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Asymmetric Alkylidene and Oxo Complexes of Tungsten(VI)

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Reactions between $(t\text{-BuO})_3W(\equiv CR)$ derivatives and 1,1′-bi-2-naphthols (H_2R_2BINO, R = Me, Br, Ph) generate mononuclear C_1-symmetric $(R_2BINO)(t\text{-BuO})_2W(=CHR)$ complexes. An analogous reaction with 2 equiv of H_2Me_2BINO generates $(Me_2BINO)_2W(=CHPh)$, while a reaction between H_2Me_2BINO and $(t\text{-BuO})_4W(=O)$ produces $(Me_2BINO)(t\text{-BuO})_2W(=O)$. This oxo complex was characterized by X-ray crystallography, which shows it to be a highly-distorted trigonal bipyramidal complex in which the Me_2BINO ligand adopts a λ chelate stereochemistry. Although the complexes show little stereoselectivity in Wittig-like alkylidene transfer to benzaldehyde, the ring opening metathesis polymerization of norbornene proceeds with modest stereoselectivity. The fraction of *cis*-polynorbornene increases in concert with the steric demands of the substituents on the R_2BINO ligand. Crystal data for $(Me_2BINO)(t\text{-BuO})_2W(=O)$ at 113 K: $a = 11.426(3)$ Å, $b = 14.733(3)$ Å, $c = 16.716(4)$ Å, $\beta = 105.87(2)°$, $Z = 4$, $D_{calc.} = 1.616$, space group $P2_1/n$ (No. 14), $R(F) = 0.053$, $R_w(F) = 0.106$ for 3451 reflections ($F_o > 0$).

Introduction

Metal alkylidene complexes engage in a wide range of cycloaddition reactions with organic substrates.[1,2] Electrophilic alkylidene moieties, which occur in electron rich transition metal complexes, participate broadly in cycloaddition reactions with unsaturated hydrocarbon derivatives, producing complex cyclic organic molecules.[3–5] Nucleophilic alkylidene moieties, found in complexes containing high oxidation state metal centers, participate in both metathesis reactions and Wittig-like alkylidene transfer processes.[6,7] The ability of alkylidenes to facilitate metathesis has been broadly employed in classical olefin metathesis reactions, alkyne polymerization, and ring opening metathesis polymerization (ROMP) processes.[8–15] While studies of asymmetric auxiliaries have contributed significantly to the development of enantiospecific Fischer carbene reagents, particularly through Hegedus' enantiospecific imine cycloadditions to chromium carbenes,[16] such strategies have not yet been broadly applied to stereocontrol in the reactions of Schrock-type alkylidene

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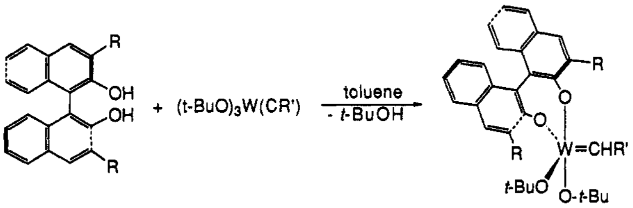
derivatives.[17] This should evoke some surprise considering that Ivin was the first to propose such a strategy for influencing the stereochemistry of ROMP processes in the early 1980s.[7]

Although chiral auxiliaries have not yet been applied to metathesis stereocontrol, a number of investigators have devoted significant attention to investigating the mechanistic details and stereochemical outcome of metathesis and ROMP reactions.[6,8,18-21] Katz, Ivin, and Basset have all made seminal contributions to understanding the reaction coordinate of alkylidene cycloadditions,[6,8,18,19] while Hegedus has outlined the probable influence of asymmetric auxiliaries on the face selectivity of 2+2 processes involving alkylidenes.[16,22] Other investigators have systematically examined the results of variations in the identity of the metal and its attendant ligands on the stereochemistry of metathesis reactions.[23,24] Basset, in particular, has shown the initial stages of the olefin metathesis reaction to be highly stereospecific, with the establishment of thermodynamic product distributions occurring through an initially uncompetitive set of branches of the reaction coordinate.[8] Early studies of ROMP stereochemistry focused on the evaluation of the microstructure of ROMP'ed materials.[19] In this area, Ivin and his co-workers have made the most important contributions, carefully unraveling the detailed stereochemistry of dozens of ROMP'ed materials through analyses of ^{13}C NMR spectra.[7,19] Both Basset and Osborn have noted the increased *cis* selectivity of isostructural catalysts as the steric demands of halide or aryloxide ligands are increased.[23,24] Most recently, Schrock and Gibson have shown that the rate of rotation about a M=C bond can directly influence the stereochemistry of cycloaddition processes.[25,26]

We have chosen to examine how introducing C_2-symmetric chelating bis(aryloxide) ligands into the coordination sphere of an alkylidene derivative influences the stereoselectivity of reactions at the alkylidene template. With this end in mind, we have synthesized a series of tungsten alkylidene complexes containing either one or two 1,1'-bi-2-naphtholate (R_2BINO) ligands.[27-30] While simple Wittig-like olefination reactions of these derivatives display no interpretable stereoselectivity, the complexes display modest stereoselectivity in ROMP processes, indicating that this strategy may hold promise in future generations of dissymmetric alkylidene reagents.

Results and Discussion

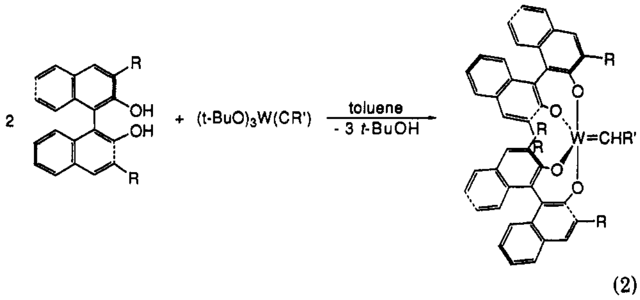
Synthesis and Structural Characteristics of (R_2BINO)(*t*-BuO)$_2$W(=CHR'), (Me_2BINO)$_2$W(=CHPh), and (Me_2BINO)(*t*-BuO)$_2$W(=O). (*t*-BuO)$_3$W(≡CR') precursors react with stoichiometric quantities of H_2R_2-BINO in toluene at ambient temperature, generating (R_2BINO)(*t*-BuO)$_2$W(=CHR') complexes (eq 1). These



(1)

reactions mimic syntheses of X_2(*t*-BuO)$_2$W(=CHR) derivatives reported by Schrock, except that, unlike Schrock's five-coordinate alkylidene complexes, in which X groups invariably adopt a *trans* relationship, the R_2BINO ligand is constrained to adopt a *cis* orientation.[31] The products are obtained as red-orange waxy crystals in yields varying from 50 to 80%. The Me_2BINO and Ph_2BINO products are stable in the solid state for weeks at ambient temperature, while the Br_2BINO derivatives decompose over several days to uncharacterized materials even under rigorous exclusion of air and moisture.

A reaction between 2 equiv of *rac*-H_2Me_2BINO and (*t*-BuO)$_3$W(≡CR') generated (Me_2BINO)$_2$W(=CHR'), which was obtained as a pure orange solid after repeated recrystallizations (eq 2). Attempts to generate an analogous bis(Ph_2BINO) complex generated only (Ph_2BINO)(*t*-BuO)$_2$W(=CHPh) and unreacted H_2Ph_2BINO. Evidently, the Ph_2BINO ligand is too sterically demanding to readily accommodate bis(Ph_2BINO) substitution around the five-coordinate template. This behavior is mimicked by the alcoholysis reactions of WCl_6 and H_2Ph_2BINO,



(2)

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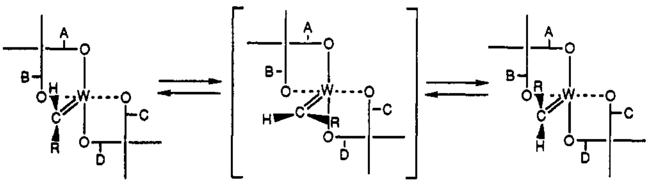
which result only in the formation of a $(Ph_2BINO)WCl_4$ complex.[32] Efforts to generate alkylidene complexes containing BINO ligands (R = H) resulted in the formation of materials with broad, essentially featureless ^1H NMR spectra. The spectra of these materials were not simplified by using optically pure H_2BINO instead of the racemic starting material, and attempts to fractionally crystallize identifiable products from the reaction mixtures were unsuccessful.

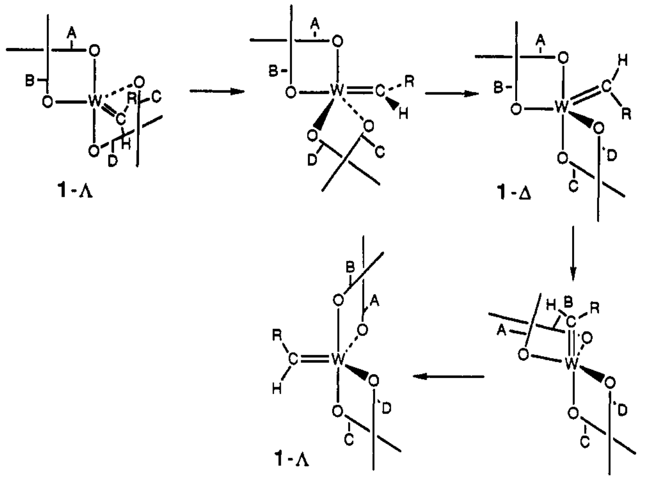
^1H and ^{13}C NMR spectra of the alkylidene fragment are indicative of the development of little or no agostic character in the α-hydrogen. Although the magnitudes of J_{W-H} and J_{W-C} (ca. 180 and 6.9 Hz, respectively) for the R_2BINO-substituted complexes fall in the range observed for some agostic alkylidene complexes, these values also fall within the respective ranges found for $X_2(t\text{-}BuO)_2W({=}CH\text{-}t\text{-}Bu)$ complexes, which were shown to have strictly nonagostic structures.[31] Furthermore, the J_{C-H_α} value for the R_2BINO-substituted complexes, which is the bellwether of agostic character for alkylidenes,[31,33,34] is approximately 136 Hz. This is well within the 130–140-Hz range typically found for nonagostic neopentylidenes, and far outside the 50–90-Hz range observed for agostic alkylidenes that display highly distorted $M{-}C{-}H_\alpha$ bond angles.[35,36]

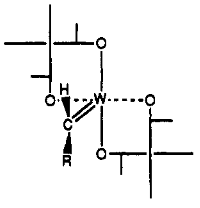
NMR spectra of the $(R_2BINO)(t\text{-}BuO)_2W({=}CHR)$ complexes suggest that they have mononuclear five-coordinate trigonal bipyramidal structures similar to those proposed by Schrock for $X_2(t\text{-}BuO)_2W({=}CH\text{-}t\text{-}Bu)$.[31] The chemical shifts of the observed alkylidene protons, δ = 8.7–7.8, are approximately 1 ppm higher than those observed for Schrock's $(ArO)_2(t\text{-}BuO)_2W({=}CH\text{-}t\text{-}Bu)$ complexes,[31] although this difference is far smaller than the 2–3 ppm shifts observed for protons that experience significant naphtholate ring currents.[30,32] Variable temperature studies show that the complexes maintain apparent C_1 symmetry over a significant temperature range (−70 to +50 °C) and exhibit no evidence of minor isomers generated by either alkylidene rotamers or diastereoisomerism in the R_2BINO chelate. $(Me_2BINO)_2W({=}CHPh)$ also shows evidence of only a single isomer in variable temperature NMR studies. An independent synthesis of this complex using (R)-H_2Me_2BINO confirmed the product to be the (R^*,R^*)-$(Me_2BINO)_2W({=}CHPh)$ diastereomer (1). The evident isomeric purity of both the $(R_2BINO)(t\text{-}BuO)_2W({=}CHR)$ and $(R_2BINO)_2W({=}CHR)$ derivatives suggests either that the substitution reactions achieve a thermodynamic product distribution through intermolecular ligand exchange or that facile intramolecular rearrangement pathways allow the initially formed isomer distributions to collapse to a thermodynamically stable structure. In either instance, the observed results indicate that one of the possible diastereoisomeric chelates (λ(3) or δ(4)) is significantly more stable in the mono- and bis(R_2BINO) isomers. Unlike the C_1-symmetric $(Me_2BINO)(t\text{-}BuO)_2W({=}CHPh)$ complex, $(Me_2BINO)_2W({=}CHPh)$ has apparent C_2-symmetry at temperatures above 40 °C. On cooling to −60 °C, the ^1H NMR spectrum of the product collapses to a C_1-symmetric structure. This fluxional behavior is consistent with rotation about the W=C (Scheme I) axis and the ΔG^*_{240} of 16.7 ± 0.5 kcal/mol found for this process is comparable to those observed for other high-valent tungsten(VI) alkylidene complexes.[17,36] A turnstile rotation involving a $W({=}CHPh)(Me_2BINO)$ subunit cannot be responsible for the fluxional process (Scheme II), because it would result in the equilibration of all four naphtholate ring environments. This is consistent with Osborn's report that alkylidene rotation in $X(t\text{-}BuCH_2O)_3W({=}CHR)$ derivatives occurred with a lower activation barrier than the intramolecular scrambling of the neopentoxide group environments through a modified turnstile or pseudorotation process.[17]

Scheme I

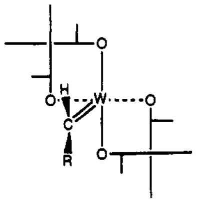


Scheme II

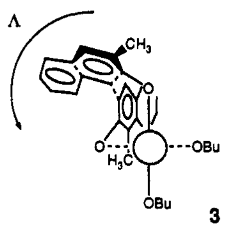




(R,R)-$(Me_2BINO)_2W({=}CHPh)$ (1)



(R,S)-$(Me_2BINO)_2W({=}CHPh)$ (2)



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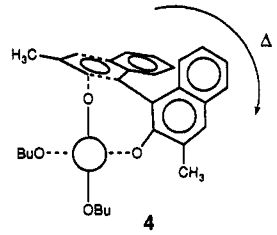

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Some of the structural questions raised in this discussion are addressed by an X-ray structure of $(Me_2BINO)(t\text{-}BuO)_2W({=}O)$, shown in a ball and stick representation in Figure 1. Positional and isotropic thermal parameters for $(Me_2BINO)(t\text{-}BuO)_2W({=}O)$ are collected in Table I, while selected bond distances and angles are shown in Table II.

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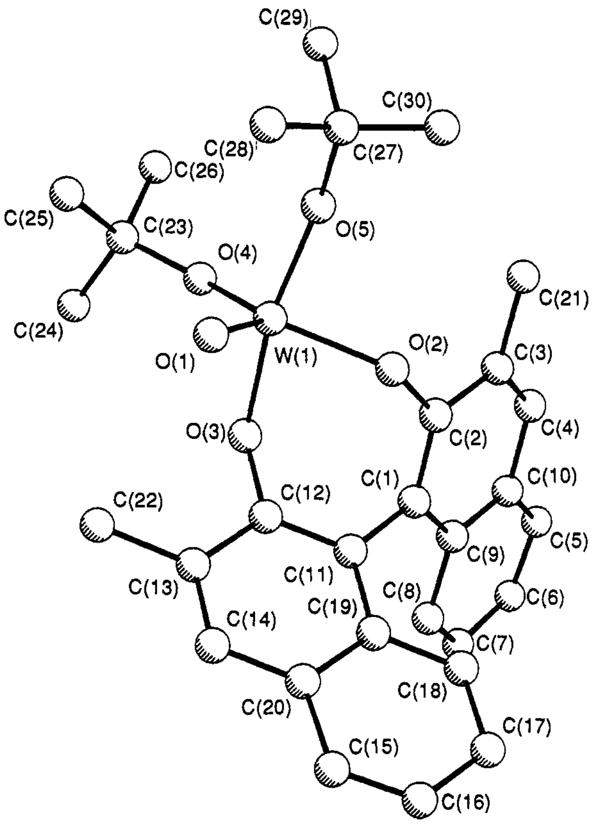

Figure 1. Ball and stick representation of the molecular structure of $(Me_2BINO)(t\text{-}BuO)_2W(=O)$.

Table I. Positional and Isotropic Thermal Parameters for $(Me_2BINO)(t\text{-}BuO)_2W(=O)$

atom	*x*	*y*	*z*	*B*(eq), Å^2
W(1)	0.30603(3)	0.41889(3)	0.80656(2)	1.70(3)
O(1)	0.2719(6)	0.4725(5)	0.7156(4)	2.6(3)
O(2)	0.3368(5)	0.2905(4)	0.7920(4)	1.9(2)
O(3)	0.4825(7)	0.4263(4)	0.8271(4)	1.7(3)
O(4)	0.3297(6)	0.4969(5)	0.8927(4)	2.8(3)
O(5)	0.1520(6)	0.3889(5)	0.8103(4)	2.5(3)
C(1)	0.5436(8)	0.2432(7)	0.8359(5)	1.9(4)
C(2)	0.4249(9)	0.2363(6)	0.8402(6)	2.0(4)
C(3)	0.3898(8)	0.1769(6)	0.8950(6)	1.9(4)
C(4)	0.4752(9)	0.1302(8)	0.9496(6)	2.5(4)
C(5)	0.693(1)	0.0929(7)	1.0163(7)	3.1(5)
C(6)	0.813(1)	0.1070(7)	1.0197(6)	2.5(4)
C(7)	0.848(1)	0.1599(7)	0.9641(7)	2.9(4)
C(8)	0.7609(8)	0.2028(6)	0.9006(5)	1.9(3)
C(9)	0.6343(8)	0.1929(6)	0.8961(6)	2.0(4)
C(10)	0.6029(9)	0.1378(7)	0.9531(5)	2.3(4)
C(11)	0.5718(8)	0.3032(7)	0.7721(5)	2.0(4)
C(12)	0.5449(8)	0.3931(6)	0.7742(5)	1.5(3)
C(13)	0.5756(8)	0.4569(7)	0.7163(6)	2.0(4)
C(14)	0.629(1)	0.4255(7)	0.6620(8)	2.9(5)
C(15)	0.697(1)	0.2945(9)	0.5871(6)	3.2(5)
C(16)	0.711(1)	0.207(1)	0.5795(7)	3.9(6)
C(17)	0.684(1)	0.1449(7)	0.6335(7)	2.6(4)
C(18)	0.6408(9)	0.1780(6)	0.6990(5)	2.1(4)
C(19)	0.6228(8)	0.2698(7)	0.7101(6)	1.9(4)
C(20)	0.648(1)	0.3336(8)	0.6519(6)	2.6(4)
C(21)	0.257(1)	0.1673(8)	0.8903(7)	3.1(5)
C(22)	0.547(1)	0.5565(8)	0.7215(8)	3.1(4)
C(23)	0.315(1)	0.5845(6)	0.9277(6)	2.4(4)
C(24)	0.439(1)	0.627(1)	0.9537(7)	3.5(5)
C(25)	0.223(1)	0.6413(8)	0.8616(8)	4.1(5)
C(26)	0.266(1)	0.5648(8)	1.0055(8)	3.6(5)
C(27)	0.0202(8)	0.3793(8)	0.7653(7)	3.0(4)
C(28)	−0.011(1)	0.448(1)	0.700(1)	4.5(6)
C(29)	−0.036(2)	0.411(1)	0.840(1)	5.2(8)
C(30)	−0.008(1)	0.283(1)	0.751(2)	10(1)
H(1)	0.4514	0.0909	0.9881	2(2)
H(2)	0.6701	0.0541	1.0552	10(6)
H(3)	0.8744	0.0784	1.0630	7(6)
H(4)	0.9326	0.1682	0.9687	5(3)
H(5)	0.7857	0.2379	0.8592	1(1)
H(6)	0.6565	0.4687	0.6268	3(2)
H(7)	0.7201	0.3352	0.5491	2(2)
H(8)	0.7413	0.1849	0.5349	13(8)
H(9)	0.6927	0.0816	0.6260	1(2)
H(10)	0.6230	0.1355	0.7380	1(1)
H(11)	0.2439	0.1848	0.9426	13(8)
H(12)	0.2096	0.2063	0.8482	13(8)
H(13)	0.2313	0.1067	0.8787	1(1)
H(14)	0.6206	0.5901	0.7341	1(1)
H(15)	0.4949	0.5759	0.6703	1(1)
H(16)	0.5081	0.5649	0.7646	1(1)
H(17)	0.4942	0.5904	0.9933	6(4)
H(18)	0.4699	0.6347	0.9061	4(3)
H(19)	0.4350	0.6858	0.9774	12(8)
H(20)	0.2120	0.7002	0.8850	1(1)
H(21)	0.2500	0.6505	0.8142	10(5)
H(22)	0.1450	0.6123	0.8467	4(3)
H(23)	0.2521	0.6197	1.0308	1(1)
H(24)	0.1890	0.5327	0.9872	1(1)
H(25)	0.3210	0.5278	1.0443	9(5)
H(26)	0.0051	0.5074	0.7235	1(1)
H(27)	0.0389	0.4403	0.6619	1(1)
H(28)	−0.0935	0.4442	0.6691	7(4)
H(29)	−0.0121	0.4724	0.8583	3(2)
H(30)	−0.1237	0.4096	0.8246	1(1)
H(31)	−0.0087	0.3728	0.8890	6(4)
H(32)	−0.0956	0.2800	0.7179	1(1)
H(33)	0.0354	0.2607	0.7125	3(1)
H(34)	0.0044	0.2510	0.7968	1(1)

Although the quality of the structure suffers due to some rotational disorder in the *t*-BuO ligands, the observed bond distances and angles are sensible and illuminate some important aspects of bonding in the "$O_4W(=O)$" core. The skeletal structure is that of a trigonal bipyramid which has undergone distortion toward a square pyramidal structure. The oxo unit occupies an equatorial site, and the W—O distance of 1.662(6) Å is typical of five-coordinate tungsten(VI) oxo complexes.[37] The angle subtended by the axial *t*-BuO and naphthoxide ligands compresses to 164.3° (O(3)—W(1)—O(5)), while the *t*-BuO and naphthoxide units that lie in the equatorial plane describe a 136.4° angle (O(2)—W(1)—O(4)). The W—O distances to the naphthoxide and *t*-BuO ligands average 1.952 and 1.818 Å, respectively. The significant 0.134-Å difference between the aryloxide and alkoxide ligands is typical of those observed in other structures containing both binaphtholate and alkoxide ligands.[27,28] The longer $M—O_{Ar}$ distances, which are inherent in aryloxide bonding, have been ascribed to both the poorer basicity and weaker π-donor character of the aryloxide ligands.[38] The somewhat extended W—O—C angles of the *t*-BuO ligands (149.9°(av)) may reflect a degree of π-donation into the d_{xy} orbital on tungsten. In contrast, the W—O—C angles of the naphthoxide moieties (126.4°(av)) are similar to those found in other complexes containing chelating R_2BINO units and are probably largely determined by the conformation of the seven-membered naphthoxide chelate ring.[28] In any case, Rothwell has demonstrated that the character of the $W—O—C_{Ar}$ angle is not a good measure of aryloxide π-donor character.[39] The Λ/Δ stereochemistry of the R_2BINO chelate is defined by the

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(38) Rothwell, I. P.; Chisholm, M. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1987; Vol. 2, Chapter 15.3.

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Table II. Selected Bond Distances and Angles for (Me$_2$BINO)(*t*-BuO)$_2$W(=O)

distances, Å		angles, deg	
W(1)–O(1)	1.662(6)	O(1)–W(1)–O(2)	110.6(3)
W(1)–O(2)	1.952(6)	O(1)–W(1)–O(3)	96.1(3)
W(1)–O(3)	1.953(6)	O(1)–W(1)–O(4)	111.9(4)
W(1)–O(4)	1.804(6)	O(1)–W(1)–O(5)	99.1(3)
W(1)–O(5)	1.832(7)	O(2)–W(1)–O(3)	82.2(2)
C$_{ar}$–O(avg)	1.36	O(2)–W(1)–O(4)	136.4(3)
C$_{Bn}$–O(avg)	1.47	O(2)–W(1)–O(5)	88.8(3)
		O(3)–W(1)–O(4)	84.3(3)
		O(3)–W(1)–O(5)	164.3(3)
		O(2)–W(1)–O(5)	88.8(3)

Scheme III

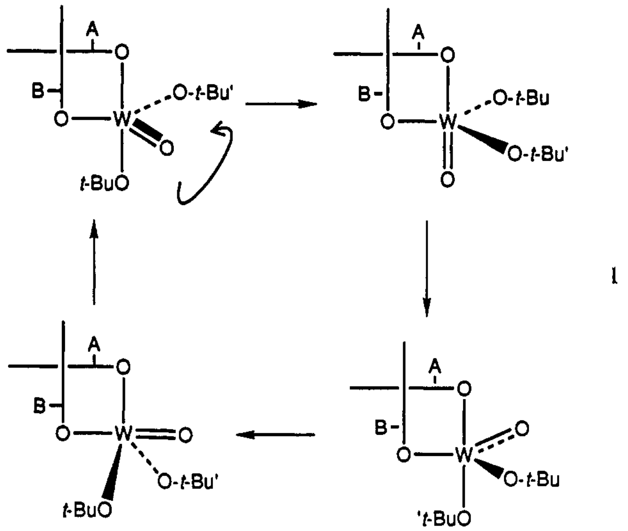

Table III

reagent	conditions	% conversion[a]	c:t ratio[b]
H$_2$BINO + (*t*-BuO)$_3$W(≡CHPh)[c]	15 min, tol	12	2.4
(Me$_2$BINO)(*t*-BuO)$_2$W(=CHPh)	3 h, tol	42	0.92
	15 min, hex	43	1.1
(Me$_2$BINO)$_2$W(=CHPh)	1 day, tol	35	2.3
(Ph$_2$BINO)(*t*-BuO)$_2$W(=CHPh)	1 h, tol	43	3.2
(Me$_2$BINO)(*t*-BuO)$_2$W(=CHPh) + GaBr$_3$	1 h, tol	69	0.41
(Ph$_2$BINO)(*t*-BuO)$_2$W(=CHPh) + GaBr$_3$	1 h, tol	72	0.50

[a] Total percent stilbene recovered. [b] *cis*- to *trans*-stilbene ratio observed by GC. [c] Reaction was run *in situ* via addition of H$_2$BINO to (*t*-BuO)$_3$W(≡CPh) prior to addition of benzaldehyde.

orientation of the ligand with respect to the pseudo-C_2 axis that is coincident with the W=C bond (**3** and **4**, respectively). In the structured (Me$_2$BINO)(*t*-BuO)$_2$W(=O) complex, the chelate adopts Λ stereochemistry.

It should be noted that unlike the (R$_2$BINO)(*t*-BuO)$_2$W(=CHR') complexes, which display C_1 symmetry up to 60 °C in ^{1}H NMR spectra, the (Me$_2$BINO)(*t*-BuO)$_2$W(=O) derivative exhibits fluxional behavior on the NMR time scale at room temperature. During the rearrangement process, the *t*-BuO ligands retain their diastereotopic character, while the two naphtholate environments become equivalent on the NMR time scale. At temperatures approaching −60 °C, the naphtholate environments decoalesce, although the slow exchange limit is not reached by the freezing point of the solvent. This exchange process is probably occurring by the rotation of the W(=O)(O-*t*-Bu)$_2$ tripod with respect to the (Me$_2$BINO)W chelate (Scheme III). It is unclear why this fluxional mechanism is favored for the oxo complex and disfavored for the analogous (R$_2$BINO)(*t*-BuO)$_2$W(=CHR) complexes (*vide infra*), although the π-bonding characteristics of the oxo and alkylidene units vary significantly.[37] Other five-coordinate d^0 complexes have been shown to exhibit such intramolecular rearrangement processes.[40] The exchange process does not proceed through associative intermolecular ligand exchange,[41] because changes in the appearance of the ^{1}H NMR spectra are not sensitive to variations in the concentration of (Me$_2$BINO)(*t*-BuO)$_2$W(=O), as would be expected in an associative (bimolecular) exchange process.

Reactions of (R$_2$BINO)(*t*-BuO)$_2$W(=CHR') and (Me$_2$BINO)$_2$W(=CHPh). In order to determine whether the R$_2$BINO chiral auxiliary ligands influence the stereochemistry of reactions at the alkylidene functionality, some alkylidenation and ring opening metathesis polymerization reactions were surveyed. The yields and stereochemical characteristics of the stilbene isolated from the alkylidenation of benzaldehyde are summarized in Table III. The results indicate that the maximum yield for formation of stilbene from benzaldehyde approaches 50% and that it is difficult to develop a clear rationale for the product stereochemistry based on the presumed steric demands of the ligands. With regard to the reduced yields, it seems likely that some facile decomposition pathway is leading to the deactivation of the alkylidene reagent. Through the choice of a benzaldehyde substrate, we have precluded the ability of alkylidene complexes to isomerize to η^2-olefins,[31] thereby avoiding this pathway for the deactivation of the reagent. Another possibility is that the presumed (R$_2$BINO)(*t*-BuO)$_2$W(=O) byproduct, which is not observable in NMR scale reactions between benzaldehyde and (R$_2$BINO)(*t*-BuO)$_2$W(=CHR), scavenges unreacted alkylidene complex to produce a nonreactive species. To test this hypothesis, (Me$_2$BINO)(*t*-BuO)$_2$W(=CHPh) and (Me$_2$BINO)(*t*-BuO)$_2$W(=O) were mixed in toluene-d_8. The ^{1}H NMR spectrum of the resulting mixture was complex, not simply a superimposition of the spectra of the two starting materials. Furthermore, on addition of a toluene-d_8 solution of benzaldehyde, no evidence of stilbene formation was observed, confirming that (Me$_2$BINO)(*t*-BuO)$_2$W(=O) can deactivate the alkylidene complex. Attempts to isolate the organometallic byproduct of the reaction between the benzylidene complexes and benzaldehyde were unsuccessful.

Both (R$_2$BINO)(*t*-BuO)$_2$W(=CHPh) and (Me$_2$BINO)$_2$W(=CHPh) act as ROMP catalysts, although there are startling differences in their reactivity. While neither catalyst produces a quantitative conversion of norbornene to polynorbornene in 15 min, (Me$_2$BINO)$_2$W(=CHPh) exhibits extremely low activity, generating only 3–5% yields of polymer. The addition of GaBr$_3$ as a Lewis acid cocatalyst markedly increases the activity of (R$_2$BINO)(*t*-BuO)$_2$W(=CHPh), generating virtually instantaneous quantitative yields of polynorbornene at 0 °C. This increased activity probably stems from the abstraction of a terminal *t*-BuO ligand by the Lewis acid gallium reagent, generating a highly active four-coordinate polymerization catalyst [(*t*-BuO)(R$_2$BINO)W(=CHR)]$^+$. This moiety is related to Osborn's structurally characterized [(RO)$_n$Br$_{3-n}$W(=CHR')$^+$][GaBr$_4^-$] systems.[42] In contrast, the addition of GaBr$_3$ to (Me$_2$BINO)$_2$W(=CHPh) has no

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[40] Heppert, J. A.; Chisholm, M. H.; Huffman, J. C.; Onteveros, C. D. *Organometallics* **1989**, *8*, 1199.

[41] Gibson, V. C.; Jolly, M.; Mitchell, J. P. *J. Chem. Soc., Dalton Trans.* **1992**, 1331.

Table IV. Analysis of Polynorbornene Prepared with Alkylidene Catalysts

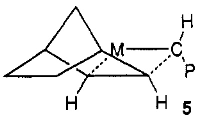
catalyst	*T*, °C	% conversion	*c:t* ratio	M_w/M_n
$(Br_2BINO)(t\text{-}BuO)_2W({=}CHPh)$	0	5	1.1	
$(Me_2BINO)(t\text{-}BuO)_2W({=}CHPh)$	0	21	3.3	
$(Ph_2BINO)(t\text{-}BuO)_2W({=}CHPh)$	0	24	4.4	
$(Me_2BINO)(t\text{-}BuO)_2W({=}CHPh)$	25	48	2.4	2.02
$(Ph_2BINO)(t\text{-}BuO)_2W({=}CHPh)$	25	31	3.9	6.40
$(Br_2BINO)(t\text{-}BuO)_2W({=}CHPh)/GaBr_3$	0	52	0.90	
$(Me_2BINO)(t\text{-}BuO)_2W({=}CHPh)/GaBr_3$	0	100	0.32	1.75
$(Ph_2BINO)(t\text{-}BuO)_2W({=}CHPh)/GaBr_3$	0	94	0.39	2.03

significant effect on the activity of the polymerization catalyst. The chelate effect of the two Me_2BINO units evidently generates a highly stable five-coordinate alkylidene that resists the productive labilization of a naphthoxide unit. This raises the interesting possibility that $(Me_2BINO)(t\text{-}BuO)_2W({=}CHPh)$ complexes may autoionize in solution to generate a catalytically active four-coordinate species. While efforts to test this hypothesis through reactions between $(Me_2BINO)(t\text{-}BuO)_2W({=}CHPh)$ and LiO-*t*-Bu-d_9 yielded evidence that the deuterium label was incorporated into the alkylidene, we were unable to fully characterize the mechanism of this exchange process due to concomitant base-catalyzed decomposition.

The characteristics of the norbornene polymer produced by catalysts derived from the mono- and bis(binaphtholate) derivatives are outlined in Table IV. The ratio of *cis*-polynorbornene generated by $(R_2BINO)(t\text{-}BuO)_2W({=}CHPh)$ varies in concert with increases in the steric demands of the 3,3′-substituents on the R_2BINO ligand (R = Ph > Me > Br). In addition to increasing the rate of the polymerization reaction, the $GaBr_3$ cocatalyst also dramatically decreases the polydispersity of the resulting norbornene polymer. The breadth of the polydispersities observed for $(R_2BINO)(t\text{-}BuO)_2W({=}CHPh)$ may result from either the nonsimultaneous initiation of polymerization in the tungsten alkylidenes or the availability of decomposition pathways akin to those observed in the LiO-*t*-Bu-d_9 initiated process (vide infra). There is circumstantial evidence that only a single catalytic species is involved in these processes, as the fractionation of the polymer with solvents including hexane, ether, and THF yields material samples with identical stereochemical characteristics. The addition of the $GaBr_3$ cocatalyst generates polymer with greater *trans*-olefin content.

To determine that the stereochemical makeup of metathesis-derived polymer is primarily a result of kinetic stereocontrol rather than an equilibrium process, a sample of 90% *cis*-polynorbornene was exposed to $(Me_2BINO)(t\text{-}BuO)_2W({=}CHPh)$ both with and without $GaBr_3$. These catalysts generate samples of polynorbornene whose *Z:E* ratios are closer to unity, and we would expect them to substantially increase the *trans* content of the 90% *cis*-polynorbornene if they induce secondary metathesis in the polymer. On a time scale 2 orders of magnitude longer than the initial polymerization event, $(Me_2BINO)(t\text{-}BuO)_2W({=}CHPh)$ failed to produce any measurable change in either the initial quantity of high polymer or the stereochemistry of the recovered sample. Mixtures of $(Me_2BINO)(t\text{-}BuO)_2W({=}CHPh)$ and $GaBr_3$ produced up to 25% degradation of the *cis* polymer over the 15-min period of the initial polymerization reaction; however, during this period, the remaining high molecular weight polymer displayed no substantial isomerization of its original *cis* double bond stereochemistry. But this experiment provides only an upper limit on the ability of secondary metathesis to influence the stereochemistry of the polymerization process. Significant concentrations of monomer, such as those present during polymer formation, can sometimes suppress secondary metathetic processes.[7a,43] A more realistic test of the influence of secondary metathesis on product stereochemistry would be obtained by polymerizing a sample of norbornene in the presence of preformed *all-cis*-polynorbornene: the isolation of a product mixture whose stereochemistry corresponds to a 1:1 mixture of the preformed *all-cis* polymer and the newly formed polynorbornene would be a strong indication that secondary metathesis processes were suppressed by the presence of the unreacted monomer.[44] This experiment was performed with the $(Me_2BINO)(t\text{-}BuO)_2W({=}CHR)/GaBr_3$ catalyst, and the isolated polymer proved to be a 1:1 mixture of preformed 90% *cis*-polynorbornene and newly formed 24% *cis*-polynorbornene. We conclude that secondary metathesis plays only a minor role, if any, in the determination of product stereochemistry.

In the instance of catalysts derived from $(R_2BINO)(t\text{-}BuO)_2W({=}CHPh)$, it is evident that the influence of the steric demands of the ligands and the coordination number of the complexes are the primary factors in determining polymer stereochemistry. While secondary metathesis processes may exert some influence over polymer stereochemistry in reaction systems employing a $GaBr_3$ cocatalyst, it is evidently steric and electronic influences on the free energies of transition states leading to *E* and *Z* bond formation that dominate the stereoselectivity observed in these results. Although it is not possible to speculate on the precise characteristics of the catalysts that control the selectivity of the polymerization, it is intuitively satisfying that increasing the steric demands of the appended ligands favors the formation of the *Z* polymer, which is derived from a less hindered *all-cis*-metallocyclobutane intermediate (**6**). This result is in accord with trends observed by Basset for variations in the steric demands of substituents on 2,6-disubstituted phenoxide ligands bound to ROMP procatalysts.[23]



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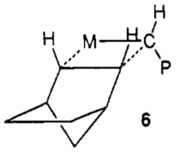

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Future studies will be directed toward improving the stability of the asymmetric tungsten catalysts, probing the ability of such complexes to control polymerization tacticity, and more fully defining the precise topological characteristics of the ligands that influence metathesis stereochemistry.

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(44) We acknowledge the insight of one of the reviewers, who suggested this experiment for setting a reasonable lower limit on the influence of secondary metathetic processes.

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Experimental Section

All reactions were carried out under a prepurified nitrogen atmosphere by using standard Schlenk, glovebox, and vacuum line techniques. All solvents were distilled under nitrogen over appropriate drying agents. NMR solvents were dried over 5-Å molecular sieves and degassed with a dry N_2 purge. ^{1}H and ^{13}C spectra were obtained on a Varian XL-300 MHz or a Bruker AM 500 MHz spectrometer. ^{1}H NMR spectra were referenced against the residual proton impurity in benzene-d_6 or toluene-d_8, while ^{13}C NMR spectra were referenced against either the resonances representing the aromatic carbon of benzene-d_6 or the methyl group carbon of toluene-d_8. Elemental analyses were performed by Desert Analytics, P.O. Box 41838, Tucson, AZ 85717, or Schwarzkopf Microanalytical Laboratory, 56-19 37th Ave., Woodside, NY 11377. 1,1′-Bi-2-naphthol (Kodak) was purified by filtration of a methylene chloride solution through silica gel, followed by recrystallization. (*R*)-(+)-1,1′-bi-2-naphthol (Aldrich) was used as received. 3,3′-Disubstituted-1,1′-bi-2-naphthols[45] (methyl, bromo, and phenyl) were prepared by slight alterations of literature methods. $\mathrm{W({\equiv}CR)(O\text{-}\mathit{t}\text{-}Bu)_3}$ and $\mathrm{W({=}O)(O\text{-}\mathit{t}\text{-}Bu)_4}$ were prepared as described in the literature.[46,47]

Typical Synthetic Details for $\mathbf{(R_2BINO)_{2-n}(\mathit{t}\text{-}BuO)_{2n}W({=}CHPh)}$ (n = 0 or 1). Synthesis of $\mathbf{(Me_2BINO)(\mathit{t}\text{-}BuO)_2W({=}CHPh)}$. $\mathrm{(\mathit{t}\text{-}BuO)_3W({\equiv}CPh)}$ (0.78 g) was placed in a small Schlenk flask (25 mL) and dissolved in dry toluene. $\mathrm{H_2Me_2BINO}$ (0.50 g) was added to the stirred solution at 0 °C. The reaction was allowed to warm slowly to room temperature. After stirring for 12 h, the solution was stripped to dryness. Redissolving the solid in toluene followed by drastic reduction of the solution volume and refrigeration at −20 °C overnight yielded an orange-brown powder. Yield: 72% (0.83 g). ^{1}H NMR data (benzene-d_6, 20 °C): δ = 8.69 (1H, s, J = 11.7 Hz, W=C*H*Ph), 7.71–7.49 (m, Ar), 7.17–6.83 (m, Ar), 6.53–6.47 (m, Ar), 2.73 (3H, s, Me), 2.43 (3H, s, Me), 1.36 (9H, s, $\mathrm{OC(CH_3)_3}$), 1.29 (9H, s, $\mathrm{OC(CH_3)_3}$, 1.29 (9H, s, $\mathrm{OC(CH_3)_3}$). ^{13}C NMR data (toluene-d_8, 20 °C): δ = 244.5 ($J_{\mathrm{W-C}}$ = 189 Hz, W*C*HPh), 166.0, 156.4 (Nap $\mathrm{C_{2,2'}}$), 133.2, 132.6, 132.0, 130.4, 130.0, 129.3, 128.7, 127.5, 127.4, 126.6, 125.0, 124.2, 122.7, 116.3 (Ar), 89.2, 80.4 ($\mathrm{O\mathit{C}(CH_3)_3}$), 31.8, 30.1 ($\mathrm{OC(\mathit{C}H_3)_3}$), 23.1, 19.3 (Me). Anal. Calcd: C, 60.66; H, 5.05. Found: C, 60.74; H, 5.54.

Presentation of Analytical Data. $\mathbf{(Ph_2BINO)(\mathit{t}\text{-}BuO)_2W({=}CHPh)}$. ^{1}H NMR data (benzene-d_6, 20 °C): δ = 8.69 (1H, s, J = 12.2 Hz, W=C*H*Ph), 7.40 (2H, d, J = 9.8 Hz, Ar), 7.69–7.67 (m, Ar), 7.58 (2H, t, J = 4.6 Hz, Ar), 7.23–6.99 (m, Ar), 6.92 (1H, t, J = 1.6 Hz, Ar), 6.83 (2H, t, J = 7.8 Hz, Ar), 6.31 (2H, d, J = 7.4 Hz, Ar), 6.23 (2H, d, J = 7.4 Hz, Ar), 1.46 (9H, s, $\mathrm{OC(CH_3)_3}$), 0.94 (9H, s, $\mathrm{OC(CH_3)_3}$). ^{13}C NMR data (benzene-d_6, 20 °C): δ = 250.6 ($J_{\mathrm{W-C}}$ = 187 Hz, WC*H*Ph) 164.9, 155.7 (Nap $\mathrm{C_{2,2'}}$), 140.8, 140.7, 135.2, 134.7, 134.2, 133.9, 133.5, 132.4, 132.3, 131.4, 130.6, 130.4, 130.3, 130.2, 130.0, 129.2, 128.7, 128.5, 128.4, 128.3, 127.5, 127.2, 127.0, 126.4, 126.2, 126.1, 125.9, 125.8, 125.6, 124.9, 123.6, 122.8, 117.8 (Ar), 88.4, 80.6 ($\mathrm{O\mathit{C}(CH_3)_3}$), 31.2, 29.9 ($\mathrm{OC(\mathit{C}H_3)_3}$). Anal. Calcd: C, 65.89; H, 5.18. Found: C, 66.54; H, 5.24.

$\mathbf{(Me_2BINO)_2W({=}CHPh)}$. ^{1}H NMR data ($\mathrm{CDCl_3}$, 20 °C): δ = 8.67 (1H, s, $J_{\mathrm{W-H}}$ = 12.0 Hz, W(=C*H*Ph)), 7.73 (2H, d, J = 8.5 Hz, Nap), 7.67 (2H, s, Nap), 7.58 (2H, d, J = 8.1 Hz, Nap), 7.52 (2H, s, Nap), 7.29–7.24 (m, Nap), 7.19–7.02 (m, Nap), 6.50 (2H, t, J = 7.7 Hz, *m*-Ar), 6.08 (1H, t, J = 7.4 Hz, *p*-Ar), 5.74 (2H, d, J = 7.9 Hz, *o*-Ar), 2.52 (6H, s, Me), 2.39 (6H, s, Me). ^{13}C NMR data ($\mathrm{CDCl_3}$, 20 °C): δ = 256.0 ($J_{\mathrm{W-C}}$ = 196 Hz, W(=*C*HPh)), 162.4, 157.5 (Nap $\mathrm{C_{2,2'}}$), 134.8, 132.3, 131.9, 131.3, 130.8, 130.0, 129.8, 129.3, 129.0, 128.7, 128.2, 128.1, 127.3, 127.0, 126.3, 125.3, 125.1, 125.0, 124.0, 123.9, 123.3, 121.6, 113.7 (Ar), 18.2, 18.0 ($\mathrm{Me_{3,3'}}$). Anal. Cald: C, 68.16; H, 4.26. Found: C, 69.17; H, 4.36.

$\mathbf{(Br_2BINO)(\mathit{t}\text{-}BuO)_2W({=}CHPh)}$. $\mathrm{(\mathit{t}\text{-}BuO)_3W({\equiv}CPh)}$ (0.500 g, 1.02 mmol) was dissolved in dry toluene under N_2 and cooled to 0 °C. $\mathrm{H_2Br_2BINO}$ (0.434 g, 1.02 mmol) was slowly added to the solution via an addition tube. The resulting solution gradually warmed to ambient temperature and was stirred overnight and stripped *in vacuo*, and the residue washed with dry hexane. The mixture was filtered, and the soluble portion was stripped to dryness. This product is unstable at ambient temperature, decomposing even in the solid state. ^{1}H NMR data (benzene-d_6, 18 °C): δ = 9.18 (1H, s, $J_{\mathrm{W-H}}$ = 13 Hz (estimated), W=C*H*Ph), 8.00 (1H, s, Nap), 7.86 (1H, s, Nap), 7.34 (2H, t, J = 9.0 Hz, Nap), 7.27 (1H, d, J = 7.5 Hz, Nap), 7.21 (1H, d, J = 7.5 Hz, Nap), 6.97–6.75 (6H, m, Nap and Ar), 6.44 (2H, d, J = 7.5 Hz, Ar), 6.29 (1H, t, J = 7.0 Hz, Ar), 1.44 (9H, s, $\mathrm{OC\mathit{Me}_3}$), 1.40 (9H, s, $\mathrm{OC\mathit{Me}_3}$). ^{13}C NMR data (benzene-d_6): δ = 249.8 (W=*C*HPh), 162.5, 154.3 (Nap $\mathrm{C_{2,2'}}$), 133.6, 132.6, 131.8, 131.7, 130.4, 129.4, 128.5, 128.4, 127.5, 127.3, 127.2, 126.3, 126.2, 126.0, 125.9, 125.7, 123.2, 118.4, 118.0 (Nap), 90.5, 81.6 ($\mathrm{O\mathit{C}Me_3}$), 31.9, 30.0 ($\mathrm{OC\mathit{Me}_3}$).

Synthesis of $\mathbf{(Me_2BINO)(\mathit{t}\text{-}BuO)_2W\{{=}CH(CH(CH_3)_2)\}}$. $\mathrm{(\mathit{t}\text{-}BuO)_3W\{{\equiv}C(CH(CH_3)_2)\}}$ (0.38 g, 0.83 mmol) was placed in a small Schlenk flask (25 mL) and dissolved in dry toluene, and the solution was cooled to 0 °C. 3,3′-Dimethyl-1,1′-bi-2-naphthol (0.26 g, 0.83 mmol) was added slowly via an addition tube. The reaction was allowed to warm to room temperature, and after stirring for 12 h, the solvent was removed *in vacuo*. Redissolving the solid in toluene followed by drastic reduction of the solution volume and refrigeration at −20 °C overnight yielded an orange powder (0.22 g, 39% yield). ^{1}H NMR data (toluene-d_8, 20 °C): δ = 8.15 (1H, d, J = 6.2 Hz, $J_{\mathrm{W-H}}$ = 13.6 Hz, $\mathrm{W\{{=}CH(CH(CH_3)_2)\}}$), 7.74 (1H, d, J = 8.2 Hz, Ar), 7.72 (1H, s, Ar), 7.60 (1H, d, J = 8.5 Hz, Ar), 7.51 (1H, s, Ar), 7.46 (1H, d, J = 8.4 Hz, Ar), 7.3 (1H, d, J = 8.9 Hz, Ar), 7.14–7.08 (2H, m, Ar), 6.95 (1H, t, J = 8.2 Hz, Ar), 6.86 (1H, t, J = 7.1 Hz, Ar), 4.60–4.53 (1H, m, $\mathrm{C\mathit{H}(CH_3)_2}$), 2.69 (6H, s, $\mathrm{Me_{3,3'}}$), 1.45 (9H, s, $\mathrm{OC(\mathit{CH}_3)_3}$), 1.24 (9H, s, $\mathrm{OC(\mathit{CH}_3)_3}$), 0.76 (3H, d, J = 6.7 Hz, $\mathrm{CH(\mathit{CH}_3)_2}$), 0.59 (3H, d, J = 6.7 Hz, $\mathrm{CH(\mathit{CH}_3)_2}$). ^{13}C NMR data (toluene-d_8, 20 °C): δ = 255.6 ($J_{\mathrm{W-C}}$ = 189 Hz, $\mathrm{W\{{=}\mathit{C}H(CH(CH_3)_2)\}}$), 165.8, 156.3 (NAP $\mathrm{C_{2,2'}}$), 133.6, 132.7, 131.7, 130.3, 130.2, 130.0, 129.5, 128.6, 128.2, 127.5, 127.3, 126.7, 124.8, 124.7, 123.2, 122.7, 116.9 (Ar), 87.7, 78.4 ($\mathrm{O\mathit{C}(CH_3)}$), 39.2 ($\mathrm{\mathit{C}H(CH_3)_2}$) 32.0, 29.9 ($\mathrm{OC(\mathit{C}H_3)_3}$), 27.4, 26.8 ($\mathrm{Me_{3,3'}}$), 19.6, 19.3 ($\mathrm{CH(\mathit{C}H_3)_2}$). Anal. Calcd: C, 58.46; H, 6.06. Found: C, 57.86; H, 6.07.

Synthesis of $\mathbf{(Me_2BINO)(\mathit{t}\text{-}BuO)_2W\{{=}CH(C(CH_3)_3)\}}$. $\mathrm{(\mathit{t}\text{-}BuO)_3W\{{\equiv}C(CH_3)_3\}}$ (0.60 g, 1.3 mmol) was placed in a small Schlenk flask (25 mL) and dissolved in dry toluene, and the solution was cooled to 0 °C. 3,3′-Dimethyl-1,1′-bi-2-naphthol (0.40 g, 1.3 mmol) was added slowly via an addition tube. The reaction was allowed to warm to room temperature, and after stirring for 12 h, the solvent was removed *in vacuo*. Redissolving the solid in methylene chloride followed by layering with hexanes and refrigeration at −20 °C overnight yielded orange microcrystals (0.29 g, 32% yield). ^{1}H NMR data (benzene-d_6, 20 °C): δ = 7.80 (1H, d, J = 8.2 Hz, Ar), 7.76 (1H, s, $J_{\mathrm{W-H}}$ = 14.1 Hz, $\mathrm{W\{{=}C\mathit{H}(C(CH_3)_3)\}}$), 7.64 (1H, d, J = 8.1 Hz, Ar), 7.54 (1H, s, Ar), 7.53 (1H, d, J = 8.8 Hz, Ar), 7.44 (1H, d, J = 8.6 Hz, Ar), 7.17–7.14 (1H, m, Ar), 7.10 (1H, t, J = 7.4 Hz, Ar), 6.97 (1H, t, J = 7.3 Hz, Ar), 6.85 (1H, t, J = 7.3 Hz, Ar), 2.72 (3H, s, Me), 2.71 (3H, s, Me), 1.46 (9H, s, $\mathrm{OC(C\mathit{H}_3)_3}$), 1.23 (9H, s, $\mathrm{OC(C\mathit{H}_3)_3}$), 0.87 (9H,

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s, C(CH_3)$_3$). ^{13}C NMR data (benzene-d_6, 20 °C): $\delta = 254.9$ ($J_{\mathrm{W-C}}$ = 191 Hz, W{=*C*H(CH(CH$_3$)$_3$)}), 165.8, 156.4 (NAP $C_{2,2'}$), 133.8, 132.7, 131.7, 130.4, 130.3, 130.0, 129.5, 128.6, 128.4, 127.5, 127.3, 126.7, 125.0, 124.8, 123.1, 122.8, 117.1 (Ar), 80.6, 78.1 (O*C*(CH$_3$)$_3$), 41.9 (*C*(CH$_3$)$_3$), 34.3, 32.6 (OC(*C*H$_3$)$_3$), 29.9 (C(*C*H$_3$)$_3$), 19.9, 19.3 (Me$_{3,3'}$). Anal. Calcd: C, 58.99; H, 6.22. Found: C, 59.12; H, 6.47.

Synthesis of (Me$_2$BINO)W(=O)(O-*t*-Bu)$_2$. W(O)(O-*t*-Bu)$_4$ (0.80 g, 1.6 mmol) was placed in a small Schlenk flask (50 mL) and dissolved in toluene (20 mL). H$_2$Me$_2$BINO (0.50 g, 1.6 mmol) was added via an addition tube to the stirred solution at 0 °C, giving an orange solution. The solution was warmed to ambient temperature overnight. The solvent was removed *in vacuo*, and the solid residue was washed with hexanes and recrystallized from CH$_2$Cl$_2$/hexanes to give yellow crystals (0.5 g, 50% yield). ^{1}H NMR data (benzene-d_6, 20 °C): $\delta = 7.69$ (2H, d, $J = 8.1$ Hz, NAP), 7.61 (2H, s, NAP), 7.50 (2H, d, $J = 8.6$ Hz, NAP), 7.14 (2H, t, $J = 6.9$ Hz, NAP), 6.94 (2H, t, $J = 7.0$ Hz, NAP), 2.67 (6H, s, Me$_{3,3'}$), 1.36, 1.18 (9H, s, OC(CH$_3$)$_3$). ^{13}C NMR data (benzene-d_6, 20 °C): $\delta = 157.8$ (NAP $C_{2,2'}$), 132.3, 130.8, 129.3, 127.3, 125.0, 124.0, 119.2 (NAP), 87.6, 85.7 (O*C*(CH$_3$)$_3$), 29.9, 29.4 (OC(*C*H$_3$)$_3$), 18.4 (Me$_{3,3'}$). Anal. Calcd: C, 54.72; H, 5.20. Found: C, 54.59; H, 5.16.

Polymerization Studies. All polymerizations were performed under N$_2$ in small round bottom flasks, which were fitted with septum caps and magnetically stirred. A stock solution of norbornene was prepared by dissolving norbornene in dry, O$_2$-free toluene over molecular sieves. This solution was degassed rigorously by two freeze–pump–thaw cycles. Appropriate quantities of this stock solution were syringed into the round bottoms. The solutions were cooled to 0 °C, except those performed at room temperature. Catalysts were dissolved in 5 mL of dry toluene under N$_2$ and syringed into the round bottoms. After 15 min, the reactions were quenched with acetone. The polymers were washed repeatedly with methanol and dried *in vacuo*. ^{1}H and ^{13}C NMR spectroscopy were used to determine polymer stereochemistry.

Secondary Metathetic Studies. (a) *cis*-Polynorbornene (90%) was dissolved in toluene (15 mL) at ambient temperature under N$_2$. Various catalysts were dissolved in dry toluene (5 mL) at ambient temperature and syringed into the magnetically stirred polynorbornene solution. After 24 h, the catalysts were quenched with acetone and washed with methanol. Residues were dried *in vacuo* and weighed to determine the mass loss of the high molecular weight polymer. Studies were also performed on the time scale of the initial polymerizations (15 min). ^{13}C NMR spectroscopy was used to determine the stereochemistry of all product fractions. (b) *cis*-Polynorbornene (90%) (163 mg) was dissolved in a toluene solution containing norbornene (163 mg) at ambient temperature under N$_2$. A catalyst solution (5 mL) containing (Me$_2$BINO)(*t*-BuO)W(=CHPh)/GaBr$_3$ was syringed into the magnetically stirred solution of the monomer and polymer. After 15 min the reaction was quenched and worked up as noted in procedure a above. Total polymer recovered = 92% (301 mg). Expected *cis:trans* ratio for a simple mixture of preformed and newly formed polymer: calcd = 1.0:1.5; obsd = 1.0:1.7. Note that the expected stereochemistry for a polymer that had undergone complete stereochemical redistribution by this catalyst would be a *cis:trans* ratio of 1.0:0.32.

X-ray Structure Analysis for (Me$_2$BINO)W(=O)(O-*t*-Bu)$_2$. A yellow prismatic crystal of approximate dimensions 0.15 × 0.15 × 0.10 mm was covered in Paratone D oil in an inert atmosphere box, transferred into the air, and mounted on a glass fiber on a goniostat head. The sample was transferred to a Rigaku AFC 5R diffractometer equipped with a low-temperature unit. X-ray diffraction data were collected with monochromated Cu Kα radiation using a 12-kW rotating anode at 113 ± 1 K. The crystal data were as follows: space group $P2_1/n$ (No. 14) based on systematic absences $h0l$: $h + 1 \neq 2n + 1$, $0k0$: $k \neq 2n + 1$; cell dimensions, $a = 11.426(3)$ Å, $b = 14.733(3)$ Å, $c = 16.716(4)$ Å, $\beta = 105.87(2)°$; $Z = 4$, $D_{\mathrm{calc}} = 1.616$ g cm^{-3}. Of the 3968 reflections collected, 3749 were unique ($R_{\mathrm{int}} = 0.104$). The intensities of three representative reflections measured after every 150 reflections remained constant throughout the data collection. An empirical absorption correction was applied (absorption coefficient for Cu Kα = 82.8 cm^{-1}), resulting in transmission factors ranging from 0.446 to 1.00. The data were corrected for Lorentz and polarization effects. The structure was solved by a combination of Patterson and direct methods. Non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed in calculated positions and their thermal parameters were refined isotropically. The final cycle of the full-matrix least squares refinement was based on 3451 observed reflections ($I > 0.01\sigma(I)$) and 359 variable parameters. The refinement converged to $R = 0.053$ and $R_w = 0.106$. The largest positional parameter shift was 0.59 times its esd. The maximum and minimum peaks in the final difference map corresponded to +2.29 and −2.03 e Å^{-3} in the vicinity of the tungsten atom. Neutral atom scattering factors were taken from Cromer and Waber.[48] Anomalous dispersion effects were included in F_{calc}; values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[49] All calculations were performed using the TEXSAN crystallographic software package from Molecular Structure Corp.[50]

Supplementary Material Available: Tables of experimental details, positional parameters, thermal parameters, and distances and angles for (Me$_2$BINO)W(=O)(O-*t*-Bu)$_2$ (14 pages). Ordering information is given on any current masthead page.

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