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

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ABSTRACT: We have synthesized and characterized tungsten oxo alkylidene biphenolate complexes with the formulas W(O)(CHR)(rac-biphenolate)-(PPhMe2)2 and (R,S)−[W(μ-O)(CHR)(biphenolate)]2 (R = CMe2Ph; biphenolate = L1 or L2 in the text). They behave as initiators for the stereoselective (cis,isotactic) polymerization of 2,3-dicarboxymethoxy-S-norbornadiene and eight enantiomerically pure S-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 PPhMe2 from the phosphine adducts or scission of the heterochiral dimer. Addition of B(C6F5)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(C6F5)3](CHR)(L1) in equilibrium with B(C6F5)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 alkylidene initiator, W(N(2,6-Me2C6H3)(CHCMe2Ph)(rac-L1), gave virtually identical results compared to the results obtained with oxo complexes.

INTRODUCTION

Although a tungsten oxo alkylidene complex1 was the first high-oxidation state tungsten complex to be prepared, largely imido alkylidene complexes were developed as metathesis catalysts2 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 alkylidene complexes have been prepared by a variety of methods.4−8 In 2012,9 a new and reliable method of synthesizing tungsten oxo alkylidenes through α-hydrogen abstraction in intermediates prepared from WO2(CH2CMe3)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=CH 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 monooanionic 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 alkylidene complexes have 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)(CHCMe3Ph)(Cl)(PPhMe2)21 and rac-Li,L1 proceeded smoothly in benzene to give rac-W(O)(CHCMe3Ph)-(L1)(PPhMe2) (rac-2a) as a light yellow powder in 86% yield. The alkylidene proton resonance in rac-2a is found in the 1H nuclear magnetic resonance (NMR) spectrum at 10.59 ppm as a doublet with a JCH of 2 Hz and a JCH of 122 Hz; both are demanding lutetium or lutetium complexes and explore them as ROMP initiators.

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characteristic of a syn alkylidene isomer. The phosphine resonance is found at 10.72 ppm ($J_{\text{HP}} = 348$ Hz) in the $^{31}\text{P}$ NMR spectrum. We propose that the structure of rac-2a is analogous to that of syn-W(O)(CH-t-Bu)(OHMT)(Me$_2$Pyr)-(PMe$_2$Ph) (OHMT = 2,6-dimethylphenoxy), 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$_6$F$_5$)$_3$ 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$_2$Cl$_2$. Its $^1$H NMR spectrum suggests that it has the empirical formula W(O)(CHCMe$_2$Ph)(L1). The chemical shift of the alkylidene proton is 8.79 ppm in CDCl$_3$ with $J_{\text{CH}}$ of 122 Hz and a $J_{\text{WH}}$ of 15 Hz, both of which are characteristic of a syn alkylidene isomer. $^{13}$ The phosphine resonance is found at 10.72 ppm (1 min, $J_{\text{WH}}$ of 348 Hz) in the $^{31}\text{P}$ NMR spectrum. We propose that the structure of rac-2a is analogous to that of syn-W(O)(CH-t-Bu)(OHMT)(Me$_2$Pyr)-(PMe$_2$Ph) (OHMT = 2,6-dimethylphenoxy), 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$_6$F$_5$)$_3$ 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 neophyldene 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); $\tau = 0.54$.](image)

![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); $\tau = 0.41$.](image)

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 $\alpha$-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...
Addition of 1 equiv of \( \text{B}[\text{C}_6\text{F}_5\text{O}](\text{CHR})_2 \) to a tol-\( d_8 \) solution of \((S)-2a \) led immediately to formation of an orange solution, the \(^1\text{H} \) 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 \( \text{B}[\text{C}_6\text{F}_5\text{O}](\text{CHR})_2 \) to \((S)-2a \) led to its complete decomposition. We cannot say that \( \text{B}[\text{C}_6\text{F}_5\text{O}](\text{CHR})_2 \) scavenges only \( \text{PPhMe}_2 \) 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., \((R,S)-(3a)_2 \) or \((S,S)-(3a)_2 \).

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

Finally, addition of 1 equiv of \( \text{B}[\text{C}_6\text{F}_5\text{O}](\text{CHR})_2 \) to \( \text{rac}-2d \) resulted in no reaction, consistent with the \( \text{PPhMe}_2 \) ligand in \( \text{rac}-2d \) being bound too strongly to be lost and scavenged by \( \text{B}[\text{C}_6\text{F}_5\text{O}](\text{CHR})_2 \).

We have found that \((R,S)-(3a)_2 \) and \((R,S)-(3b)_2 \) initiate the polymerization of monomers \( \text{M1} \rightarrow \text{M9} \) (see below and Table 1), often in a highly stereoselective manner, to give cis-isotactic polymers. The enantiomerically pure monomers include \( S-[\text{endo}-(R)-\text{carboxyl}-\text{C}_6\text{F}_5\text{O}]-\text{norbornene} \) \( \text{(M2)} \), \( S-[\text{endo}-(R)-\text{carboxyl}-\text{C}_6\text{F}_5\text{O}]-\text{norbornene} \) \( \text{(M3)} \), a \( S-[\text{endo}-(R)-\text{carboxyl}-\text{C}_6\text{F}_5\text{O}]-\text{norbornene} \) monomer that contains a (+)-menthol \( \text{(M4)} \), \( \alpha\text{-d-mannofuranose} \) \( \text{(M5)} \), or \( \text{N-hydroxysuccinimide} \) \( \text{(M6)} \), \( S-[\text{endo}-(S)-\text{methyl-acetate}]-\text{norbornene} \) \( \text{(M7)} \), \( S-[\text{endo}-(S)-\text{methyl-acetate}]-\text{norbornene} \) \( \text{(M8)} \), \( \text{endo} \)-\( \text{polymerize in CCl}_3 \) \( \text{tol} \)-\( d_8 \), a 5-\( \text{endo} \)-\( \text{pantolactone ester} \)-norbornene 20 min >95
ethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate\(^2^3\) (M8), and N-TMS-(+)-Vince Lactam\(^2^4\) (M9).

Polymerization of 100 equiv of 2,3-dicarbomethoxy-5-norbornadiene (M1) with (R,S)-(3a)\(^2\) (Table 1, run 1) yields polyM1 that has a characteristic second-order olefinic resonance in its proton NMR spectrum near 5.4 ppm (Figure 5a), while enantiomerically pure monosubstituted norbornenes 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\(_6\)F\(_5\))\(_3\) can “activate” a tungsten oxo alkylidene complex toward a ROMP reaction.\(^1^5^a\) However, addition of 2 equiv of B(C\(_6\)F\(_5\))\(_3\) to (R,S)-(3a)\(^2\) produced a poor initiator for polymerization of M1 with yields of \(~15\%\) polyM1 in 15 min (\(~80\%\) in 6 h), and polyM1 is only \(~70\%\) cis,isotactic. We ascribe the relatively slow rate of polymerization in part to the formation of W[OB(C\(_6\)F\(_5\))\(_3\)]-(CHR)(L1) (Figure 4) that is relatively unreactive toward M1 (we presume for steric reasons). Decomposition of W[OB(C\(_6\)F\(_5\))\(_3\)](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 \(~1/10\)th 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\(_2\)Ph)-(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\(_2\)Ph)(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 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\(_2\)Ph)(L1) and (R)-W(O)(CHCMe\(_2\)Ph)(L1) through enantimorphic site control are approximately the same and both produce the same polymer structure.
We have explored the stereospecific polymerization of endo-dicyclopentadiene (DCPD), tetracyclododecene (TCD), and norbornene with a large number of molybdenum and tungsten initiators, among them \( W(NAr')\) (CHCMePh)(rac-L1) (rac-4; \( NAr' = N\text{-}2,6\text{-}Me_2C_6H_{13} \)), which was usually the most stereoselective (\( >98\% \) cis,iso)active. 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,isoactive polymers result from enantiomorphically pure site control in 14e \( W(O)(\text{CHCMePh})\)(L1) or \( W(O)(\text{CHCMePh})\)(L2) formed through either loss of PPhMe2 from a phosphine adduct or scission of a dimeric heterocirrter. We have no evidence that \( W(O)(\text{CHCMePh})\)(L1) or \( W(O)(\text{CHCMePh})\)(L2) is unstable in solution as a 14e monomer, only that reversible formation of a bis-μ-oxo heterocirrteris facile and favored, at least for neophyldene complexes, over any alkylidene coupling to give olefins. Evidence in the literature suggests that the propagating alkylidene in a M=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. Therefore, monomeric \( W(O)(\text{CHCMePh})\)(L1) complexes are also likely to form dimers and phosphine adducts analogous to the neophyldene complexes and be relatively resistant to alkylidene coupling.

It should be noted that tungsten imido alkylidenes (imido = \( N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_{13} \)) are unstable toward bimolecular coupling of alkylidenes after a smaller alkylidene is formed from a neopentyldiene or neophyldiene complex. Reactions between \( (R,S)-3a \) or \( (R,S)-3b \) 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 \( (R,S)-3a \) or \( (R,S)-3b \) 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 steriac reasons, as appears to be the case in \( W(O)(\text{CHCMePh})\)(L1) or \( W(O)(\text{CHCMePh})\)(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 \( (R,S)-3a \) breaks up to give the 14e monomeric oxo alkylidene complex much more readily than \( rac-2a \) loses PPhMe2. We can propose two reasons. \( W(O)(\text{CHCMePh})\)(L1) or \( W(O)(\text{CHCMePh})\)(L2) is the "base" in \( (R,S)-3a \) or \( (R,S)-3b \), respectively, and each should be sterically more demanding than PPhMe2 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 biphensolate alkylidene complexes (dimers or phosphine complexes) that behave as initiators for the stereoselective cis,isoactive ROMP of 2,3-dicarbomethoxy-5-norbornadiene and a selection of enantio-merically pure 3-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 \( B(C_6F_5)_3 \), accelerating metathesis reactions through binding to the oxo ligand, \( B(C_6F_5)_3 \) 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 enantio-merically pure monomer at approximately the same rate and to give the same cis,isoactive 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 enantio-merically 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 \( N\text{-}2,6\text{-}Me_2C_6H_3 \) analogues are equally efficient in polymerizing five of the monomers that were explored here to give a single cis,isoactive 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-d6 and toluene-d8 were dried over Na/benzophenone, vacuum transferred onto molecular sieves, 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)(CHCMePh)Cl)(PPhMe2)(1).** Complex 1 was synthesized as previously reported with minor modifications. Trimethylchlorosilane (1.37 mL, 2.3 equiv) was added dropwise to a 50 mL toluene suspension of \( W(O)(\text{CHCMePh})(\text{Bipy}) \) (Bipy = 2-bipyrindine; 3 g, 4.70 mmol), and ZnCl2(dioxane) (1.11 g, 1.05 equiv) was purchased from Strem and degassed and stored over 4 Å molecular sieves prior to use. Starting materials were prepared as described in the Supporting Information.

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W[O(CHCMe3)2][L1](PPhMe2) (rac-2a and (S)-2a). A mixture of 1 and Li3Li+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 was synthesized from 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 PPhMe2.

W[O(CHCMe3)2][L2](PPhMe2) (rac-2b and (R)-2b). Complex rac-2b was synthesized from complex 1 and Li3Li+THF through the same procedure that was used to synthesize rac-2a (65% yield). Anal. Calc. for C64H79O3PW: 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(CHCMe3)2][L3](PPhMe2) (rac-2c). rac-2c was synthesized from 1 and Li3Li+THF through the same procedure that was used to synthesize rac-2a (65% yield). Anal. Calc. for C60H63O2PW: C, 70.46%; H, 6.87%. Found: C, 70.58%; H, 6.81%.

W[O(CHCMe3)2][L4](PPhMe2) (rac-2d). Complex rac-2d was synthesized from 1 and Li4Li+THF through the same procedure that was used to synthesize rac-2a (50% yield). Anal. Calc. for C66H79O3PW: C, 70.20%; H, 6.80%. Found: C, 70.59%; H, 6.16%.

(R,S)-[Wμ-O(CHCMe3)2][L1] (R,S-3a). The addition of B(C6F5)3 (318 mg, 0.56 mmol) to a stirred diethyl ether solution (20 mL) of B(C6F5)3 (318 mg, 0.56 mmol) in room temperature (rt) overnight. The reaction mixture was filtered to give a yellow precipitate (65% yield). Anal. Calcd for C68H79O3PW: C, 70.20%; H, 5.80%. Found: C, 70.59%; H, 6.16%.

(R,S)-[Wμ-O(CHCMe3)2][L2] (R,S-3b). B(C6F5)3 (129 mg, 0.25 mmol) was added to room temperature to a stirred benzene solution (20 mL) of rac-W(μ-O)(CHCMe3)2[PPhMe2] (rac-2b, 450 mg, 0.51 mmol) at 51 room temperature. The product was filtered off and washed with pentane [102 mg yield (69%)].

Notes
The authors declare no competing financial interest.

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