1698 *Inorg. Chem.* **1993,** *32,* 1698–1705

Binaphtholate and Binaphtholate Chloride Complexes of Tungsten(VI)

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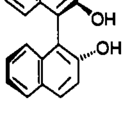
Received July 29, 1992

A range of 1,1′-bi-2-naphthol (H_2BINO) derivatives react with WCl_6 in toluene to generate a new family of $W(R_2BINO)_{3-n}Cl_{2n}$ derivatives. Reactions between excess 3,3′-diphenyl-1,1′-bi-2-naphthol (H_2Ph_2BINO) and WCl_6 generate only the monosubstituted $W(Ph_2BINO)Cl_4$ product. The less sterically demanding H_2Me_2BINO ligand produces minor quantities of various bis-Me_2BINO-substituted isomers, together with *trans*-(R^*,R^*)-$W(Me_2BINO)_2Cl_2$, which is the overwhelmingly favored product. The parent H_2BINO ligand generates two of four possible $W(BINO)_3$ diastereomers, with (S^*,S^*,S^*)-$W(BINO)_3$ and (S^*,S^*,R^*)-$W(BINO)_3$ diastereomers being produced in statistically predicted quantities. Molecular modeling and spectroscopic studies indicate that the S^*,S^*,S^* and S^*,S^*,R^* isomers prefer to adopt Δ^* rather than Λ^* overall complex stereochemistry. This preference stems from a minimization of interligand interactions between (*S*)-BINO ligands in Δ diastereomers. There is relatively little difference between the stereochemistry of polynorbornene prepared employing the $W(R_2BINO)_{3-n}Cl_{2n}$ complexes as precatalysts. This may arise, in part, from the ability of the catalysts to engage in secondary metathesis reactions. The $(BINO)_3W$ complexes are not activated for ring opening metathesis polymerization catalysis at −70 °C, apparently because the slow rate of ligand exchange at this temperature does not allow the metal to open a coordination site.

Complexes containing early transition metals in either their highest or penultimate oxidation states have recently matured as reagents and catalysts for bond-forming reactions.[1-26] Such species operate through a variety of fundamental reaction types, including insertion,[1-14] C–H bond activation,[15] O-atom transfer,[16-20] and electrocyclic pathways.[21-23] As exemplified by the Sharpless–Katsuki epoxidation catalyst, the potential significance of early transition metal species bearing chiral auxiliary ligands in asymmetric transformations is now genuinely appreciated.[19] A range of related complexes designed to catalyze stereo- and enantiospecific oxidation reactions, electrocyclic processes, and α-olefin polymerizations are now being developed.[8-14,16-26]

Among this range of elegant and selective catalyst systems, it is apparent that there is a continued need to obtain fundamental knowledge about the structure and function of the catalytically active species. In part, this stems from the sheer complexity of the catalytic processes in question. For example, controversy continues to surround the structure of the active intermediate and mechanism of action of the Sharpless–Katsuki catalyst, despite the extensive structural and mechanistic characterization of this system.[19,20] While the empirical approach to the development of asymmetric early transition metal catalysts has been a useful strategy, more and more efforts to effect the rational design of such catalysts are gaining success.[16-18] The continued development of structure–reactivity and structure–selectivity relationships will be a step toward fully defining the mechanisms through which these systems act and toward the rational development of future generations of catalysts.



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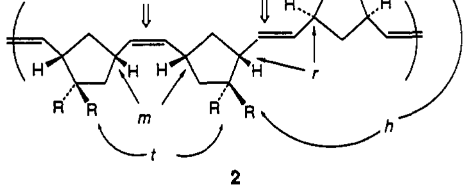

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Over the past several years, we have been particularly concerned with the coordination chemistry of 1,1′-bi-2-naphthol (**1**, H_2BINO),[27-29] a C_2-symmetric bis(phenoxide) that has become an important ligand in Lewis-acidic metal catalysts.[30-33] The goals of these studies have been to (1) examine the fundamental

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chemistry of the BINO ligand, (2) explore the stereochemistry and structural characteristics of group 4 and 6 complexes bearing one or more R_2BINO ligands, (3) evaluate the potential stereoelectronic influences introduced by this bidentate asymmetric moiety and (4) establish new classes of stoichiometric and catalytic reactions whose stereochemistry can be influenced by the R_2BINO unit. Asymmetric group 6 complexes could find a particularly important application as precatalysts for ring opening metathesis polymerization (ROMP). From the inception of metathesis polymerization, d^0 tungsten catalysts, in particular WCl_6, have been a mainstay of industrial polymerization methodology.[34,35] The modern relatives of these early high-oxidation-state catalysts, including $W(OAr)_{4-n}Cl_n({=}O)$[36] and polyoxomolybdate procatalysts,[37] as well as the Schrock $W(OR)_2({=}CH\text{-}t\text{-}Bu)({=}NAr)$[38] and Osborn $[W(OR)_{3-n}Cl_n({=}CHR)]^+$[39] living homogeneous catalysts, maintain a central role in both industrial and academic investigations.

Conceptually, variations in the three pertinent aspects of polynorbornene stereochemistry—the cis/trans ratio, the tacticity, and the head-and-tail relationship (2)—should be controllable within the framework of a series of isostructural polymerization catalysts, providing that the choice of ligand systems allows the convenient systematic variation of ligand topology, and the steric and electronic characteristics of the metal center. One logical strategy for influencing the stereochemistry of ROMP processes is to modify a simple "industrial" precatalyst such as WCl_6 with asymmetric diolate ligands.[40] In this paper, we outline our studies of the coordination chemistry of R_2BINO ligands at an octahedral d^0 tungsten center and discuss the use of these asymmetric chelate complexes as precatalysts for the ROMP of norbornene.

Results and Discussion

Synthesis of W(Ph_2BINO)Cl_4. A direct alcoholysis reaction between WCl_6 and H_2Ph_2BINO produces W(Ph_2BINO)Cl_4 (3) in good yield as a purple microcrystalline powder (eq 1). Repeated

$$H_2Ph_2BINO + WCl_6 \xrightarrow{\text{toluene}} W(Ph_2BINO)Cl_4 + 2HCl \quad (1)$$

attempts to obtain X-ray quality crystals of 3 from a variety of solvents were unsuccessful, as were similar efforts for all of the binaphtholate tungsten(VI) halides prepared in this study. The NMR spectroscopy of 3 was consistent with the expected C_2-symmetric structure of the complex and betrayed the presence of a small quantity of cocrystallized CH_2Cl_2. Attempts to synthesize a bis-Ph_2BINO-substituted analog of 3 were unsuccessful, even on refluxing excess H_2Ph_2BINO and WCl_6 in toluene.

Efforts to prepare other examples of W(R_2BINO)Cl_4 derivatives were frustrated by a variety of factors. Syntheses employing stoichiometric quantities of H_2Me_2BINO and WCl_6 invariably led to the isolation of W(Me_2BINO)$_2Cl_2$ products (vide infra). It appears, based on the dearth of evidence for a mono-Me_2BINO product in NMR spectra of crude reaction mixtures, that the bis-Me_2BINO complex is a thermodynamically more stable product. Attempts to generate $(R_3Si)_2$BINO-substituted tungsten(VI) halides via either alcoholysis reactions or metathesis reactions with a $Li_2(R_3Si)_2$BINO reagent also failed (Scheme I), in the former case because facile protodesilylation of the $(R_3Si)_2$BINO ligand resulted in the isolation of a W(BINO)$_3$ product (vide infra) and in the latter case because the material obtained was uncharacterizable. Unlike some previously reported titanium(IV) chemistry, repeated attempts to employ lithium binaphtholate salts in anion metathesis methodology proved unsuccessful in this study of tungsten(VI) species.[27]

Scheme I

$$\begin{tikzcd}
H_2(t\text{-}BuMe_2Si)_2BINO + WCl_6 \arrow[r, "\text{toluene}", "\text{reflux}"'] \arrow[d, "\text{2 }n\text{-BuLi}"', "\text{ether}"] & W(BINO)_3 + t\text{-}BuMe_2SiCl \\
Li_2(t\text{-}BuMe_2Si)_2BINO + WCl_6 \arrow[r, "\text{ether}"] & \text{uncharacterized material}
\end{tikzcd}$$

The stereochemistry of 3 is quite straightforward even by comparison with monoethylenediamine complexes.[41] Of course, the single chelate interaction between the R_2BINO unit and the metal generates no element of metal-derived stereochemistry. This is distinct from bridging R_2BINO ligands in $W_2(R_2\text{BINO})_{3-n}(O\text{-}t\text{-}Bu)_{2n}$ complexes, in which even a single R_2BINO bridge generates an O–W–W–O dihedral that possesses inherent λ or δ stereochemistry (Scheme IIa).[28] Furthermore, unlike ethylenediamine, the R_2BINO unit possesses a fixed element of conformational (helical) stereochemistry based on the restricted torsional ability of the 1,1′-fused binaphtholate unit (Scheme IIb). Consequently, the (*R*)-R_2BINO ligand exhibits persistent λ stereochemistry as a ligand, while the (*S*)-R_2BINO unit necessarily exhibits δ stereochemistry.

Synthesis and Stereochemistry of (Me_2BINO)$_2WCl_2$. When *rac*-H_2Me_2BINO and WCl_6 are allowed to react in toluene solution, ^{1}H NMR spectra of the crude reaction mixtures indicate that a range of products is formed. The major dark red-purple product formed at ambient temperature can be purified by fractional crystallization from CH_2Cl_2/hexane and is identified as W(Me_2BINO)$_2Cl_2$ (4) (eq 2). Compound 4 possesses high

$$2H_2Me_2BINO + WCl_6 \xrightarrow{\text{toluene}} W(Me_2BINO)_2Cl_2 + 4HCl \quad (2)$$

symmetry, based on ^{1}H NMR spectra acquired over a broad temperature range (−50 to +23 °C). Attempts to synthesize isolable yields of tris-Me_2BINO-substituted complexes in refluxing toluene or mono-Me_2BINO complexes at reduced temperature using H_2Me_2BINO as a limiting reagent were equally unsuccessful. All of these reactions resulted in varying yields of the products observed in the initial reaction to form 4.

Five distinct isomers, not considering enantiomers, of W(Me_2BINO)$_2Cl_2$ could be formed during reactions with *rac*-H_2Me_2BINO (Chart I). The complexity of spectra of the crude reaction mixture obviously indicates that many of these isomers are either formed kinetically or possess similar (±2 kcal/mol) relative thermodynamic stabilities. The two trans-substituted isomers are the C_{2h}-symmetric *trans*-(*R*,*S*)-W(Me_2BINO)$_2Cl_2$ which is a *meso* compound, and the D_2-symmetric *trans-rac*-W(Me_2BINO)$_2Cl_2$, which exists as (*R*,*R*) and (*S*,*S*) optical antipodes (Chart I). The cis isomers, differentiated by both the stereochemistry of the appended R_2BINO ligands and the Δ/Λ isomerism of the cis chelates, exist as three pairs of enantiomers. Table I lists the ratio of the products expected for a statistical distribution of the W(Me_2BINO)$_2Cl_2$ complexes and the relative number and intensity of the methyl resonances expected in the

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Scheme II. Stereochemistry of the R_2BINO Ligand

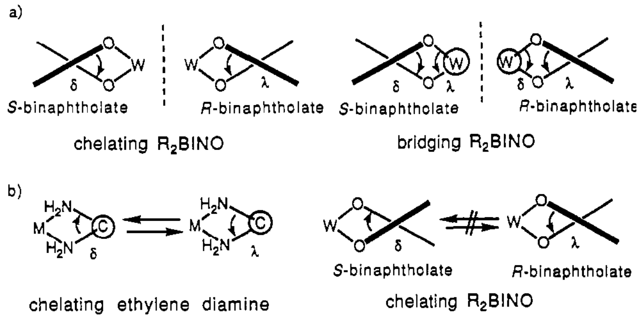

Chart I. Structural Isomers of $W(Me_2BINO)_2Cl_2$

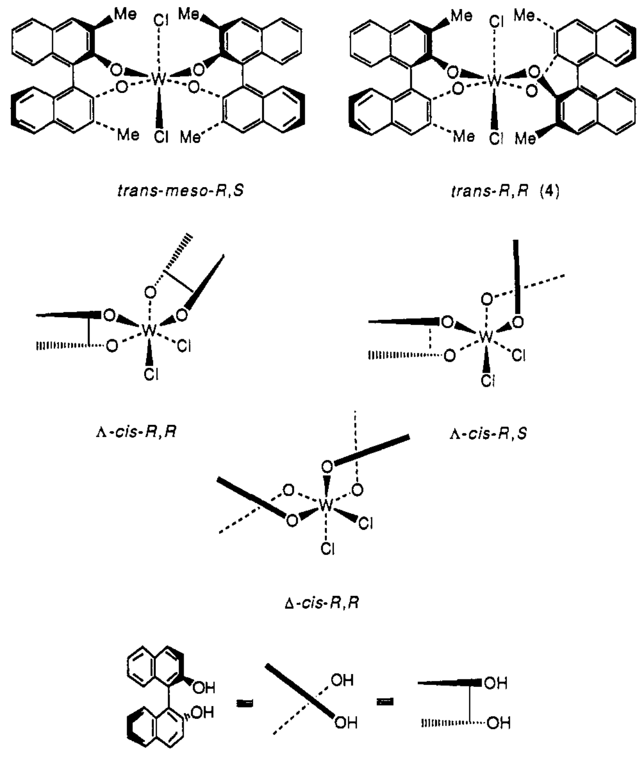

Table I. Expected Symmetry and Spectroscopic Characteristics of $W(Me_2BINO)_2Cl_2$ and $W(BINO)_3$ Isomers

isomer	symmetry	pop. based[a] on statistics	rel no.[b] (intensity) of resonances
trans-R,R**	D_2	1	1 (4)[c]
trans-meso-R,S**	C_{2h}	1	1 (4)[c]
cis-R,R**	C_2	2	2 (2:2)[c]
cis-R,S**	C_1	2	4 (1:1:1:1)[c]
Δ-*S*,S*,S**	D_3	1	1 (6)[d]
Δ-*S*,S*,R**	C_2	3	3 (2:2:2)[d]

[a] Statistical population, based on an assumption of equivalent thermodynamic stability of the isomers. [b] Not corrected for the statistical isomer population. [c] Calculated for 3,′3′-methyl substituents in ^1H NMR spectra. [d] Calculated for 3,3′-proton substituents in ^1H NMR spectra.

^1H NMR spectrum of each isomer. A comparison of the product ratios obtained during the synthesis of **4** with the theoretical ratios shows that the $W(Me_2BINO)_2Cl_2$ isomers are not formed in a purely statistical distribution. An inspection of the data outlined in Table I clearly indicates that **4**, which is the prevalent isomer formed at ambient temperature and which exhibits only a single naphtholate environment, is one of the two *trans*-$W(Me_2BINO)_2Cl_2$ isomers. Furthermore, prolonged heating of the $(Me_2BINO)_2WCl_2$ product mixture results in the slow disappearance of the minor products in favor of **4**. On the basis of the existing literature detailing intermolecular ligand exchange in high-oxidation-state early transition metal complexes[42] and our previous experience with intermolecular R_2BINO ligand exchange processes,[28] it seems unreasonable to suggest that the observed product distribution results from a kinetic (stereospecific) substitution process. The involvement of intermolecular ligand exchange is implicated by the noteworthy increase in the quantity of **4** at the expense of minor isomers, as the crude reaction mixture is refluxed in toluene over a period of several days. From this information, we conclude that the major product **4** is the most thermodynamically favored $W(Me_2BINO)_2Cl_2$ diastereomer over temperatures ranging from 0 to 120 °C.

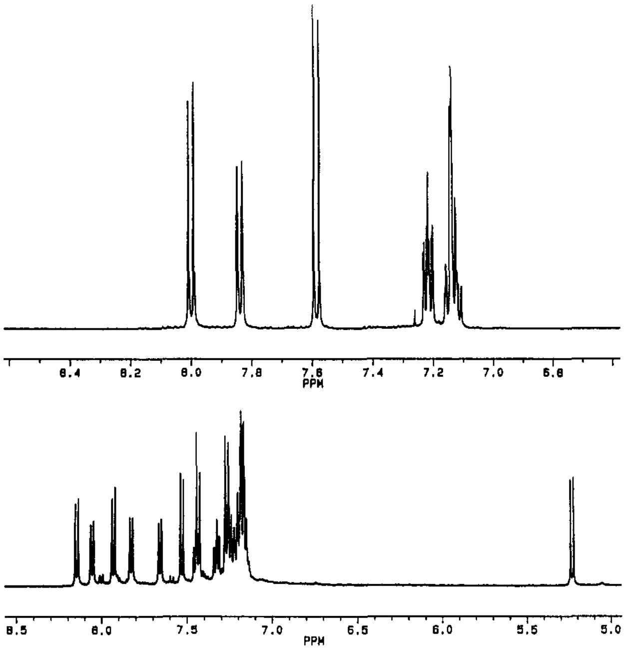

Figure 1. Top: (a) ^1H NMR spectrum of (S^*,S^*,S^*)-$W(BINO)_3$ at 500 MHz. Bottom: (b) ^1H NMR spectrum of (S^*,S^*,R^*)-$W(BINO)_3$ at 500 MHz. The figure shows the aromatic region of the spectrum.

In order to assign **4** unequivocally as either the *meso* or *rac* form of *trans*-$W(Me_2BINO)_2Cl_2$, an NMR-scale reaction was performed between (*R*)-H_2Me_2BINO and WCl_6. The ^1H NMR spectrum of the crude reaction mixture showed a resonance at $\delta = 2.70$, indicating that **4** was the only major product. Consequently, **4** is the *trans*-(R^*,R^*)-$W(Me_2BINO)_2Cl_2$ isomer, which possesses Me_2BINO ligands of like stereochemistry. This result could have been predicted on the basis of simple models of the two *trans*-$W(Me_2BINO)_2Cl_2$ isomers. The like stereochemistry of the Me_2BINO ligands in *trans*-(R^*,R^*)-**4** orients the methyl substituents on adjacent naphtholate units away from one another, while these methyl groups are in close proximity in the *meso* isomer (Chart I).

Synthesis and Stereochemistry of $(BINO)_3W$. Three equivalents of *rac*-H_2BINO and WCl_6 react in toluene to produce a mixture of two *tris*-substituted products (eq 3). Fractional

$$3H_2BINO + WCl_6 \xrightarrow{\text{toluene}} W(BINO)_3 + 6HCl \qquad (3)$$

crystallization from CH_2Cl_2 yields a red microcrystalline sample of one of these compounds. The relative simplicity of its ^1H NMR spectrum (Figure 1a) implies that the complex possesses a high degree of symmetry, with the result that it is assigned as a D_3-symmetric (S^*,S^*,S^*)-$W(BINO)_3$ (**5**) isomer. An independent synthesis, employing (*R*)-H_2BINO, produced a sample of (*R*,*R*,*R*)-$(BINO)_3W$ that is identical to **5** based on ^1H NMR spectroscopy. Further crystallization from the residue of the reaction using *rac*-H_2BINO yields a small quantity of a second

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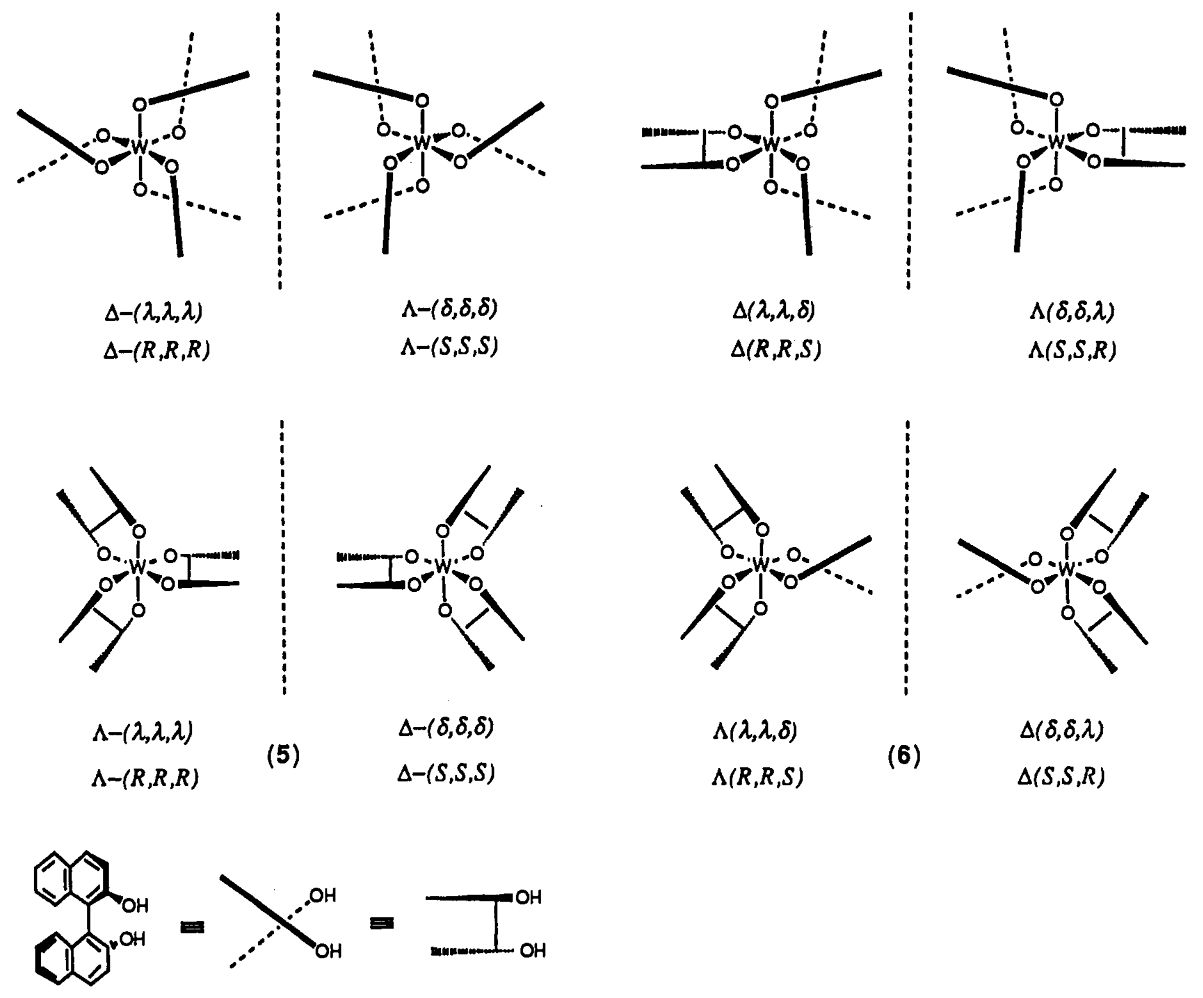
Chart II. Structural and Optical Isomers of W(BINO)$_3$



isomer, which exhibits 18 independent ^{1}H NMR resonances (Figure 1b). The multiplicity of this spectrum is consistent with a C_2-symmetric (S^*,S^*,R^*)-W(BINO)$_3$ (**6**) derivative. ^{1}H NMR spectra of crude reaction mixtures indicate that **5** and **6** are formed in a statistical 1:3 molar ratio. Both **5** and **6** could exist as pairs of Δ and Λ diastereomers (Chart II), and of course, each of these diastereomers exists as a pair of optical antipodes. Despite the potential for obtaining four isomers that could be distinguished via NMR spectroscopy, **5** and **6** are the only observable products of the H$_2$BINO substitution process. To ensure that the other two diastereomers were not thermally accessible, a synthesis of **5** and **6** in refluxing toluene was monitored over a 140 h period. While small changes in the quantities of **5** and **6** were observed during this study, the ratio of the products stabilized at 3:1 after 22 h. Minor isomers remained below the NMR detection limit (≤5%) during the entire experiment, supporting the assertion that **5** and **6** are more stable than their alternative diastereomers. This phenomenon could be caused by a tendency for Δ and Λ forms of the W(BINO)$_3$ complexes to incorporate BINO ligands of differing stereochemistry. Such behavior has ample precedent in other tris-chelated transition metal complexes bearing asymmetric bidentate ligands.[43] These preferences arise not from dramatic changes in conformation of the BINO chelate but, rather, from changes in the nature of interligand interactions induced by the Δ- and Λ-complex stereochemistry.

Considering the evident energetic differences between the Λ and Δ isomers of **5**, it should come as little surprise that these diastereomers are predicted to exhibit some dramatic structural differences. Molecular modeling studies show that both isomers adopt a "dual-bladed" paddle wheel structure although the Δ-(S,S,S)-W(BINO)$_3$ complex (Figure 2a) is substantially flattened along the C_3 principle axis by comparison with its Λ-(S,S,S)-W(BINO)$_3$ analog (Figure 2b).[44] As the structural models indicate, the flattening of the Δ isomer allows efficient cogging of the BINO ligands, thereby eliminating close gauche contacts. More net strain is engendered by gauche interactions in the corresponding Λ isomer, resulting in a much greater total energy than the less hindered Δ isomer. Due to the lack of accurate basis functions for W(VI), it is clearly the *trend* in these total energies, and not their absolute magnitude, that should be considered.

A peculiar spectroscopic characteristic of the (S^*,S^*,R^*)-W(BINO)$_3$ diastereomer gives us another opportunity to probe the Δ/Λ stereochemical preferences of the R and S optical antipodes of BINO. One of the 3-position hydrogen resonances of a naphtholate unit in the observed (S^*,S^*,R^*) diastereomer is shielded by between 2 and 3 ppm (Figure 1b) from its "normal" position at δ = 7.8–7.3. Similar anisotropically shifted hydrogen resonances have been observed in other complexes containing R$_2$BINO ligands.[29] These effects clearly stem from the proximity of the affected hydrogen to the shielding cone of either the *a*- or *b*-ring of a naphthoxide unit. For the (S,S,R^*) diastereomer, the shifted 3-position hydrogens could be either on the unique (R^*)-BINO ligand, which lies on the C_2-axis, or the *gauche*-naphthoxide

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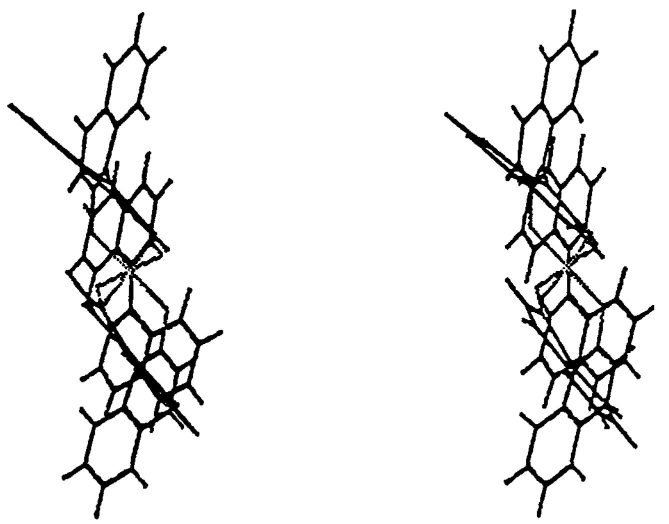
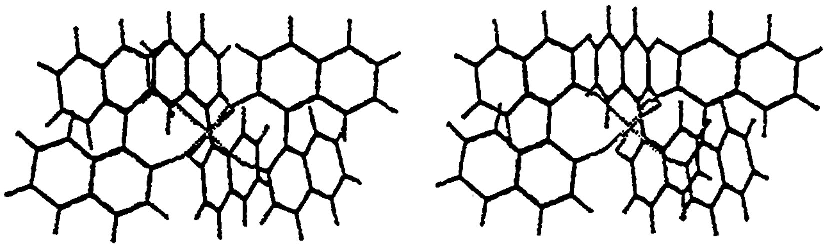
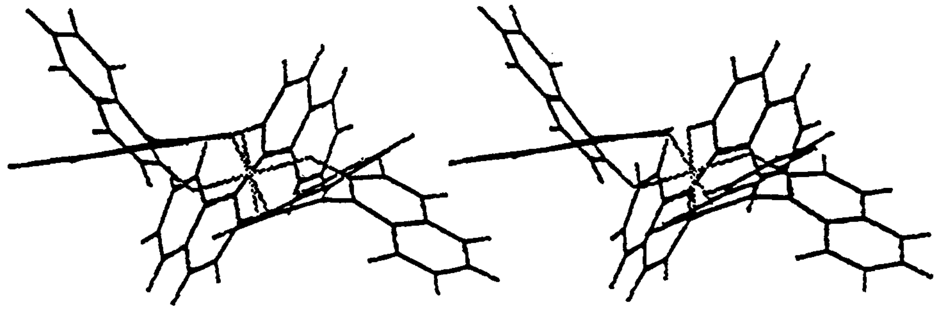


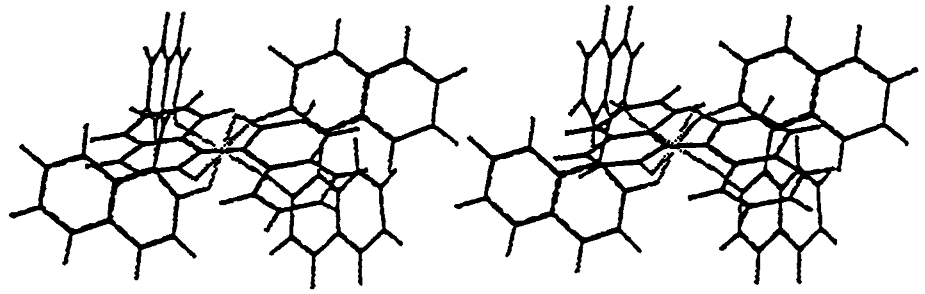
(a) Δ-(*S*,*S*,*S*)-W(BINO)$_3$



(b) Λ-(*S*,*S*,*S*)-W(BINO)$_3$



(c) Δ-(*S*,*S*,*R*)-W(BINO)$_3$



(d) Λ-(*S*,*S*,*R*)-W(BINO)$_3$

Figure 2. (a) Stick figure diagram from the molecular modeling study of Δ-(*S*,*S*,*S*)-W(BINO)$_3$. (b) Stick figure diagram from the molecular modeling study of Λ-(*S*,*S*,*S*)-W(BINO)$_3$. (c) Stick figure diagram from the molecular modeling study of Δ-(*S*,*S*,*R*)-W(BINO)$_3$. (d) Stick figure diagram from the molecular modeling study of Λ-(*S*,*S*,*R*)-W(BINO)$_3$.

units of the C_2-related BINO ligands. Models of the Λ and Δ diastereomers of the (*S**,*S**,*R**)-W(BINO)$_3$ complexes indicate that both isomers possess hydrogen atoms that could exhibit a ring current effect. The Λ-(*S*,*S*,*R*)-(BINO)$_3$W isomer orients the 3,3-position hydrogens of its (*R*)-BINO ligand toward the *a*-ring of the *gauche*-naphthol units belonging to the (*S*)-BINO ligands (Figure 2c). On the basis of simple model studies, the closest approach of this hydrogen atom to the ring centroid of the *gauche*-BINO unit is 2.9 Å. It is also noteworthy that this Λ isomer still remains higher in energy than the alternative Δ-(*S*,*S*,*R*) isomer. In the Δ-(*S*,*S*,*R*)-W(BINO)$_3$ complex, the 3-position hydrogens of the *gauche*-naphthoxide belonging to the (*S*)-BINO ligands are directed toward the *a*-rings of the unique (*R*)-BINO ligand (Figure 2d). The closest approach of these hydrogens to the aromatic ring is 2.5 Å. Estimations of the shielding influence of the naphtholate units based on the structures generated in the modeling study indicate that the well-centered hydrogen of the Δ-(*S*,*S*,*R*) isomer, approaching within 2.5 Å of the arene centroid, should experience a Δδ of >1.3 ppm, while the poorly-centered hydrogen of the Λ-(*S*,*S*,*R*) isomer, approaching within 2.9 Å of the arene centroid, would experience a Δδ of <0.5 ppm.[45] Consequently, the 3-position hydrogens of the (*S*)-BINO ligand in the Δ-(*S*,*S*,*R*) isomer have the angular relationships and distances from the arene ring which best account for the observed 2–3 ppm shielding effect. This result correlates with the total energies obtained from molecular modeling calculations, which predict the Δ-(*S*,*S*,*R*) isomer to be more stable than the alternative Λ-(*S*,*S*,*R*) complex.

The trend in the total energies obtained from modeling studies and the results of NMR shielding calculations indicate that the Δ-(*S*,*S*,*R*) and Δ-(*S*,*S*,*S*) isomers of the W(BINO)$_3$ complexes are more thermodynamically stable than their Λ counterparts. The relative instability of the Λ isomers appears to result from unfavorable gauche interactions between adjacent (*S*)-BINO ligands. As complexes containing two or more *S*(δ)-BINO ligands are more stable in a Δ metal stereochemistry, so the presence of two or more *R*(λ)-BINO ligands clearly favors a Λ metal stereochemistry. Such preferences for Δ or Λ stereochemistry are often observed, although some notable exceptions do occur.[46a] In some instances, these exceptions may be mitigated by flexible chelates, long M–X distances that act to relieve interligand interactions, and concomitant electronic effects engendered by the poor π-donor capacity of the ligand set.[46]

Comparisons with the Structural and Spectroscopic Characteristics of Other Aryloxy Tungsten(VI) Halide Complexes. A significant body of information about the structure and reactivity of aryloxide-substituted tungsten(VI) complexes has been obtained through studies by Schrock, Rothwell, and Bassett.[47–49] Conceptually, the tied-back binaphthol molecule could generate stereochemically different complexes in reactions with WCl$_6$ than those that proceed from reactions with simple phenols. Interestingly, both W(OAr)$_2$Cl$_4$ and W(OAr)$_4$Cl$_2$ complexes, isolated and structurally characterized in other laboratories,[48,49] showed similar structures to those of the W(Ph$_2$BINO)Cl$_4$ and *trans*-(*R**,*R**)-W(Me$_2$BINO)$_2$Cl$_2$ products isolated in this study. The origin of the preferences of the bis- and tetrakis(aryloxide) derivatives for their respective cis and trans geometries is, at present, unclear. For example, unlike W(Ph$_2$BINO)Cl$_4$, which is constrained to adopt a cis geometry, the stereochemistry of the *cis*-W(OAr)$_2$Cl$_4$ product could be controlled either by kinetic considerations or by a favorable electronic arrangement of the π-donor aryloxide ligands.[48,49]

Phenoxide substituted tungsten(VI) complexes are, in general, highly colored. The Δ-(*S**,*S**,*S**)-W(BINO)$_3$ complex, **5**, is intense red in solution like its W(OPh)$_6$ analog and unlike W(OMe)$_6$, which is pale yellow.[50] The intense color of the phenoxide complexes is attributed to the tailing of LMCT bands into the upper region of the visible spectrum.[51] This tailing is clearly observable in the UV/vis spectrum **5**, which is dominated by the exciton and E-band transitions of the BINO ligands at 220 (ϵ = 170 000) and 325 (ϵ = 36 000), respectively. The CD spectrum of the Λ-(*R*,*R*,*R*)-W(BINO)$_3$ antipode (Figure 3) exhibits corresponding Cotton effects for these bands at 218 nm (only half of this band is evident in Figure 3) and a band showing a positive Cotton effect at 327 nm. The sense of the sinusoidal exciton band, which shows a maximum positive Cotton effect at 207 nm and a maximum negative Cotton effect at 229 nm, confirms that the (*R*)-BINO ligand has maintained its absolute stereochemistry during substitution. The spectrum also exhibits a range of minor bands that are distinct from the CD spectrum of the ligand. These include a sharp band exhibiting a positive Cotton effect at 249 nm, a broad indistinct band between 265 and 280 nm, and a weak band that tails into the visible region. As we observed in optically pure complexes of the W$_2^{6+}$ core, these minor bands are evidentally associated with pπ–dπ LMCT transitions.[29]

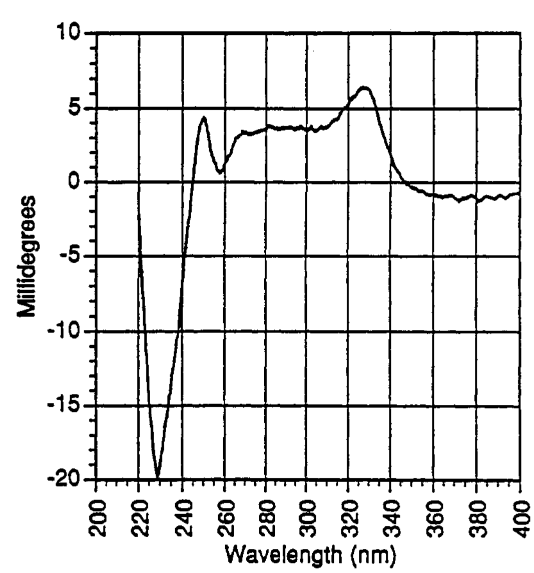


Figure 3. CD spectrum of Λ-(*R*,*R*,*R*)-W(BINO)$_3$ in toluene solution.

Polymerization Catalysis Employing W(R$_2$BINO)$_{3-n}$Cl$_{2n}$ Precatalysts. One of our initial objectives in investigating the coordination chemistry of R$_2$BINO complexes of tungsten(VI) was to determine whether the steric demands and defined topology of the asymmetric ligands could influence the stereochemistry of metathesis polymerization processes employing two-component catalysis. Basset has performed an extensive series of studies of olefin metathesis and ROMP processes employing isostructural (aryloxy)tungsten halide precatalysts and tungsten alkylidene complexes bearing aryloxide ligands.[52] Among a range of factors that influence the stereochemistry of ROMP processes, Basset confirmed that increasing the steric demands of ligands bound to the metal generally increases the fraction of *cis* double bonds in the polynorbornene product.[52] While several series of isostructural binaphtholate-functionalized coordination compounds and binaphtholate-substituted tungsten alkylidenes prepared in our laboratory conform to Basset's correlation between increased steric demand at the metal and increased *cis*-olefin content in polynorbornene,[53] efforts to establish a systematic relationship between the steric demands of the R$_2$BINO ligands and the stereochemistry of the product polymer are obviously hampered

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Table II. Stereochemical Analysis of Polynorbornene Prepared with $W(R_2BINO)_{3-n}Cl_{2n}$ Precatalysts

catalyst[a]	temp (°C)	cis/trans ratio	$r_t r_c$
WCl_6	−78	0.86	*b*
Δ-(S^*,S^*,S^*)-W(BINO)$_3$	−78		
Δ-(S^*,S^*,R^*)-W(BINO)$_3$	−78		
trans-(R^*,R^*)-W(Me_2BINO)$_2$$Cl_2$	−78	0.65	2
W(Ph_2BINO)Cl_4	−78	1.5	5
WCl_6	0	0.79	2
Δ-(S^*,S^*,S^*)-W(BINO)$_3$	0	0.70	1
Δ-(S^*,S^*,R^*)-W(BINO)$_3$	0	0.60	2
trans-(R^*,R^*)-W(Me_2BINO)$_2$$Cl_2$	0	0.58	2
W(Ph_2BINO)Cl_4	0	0.78	3

[a] The initiator is Et_2AlCl. [b] A reasonable ^{13}C NMR spectrum could not be obtained due to the partial solubility of the polymer in $CDCl_3$.

in this instance by our inability to control in a systematic fashion the number of R_2BINO ligands attached to the tungsten center.

Table II summarizes the results of the polymerization of norbornene by the $W(R_2BINO)_{3-n}Cl_{2n}$ precursors isolated in this study, using a Et_2AlCl cocatalyst. It is noteworthy that, while all of the tungsten precatalysts are active for metathesis polymerization at 0 °C, the W(BINO)$_3$ isomers alone remain inactive at −78 °C. In a related study, we observed dramatically reduced ROMP activity in W(Me_2BINO)$_2$(=CHPh) as compared with its W(Me_2BINO)(O-*t*-Bu)$_2$(=CHR) analog.[54] Evidentally, the fully-chelated tungsten centers in **5** and **6** cannot be induced to open a coordination site at −78 °C. The kinetic inactivity of the W(BINO)$_3$ precatalysts at −78 °C is consistent with the traditional model for precatalyst activation: dialkylation, succeeded by α-H elimination to produce the reactive alkylidene. It could also be consistent with the more recent hypothesis that the reduction of the tungsten(VI) precursor by the cocatalyst is the initial step in the formation of an active catalyst.[36] Both Schrock and Rothwell have demonstrated that the result of a single electron reduction of a $W(OAr)_{6-n}Cl_n$ complex is the labilization of a halide ligand and the isolation of a $W(OAr)_{5-n}Cl_n(L)$ derivative (where L = an ether or phosphine ligand).[47,48] The reduction of a W(BINO)$_3$ species would initially result in a $[W(BINO)_3]^{\bullet-}$ moiety, in which a naphthoxide unit, even though effectively labilized by the presence of the single d electron, would remain in the vicinity of the metal and compete for the open coordination site by virtue of the chelate effect.

The second striking trend found in Table II is the similarity of the cis/trans double bond ratios of polynorbornene samples obtained with all of the $W(R_2BINO)_{3-n}Cl_{2n}$ precatalysts and the parent precatalyst, WCl_6. The stereochemistry of most of the polyolefin products are sufficiently similar that the catalysts could be identical. This might result from the complete loss of R_2BINO ligands from the metal through Et_2AlCl-catalyzed ligand exchange. This hypothesis, together with speculation about how transition state energies would affect isomer ratios in unlike catalysts, cannot be fully elucidated given the complex nature of the catalyst systems. An alternative explanation for the similarity of the polymer sample is that the stereochemistry of the polymer is reorganized subsequent to the initial polymerization event in a secondary metathesis process. The secondary metathesis activities of some of the catalysts were examined by exposing samples of 95% *cis*-polynorbornene to solutions of a variety of active metathesis polymerization catalysts. The quantity of high polymer recovered, together with the stereochemical characteristics of both the recovered polymer and soluble oligomeric residue, was examined by ^1H and ^{13}C NMR spectroscopy. While some other classes of precatalyst molecules leave the 95% cis polymer essentially unchanged, a two-component W(Ph_2BINO)Cl_4/Et_2AlCl catalyst degrades 22% of the high polymer into soluble oligomers over a 15-min period, although the cis-olefin content of the recovered high polymer remains essentially unchanged. Over a 24-h time scale, far longer than that of the initial polymerization process, the same quantity of high polymer is recovered, with its cis content reduced to 71%. These results confirm that secondary metathesis is, by no means, fully responsible for the product distributed noted in Table II, although it could be a minor factor contributing to the evident lack of selectivity of the $(R_2BINO)_{3-n}WCl_{2n}$-catalyzed ROMP processes.

Conclusions

The extent of R_2BINO substitution on a WCl_6 template is controlled by the steric demands of the substituent in the 3,3-position, for a $W(R_2BINO)_{3-n}Cl_{2n}$ product, where R = H (unsubstituted), $n = 0$; R = Me, $n = 1$; and R = Ph, $n = 2$. The W(Me_2BINO)$_2$$Cl_2$ product preferentially forms a *trans*-(R^*,R^*) complex, as confirmed by reactions employing optically pure (R)-H_2Me_2BINO. Two diastereomers of W(BINO)$_3$ are isolated, with the Δ^*-(S^*,S^*,S^*) and Δ^*-(S^*,S^*,R^*) complexes being favored, because the Δ^* complex stereochemistry minimizes interligand interactions. Studies of norbornene polymerization using the $W(R_2BINO)_{3-n}Cl_{2n}$ complexes as precatalysts generated little variation in product stereochemistry. This result may be influenced slightly by the activity of some of the resulting catalysts in secondary metathesis processes. The fully chelated W(BINO)$_3$ complexes are not activated by Et_2AlCl at −78 °C, suggesting that ligand exchange processes are crucial for the formation of a catalytically active system.

Experimental Section

All reactions were carried out under a prepurified nitrogen atmosphere 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. ^1H and ^{13}C spectra were obtained on a Varian XL-300 MHz or a Bruker AM 500 MHz spectrometer. ^1H NMR spectra were referenced against the residual proton impurity in benzene-d_6, toluene-d_8, or chloroform-d_1, respectively. UV–vis spectra were acquired on a Hewlett Packard 8450A spectrometer. Circular dichroism spectra were acquired on a AVIV Model 60DS spectrometer, and optical rotations were determined using a Perkin-Elmer Model 241 polarimeter. Elemental analyses were performed by Desert Analytics, Tucson, AZ, or Schwarzkopf Microanalytical Laboratory, Woodside, NY. 1,1′-Bi-2-naphthol (Kodak), *R*-(+)-1,1′-bi-2-naphthol (Aldrich), and WCl_6 (Pressure Chemical) were used as received. 3,3-Disubstituted-1,1′-bi-2-naphthols (methyl, phenyl, *t*-BuMe$_2$Si) and (R)-H_2Me_2BINO were prepared using published procedures.[55]

W(Ph_2BINO)Cl_4 (3). WCl_6 (0.23 g, 0.58 mmol) was placed in a small Schlenk flask (50 mL) and dissolved in dry toluene (20 mL), followed by addition of solid H_2Ph_2BINO (0.25 g, 0.57 mmol). A reflux condenser was added and the dark purple solution was refluxed with stirring. After 12 h, the solvent was removed in vacuo. Redissolving the solid in CH_2Cl_2 followed by drastic reduction of the solution volume and refrigeration at −20 °C yielded a dark purple powder of **3** (0.33 g, 71% yield). ^1H NMR data ($CDCl_3$, 20 °C): δ = 8.07 (2H, s, NAP), 8.05 (2H, d, J = 8.2 Hz, NAP), 7.69 (4H, d, J = 8.3 Hz, Ar), 7.51 (4H, t, J = 7.6 Hz, Ar), 7.39 (2H, t, J = 7.4 Hz, Ar), 7.35 (2H, t, J = 8.3 Hz, Ar), 7.16 (2H, t, J = 6.9 Hz, Ar), 7.05 (2H, d, J = 8.5 Hz, NAP). ^{13}C NMR data ($CDCl_3$, 20 °C): δ = 165.9 (NAP $C_{2,2}$), 136.0, 135.0, 131.3, 130.6, 130.4, 130.1, 130.0, 129.6, 128.1, 127.5, 125.6, 123.6 (Ar). Anal. Calcd for W(Ph_2BINO)Cl_4·$^1/_2$$CH_2Cl_2$: C, 48.89; H, 2.61. Found: C, 48.45; H, 2.88.

(R^*,R^*)-W(Me_2BINO)$_2$$Cl_2$ (4). WCl_6 (0.32 g, 0.81 mmol) was placed in a small Schlenk flask (50 mL) and dissolved in dry toluene (20 mL), followed by addition of solid H_2Me_2BINO (0.50 g, 2.6 mmol). A reflux condenser was added, and the dark purple solution was refluxed with stirring. After 12 h the solvent was removed in vacuo. Redissolving the solid in CH_2Cl_2, followed by drastic reduction of the solution volume and

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refrigeration at −20 °C, yielded a dark purple powder of **4** (0.49 g, 60% yield). ^{1}H NMR data ($CDCl_3$, 20 °C): δ = 7.82 (4H, s, NAP), 7.81 (4H, d, J = 8.8 Hz, NAP), 7.20 (4H, t, J = 7.1 Hz, NAP), 7.10 (4H, t, J = 7.4 Hz, NAP), 6.93 (4H, d, J = 8.6 Hz, NAP), 2.70 (12H, s, Me). ^{13}C NMR data ($CDCl_3$, 20 °C): δ = 162.6 (NAP $C_{2,2'}$), 132.7, 131.7, 129.5, 128.4, 127.7, 127.0, 126.4, 124.9, 119.3 (NAP), 17.9 (Me). Anal. Calcd for $W(Me_2BINO)_2Cl_2 \cdot {}^3/_2CH_2Cl_2$: C, 55.08; H, = 3.44. Found: C, 55.54; H, 3.50.

(S^*,S^*,S^*)-W(BINO)$_3$ (5) and (S^*,S^*,R^*)-W(BINO)$_3$ (6). WCl_6 (2.5 g, 6.3 mmol) was placed in a large Schlenk flask (500 mL) and dissolved in dry toluene (100 mL), followed by addition of solid H_2BINO (5.4 g, 18.9 mmol). The apparatus was fitted with a reflux condenser, and the dark red solution was refluxed with stirring. After 12 h the solvent was removed in vacuo. Redissolving the solid in CH_2Cl_2 followed by drastic reduction of the solution volume and refrigeration at −20 °C yielded dark red crystals of **5** (1.6 g, 24% yield). Removal of the mother liquor, followed by further reduction of the solution volume, resulted in a dark red powder that after repeated recrystallizations resulted in pure **6** (0.42 g, 6% yield).

5. ^{1}H NMR data (C_6D_6, 20 °C): δ = 7.79 (6H, d, J = 8.8 Hz, NAP), 7.71 (6H, d, J = 8.8 Hz, NAP), 7.54 (6H, d, J = 8.1 Hz, NAP), 7.16 (6H, d, J = 7.9 Hz, NAP), 6.90 (6H, t, J = 7.2 Hz, NAP), 6.70 (6H, t, J = 7.3 Hz, NAP). ^{13}C NMR data ($CDCl_3$, 20 °C): δ = 160.4 (NAP $C_{2,2'}$), 132.5, 131.6, 129.3, 127.8, 127.5, 125.6, 125.0, 119.7, 119.3 (NAP). Anal. Calcd for (R^*,R^*,R^*)-$W(BINO)_3 \cdot {}^1/_2CH_2Cl_2$: C, 67.51; H, 3.44. Found: C, 67.96; H, 3.36.

6. ^{1}H NMR data ($CDCl_3$, 20 °C): δ = 8.13 (2H, d, J = 8.1 Hz, NAP), 8.05 (2H, d, J = 7.8 Hz, NAP), 7.92 (2H, d, J = 8.9 Hz, NAP), 7.82 (2H, d, J = 8.1 Hz, NAP), 7.65 (2H, d, J = 7.7 Hz, NAP), 7.51 (2H, d, J = 8.8 Hz, NAP), 7.44 (2H, t, J = 6.5 Hz, NAP), 7.41 (2H, d, J = 8.9 Hz, NAP), 7.31 (2H, t, J = 7.8 Hz, NAP), 7.23–7.14 (16H, m, NAP), 5.20 (2H, d, J = 9.0 Hz, NAP). ^{13}C NMR data ($CDCl_3$, 20 °C): δ = 162.5, 161.7, 158.1 (NAP $C_{2,2'}$), 132.7, 132.3, 132.3, 132.2, 131.2, 131.0, 129.6, 129.5, 129.2, 128.0, 127.9, 127.7, 127.7, 127.3, 127.2, 126.0, 125.8, 125.6, 125.5, 125.0, 124.6, 120.3, 120.1, 119.0, 118.3, 118.3, 117.5 (NAP). Anal. Calcd for (R^*,R^*,S^*)-$W(BINO)_3 \cdot {}^1/_2CH_2Cl_2$: C, 66.58; H, 3.41. Found: C, 66.46; H, 3.43.

Equilibrium Studies in the Synthesis of 5 and 6. WCl_6 (0.78 g, 1.96 mmol) was placed in a Schlenk flask (200 mL) and dissolved in dry toluene (25 mL) to form a purple solution to which solid H_2BINO (1.74 g, 6.07 mmol) was added. The solution was heated to reflux, and 1.0-mL aliquots of the reaction mixture were sampled at time intervals of 2.5, 8.5, 22.5, 46.5, and 142 h. Each aliquot was immediately dried in vacuo, and the quantities of **5** and **6** in the sample were analyzed by ^{1}H NMR spectroscopy.

Polymerization (ROMP) Studies. The precatalyst (0.020 g) was placed in a small round bottom flask with a septum and a nitrogen purge and subsequently dissolved in dry toluene (2 mL). Two equivalents of Et_2AlCl were added to the cooled solution (0 or −78 °C) via syringe. After 10 min, a precooled solution of norbornene in toluene was introduced via syringe. While being stirred, the solution became very viscous, and after 15 min the reaction was quenched with acetone. The polymer was precipitated by the addition of methanol, giving a white solid. The solvent was removed by filtration and the polymer dried in vacuo. All of the yields of polynorbornene were within 5% of quantitative. The stereochemistry of the resulting polynorbornene was determined by ^{1}H and ^{13}C NMR spectroscopy.[56]

Table III. Summary of Energies for the Δ and Λ Diastereomers of (S,S,S)-W(BINO)$_3$ and (S,S,R)-W(BINO)$_3$

	calcd tot. energy[a] (kcal/mol)		
	W–O = 1.80 Å	W–O = 1.85 Å	W–O = 1.90 Å
Δ-(S,S,R) (**6**)	21.368	6.882	6.583
Λ-(S,S,R)	26.127	14.419	13.903
Δ-(S,S,S) (**5**)	16.865	3.475	3.187
Λ-(S,S,S)	25.629	10.093	8.859

[a] The total energy is a sum of the calculated strain energy and the energy of the WO_6 aggregate. The aggregate energy is constant over a set of calculations performed at a specific W–O bond distance.

Secondary Metathesis Studies. Catalysts were prepared as noted above and allowed to stand for 15 min at ambient temperature in toluene solution. A quantity of 95% *cis*-polynorbornene, prepared from a $W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$ catalyst, was dissolved in toluene and added to the catalyst solution. Ratios of the monomer to the tungsten precatalyst were held at 200:1. After 15 min at 0 °C, the reaction was quenched with acetone and washed with three volumes of methanol. The solid residue was isolated, dried in vacuo, and analyzed by ^{1}H and ^{13}C NMR spectroscopy.[56] The methanol washes were combined, stripped to a viscous oil and analyzed by ^{1}H and ^{13}C NMR spectroscopy. Results for $W(Ph_2BINO)Cl_4/Et_2AlCl$ catalyst: high polymer recovered, 78%, 95% cis stereochemistry. Results for a similar experiment performed at 25 °C for 24 h: high polymer recovered, 78%, 71% cis stereochemistry. Reducing the contact time between the catalyst and the *cis*-polymer and the reaction temperature resulted in a substantial reduction in the quantity of secondary metathesis.

Molecular Modeling Calculations. Molecular modeling calculations were performed using the SYBYL 5.4 Molecular Modeling package on a VAX 9000-210 computer, and a summary of these results is included in Table III. In the absence of adequate potential functions to model W(VI), a dummy atom was used to model the tungsten center. On the basis of structural data available from a range of octahedral aryloxide-substituted W(VI) complexes, tungsten–oxygen bond distances were set at 1.85 Å. The octahedral "MO_6" core was defined as an aggregate and was not directly minimized by the normal SYBYL algorithm. The W–O bond distances of the central MO_6 were varied by ±0.05 Å and the O–W–O angle of the BINO chelate was compressed by up to 5° without changing the relative stability of the Δ and Λ isomers. Checks of critical bond angles, including W–O–C (128° average) and binaphthyl dihedrals (60° averages) were found to be within acceptable limits in all of the minimized structures.

Acknowledgment. We thank the University of Kansas General Research Fund and the donors of Petroleum Research Fund, administered by the American Chemical Society, for support. We further acknowledge the assistance of Cynthia Stevenson for help with CD spectroscopy and, Professor George Stanley, Kit Gunn, and Dr. David Huhta for assistance with modeling studies.

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(56) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983; Chapter 11.