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Synthesis of Tungsten Oxo Alkylidene Biphenolate Complexes and Ring-Opening Metathesis Polymerization of Norbornenes and Norbornadienes

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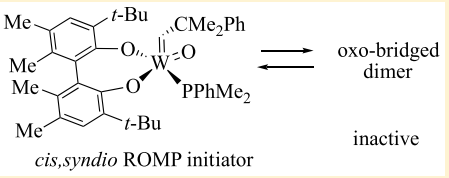
Supporting Information

ABSTRACT: We have synthesized and characterized tungsten oxo alkylidene biphenolate complexes with the formulas W(O)(CHR)(*rac*-biphenolate)-($PPhMe_2$) and (*R*,*S*)-[W(μ-O)(CHR)(biphenolate)]$_2$ (R = CMe_2Ph; biphenolate = **L1** or **L2** in the text). They behave as initiators for the stereoselective (*cis*,*isotactic*) polymerization of 2,3-dicarbomethoxy-5-norbornadiene and eight enantiomerically pure 5-substituted norbornenes with a *cis*,*isotactic* precision of 95−98% in most cases. The active initiators are 14e W(O)(CHR)(biphenolate) complexes, which are formed through either dissociation of $PPhMe_2$ from the phosphine adducts or scission of the heterochiral dimer. Addition of $B(C_6F_5)_3$ (one per W) to (*R*,*S*)-[W(μ-O)(CHR)(**L1**)]$_2$ led to formation of what we propose to be monomeric W[$OB(C_6F_5)_3$](CHR)(**L1**) in equilibrium with $B(C_6F_5)_3$ and (*R*,*S*)-[W(μ-O)(CHR)(**L1**)]$_2$. This mixture decomposed over a period of 1−2 h, was much slower to initiate polymerization than (*R*,*S*)-[W(μ-O)(CHR)(**L1**)]$_2$, and was much less stereoselective. Polymerization of five of the monomers with the imido alkyidene initiator, W(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)(*rac*-**L1**), gave virtually identical results compared to the results obtained with oxo complexes.



INTRODUCTION

Although a tungsten oxo alkylidene complex[1] was the first high-oxidation state tungsten complex to be prepared, largely imido alkylidene complexes were developed as metathesis catalysts[2] because they were predicted to be more stable toward bimolecular decomposition reactions than oxo alkylidenes. Bimolecular decomposition (alkylidene coupling) of tungsten (and molybdenum) imido alkylidene complexes has been shown to be one of the main modes of decomposition whenever some steric hindrance that would slow such bimetallic reactions is insufficient.[3]

Over the years, tungsten oxo alkylidenes have been prepared by a variety of methods.[1,4−8] In 2012,[9] a new and reliable method of synthesizing tungsten oxo alkylidenes through α-hydrogen abstraction in intermediates prepared from $WO_2(CH_2CMe_3)_2(Bipy)$[10] made tungsten oxo alkylidene complexes more readily available. Since then, neutral tungsten oxo alkylidene complexes, similar to analogous imido alkylidene complexes, that contain pyrrolide and sterically demanding OR ligands have been prepared and explored.[11] Cationic versions of tungsten oxo alkylidene complexes that contain an NHC ligand have also been reported.[12] Metathesis active molybdenum oxo alkylidene complexes also have been prepared recently,[13] but their metathesis chemistry has not been explored to any significant extent.

An important application of high-oxidation state Mo and W complexes is ring-opening metathesis polymerization (ROMP), often of norbornenes and norbornadienes, to give polymers with a single primary structure.[14] Two structures are obtained most reliably. *Cis*,*isotactic* polymers are formed through enantiomorphic site control when a sterically demanding biphenolate or binaphtholate ligand is present. Isotacticity results from addition of the monomer to the same face of each M=C bond as the polymer grows. When initiators contain a stereogenic metal center, but initially no chiral ligands, the monomer approaches the metal preferentially *trans* to one of the two types of monoanionic ligands, the configuration at the metal inverts with each polymerization step, and a *cis*,*syndiotactic* structure therefore is formed. This phenomenon has been called "stereogenic metal control". Although tungsten oxo alkylidenes have been explored as initiators to some degree to date,[15] no molybdenum or tungsten oxo alkylidene complexes that contain a biphenolate or binaphtholate ligand have been prepared, imido alkylidene versions of which were first reported in 1993.[16] In this work, we prepare some examples of W oxo biphenolate and binaphtholate complexes and explore them as ROMP initiators.

RESULTS

We explored the synthesis of complexes that contain one of the four ligands shown below (**L1**−**L4**). The reaction between W(O)($CHCMe_2Ph$)$(Cl)_2(PPhMe_2)_2$[1] and *rac*-Li_2**L1** proceeded smoothly in benzene to give *rac*-W(O)($CHCMe_2Ph$)-(**L1**)($PPhMe_2$) (*rac*-**2a**) as a light yellow powder in 86% yield. The alkylidene proton resonance in *rac*-**2a** is found in the ^{1}H nuclear magnetic resonance (NMR) spectrum at 10.59 ppm as a doublet with a $^3J_{PH}$ of 2 Hz and a $^1J_{CH}$ of 122 Hz; both are

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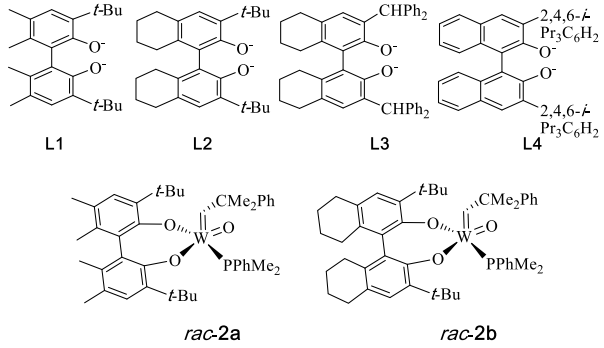
characteristic of a *syn* alkylidene isomer.[17] The phosphine resonance is found at 10.72 ppm ($^1J_{WP}$ = 348 Hz) in the ^{31}P NMR spectrum. We propose that the structure of *rac*-**2a** is analogous to that of *syn*-W(O)(CH-*t*-Bu)(OHMT)(Me_2Pyr)-(PMe_2Ph) (OHMT = 2,6-dimesitylphenoxide),[18] which is essentially a square pyramid with the alkylidene ligand in the apical position, but "distorted" structures between a TBP and SP are often encountered. Analogous complexes that contain *rac*-**L2** (*rac*-**2b**), *rac*-**L3** (*rac*-**2c**), *rac*-**L4** (*rac*-**2d**), (*S*)-**L1** [(*S*)-**2a**], and (*R*)-**L2** [(*R*)-**2b**] were prepared in good yield using a procedure analogous to that used to prepare *rac*-**2a**.



Addition of 1 equiv of $B(C_6F_5)_3$ to a solution of *rac*-**2a** in diethyl ether led to the rapid precipitation of a yellow powder (65% yield) that is only sparingly soluble in ether, toluene, $CDCl_3$, or CD_2Cl_2. Its ^{1}H NMR spectrum suggests that it has the empirical formula W(O)($CHCMe_2Ph$)(**L1**). The chemical shift of the alkylidene proton is 8.79 ppm in $CDCl_3$ with a $^1J_{CH}$ of 122 Hz and a $^2J_{WH}$ of 15 Hz, both of which are characteristic of a *syn* alkylidene[17] complex. *rac*-W(O)($CHCMe_2Ph$)(**L1**) can be recrystallized from dichloromethane in the form of yellow needles.

An X-ray diffraction study revealed that *rac*-W(O)-($CHCMe_2Ph$)(**L1**) is a heterochiral dimer, (*R*,*S*)-(**3a**)$_2$, in which one oxo ligand (with a W1−O1 distance of 1.78 Å) behaves as a donor to the second W, with the W1−O1* ("donor") distance being 2.17 Å (Figure 1). The arrangement around each metal in the centrosymmetric dimer is approximately halfway between a TBP and a SP (τ = 0.54[19]). The W1−O1 distance is slightly longer than a typical distance in a four-coordinate complex such as that reported (1.69 Å) for W(O)(CH-*t*-Bu)(Ph_2Pyr)(OHMT) (Pyr = pyrrolide)[9] as a consequence of O1 on W1 acting as a donor to W2. For comparison, in W[$OB(C_6F_5)_3$](CH-*t*-Bu)-(OHMT)(Me_2Pyr),[11] the W−O bond is lengthened to 1.76 Å as a consequence of boron bonding to W=O. (*R*,*S*)-(**3a**)$_2$ is stable in air in the solid state, with no significant decomposition being observed after 10 days (see the Supporting Information). The fact that $PPhMe_2$ can be scavenged from *rac*-**2a** through addition of $B(C_6F_5)_3$ suggests that $PPhMe_2$ dissociates readily.

Addition of 1 equiv of $B(C_6F_5)_3$ to a benzene solution of *rac*-**2b** yielded (*R*,*S*)-(**3b**)$_2$ as a yellow powder that was isolated in a 60% yield. The chemical shift of the neophylidene proton is 8.78 ppm in $CDCl_3$. X-ray diffraction showed that (*R*,*S*)-(**3b**)$_2$ is a heterochiral dimer analogous to (*R*,*S*)-(**3a**)$_2$ in the solid state (Figure 2). The W1−O1 distance in (*R*,*S*)-(**3b**)$_2$ is 1.79 Å [vs 1.78 Å in (*R*,*S*)-(**3a**)$_2$], and the W1−O1* distance is 2.15 Å [vs 2.17 Å in (*R*,*S*)-(**3a**)$_2$].

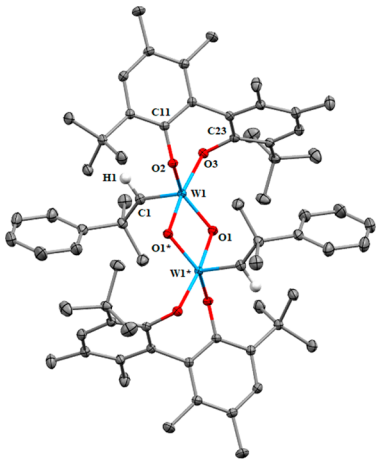


Figure 1. Thermal ellipsoid plot (50% probability) of (*R*,*S*)-(**3a**)$_2$. Solvent and hydrogen atoms in (*R*,*S*)-(**3a**)$_2$ have been omitted for the sake of clarity, except for the two alkylidene protons. Selected bond distances (angstroms) and angles (degrees): W1−O1, 1.7780(10); W1−O1*, 2.1681(10); W1−C1, 1.8813(14); W1−C1−C2, 144.14(11); W1−C1−H1, 103.1(12); τ = 0.54.

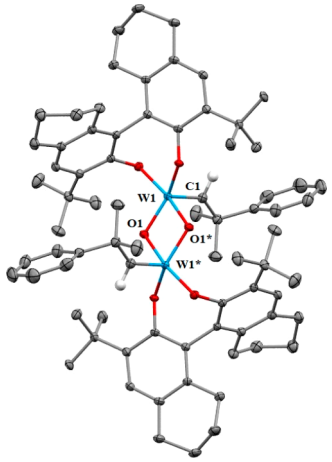


Figure 2. Thermal ellipsoid plot (50% probability) of (*R*,*S*)-(**3b**)$_2$. Solvent and hydrogen atoms in (*R*,*S*)-(**3b**)$_2$ have been omitted for the sake of clarity, except for the two alkylidene protons. Selected bond distances (angstroms) and angles (degrees): W1−O1, 1.7886(14); W1−O1*, 2.1495(15); W1−C1, 1.878(2); W1−C1−C2, 143.23(17); W1−C1−H1, 102.4(18); τ = 0.41.

The ^{1}H NMR spectrum of a mixture of (*R*,*S*)-(**3a**)$_2$ and (*R*,*S*)-(**3b**)$_2$ (1:1) in $CDCl_3$ revealed a total of four sharp alkylidene α-proton resonances in a 1:1:1:1 ratio (Figure 3), one each for (*R*,*S*)-(**3a**)$_2$ (8.79 ppm) and (*R*,*S*)-(**3b**)$_2$ (8.78 ppm) and two (the "outer" resonances at 8.77 and 8.80 ppm) that we attribute to the "mixed" heterochiral dimer, (*R*,*S*)-**3a**/**3b**. We therefore conclude that (*R*,*S*)-(**3a**)$_2$ and (*R*,*S*)-(**3b**)$_2$ are dimers in solution also and that they dissociate readily to give a mixture of unobservable monomers that then recombine to give an equilibrium mixture of (*R*,*S*)-(**3a**)$_2$, (*R*,*S*)-**3a**/**3b**, and (*R*,*S*)-(**3b**)$_2$ in a 1:2:1 ratio.

The rate-limiting step of scrambling should be breakup of any dimer into monomers. A time-dependent analysis of the approach to the equilibrium shown in Figure 3 (at 10 °C; see Figure S50) is consistent with dimer breakup being rate-limiting and a k of 0.03 min^{-1} (0.0005 s^{-1}) with a $t_{1/2}$ of ∼20 min at 10 °C. (A more precise determination of the rate of

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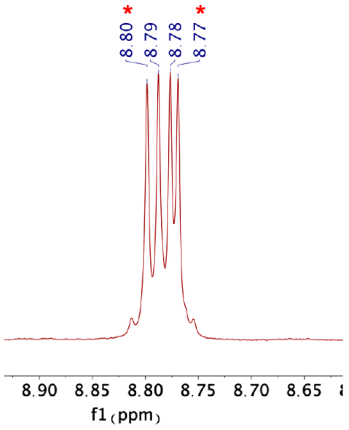

Figure 3. Alkylidene proton resonances in an initial mixture of (*R*,*S*)-(**3a**)$_2$ and (*R*,*S*)-(**3b**)$_2$ (1:1) [*(*R*,*S*)-**3a**/**3b**].

scrambling is not possible due to the overlap of resonances seen in Figure 3 at 500 MHz.) An estimated rate constant at 20 °C (~2 × 0.0005 s^{-1}) is orders of magnitude too small compared to what is required (>5 Hz at 500 MHz) to lead to broadening of the resonances shown in Figure 3.

Addition of B(C$_6$F$_5$)$_3$ to a 1:1 mixture of (*S*)-**2a** and (*R*)-**2b** leads to the formation of a "mixed" dimer, (*S*)-**3a**/(*R*)-**3b**, which has alkylidene proton resonances at 8.77 and 8.80 ppm. This result proves that the "outer" resonances in the spectrum of 1:1:1:1 resonances shown in Figure 3 are those for (*S*)-**3a**/(*R*)-**3b** and (*R*)-**3a**/(*S*)-**3b** (one part of each) in the mixture along with one part of (*R*,*S*)-(**3a**)$_2$ and one part of (*R*,*S*)-(**3b**)$_2$.

Addition of 1 equiv of B(C$_6$F$_5$)$_3$ (per W) to a solution of (*R*,*S*)-(**3a**)$_2$ in CDCl$_3$ at 22 °C leads to formation of a single new alkylidene complex with a chemical shift for the alkylidene proton of 9.35 ppm (Figure 4). We propose that the new

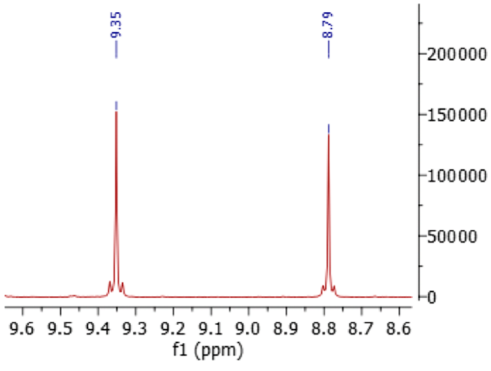

Figure 4. Alkylidene proton resonance for W[OB(C$_6$F$_5$)$_3$](CHR)(*rac*-**L1**) (at 9.35 ppm) that is formed upon addition of B(C$_6$F$_5$)$_3$ to (*R*,*S*)-(**3a**)$_2$ (at 8.79 ppm).

alkylidene resonance is that for W[OB(C$_6$F$_5$)$_3$](CHR)(*rac*-biphenolate) and that W[OB(C$_6$F$_5$)$_3$](CHR)(*rac*-biphenolate) is in equilibrium with (*R*,*S*)-(**3a**)$_2$ and B(C$_6$F$_5$)$_3$. W[OB(C$_6$F$_5$)$_3$](CHR)(*rac*-biphenolate) decomposes to unknown products over a period of 1−2 h at 22 °C, which has prevented its isolation so far. The rapid formation of relatively insoluble (*R*,*S*)-(**3a**)$_2$ when 1 equiv of B(C$_6$F$_5$)$_3$ is added to a solution of *rac*-**2a** allows (*R*,*S*)-(**3a**)$_2$ to be separated from (C$_6$F$_5$)$_3$B(PPhMe$_2$), which slows any further possible reaction of (*R*,*S*)-(**3a**)$_2$ with B(C$_6$F$_5$)$_3$ under those conditions.

Addition of 1 equiv of B(C$_6$F$_5$)$_3$ to a tol-d_8 solution of (*S*)-**2a** led immediately to formation of an orange solution, the ^{1}H NMR spectrum of which shows multiple weak and indistinct alkylidene resonances that we attribute to decomposition products (for details, see the Supporting Information). Addition of 2 equiv of B(C$_6$F$_5$)$_3$ to (*S*)-**2a** led to its complete decomposition. We cannot say that B(C$_6$F$_5$)$_3$ scavenges only PPhMe$_2$ that has dissociated from (*S*)-**2a**; i.e., it could be involved in reactions that result in decomposition in this experiment. We also cannot draw any conclusions concerning the formation and stability of any enantiomerically pure dimer, e.g., (*R*,*R*)-(**3a**)$_2$ or (*S*,*S*)-(**3a**)$_2$.

Addition of 1 equiv of B(C$_6$F$_5$)$_3$ in tol-d_8 to *rac*-**2c** led to slow decomposition. The decomposition is slow because PPhMe$_2$ in *rac*-**2c** is likely (for steric reasons) to be bound more strongly than it is in *rac*-**2a** or *rac*-**2b**. Apparently, 14e W(O)(CHCMe$_2$Ph)(**L3**) does not yield a stable dimer before it begins to decompose in the presence of B(C$_6$F$_5$)$_3$ in an unknown manner. Again, we cannot eliminate B(C$_6$F$_5$)$_3$ being involved in the decomposition process.

Finally, addition of 1 equiv of B(C$_6$F$_5$)$_3$ to *rac*-**2d** resulted in no reaction, consistent with the PPhMe$_2$ ligand in *rac*-**2d** being bound too strongly to be lost and scavenged by B(C$_6$F$_5$)$_3$.

We have found that (*R*,*S*)-(**3a**)$_2$ and (*R*,*S*)-(**3b**)$_2$ initiate the polymerization of monomers **M1**−**M9** (see below and Table 1), often in a highly stereoselective manner, to give *cis,isotactic*

Table 1. Polymerizations of M1−M9

run	monomer	initiator	solvent	time	select (%)
1	**M1**	(*R*,*S*)-(**3a**)$_2$	CDCl$_3$	20 min	>95
2	**M2**	(*R*,*S*)-(**3a**)$_2$	CDCl$_3$	20 min	>95
3	**M2**	(*R*,*S*)-(**3b**)$_2$	CDCl$_3$	20 min	>95
4	**M3**	(*R*,*S*)-(**3a**)$_2$	CDCl$_3$	20 min	>95
5	**M3**	(*R*,*S*)-(**3b**)$_2$	CDCl$_3$	20 min	>98
6	**M4**	(*R*,*S*)-(**3a**)$_2$	CDCl$_3$[a]	20 min	>98
7	**M5**	(*R*,*S*)-(**3a**)$_2$	CDCl$_3$	20 min	>90
8	**M6**	(*R*,*S*)-(**3a**)$_2$	CD$_2$Cl$_2$	60 min	>90
9	**M7**	(*R*,*S*)-(**3a**)$_2$	CDCl$_3$[a]	20 min	>98
10	**M8**	(*R*,*S*)-(**3a**)$_2$	tol-d_8	20 min	>98
11	**M9**	(*R*,*S*)-(**3a**)$_2$	tol-d_8	3 h	>98
12	**M3**	(*rac*)-**2a**	CDCl$_3$	3 h	>95
13	**M3**	(*S*)-**2a**	CDCl$_3$	3 h	>90
14	**M4**	(*rac*)-**2a**	CDCl$_3$	3 h	>95
15	**M4**	(*S*)-**2a**	CDCl$_3$	3 h	>95
16	**M8**	(*rac*)-**2a**	tol-d_8	3 h	>95
17	**M8**	(*S*)-**2a**	tol-d_8	3 h	>95
18	**M2**	*rac*-**4**	CDCl$_3$	20 min	>98
19	**M3**	*rac*-**4**	CDCl$_3$	20 min	>98
20	**M4**	*rac*-**4**	CDCl$_3$	20 min	>98
21	**M5**	*rac*-**4**	CDCl$_3$	20 min	>90
22	**M8**	*rac*-**4**	tol-d_8	20 min	>95

[a]Reaction solvent = CH$_2$Cl$_2$; the polymer was precipitated in methanol.

polymers. The enantiomerically pure monomers include 5-[*endo*-(*R*)-carboxylic-(*S*)-pantolactone ester]-norbornene[20] (**M2**), 5-[*endo*-(*R*)-carboxylic-(*R*)-pantolactone ester]-norbornene (**M3**), a 5-[*endo*-(*R*)-carboxylic ester]-norbornene monomer that contains a (+)-menthol (**M4**), α-D-mannofuranose[21] (**M5**), or *N*-hydroxysuccinimide[22] (**M6**), 5-[*endo*-(*S*)-methyl-acetate]-norbornene (**M7**), (*S*)-methyl-*N*-(1-phenyl-

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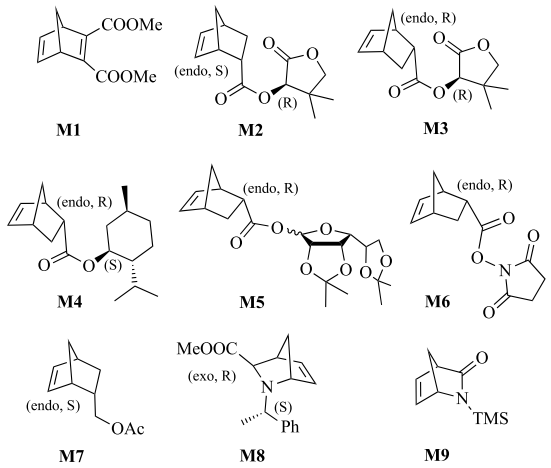
ethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate[23] (**M8**), and *N*-TMS-(+)-Vince Lactam[24] (**M9**).



Polymerization of 100 equiv of 2,3-dicarbomethoxy-5-norbornadiene (**M1**) with (*R*,*S*)-(**3a**)$_2$ (Table 1, run 1) yields poly**M1** that has a characteristic second-order olefinic resonance in its proton NMR spectrum near 5.4 ppm (Figure 5a), while enantiomerically pure monosubstituted norbornenes

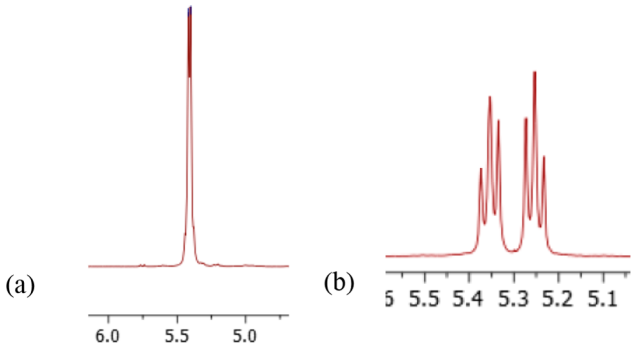


Figure 5. Olefinic proton resonances in (a) *cis,isotactic*-poly**M1** prepared in run 1 and (b) *cis,isotactic*-poly**M4** prepared in run 6.

M2–**M9** gave *cis,isotactic* polymers that contain inequivalent protons on the same double bond and therefore two pseudotriplets for olefinic protons in proton NMR spectra (see Figure 5b for an example). The same result is observed with each initiator in runs 2 and 3 and in runs 4 and 5. All details can be found in the Supporting Information.

Previous results showed that B(C_6F_5)$_3$ can "activate" a tungsten oxo alkylidene complex toward a ROMP reaction.[15a] However, addition of 2 equiv of B(C_6F_5)$_3$ to (*R*,*S*)-(**3a**)$_2$ produced a poor initiator for polymerization of **M1** with yields of ~15% poly**M1** in 15 min (~80% in 6 h), and poly**M1** is only ~70% *cis,isotactic*. We ascribe the relatively slow rate of polymerization in part to the formation of W[OB(C_6F_5)$_3$]-(CHR)(**L1**) (Figure 4) that is relatively unreactive toward **M1** (we presume for steric reasons). Decomposition of W[OB-(C_6F_5)$_3$](CHR)(**L1**) over a period of 1–2 h also is likely to lead to a loss of polymerization activity and selectivity.

Because the phosphines are labile in *rac*-**2a** and *rac*-**2b**, both should also behave as initiators for ROMP. **M3**, **M4**, and **M8** were found to be polymerized by (*rac*)-**2a** or (*S*)-**2a**, but much more slowly than polymerizations initiated by (*R*,*S*)-(**3a**)$_2$ or (*R*,*S*)-(**3b**)$_2$; 3 h is required to consume 100 equiv of norbornene, which amounts to an estimated rate that is ~1/10th of the rate of polymerization by (*R*,*S*)-(**3a**)$_2$ or (*R*,*S*)-(**3b**)$_2$. The stereoselectivities are essentially the same as or slightly inferior to the stereoselectivities produced by (*R*,*S*)-(**3a**)$_2$ or (*R*,*S*)-(**3b**)$_2$ (see the Supporting Information for details). These data suggest that less 14e W(O)($CHCMe_2Ph$)-(**L1**) is available when a $PPhMe_2$ adduct is used as the initiator compared to the amount available when (*R*,*S*)-(**3a**)$_2$ dissociates to give W(O)($CHCMe_2Ph$)(**L1**). These data also suggest that the presence of $PPhMe_2$ does not dramatically alter the selectivity of the polymerization.

A polymerization of **M2** (30 equiv) in $CDCl_3$ by (*S*)-**2a** after 15 min showed that 90% was polymerized to give a growing polymer with an alkylidene resonance for the last-inserted unit at 10.98 ppm along with an alkylidene resonance for the initiator at 10.58 ppm (Figure 6). When *rac*-**2a** was the

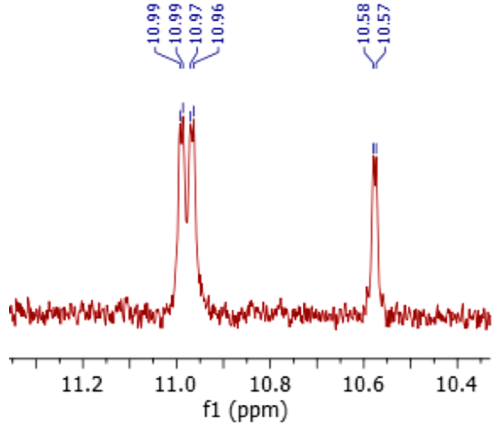


Figure 6. Alkylidene protons observed in the polymerization of 30 equiv of **M2** by (*S*)-**2a**.

initiator, ~80% of **M2** was polymerized in 15 min with now two alkylidene resonances appearing for the last-inserted units at 10.98 and 10.86 ppm in a ratio of ~4:3 (Figure 7). This result suggests that the rates of polymerization of **M2** by (*S*)-W(O)($CHCMe_2Ph$)(**L1**) and (*R*)-W(O)($CHCMe_2Ph$)(**L1**) through enantiomorphic site control are approximately the same and both produce the same polymer structure.

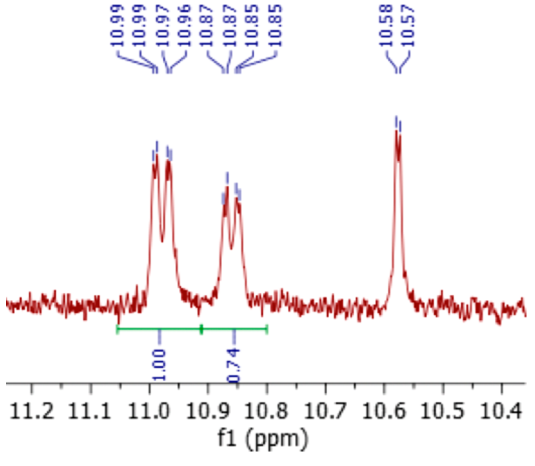


Figure 7. Alkylidene protons observed in the polymerization of 30 equiv of **M2** by *rac*-**2a**.

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We have explored the stereospecific polymerization of *endo*-dicyclopentadiene (DCPD), tetracyclododecene (TCD), and norbornene with a large number of molybdenum and tungsten initiators,[25] among them W(NAr′)(CHCMe$_2$Ph)(*rac*-**L1**) (*rac*-**4**; NAr′ = *N*-2,6-Me$_2$C$_6$H$_3$), which was usually the most stereoselective (>98% *cis,isotactic*). Therefore, we also explored the polymerization of **M2**−**M5** and **M8** with *rac*-**4** (runs 18−22 in Table 1). We found that the selectivities with *rac*-**4** as an initiator were indistinguishable from those obtained with the analogous oxo initiators.

DISCUSSION

We propose that *cis,isotactic* polymers result from enantiomorphic site control in 14e W(O)(CHCMe$_2$Ph)(**L1**) or W(O)(CHCMe$_2$Ph)(**L2**) formed through either loss of PPhMe$_2$ from a phosphine adduct or scission of a heterochiral dimer. We have no evidence that W(O)(CHCMe$_2$Ph)(**L1**) or W(O)(CHCMe$_2$Ph)(**L2**) is unstable in solution as a 14e monomer, only that reversible formation of a bis-μ-oxo heterochiral dimer is facile and favored, at least for neophylidene complexes, over any alkylidene coupling to give olefins. Evidence in the literature suggests that the propagating alkylidene in a Mo=CHPoly complex (where Poly is the growing polymer chain) made from a substituted norbornene is operationally relatively sterically demanding, judging from the relatively selective formation of a "first insertion product" in a polymerization of **M1**.[13b] Therefore, monomeric W(O)(CHPoly)(**L1**) complexes are also likely to form dimers and phosphine adducts analogous to the neophylidene complexes and be relatively resistant to alkylidene coupling.

It should be noted that tungsten imido alkylidenes (imido = *N*-2,6-*i*-Pr$_2$C$_6$H$_3$) are unstable toward bimolecular coupling of alkylidenes after a smaller alkylidene is formed from a neopentylidene or neophylidene complex.[3a−c] Reactions between (*R*,*S*)-(**3a**)$_2$ or (*R*,*S*)-(**3b**)$_2$ and 3-hexenes did not lead to formation of analogous oxo propylidene dimers (see the Supporting Information), only decomposition, so bimolecular coupling of "small" alkylidenes is also found in oxo alkylidene complexes, in spite of the ability of the oxo ligand to form dimers (reversibly) through oxo bridging between metals. Formation of complexes analogous to (*R*,*S*)-(**3a**)$_2$ and (*R*,*S*)-(**3b**)$_2$ would seem to be possible only when alternative bimolecular coupling to give (ultimately) metal−metal bonded imido complexes or W(IV) olefin or metallacyclobutane complexes is slow for steric reasons,[3a−c] as appears to be the case in W(O)(CHCMe$_2$Ph)(**L1**) or W(O)(CHCMe$_2$Ph)(**L2**) initiators and CHPoly analogues formed in the polymerizations explored here. Alkylidene coupling could be competitive with chain extension when less reactive monomers are used (e.g., cyclooctene), which yield less sterically demanding alkylidenes.

We proposed earlier that (*R*,*S*)-(**3a**)$_2$ breaks up to give the 14e monomeric oxo alkylidene complex much more readily than *rac*-**2a** loses PPhMe$_2$. We can propose two reasons. W(O)(CHCMe$_2$Ph)(**L1**) or W(O)(CHCMe$_2$Ph)(**L2**) is the "base" in (*R*,*S*)-(**3a**)$_2$ or (*R*,*S*)-(**3b**)$_2$, respectively, and each should be sterically more demanding than PPhMe$_2$ and lost more readily to give a 14e complex. Second, the W=O bond is likely to be shorter in the resulting monometallic complex than in the dimer and should provide a small additional driving force for scission of the dimer.

The fact that the results of polymerization of **M2**−**M5** and **M8** with *rac*-**4**, a monomeric initiator (runs 18−22, respectively, in Table 1), are indistinguishable from those obtained with the oxo initiators supports the proposal that 14e monomeric oxo complexes are the active species.

CONCLUSIONS

We have synthesized tungsten oxo biphenolate alkylidene complexes (dimers or phosphine complexes) that behave as initiators for the stereoselective *cis,isotactic* ROMP of 2,3-dicarbomethoxy-5-norbornadiene and a selection of enantiomerically pure 5-substituted norbornenes. Monomeric 14e oxo alkylidene complexes are the active initiators. The dimeric oxo alkylidene complexes are the faster and marginally more stereoselective catalysts compared to the phosphine adducts. Instead of B(C$_6$F$_5$)$_3$ accelerating metathesis reactions through binding to the oxo ligand, B(C$_6$F$_5$)$_3$ binds to the oxo ligand in complexes that contain **L1** to give a relatively unreactive adduct, we propose for steric reasons. Both enantiomers of a 14e oxo alkylidene complex appear to polymerize an enantiomerically pure monomer at approximately the same rate and to give the same *cis,isotactic* structure. Therefore, there would seem to be little possibility of a kinetic resolution of a *rac* monomer through selective polymerization of one of the two enantiomers with an enantiomerically pure initiator. The results presented here suggest that five-coordinate 14e oxo alkylidene complexes in general are not necessarily unstable toward bimolecular decomposition because the oxo ligand bridges between metals but because alkylidenes ultimately can couple when the alkylidenes are relatively "small" and/or steric protection provided by other ligands is insufficient. Finally, oxo complexes and their monomeric *N*-2,6-Me$_2$C$_6$H$_3$ analogues are equally efficient in polymerizing five of the monomers that were explored here to give a single *cis,isotactic* structure.

EXPERIMENTAL SECTION

General Procedures. All air- and moisture-sensitive compounds were manipulated under a nitrogen atmosphere in a glovebox or on a Schlenk line. Glassware was oven-dried prior to use. Solvents were degassed and dried by being passed through columns of activated alumina or 4 Å molecular sieves and stored over activated molecular sieves. Pentane was shaken with sulfuric acid and then water before use in the solvent purification system. Benzene-d_6 and toluene-d_8 were dried over Na/benzophenone, vacuum transferred onto molecular sieves, and stored in the glovebox. ^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to the NMR solvent residual peak, and ^{31}P{^{1}H} spectra were referenced externally to H$_3$PO$_4$ in a D$_2$O standard. B(C$_6$F$_5$)$_3$ was purchased from Strem and used as received. PPhMe$_2$ was purchased from Strem and degassed and stored over sieves prior to use. Starting materials were prepared as described in the literature in the Supporting Information. Elemental analyses were performed at the elemental analysis facility at the University of Rochester (Rochester, NY), Midwest Microlab (Indianapolis, IN), or Atlantic Microlab (Norcross, GA). All NMR data and spectra can be found in the Supporting Information.

W(O)(CHCMe$_2$Ph)(Cl)$_2$(PPhMe$_2$)$_2$ (1). Complex **1** was synthesized as previously reported with minor modifications.[9] Trimethylchlorosilane (1.37 mL, 2.3 equiv) was added dropwise to a 50 mL toluene suspension of W(O)$_2$(CH$_2$CMe$_2$Ph)$_2$(Bipy) (Bipy = 2-bipyridine; 3 g, 4.70 mmol), and ZnCl$_2$(dioxane) (1.11 g, 1.05 equiv) and PPhMe$_2$ (1.23 g, 1.90 equiv) were then added. The orange mixture was stirred at room temperature for 30 min, before being heated at 60 °C for 30 min and then 100 °C for 2 h. The mixture turned black during this period. The mixture was cooled to room temperature and filtered through Celite, and all solvents were removed from the filtrate under vacuum. Acetonitrile (20 mL) was added to the residue, and a yellow powder was filtered off from the dark solution. The mixture was held at −28 °C overnight to give a second crop as yellow crystals [overall yield of 2.06 g (65%)].

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W(O)(CHCMe$_2$Ph)(L1)(PPhMe$_2$) [*rac*-2a and (*S*)-2a]. A mixture of **1** and Li$_2$**L1**·*n*THF (1.2 equiv, *n* = 1−1.5) in benzene was stirred at room temperature (rt) overnight. The reaction mixture was filtered through Celite to give a light yellow filtrate, from which all solvent was removed *in vacuo*. Pentane was added to the residue, and the suspension was stirred at rt for 30 min, followed by filtration to give the product as a very pale yellow powder that can be used for further syntheses of derivatives described below (86% yield). The product can also be recrystallized from a mixture of ether and pentane. Anal. Calcd for $C_{42}H_{55}O_3PW$: C, 61.32%; H, 6.74%. Found: C, 61.36%; H, 6.78%. Complex (*S*)-**2a** was synthesized through the same protocol (40% yield).

W(O)(CHCMe$_2$Ph)(L2)(PPhMe$_2$) [*rac*-2b and (*R*)-2b]. Complex *rac*-**2b** was synthesized from complex **1** and Li$_2$**L2**·*n*THF through the same procedure that was used to synthesize *rac*-**2a** (60% yield). Complex (*R*)-**2b** was synthesized in the same way (32% yield). Satisfactory elemental analyses could not be obtained for *rac*-**2b**, possibly as a consequence of the greater lability of PPhMe$_2$.

W(O)(CHCMe$_2$Ph)(L3)(PPhMe$_2$) (*rac*-2c). *rac*-**2c** was synthesized from **1** and Li$_2$**L3**·*n*THF through the same procedure that was used to synthesize *rac*-**2a** (65% yield). Anal. Calcd for $C_{68}H_{79}O_3PW$: C, 70.46%; H, 6.87%. Found: C, 70.58%; H, 6.81%.

W(O)(CHCMe$_2$Ph)(L4)(PPhMe$_2$) (*rac*-2d). Complex *rac*-**2d** was synthesized from **1** and Li$_2$**L4**·*n*THF through the same procedure that was used to synthesize *rac*-**2a** (50% yield). Anal. Calcd for $C_{68}H_{79}O_3PW$: C, 70.20%; H, 5.80%. Found: C, 70.59%; H, 6.16%.

(*R*,*S*)-[W(μ-O)(CHCMe$_2$Ph)(L1)]$_2$ [(*R*,*S*)-(3a)$_2$]. The addition of B(C$_6$F$_5$)$_3$ (318 mg, 0.56 mmol) to a stirred diethyl ether solution (20 mL) of *rac*-W(O)(CHCMe$_2$Ph)(**L1**)(PPhMe$_2$) (*rac*-**2a**, 450 mg, 0.51 mmol) at room temperature led to the precipitation of a yellow powder in <1 min. The product was filtered off and washed with pentane [240 mg yield (69%)]. Yellow needles were obtained by cooling a dichloromethane solution of the product in the freezer overnight. Anal. Calcd for $C_{34}H_{44}O_3W$: C, 59.65%; H, 6.48%. Found: C, 59.55%; H, 6.56%.

(*R*,*S*)-[W(μ-O)(CHCMe$_2$Ph)(L2)]$_2$ [(*R*,*S*)-(3b)$_2$]. B(C$_6$F$_5$)$_3$ (129 mg, 0.25 mmol) was added at room temperature to a stirred benzene solution (20 mL) of *rac*-W(O)(CHCMe$_2$Ph)(**L2**)(PPhMe$_2$) (*rac*-**2b**, 201 mg, 0.23 mmol). A yellow powder precipitated in <5 min. The product was filtered off and washed with pentane [102 mg yield (60%)]. Yellow crystals were obtained by cooling a chloroform solution of the product in the freezer overnight. Anal. Calcd for $C_{38}H_{48}O_3W$: C, 61.96%; H, 6.57%. Found: C, 61.66%; H, 6.90%.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00377.

Detailed NMR data, spectra for all compounds, and details of X-ray studies (PDF)

Structural data (XYZ)

Accession Codes

CCDC 1919810−1919811 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

T.Y. performed the majority of the synthetic work, while P.M. performed all X-ray structural studies.

Notes

The authors declare no competing financial interest.

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