; N, 1.50.

W(O)(CHCMe₂Ph)(Me₂Pyr)(OHMT)(MeCN) (3a(N)). Compound **3a**(MeCN) was prepared by stirring compound **3a**(PPh₂Me) (0.560 g, 0.586 mmol) in MeCN (5 mL) at room temperature overnight. The resulting orange suspension was filtered and the yellow product was washed several times with cold (-30 °C) MeCN. The MeCN filtrate was reduced in volume to *ca.* 4 mL and was left in the freezer (-30 °C) overnight to yield more of the yellow product. Two crops were combined (0.220 g, 0.399 mmol, 68%). ¹H NMR (C₆D₆, 20 °C): δ [ppm] 8.51 (s, 1H, WCHCMe₂Ph, $^1J_{CH}$ = 122 Hz, $^2J_{HW}$ = 12 Hz), 7.36 (d, 2H, ArH), 7.13 (t, 2H, ArH), 7.01 (t, 1H, ArH), 6.93-6.88 (multiplet, 3H, ArH), 6.85 (bs, 2H, ArH), 6.80 (bs, 2H, ArH), 5.98 (s, 2H, Me₂PyrH), 2.17 (s, 6H, Me₂Pyr), 1.96 (s, 6H, Ar-*para*-Me), 1.91 (merged singlets, 12H, Ar-*ortho*-Me), 1.74 (s, 3H, WCHCMe₂Ph), 1.51 (s, 3H, WCHCMe₂Ph), 0.58 (s, 1.5H, MeCN); ¹³C NMR (C₆D₆, 20 °C): δ [ppm] 274.8 (WCHCMe₂Ph), 156.8, 150.6, 137.4, 136.6, 136.5, 135.7, 134.2, 132.0, 130.0, 129.3, 128.6, 128.5, 126.6, 126.3, 124.1, 110.9 (MeCN), 49.2 (WCHCMe₂Ph, $^3J_{CW}$ = 12 Hz), 32.8, 30.5, 21.2, 20.9, 19.9 (WCHCMe₂Ph), 16.7, 0.11 (MeCN). Anal. Calcd for C₄₀H₄₅NO₂W·0.5MeCN: C, 63.45; H, 6.04, N, 2.71. Found: C, 63.26, H, 6.00, N, 2.76.

W(O)(CHCMe₂Ph)(Me₂Pyr)(OHMT) (3a). Compound **3a** was prepared by treating a stirring solution of **3a**(MeCN) (0.075 g, 0.094 mmol) in cold (-30 °C) toluene (5 mL) with a suspension of B(C₆F₅)₃ (0.047 g, 0.092 mmol, 0.98 equiv) in toluene (1 mL) at room temperature. The reaction mixture was allowed to stir for 4 h before the solvent was removed *in vacuo*. To the resulting yellow residue was added pentane (~ 5 mL) which created a yellow suspension. The suspension was filtered through Celite and the solvent was removed from the filtrate *in vacuo* to

yield a yellow residue once again. Recrystallization from a saturated pentane solution at $-30\text{ }^{\circ}\text{C}$ yielded yellow needles (0.057 g, 0.075 mmol, 80%). ^1H NMR (C_6D_6 , $20\text{ }^{\circ}\text{C}$): δ [ppm] 8.46 (s, 1H, WCHCMe_2Ph , $^1J_{\text{CH}} = 121\text{ Hz}$, $^2J_{\text{HW}} = 12\text{ Hz}$), 7.35 (d, 2H, ArH), 7.13 (t, 2H, ArH), 7.01 (t, 1H, ArH), 6.94-6.87 (multiplet, 3H, ArH), 6.85 (bs, 2H, ArH), 6.80 (bs, 2H, ArH), 5.97 (s, 2H, Me_2PyrH), 2.17 (s, 6H, Me_2Pyr), 1.95 (s, 6H, Ar-para-Me), 1.90 (s, 12H, Ar-ortho-Me), 1.73 (s, 3H, WCHCMe_2Ph), 1.51 (s, 3H, WCHCMe_2Ph). ^{13}C NMR (C_6D_6 , $20\text{ }^{\circ}\text{C}$): δ [ppm] 270.7 (WCHCMe_2Ph , $^1J_{\text{CW}} = 204\text{ Hz}$), 156.7, 150.6, 137.4, 136.6, 136.5, 135.7, 134.2, 132.0, 129.9, 129.3, 128.6, 128.5, 126.5, 126.3, 124.1, 49.2 (WCHCMe_2Ph , $^3J_{\text{CW}} = 12\text{ Hz}$), 32.8, 30.5, 21.2, 20.9, 19.8 (WCHCMe_2Ph , $^2J_{\text{CW}} = 45\text{ Hz}$), 16.6. Anal. Calcd for $\text{C}_{40}\text{H}_{45}\text{NO}_2\text{W}$: C, 63.58; H, 6.00, N, 1.85. Found: C, 63.64, H, 6.14, N, 1.78.

W(O)(CHCMe₂Ph)(Me₂Pyr)(ODFT)(PPh₂Me) (3b(P)). A solid portion of $\text{Li}(\text{Me}_2\text{Pyr})$ (0.014 g, 0.13 mmol, 1.1 equiv) was added to a cold ($-30\text{ }^{\circ}\text{C}$) solution of **2b** (0.125 g, 0.126 mmol) in toluene (8 mL). The reaction mixture was stirred at room temperature overnight (turns from yellow to orange) then was filtered directly through a bed of Celite to remove LiCl . Removal of toluene *in vacuo* followed by trituration with pentane (4 mL) and recrystallization from a saturated pentane solution at $-30\text{ }^{\circ}\text{C}$ yielded a yellow solid (0.094 g, 0.089 mmol, 71%). ^1H NMR (C_6D_6 , $20\text{ }^{\circ}\text{C}$): δ [ppm] 9.32 (bs, 1H, WCHCMe_2Ph), 7.22 (broad s, 2H, ArH), 6.94-6.78 (overlapping multiplets, 16H, Ar-H), 5.87 (bs, 2H, $\text{Me}_2\text{Pyr-H}$), 2.26 (bs, 3H, Me_2Pyr), 1.66 (s, 3H, Me_2Pyr), 1.25 (s, 6H, WCHCMe_2Ph), 1.11 (bd, 3H, $^2J_{\text{HP}} = 8\text{ Hz}$). ^{13}C NMR (C_6D_6 , $20\text{ }^{\circ}\text{C}$): δ [ppm] 288.0 (bs), 149.3, 133.3, 132.8(b), 130.7, 128.9, 128.6 (d, $^3J_{\text{CP}} = 9\text{ Hz}$), 128.4 (b), 126.5, 125.8, 120.1, 118.7, 109.5 (b), 51.1 (WCHCMe_2Ph , $^3J_{\text{CW}} = 13\text{ Hz}$), 33.1, 27.9, 15.8 (WCHCMe_2Ph), 12.7 (d, $^1J_{\text{CP}} = 24\text{ Hz}$). ^{19}F NMR (C_6D_6 , $20\text{ }^{\circ}\text{C}$): δ [ppm] -135.7 (b, 1F), -136.8 (b, 1F), -141.0 (b, 1F), -144.3 (b, 1F), -158.3 (b, 2F), -159.8 (b, 1F), -164.9 (b, 2F). ^{31}P NMR (C_6D_6 , $20\text{ }^{\circ}\text{C}$): δ [ppm] 19.31 (bs). Anal. Calcd for $\text{C}_{47}\text{H}_{36}\text{F}_{10}\text{NO}_2\text{PW}$: C, 53.68; H, 3.45, N, 1.33. Found: C, 53.34, H, 3.48, N, 1.26.

W(O)(CHCMe₂Ph)(Me₂Pyr)(OTPP)(PPh₂Me) (3c(P)). A solid portion of Li(Me₂Pyr) (0.015 g, 0.144 mmol, 1.1 equiv) was added to a cold (-30 °C) solution of **2c** (0.100 g, 0.131 mmol) in toluene (8 mL). The reaction mixture was stirred at room temperature overnight then was filtered directly through a bed of Celite to remove LiCl. Removal of toluene *in vacuo* followed by trituration with pentane (4 mL) then washing with cold (-30 °C) pentane (3 x 5 mL) yielded a pale yellow solid (0.117 g, 0.110 mmol, 88%). ¹H NMR (C₆D₆, 20 °C): δ [ppm] 9.98 (broad s, 1H, WCHCMe₂Ph), 7.34 (m, 6H, ArH), 7.09-6.94 (overlapping multiplets, 20H, Ar-H), 6.22 (s, 2H, Me₂Pyr-H), 2.20 (s, 6H, Me₂Pyr), 1.53 (s, 3H, PPh₂Me), 1.41 (s, 3H, WCHCMe₂Ph), 1.37 (s, 3H, WCHCMe₂Ph); ³¹P NMR (C₆D₆, 20 °C): δ [ppm] 19.38 (broad). ¹³C NMR (C₆D₆, 20 °C): δ [ppm] *WCHMe₂Ph resonance was not observed at RT, 158.4, 150.2, 142.3 (d, ¹J_{CP} = 53 Hz), 139.8, 137.4, 135.6, 133.4, 132.6 (d, ²J_{CP} = 14 Hz), 131.8, 131.1, 130.7, 130.1, 129.8, 128.9 (d, ³J_{CP} = 9 Hz), 128.4, 127.0, 126.6, 126.5, 126.2, 109.6, 50.3 (WCHCMe₂Ph, ³J_{CW} = 12 Hz), 32.2, 31.8, 30.1, 19.0, 13.6 (d, ¹J_{CP} = 11 Hz). Anal. Calcd for C₅₉H₅₄NO₂PW: C, 69.21; H, 5.32, N, 1.37. Found: C, 69.33, H, 5.13, N, 1.38.

W(O)(CHCMe₂Ph)(Me₂Pyr)(OdAdP) (3d). A solid portion of Li(Me₂Pyr) (0.011 g, 0.109 mmol, 1.1 equiv) was added to a cold (-30 °C) solution of **2d** (0.095 g, 0.101 mmol) in toluene (5 mL). The reaction mixture was stirred at room temperature overnight then was filtered directly through a bed of Celite to remove LiCl. Removal of toluene *in vacuo*, trituration with pentane (3 mL) for 8 h, then washing with cold (-30 °C) pentane (2 mL) yielded a pale yellow solid (0.071 g, 0.089 mmol, 88%). ¹H NMR (C₆D₆, 20 °C): δ [ppm] 9.80 (s, 1H, WCHCMe₂Ph, ²J_{HW} = 11 Hz), 7.13 (s, 2 H, ArH), 7.02 (m, 5H, ArH), 6.02 (s, 2H, Me₂PyrH), 2.34 (s, 6H, Me₂Pyr), 2.18 (dd, 12H), 2.03 (s, 6H), 1.73 (s, 6H, WCHCMe₂Ph), 1.66 (s, 12H). ¹³C NMR (C₆D₆, 20 °C): δ [ppm] 270.3 (s, WCHCMe₂Ph), 163.6, 150.4, 139.1, 131.6, 128.6, 126.5, 126.4, 126.1, 50.1, 42.8, 41.6, 38.2, 37.4, 36.8, 32.4, 31.5, 29.7, 29.6, 21.5. Anal. Calcd for C₄₃H₅₅NO₂W: C, 64.42; H, 6.91, N, 1.75. Found: C, 64.27, H, 6.95, N, 1.71.

W(O)(CHCMe₂Ph)(Me₂Pyr)(ODBMP)(PPh₂Me) (3e(P)). A solid portion of Li(Me₂Pyr) (0.009 g, 0.090 mmol, 1.1 equiv) was added to a cold (-30 °C) solution of **2e** (0.080 g, 0.080 mmol) in Et₂O (10 mL). The yellow-orange reaction mixture was stirred at room temperature overnight then was filtered directly through a bed of Celite. Removal of the solvent *in vacuo* gave an orange residue which was triturated with pentane (2 mL) for 5 h then filtered, washed with cold (-30 °C) pentane (1 mL) and vacuum dried to yield a yellow solid (0.054 g, 0.051 mmol, 63%). Two isomers present (4:6 ratio). ¹H NMR (C₆D₆, 20 °C): δ [ppm] 11.13 (bs, 1H, WCHCMe₂Ph), 10.83 (very bs, 1H, WCHCMe₂Ph). ³¹P NMR (C₆D₆, 20 °C): δ [ppm] 18.70 (b). Anal. Calcd for C₆₂H₆₀NO₂PW: C, 69.86; H, 5.67; N, 1.31. Found: C, 69.70; H, 5.47; N, 1.16.

W(O)(CHCMe₂Ph)(OHMT)₂ (4a). To a Schlenk flask (25 mL) was added HMTOLi (0.241 g, 0.717 mmol, 2.4 equiv) followed by a toluene solution (15 mL) of **1** (0.240 g, 0.299 mmol). The reaction mixture was stirred at room temperature for 30 min then was heated at 100 °C for 48 h during which time the reaction mixture changed colors from yellow to orange. Cooled to room temperature then filtered directly through a Celite plug to remove LiCl. Removal of the solvent *in vacuo* yielded an orange residue which following trituration with MeCN (4 mL) then washing with cold (-30 °C) MeCN (3 x 4 mL) gave a yellow solid (0.220 g, 0.222 mmol, 74%). ¹H NMR (C₆D₆, 20 °C): δ [ppm] 7.51 (s, 1H, WCHCMe₂Ph, ¹J_{CH} = 126 Hz, ²J_{HW} = 12 Hz), 7.08 (t, 2H, ArH), 7.03 (t, 1H, Ar-H), 6.89 (broad s, 4H, Ar-H), 6.86 (d, 2H, Ar-H), 6.84 (s, 3H, Ar-H), 6.82 (s, 1H, Ar-H), 6.80 (d, 2H, Ar-H), 6.75 (s, 4H, Ar-H), 2.24 (s, 12H, Ar-*para*-Me), 2.03 (s, 12H, Ar-*ortho*-Me), 1.98 (s, 12H, Ar-*ortho*-Me), 1.41 (s, 6H, WCHCMe₂Ph). ¹³C NMR (C₆D₆, 20 °C): δ [ppm] 253.0 (WCHCMe₂Ph, ¹J_{CW} = 214 Hz), 158.5, 152.4, 137.0, 136.8, 136.7, 135.4, 135.0, 131.8, 131.0, 129.1, 128.9, 128.8, 126.6, 125.8, 48.1, 33.7, 21.5, 21.4, 20.8. Anal. Calcd for C₅₈H₆₂O₃W: C, 70.30; H, 6.31. Found: C, 70.48, H, 6.40.

W(O)(CHCMe₂Ph)(ODFT)₂(PPh₂Me) (4b(P)). To a Schlenk flask (25 mL) was added DFTOLi (0.088 g, 0.203 mmol, 1.1 equiv) followed by a toluene solution (12 mL) of **2b** (0.148 g, 0.184 mmol). The reaction mixture was heated at 80 °C for 48 h during which time the

reaction mixture changed colors from yellow to orange and a white precipitate formed. Cooled to room temperature then filtered directly through a Celite plug to remove LiCl. Removal of the solvent *in vacuo* yielded an orange residue which following trituration with pentane (4 mL) for 3 h gave a yellow-orange solid (0.098 g, 0.072 mmol, 40%). *Syn/anti* isomer ratio is 7:3. Signals for the *syn/anti* alkylidene resonances listed only. ^1H NMR (C_6D_6 , 20 °C): δ [ppm] 11.85 (s, 1H, WCHCMe_2Ph , $^1J_{\text{CH}} = 122$ Hz, *syn*), 10.91 (s, 1H, WCHCMe_2Ph , $^1J_{\text{CH}} = 141$ Hz, *anti*). ^{13}C NMR (C_6D_6 , 20 °C): δ [ppm] 295.0 (WCHCMe_2Ph , *anti*), 286.7 (WCHCMe_2Ph , *syn*). ^{31}P NMR (C_6D_6 , 20 °C): δ [ppm] 19.14 (bs), 16.24 (bs). Anal. Calcd for $\text{C}_{59}\text{H}_{31}\text{F}_{20}\text{O}_3\text{PW}$: C, 51.25; H, 2.26. Found: C, 51.66, H, 2.45.

$\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{OTPP})_2(\text{PPh}_2\text{Me})$ (4c(P)). To a Schlenk flask (25 mL) was added LiOTPP (0.265 g, 0.554 mmol, 2.2 equiv) followed by a THF solution (12 mL) of **1** (0.202 g, 0.251 mmol). The reaction mixture was heated at 60 °C for 16 h during which time the reaction mixture changed colors from yellow to orange. The reaction mixture was cooled to room temperature and the solvent was removed *in vacuo* before benzene (4 mL) was added. The reaction mixture was then filtered directly through a Celite plug and the solvent was removed from the filtrate *in vacuo* to yield a yellow residue. Trituration with MeCN (4 mL) overnight at room temperature gave a yellow solid (0.240 g, 0.181 mmol, 72%). ^1H NMR (CDCl_3 , 20 °C): δ [ppm] 8.89 (bs, 1H, WCHCMe_2Ph), 7.29 (m, 12H, *ArH*), 7.13-7.03 (m, 29H, *ArH*), 6.86 (broad s, 10H, *ArH*), 6.75 (m, 6H, *ArH*), 1.18 (bs, 3H, PPh_2Me), 1.08 (s, 6H, WCHCMe_2Ph); ^{31}P NMR (CDCl_3 , 20 °C): δ 16.5, -12.2 (broad, unbound PPh_2Me). ^{13}C NMR (C_6D_6 , 20 °C): δ [ppm] * WCHCMe_2Ph resonance was not observed at RT, 159.6, 151.6, 142.0, 141.4, 136.9, 132.3 (d, $^2J_{\text{CP}} = 15$ Hz), 129.9, 129.2, 128.5 (d, $^3J_{\text{CP}} = 8$ Hz), 48.5, 31.3, 11.9. Anal. Calcd for $\text{C}_{83}\text{H}_{67}\text{O}_3\text{PW}$: C, 75.11; H, 5.09. Found: C, 74.87, H, 4.97.

$\text{W}(\text{O})(\text{CHCMe}_2\text{Ph})(\text{OdAdP})_2$ (4d). A solution of **1** (0.148 g, 0.184 mmol) in 10 mL of toluene was added to a solid portion of $\text{LiOdAdP}(\text{THF})_2$ (0.213 g, 0.404 mmol, 2.2 equiv). The yellow reaction mixture was stirred for 4 h and then filtered through a bed of Celite to remove LiCl.

Toluene was removed *in vacuo* to yield a brown residue. The product was triturated with pentane (5 mL) overnight and then the resulting suspension was filtered. After washing the solid with cold (-30 °C) pentane (3 x 4 mL), an off-white solid was isolated (0.146 g, 0.135 mmol, 75% yield). ¹H NMR (C₆D₆, 20 °C): δ [ppm] 9.31 (s, 1H, WCHCMe₂Ph, ¹J_{CH} = 122 Hz, ²J_{HW} = 12 Hz), 7.13 (s, 4H, ArH), 7.00 (m, 5H, ArH), 2.34 (m, 30H), 2.09 (bs, 12H, Ar-Me), 1.79 (dd, 24H), 1.62 (s, 6H, WCHCMe₂Ph). ¹³C NMR (C₆D₆, 20 °C): δ [ppm] 260.1 (WCHCMe₂Ph), 164.2, 152.1, 139.4, 130.8, 127.0, 126.2, 125.9, 43.7, 39.0, 37.1, 33.4, 29.7, 21.4. Anal. Calcd for C₆₄H₈₂O₃W: C, 70.97; H, 7.63. Found: C, 71.21; H, 7.92.

W(O)(CHCMe₂Ph)(ODBMP)₂(MeCN) (4e(N)). A solution of **1** (0.102 g, 0.127 mmol) in toluene (15 mL) was added to a solid portion of LiODBMP(Et₂O) (0.218 g, 0.418 mmol) and the resulting mixture was stirred for 6 h at room temperature, during which time the color gradually changed to dark yellow. The reaction mixture was then filtered directly through Celite and the solvent was removed from the filtrate *in vacuo* to yield a residue. The residue was triturated with MeCN (~ 2 mL) overnight at room temperature to give an off-white powder, which was isolated by filtration then vacuum dried. The solvent was removed from the filtrate *in vacuo* to give a residue which was triturated with pentane and filtered to give a light yellow solid (2 crops combined, 0.071 g, 0.057 mmol, 45% yield). ¹H NMR (C₆D₆, 20 °C): δ [ppm] 10.97 (bs, 1H, WCHCMe₂Ph), 7.22–7.16 (m, 10H, ArH), 7.12–6.86 (m, 39H, ArH), 6.44 (bs, 4H, 2,6-(Ph₂CH)₂-4-Me-C₆H₂), 1.94 (s, 6H, 2,6-(Ph₂CH)₂-4-Me-C₆H₂), 1.81 (s, 6H, WCHMe₂Ph), 0.33 (s, 3H, MeCN). ¹³C NMR (CDCl₃, 20 °C): δ [ppm] *WCHMe₂Ph resonance was not observed at RT, 151.7, 145.3, 144.6, 144.1, 143.6, 133.9, 133.5, 130.6, 130.2, 130.1, 129.9, 129.8, 128.9, 128.7, 128.6, 128.5, 127.0, 126.7, 126.6, 126.6, 126.4, 126.1, 126.0, 125.9, 50.8, 50.7, 49.0, 38.2, 32.6, 31.7, 21.1, 21.0, 18.0. Anal. Calcd for C₇₈H₆₉NO₃W: C, 74.81; H, 5.55; N, 1.12. Found: C, 74.51; H, 5.38; N, 1.11.

W(O)(CHCMe₂Ph)(OC(CF₃)₃)₂(PPh₂Me) (5(P)). A solution of **1** (0.207 g, 0.258 mmol) in 10 mL of cold (-30 °C) toluene was added to a solid portion of LiOC(CF₃)₃ (0.141 g, 0.583 mmol,

2.2 equiv). The reaction mixture was stirred for 3 h at room temperature during which time the reaction mixture turned bright yellow. The reaction mixture was then filtered through Celite to remove LiCl. The solvent was removed *in vacuo* to yield a yellow residue. The residue was triturated with pentane (4 mL) for 3 h then the mixture was placed in the freezer at -30 °C overnight. The light-yellow solid was filtered, washed with cold pentane (-30 °C), then vacuum dried (0.084 g, 0.134 mmol, 52% yield). *Syn/anti* isomers present in a 91:9 ratio. ^1H NMR (C_6D_6 , 20 °C): δ [ppm] 12.09 (d, 1H, WCHCMe_2Ph , $^1J_{\text{CH}} = 142$ Hz, $^2J_{\text{HW}} = 10$ Hz, $^3J_{\text{HP}} = 5$ Hz, *anti*), 11.35 (d, 1H, WCHCMe_2Ph , $^1J_{\text{CH}} = 115$ Hz, $^2J_{\text{HW}} = 10$ Hz, $^3J_{\text{HP}} = 5$ Hz, *syn*). ^{19}F NMR (C_6D_6 , 20 °C): δ [ppm] -71.4 (9F, *anti*), -71.8 (9F, *syn*), -73.0 (9F, *anti*), -73.3 (9F, *syn*). ^{31}P NMR (C_6D_6 , 20 °C): δ [ppm] 23.08 (s, $^1J_{\text{PW}} = 403$ Hz, *anti*), 25.51 (s, $^1J_{\text{PW}} = 418$ Hz, *syn*). ^{13}C NMR (C_6D_6 , 20 °C): δ [ppm] 295.8 (d, $^2J_{\text{CP}} = 24$ Hz, $^1J_{\text{CW}} = 178$ Hz, *anti*), 285.8 (d, $^2J_{\text{CP}} = 21$ Hz, $^1J_{\text{CW}} = 186$ Hz, *syn*). Anal. Calcd for $\text{C}_{31}\text{H}_{25}\text{F}_{18}\text{O}_3\text{PW}$: C, 37.15; H, 2.51. Found: C, 37.34; H, 2.48.

ROMP of DCMNBD.

General Procedure. This description is representative for the ROMP of DCMNBD with all initiators discussed herein. In reactions employing $\text{B}(\text{C}_6\text{F}_5)_3$ (4.60 or 9.20 μmol %), the $\text{B}(\text{C}_6\text{F}_5)_3$ was mixed with the initiator prior to addition to monomer. To a stirring CDCl_3 solution (1 mL) of DCMNBD (50.0 mg, 0.240 mmol, 50 equiv) was added a CDCl_3 solution (1 mL) of initiator (4.60 μmol , 2 mol %). The progress of the reaction was monitored by diluting aliquots of the reaction mixture with CDCl_3 (wet) and recording the ^1H NMR spectra. The polymer was precipitated by adding the reaction mixture dropwise to a stirring solution of MeOH (20 - 25

mL), affording a white solid. The polymer was isolated by centrifugation, washed with MeOH, and then was dried under vacuum.

cis,syndiotactic-poly(DCMNBD): ^1H NMR (CDCl_3 , 20 $^\circ\text{C}$): δ [ppm] 5.33 (m, 2, H_a), 4.00 (m, 2, H_b), 3.72 (s, 1, H_c), 2.52 (m, 1, H_d), 1.45 (m, 1, H_e); ^{13}C NMR (CDCl_3 , 20 $^\circ\text{C}$): δ [ppm] 165.45 (s, C_8), 142.35 (s, C_2), 131.58 (s, C_6), 52.13 (s, C_9), 44.52 (s, C_1), 38.06 (s, C_7).

cis,isotactic-poly(DCMNBD): ^1H NMR (CDCl_3 , 20 $^\circ\text{C}$): δ [ppm] 5.41 (m, 2, H_a), 3.92 (m, 2, H_b), 3.71 (s, 1, H_c), 2.49 (m, 1, H_d), 1.43 (m, 1, H_e). ^{13}C NMR (CDCl_3 , 20 $^\circ\text{C}$): δ 165.30 (s, C_8), 142.35 (s, C_2), 131.53 (s, C_6), 52.13 (s, C_9), 44.32 (s, C_1), 38.83 (s, C_7).

Table 1. Poly(DCMNBD) Prepared from 50 equivalents of DCMNBD from initiators W(O)(CHCMe₂Ph)(Me₂Pyr)(OAr)(L) or W(O)(CHCMe₂Ph)(Me₂Pyr)(OAr).

Initiator	OAr	<i>cis</i> (%)	major tacticity (%)
3a(P)	OHMT	98	<i>syndio</i> (97)
3a(N)	OHMT	98	<i>syndio</i> (97)
3a	OHMT	>99	<i>syndio</i> (99)
3b(P)	ODFT	97	<i>syndio</i> (96)
3c(P)	OTPP	>99	<i>syndio</i> (>98)
3c*	OTPP	96	<i>syndio</i> (97)
3d	OdAdP	86	<i>syndio</i> (83)
3e(P)	ODBMP	~99	<i>syndio</i> (96)
3e*	ODBMP	96	<i>syndio</i> (96)

* Generated *in situ* employing B(C₆F₅)₃.

Table 2. Poly(DCMNBD) Prepared from 50 equivalents of DCMNBD from W(O)(CHCMe₂Ph)(OAr)₂ and W(O)(CHCMe₂Ph)(OR)₂(L) initiators .

Initiator	OR	<i>cis</i> (%)	major tacticity (%)
4a	OHMT	96	<i>syndio</i> (90)
4b(P)	ODFT	>99	<i>iso</i> (83)
4c(P)	OTPP	90	<i>iso</i> (84)
4c	OTPP	93	<i>syndio</i> (96)
4d	OdAdP	>99	<i>syndio</i> (84)
4e(N)	ODBMP	>99	<i>iso</i> (90)
4e**	ODBMP	96	<i>syndio</i> (86)
5(P)	OC(CF ₃) ₃	98	<i>iso</i> (80)
5*	OC(CF ₃) ₃	99	<i>syndio</i> (95)

* Generated *in situ* employing B(C₆F₅)₃. ** Generated through repeated removal *in vacuo* of all solvent from toluene solutions of **4e(N)**.

Figure 2. (Top) ^1H NMR (CDCl_3 , 500 MHz) spectrum of *cis,syndiotactic*-poly(DCMNBD): 5.33 (m, 2, H_a), 4.00 (m, 2, H_b), 3.72 (s, 1, H_c), 2.52 (m, 1, H_d), 1.45 (m, 1, H_e); (bottom) ^1H NMR (CDCl_3 , 500 MHz) spectrum of *cis,isotactic*-poly(DCMNBD): 5.41 (m, 2, H_a), 3.92 (m, 2, H_b), 3.71 (s, 1, H_c), 2.49 (m, 1, H_d), 1.43 (m, 1, H_e).

Figure 3. (Top) ^{13}C NMR (CDCl_3 , 125 MHz) spectrum of *cis,syndiotactic*-poly(DCMNBD): 165.45 (s, C_8), 142.35 (s, C_2), 131.58 (s, C_6), 52.13 (s, C_9), 44.52 (s, C_1), 38.06 (s, C_7); (bottom) ^{13}C NMR (CDCl_3 , 125 MHz) spectrum of *cis,isotactic*-poly(DCMNBD): 165.30 (s, C_8), 142.35 (s, C_2), 131.53 (s, C_6), 52.13 (s, C_9), 44.32 (s, C_1), 38.83 (s, C_7).

Figure 4. Olefinic region of the ^1H NMR (CDCl_3 , 500 MHz) spectra (left) and methylene C(7) region of the ^{13}C NMR (CDCl_3 , 500 MHz) spectra of the isolated poly(DCMNBD) prepared with MAP initiators **3a(P)**, **3a(N)**, **3a**, **3b(P)**, **3c(P)**, **3d**, and **3e(P)** (* = *trans*, syndiotactic polymer).

Figure 5. Olefinic region of the ^1H NMR (CDCl_3 , 500 MHz) spectra (left) and methylene region C(7) region of the ^{13}C NMR (CDCl_3 , 500 MHz) spectra of the isolated poly(DCMNBD) prepared with initiators **4a**, **4b(P)**, **4c(P)**, **4d**, **4e(N)**, and **5(P)**.

Figure 6. Polymerization of DCMNBD catalyzed by **4a** without Lewis acid (blue) and in the presence of BPh₃ (red) and B(C₆F₅)₃ (green).

Figure 7. Poly(DCMNBD) prepared employing **4a** (a), **4a** plus BPh₃ (b), and **4a** plus B(C₆F₅)₃ (c) .

Figure 8. Olefinic region of the ¹H NMR (CDCl₃, 500 MHz) spectra of poly(DCMNBD) formed with initiators **4c**, **4e**, and **5(P)** and (right) in the presence of one or two equivalents of B(C₆F₅)₃ (* = *trans* polymer).

Supporting Information Available. Details for the synthesis and characterization of all complexes and polymers as well as the X-ray structure for compound **4c** is available free of charge via the Internet at <http://pubs.acs.org>.

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