Synthesis and Reactivity of Binaphtholate Complexes of a d^3–d^3 Ditungsten Template

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W_2(O-*t*-Bu)$_6$ reacts with binaphthol derivatives (H_2BINO, R = H (**1**); H_2Me_2BINO, R = CH_3 (**2**)) to produce monosubstituted products of the formula (R_2BINO)W_2(O-*t*-Bu)$_4$. The presence of a single product in the ^{1}H NMR spectra of these compounds supports the hypothesis that the binaphtholate ligand adopts a preferential mode of binding. Disubstituted products can be formed when 2 equiv of binaphthol is reacted with W_2(O-*t*-Bu)$_6$: racemic binaphthol generates *anti*-(*R*,*S*)-(BINO)$_2W_2$(O-*t*-Bu)$_2$ (**3**) with small quantities of *anti*-(*R**,*R**)-(BINO)$_2W_2$(O-*t*-Bu)$_2$ (**5**), while optically pure (*R*)-binaphthol yields *gauche*-(*R*,*R*)-(BINO)$_2W_2$(O-*t*-Bu)$_2$ (**6**). The enantiomers of **6** appear to undergo intermolecular exchange reactions in the presence of *tert*-butyl alcohol, forming **3** as the main product along with small quantities of (*R**,*R**,*R**)-(BINO)$_3W_2$ (**4**). A reaction between **2** and 2 equiv of acetylene generates a flyover complex, (μ_2-C_4H_4)(Me_2BINO)W_2(O-*t*-Bu)$_4$ (**7**), as identified by ^{1}H and ^{13}C NMR spectroscopy. When greater than 6 equiv of acetylene is employed, (η^2-C_2H_2)(μ_2-C_4H_4)(Me_2BINO)$_2W_2$(O-*t*-Bu)$_2$ (**8**), a complex containing a flyover fragment with an additional terminal acetylene ligand, is produced. Complex **3** is also reactive toward acetylene, generating diastereomeric tris(acetylene) derivatives of the formula (μ_2-C_4H_4)-(η^2-C_2H_2)(BINO)$_2W_2$(O-*t*-Bu)$_2$ (**9**) in a nonstatistical ratio. This result suggests that the presence of chiral chelating ligands in the coordination sphere can influence the stereochemistry of complex formation at the W_2 template.

Introduction

Considerable attention has been devoted to the study of d^3–d^3 ditungsten complexes containing a variety of ligand systems.[1] Such complexes have versatile reactivity with small unsaturated molecules such as acetylenes,[2-5] olefins,[6-8] allenes,[9] ketones,[10,11] and carbon monoxide,[12] frequently producing dinuclear organometallic products with complex bridging hydrocarbyl functionality. The interest excited by this class of inorganic functional groups stems not merely from this range of functionality but also from the scope of fundamental reaction types exhibited by the metal–metal bond, including ligand addition,[13] anion metathesis,[14] cycloaddition,[15] insertion,[16] C–H bond activation,[17] and multiple-bond metathesis processes.[18-22] These reactions are so diverse and readily influenced by the steric and electronic characteristics of the ancillary ligands that they provide a window into the potential scope of metal cooperativity in the chemistry of the early transition metals. A significant number of organometallic ditungsten complexes are inherently asymmetric;[3,6,8,10,23] consequently, it seems a logical extension of this work to incorporate ancillary chiral ligands into the metal coordination sphere. This would afford an opportunity to study the stereochemistry of the substitution reactions of the ligands, as well as the effect of the chirality on the stereoselectivity of reactions at the W_2 unit.

Several years ago we chose to study the chemistry of transition metal complexes containing the 1,1′-bi-2-naphtholate (R_2BINO) ligand.[24-27] Our interest in this asymmetric bidentate ligand was stimulated because its ability to mimic the 2,6-disubstituted

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phenoxide moieties, which are ubiquitous ligands in numerous group 3 through group 7 complexes, should make it a compatible auxiliary ligand for an extensive range of early transition metal complexes. At the onset of our studies we were surprised to find little firm structural data concerning the bonding modes and structures of complexes containing these units.[28] In the early 1980s Brintzinger structurally characterized some BINO-chelated *ansa*-metallocene complexes which, until our studies, remained the only unequivocally characterized coordination mode for the BINO ligand.[28] We have since identified novel bridging, unidentate bridging, and naphthol–naphtholate chelating environments in a variety of R_2BINO-substituted complexes.[24-27]

The binaphtholate ligand has already found applications in controlling the stereochemistry of macrocycles,[29] enforcing enantioselectivity in reactions catalyzed by metallic Lewis acids,[30] effecting reductions by main-group hydride reagents,[31] and inducing the production of isotactic polypropylene.[32] Some of the complexity evident in catalyst systems bearing BINO functionality may stem from the difficulty in predicting the stoichiometry and stereochemical outcome of alkoxide-exchange reactions involving chiral ligands at early transition metal centers, an issue on which our research has recently focused.[25] In this paper, we report the details of the coordination of chiral 1,1′-bi-2-naphtholate derivatives at the $W_2(OR)_6$ template and the influence of these ligands on the reaction of the d^3–d^3 W_2 functional group with acetylene. Portions of this work have appeared previously in communication form.[24,26]

Results and Discussion

Synthesis of $(R_2BINO)_{3-n}W_2(O\text{-}t\text{-}Bu)_{2n}$ Derivatives. Reactions between $W_2(O\text{-}t\text{-}Bu)_6$ and binaphthol (H_2BINO), R = H (**1**); H_2Me_2BINO, R = CH_3 (**2**)) afford monosubstituted products containing bridging naphtholate units (eq 1), while the bulkier

$$W_2(O\text{-}t\text{-}Bu)_6 + R_2BINO \xrightarrow{\text{toluene}} (R_2BINO)W_2(O\text{-}t\text{-}Bu)_4 \quad (1)$$

1: R=H
2: R=CH$_3$

Ph_2BINO ligand is unreactive toward this dimetallic center. Similar reactions of these ligands with $W_2(NMe_2)_6$ produce mixtures whose ^{1}H NMR spectra contain no evidence of a major substitution product.[33] The structure of $(Me_2BINO)W_2(O\text{-}t\text{-}Bu)_4$ (**2**), shown in the ball and stick representation in Figure 1, confirms that the compound is monomeric in the solid state.[34] The binaphtholate ligand is oriented such that the two gauche alkoxide ligands lie in the shielding cones of the aromatic rings. The ^{1}H NMR spectrum of **2** shows two environments for the O-*t*-Bu ligands, with the resonance appearing at δ = 0.68 representing the O-*t*-Bu ligands that experience the group anisotropy of the naphtholate unit. This inference is further supported by NOE difference ^{1}H NMR spectroscopy, which shows a modest energy transfer from the protons of the O-*t*-Bu resonance at δ = 0.68 to the protons associated with the 4-position naphthalene singlet at δ = 7.83 during irradiation. On the basis of the observation of such a shielding effect in the ^{1}H NMR spectrum of **2**, we can suggest the existence of a close correspondence between the molecular structure in the solid and solution states.

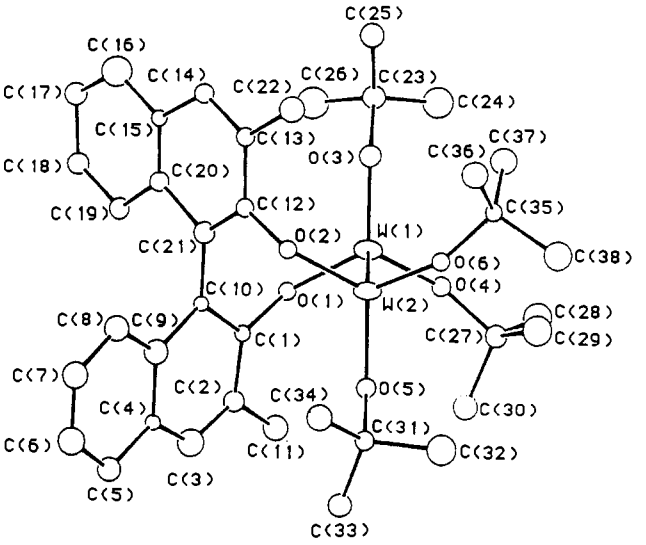

Figure 1. ORTEP drawing of $(Me_2BINO)W_2(O\text{-}t\text{-}Bu)_4$ (**2**), showing an oblique view down the W–W bond axis. A representative sampling of bond distances (Å), angles (deg), and torsional relationships (deg) follows: W(1)–W(2) = 2.324(1), W(1)–O(1) = 1.934(1), W(1)–O(4) = 1.889(16), W(1)–O(3) = 1.869(16); W(2)–W(1)–O(1) = 101.52(32), W(2)–W(1)–O(4) = 110.86(30), W(2)–W(1)–O(3) = 97.86(48), O(1)–W(1)–O(3) = 120.05(43), O(1)–W(1)–O(4) = 107.32(46), W(1)–O(1)–C(1) = 129.59(91), W(1)–O(3)–C(23) = 128.3(14), W(1)–O(4)–C(27) = 145.86(94); C(1)–C(10)–C(21)–C(12) = –89.3(20).

The presence of only a single product in both the solution- and solid-state structures of **2** suggests that the binaphtholate ligand may have a stereochemical preference in binding. In the X-ray structure of **2**, the molecule adopts the classic staggered ethane-like structure of many structurally-characterized $M_2(OR)_6$ complexes. It is noteworthy that the R_2BINO ligand spans the W–W bond without either adopting a unidentate bridging bonding mode or enforcing an eclipsed conformation on the "W_2O_6" skeleton. Eclipsed structures are produced by ethylene glycolate- and ethylenediamine-derived ligands, and it may be that the eight-membered-ring bridge formed by the R_2BINO ligands better accommodates the 3.5-Å O···O distance of the staggered $W_2(OR)_6$ structure than glycolate-derived ligands.[22,35] A bridging binaphtholate unit generates two skew axes on bonding: (1) the natural skew axis of the chiral ligand, which is always λ in the case of (*R*)-BINO, and (2) the skew axis defined by the O–W–W–O dihedral angle, which could produce either a λ or δ linkage. Consequently, diastereomeric λ and δ structures are possible for a staggered $(Me_2BINO)W_2(O\text{-}t\text{-}Bu)_4$ complex, as illustrated in Figure 2. The (*R*)-BINO ligand in **2** adopts a λ conformation with respect to the metal stereochemistry, with the C(10)–C(21) junction between the naphthalene units oriented perpendicular to the W–W bond vector. The invariance of the ^{1}H NMR spectra

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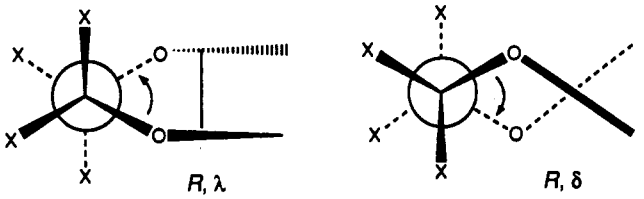

Figure 2. λ and δ chelating modes of (*R*)-BINO.

of complexes **1** and **2** over a wide temperature range (−50 to +25 °C) suggests either that the barrier to exchange between the δ and λ conformers is low or that one conformer is strongly preferred. Binuclear molybdenum complexes containing flexible chiral phosphine ligands have been shown to generate two diastereomeric bridging structures in unequal amounts, demonstrating that such chiral bridging ligands may significantly affect the stability of particular diastereomeric structures.[36] Unlike these asymmetric phosphine ligands, the R_2BINO ligand can also superimpose π-donor effects on the steric influences generated by the ditungstadioxacycle. The λ diastereomer of the (*R*)-BINO chelate, shown in Figure 2, orients the oxygen pπ donor orbitals of BINO perpendicular to the W–W bond vector. This orientation favors maximum π-donor capacity in simple W_2X_6 (X = OR, NMe_2) complexes and is consistent with the BINO conformation observed in the X-ray structure of **2**.[37] In contrast, the δ diastereomer of the (*R*)-BINO chelate aligns the oxygen pπ orbitals along the W–W bond. In this orientation, at least one symmetry combination of the BINO pπ orbitals will π-donate into a filled W–W π-bonding orbital. The relative rigidity of the BINO ligand and π-donor effects introduced by the bis(naphthoxide) moieties may result in enhanced selectivity in binding, perhaps to the extent of significantly destabilizing some ligating modes.

The UV–vis spectra of compounds **1** and **2** contain three major bands at 235, 278, and 332 nm (ε = >80 000, 23 000, and 12 000, respectively), consistent with the expected major exciton absorbance and E-band absorbance of the binaphtholate ligand. A shoulder on the 332-nm band which tails into the visible region is consistent with the metal-derived π → π* transition observed in homoleptic $W_2(OR)_6$ complexes, and a corresponding weak transition is visible at 421 nm (ε ≤1800). These latter two transitions are also seen in the UV spectrum of a recently reported homoleptic asymmetric ditungsten menthoxide complex, (+)-$[W_2(OC_{10}H_{19})_6]$.[38] The complex (*R*)-(BINO)W_2(O-*t*-Bu)$_4$ (*R*-**1**), prepared from (*R*)-H_2BINO, displayed an optical rotation of $[\alpha]_D^{20}$ = +23.4°. CD spectra of this compound exhibit bands with positive Cotton effects at 226 and 350 nm, representing the E-band and magnetically allowed component of the W-based π → π* transitions observed in the UV–vis spectrum of the complex. Unlike the CD spectrum of (+)-$[W_2(OC_{10}H_{19})_6]$,[38] a band corresponding to the visible transition at 421 nm was not detected in the CD spectrum of *R*-**1**. In addition to the spectral features noted above, an intense exciton-derived CD absorption consistent with retention of the *R* configuration of the binaphtholate ligand appears at 231 nm.

The addition of 2 equiv of racemic H_2BINO to a solution of W_2(O-*t*-Bu)$_6$ in toluene at room temperature results in the formation of an analytically pure pale yellow precipitate of empirical formula (BINO)$_2W_2$(O-*t*-Bu)$_2$ (**3**) (eq 2). Substitution of two binaphtholate ligands onto the ditungsten framework can generate up to six isomers, not including enantiomers, which are illustrated in Figure 3. These isomers differ in the chirality of the binaphtholate ligand, in the δ or λ conformation of the binaphtholate chelate, and in the placement of the *t*-BuO groups.

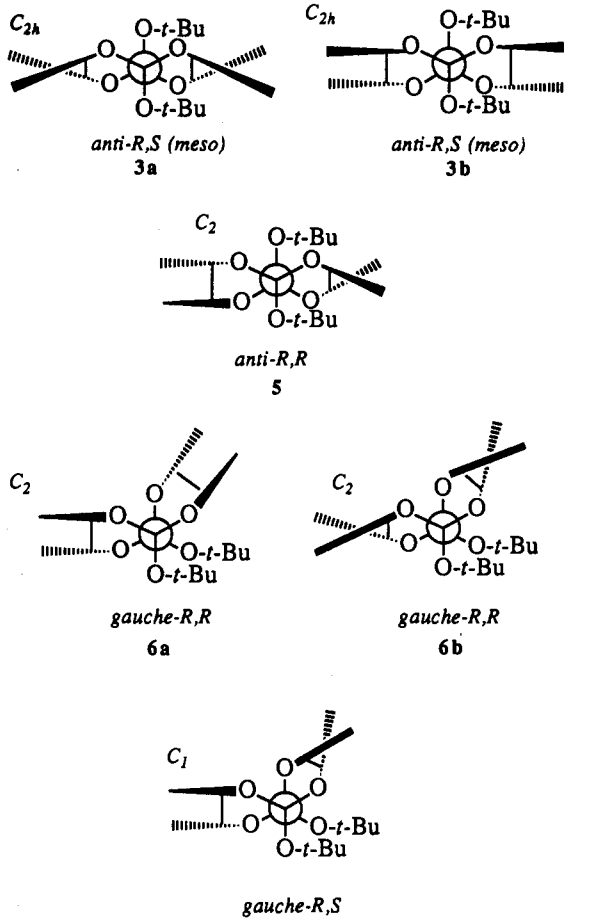

Figure 3. Possible isomers of (BINO)$_2W_2$(O-*t*-Bu)$_2$ (**3**).

$$W_2(O\text{-}t\text{-}Bu)_6 + 2\ rac\ H_2BINO \xrightarrow{toluene} anti\text{-}(R,S)\text{-}(BINO)_2W_2(O\text{-}t\text{-}Bu)_2 \quad (2)$$

3

Notably, the gauche isomers **6a** and **6b** could interconvert through rotation about the W–W bond. The ^{1}H and ^{13}C NMR spectra of **3**, like the spectra of **1** and **2**, are invariant over a wide temperature range. These spectra are consistent with the magnetic equivalence of both the *t*-BuO and the naphtholate ligand environments in **3**. The resonance associated with *t*-BuO ligands appears at δ = 0.1 for this complex, a dramatic upfield shift from the *t*-BuO resonance of W_2(O-*t*-Bu)$_6$, which occurs at δ = 1.6. This effect is consistent with the *t*-BuO ligands experiencing the shielding influence of two proximal naphtholate groups. Combined with symmetry considerations, this anisotropic shift indicates that **3** is a *trans-meso* complex, containing both *R* and *S* enantiomers of the BINO unit. Because the binaphtholate ligands can bind in either a λ or a δ fashion, there are two possible conformers of the *anti*-(*R*,*S*)-(BINO)$_2W_2$(O-*t*-Bu)$_2$ product (**3**). Stereopictures of these two isomers are shown in Figure 4. The dramatic upfield shift of the *t*-BuO ligands could be seen in either of these isomers, depending upon the orientation of the *t*-BuO ligand with respect to the W–W bond. In order for such a shielding effect to occur in structure **3b**, in which the 1,1′-binaphthyl vectors are oriented parallel to the W–W bond axis, the *t*-BuO ligands would have to adopt an endo orientation with respect to the W–W bond. This geometry should create steric congestion in the vicinity of the W–W bond, with the result that such an endo orientation would presumably not be preferred for simple $W_2(OR)_6$ complexes. In structure **3a**, the shielding requirement of the *t*-BuO ligands is satisfied by their placement in a favorable exo orientation. Furthermore, the (*R*)- and (*S*)-BINO ligands, respectively, adopt λ and δ stereochemistries at the metal. The diastereoisomerism of these linkages is identical to the stereo-

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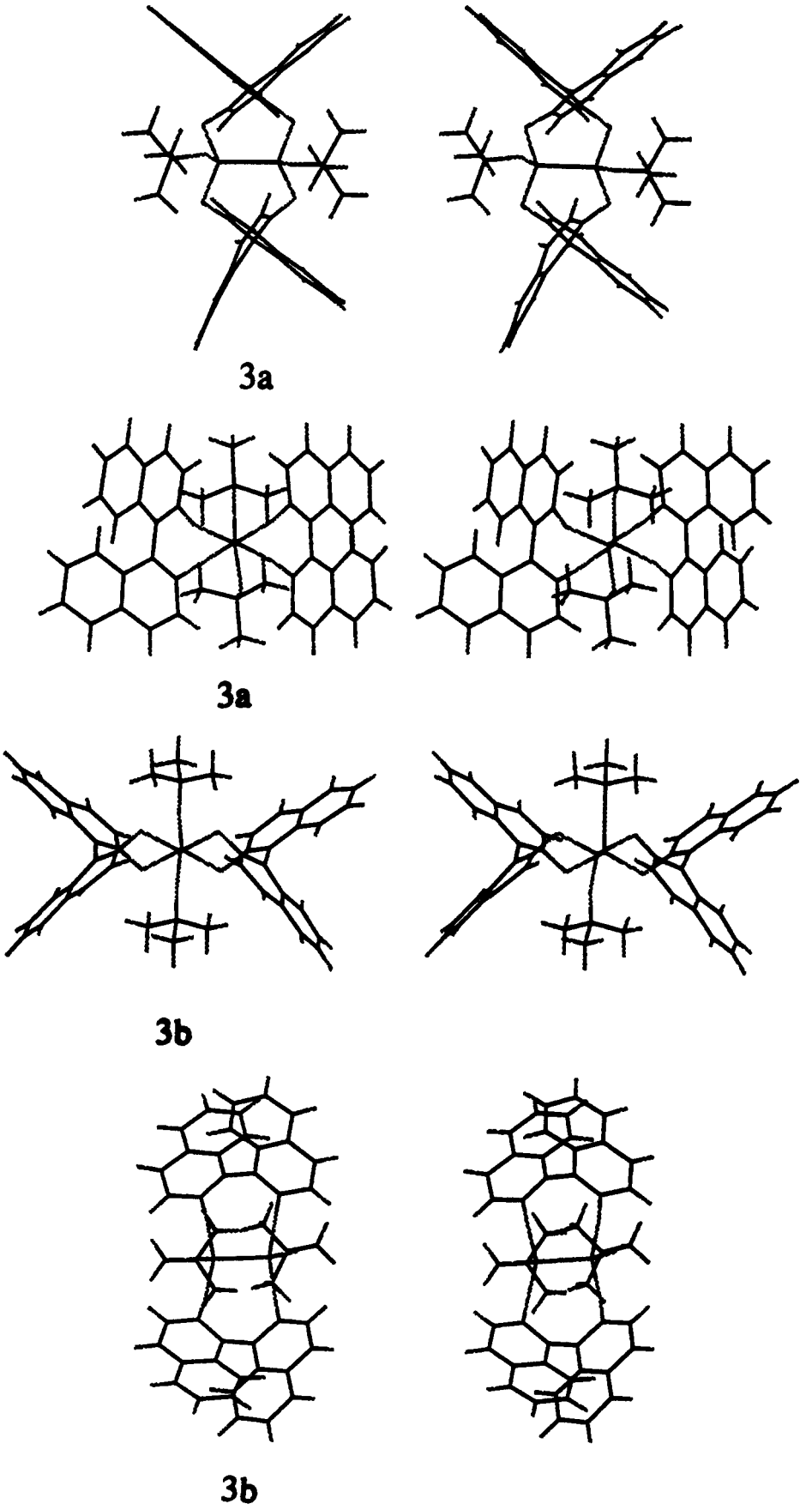
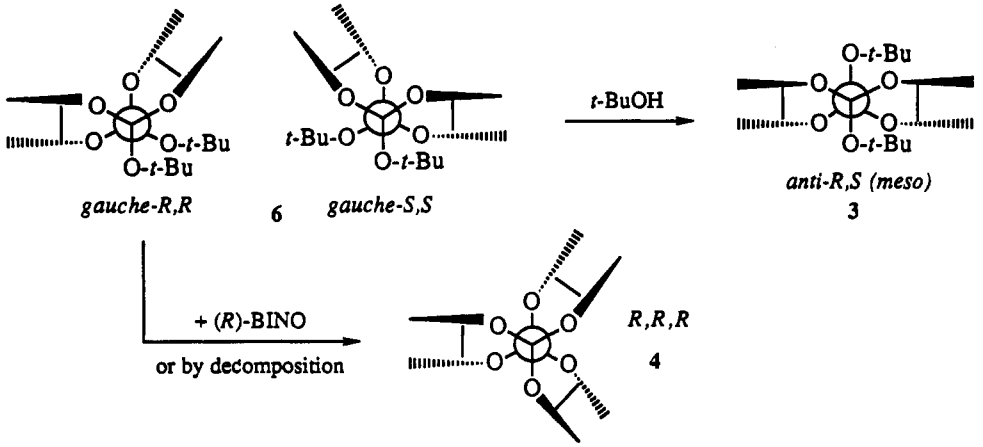


Figure 4. Stereodiagrams of *anti*-(*R*,*S*)-$(BINO)_2W_2(O\text{-}t\text{-}Bu)_2$ isomers (**3a** and **3b**).

chemistry found in the crystallographically characterized diastereomer **2**. From this information, we conclude that **3a** is the most likely structure of the complex.

Two minor products (<10% each) are also observed in the ^1H NMR spectra of the soluble residues of this reaction mixture. One, which exhibits no *t*-BuO resonances and possesses high symmetry, was identified as (*R**,*R**,*R**)-$(BINO)_3W_2$ (**4**) (vide infra). The other minor product exhibits apparent C_2 symmetry,

Scheme I. Intermolecular Ligand-Exchange Reactions Involving Enantiomeric Gauche Isomers of **6**



with signals consistent with two inequivalent naphthoxide environments and a single *t*-BuO environment. Either the *anti*-(*S**,*S**)-$(BINO)_2W_2(O\text{-}t\text{-}Bu)_2$ isomer (**5**) or the *gauche*-(*S**,*S**)-$(BINO)_2W_2(O\text{-}t\text{-}Bu)_2$ isomer (**6**) would satisfy these symmetry requirements. After **6** was prepared by an independent synthesis and found not to correspond to the spectrum of this minor product, the identity of the minor isomer was assigned as **5**.

Compound **6** is obtained as the only product of the reaction between 2 equiv of (*R*)-H_2BINO and $W_2(O\text{-}t\text{-}Bu)_6$ (eq 3). The

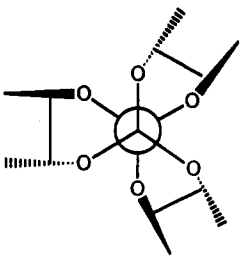
$$W_2(O\text{-}t\text{-}Bu)_6 + 2\ (R)\text{-}H_2BINO \longrightarrow \underset{\mathbf{6}}{gauche\text{-}(R,R)\text{-}(BINO)_2W_2(O\text{-}t\text{-}Bu)_2} \quad (3)$$

proton resonance generated by the *t*-BuO ligand of this product appears at $\delta = 0.97$, which is consistent with the presence of only one gauche interaction between the *t*-BuO and naphtholate ligands. By comparison, the alternative anti-*R**,*R** structure (**5**) could expose the *t*-BuO ligand to stronger shielding by two naphthoxide units. The two sets of resonances associated with the naphthalene rings are also consistent with the expected C_2 symmetry of **6**. Further circumstantial evidence for the gauche orientation of the *t*-BuO ligands is derived from the relative instability of the complex, which, unlike **3**, decomposes in solution with a half-life of 30 min at 20 °C, forming *tert*-butyl alcohol, isobutylene, and significant quantities of the minor product **4**. Such a decomposition process could be facilitated by the proximal orientation of the *t*-BuO ligands. Compound **4** can also be formed by the addition of 3 equiv of (*R*)-H_2BINO (vide infra), and this reaction presumably proceeds through an intermediate such as **6**.

The reaction of 3 equiv of (*R*)-H_2BINO with $W_2(O\text{-}t\text{-}Bu)_6$ yields the yellow "homostereoleptic" decomposition product **4** in higher yields (eq 4). Traces of this product are also evident in

$$W_2(O\text{-}t\text{-}Bu)_6 + 3\ (R)\text{-}H_2BINO \longrightarrow \underset{\mathbf{4}}{(R,R,R)\text{-}(BINO)_3W_2} \quad (4)$$

the largely uninterpretable ^1H NMR spectrum of the material produced in an analogous reaction involving *rac*-H_2BINO. There are three most logical conformations for this molecule: a staggered form, whose global stereochemistry could be either Λ or Δ, or an eclipsed form, as occurs in the tris(binaphtholate)-bridged main-group compound $(BINO)_3B_2$.[39] Other ditungsten systems containing chelating alkoxide groups, such as $W_2(OCMe_2CMe_2O)_3$,[35] adopt an eclipsed orientation, although this preference may be in part due to steric interactions between the ligands or to the limited size of the six-membered ditungstadioxacyclohexane. The solid-state structure of **2** suggests that binaphtholate chelates prefer a staggered conformation, although this preference may be dominated by interligand interactions with the *t*-BuO ligands, rather than by an inherently favored conformation of the R_2-BINO chelate ring.



4

Facile intermolecular ligand exchange must be occurring to account for the formation of **4** via the decomposition of **6**. To test for evidence of such intermolecular exchange processes, solutions of *gauche*-(*R*,*R*)-$(BINO)_2W_2(O\text{-}t\text{-}Bu)_2$ and *gauche*-(*S*,*S*)-$(BINO)_2W_2(O\text{-}t\text{-}Bu)_2$ were mixed in the presence of *t*-BuOH at 0 °C (eq 5). After several hours at ambient

$$\underset{\mathbf{R\text{-}6}}{gauche\text{-}(R,R)\text{-}(BINO)_2W_2(O\text{-}t\text{-}Bu)_2} + \underset{\mathbf{S\text{-}6}}{gauche\text{-}(S,S)\text{-}(BINO)W_2(O\text{-}t\text{-}Bu)_2} \xrightarrow{t\text{-}BuOH} \underset{\mathbf{3}}{anti\text{-}(R,S)\text{-}(BINO)_2W_2(O\text{-}t\text{-}Bu)_2} \quad (5)$$

temperature, the reaction yielded **3** as the major identifiable product, along with trace quantities of **4**. This result confirms that intermolecular ligand migration can occur in these systems and that **3** is thermodynamically more stable than its gauche counterparts. The production of a small amount of the tris-substituted product **4** during the synthesis of **3** requires that some amount of **6** be formed during the initial substitution process. This conclusion is founded on the observation that **4** cannot be formed through the addition of *rac*-H_2BINO to **3**, but only through the decomposition of **6** or through the further substitution of **6** by a BINO ligand of like stereochemistry (Scheme I).

Reactions with Acetylene. A characteristic reaction of the $W_2(OR)_6$ parent molecule is the addition of between 1 and 3 equiv of acetylene to the ditungsten unit to form stable organometallic complexes.[40,41] Although the hydrocarbyl fragment is not readily

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(40) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Chem. Soc. Rev.* **1985**, *14*, 69.

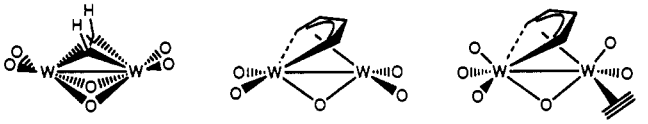


Figure 5. Possible products of reactions between $W_2(OR)_6$ and C_2H_2.

eliminated in these ditungsten complexes, such compounds can serve as models for C–C bond formation in the cyclotrimerization and/or polymerization of alkynes at a bimetallic center.[42] Reactions involving acetylenes and homoleptic ditungsten alkoxides can produce complexes containing a single bridging acetylene,[2] a diacetylene flyover moiety,[3] or a flyover unit and an additional terminal acetylene ligand[3] (Figure 5). Earlier work by Chisholm,[41] Schrock,[31] and Cotton[43] elucidated the course of reactions between $W_2(OR)_6$ compounds and a variety of acetylenes and demonstrated that the products formed depend on the steric bulk of the alkoxide, the substituents on the alkyne, and the reaction conditions. Such processes can formally be viewed as oxidative addition reactions, with electron density being transferred from the W–W bond to form W–C bonds. Survey reactions between a range of mono- and disubstituted alkynes and complexes **2** and **3** indicated that the R_2BINO-substituted complexes were generally only reactive with the parent ethyne molecule.

The reaction between **2** and 2 equiv of acetylene generates a flyover molecule, $(\mu_2,\eta^4\text{-}C_4H_4)(Me_2BINO)W_2(O\text{-}t\text{-}Bu)_4$ (**7**) (eq 6), as identified by ^1H and ^{13}C NMR spectroscopy. Consistent

$$\underset{\mathbf{2}}{(Me_2BINO)W_2(O\text{-}t\text{-}Bu)_4} + 2C_2H_2 \longrightarrow \underset{\mathbf{7}}{(\mu_2\text{-}C_4H_4)(Me_2BINO)W_2(O\text{-}t\text{-}Bu)_4} \quad (6)$$

with the observations of earlier reactions involving $W_2(O\text{-}t\text{-}Bu)_6$ and 2-butyne,[3] reactions between **2** and only 1 equiv of acetylene result in the formation of the same flyover molecule, leaving unreacted **2**. Interestingly, the spectroscopic characterization of the product indicates that only one of the possible product isomers is formed. The ^1H NMR spectrum reveals four inequivalent resonances associated with the C_4H_4 moiety, as is expected on the basis of the C_1 symmetry of **7**. The signal representing one of these protons is shifted approximately 3 ppm upfield from its expected chemical shift location, which we attribute to its position in the shielding cone of one of the naphthalene rings. Further evidence of the formation of a flyover complex is found in the ^{13}C NMR spectrum, which shows ^{183}W couplings (J = 68 Hz and J = 82 Hz, respectively) to the ^{13}C resonances at δ = 202.0 and 172.5, which are in the expected range for the 1- and 4-position carbons of the flyover ligand.[3]

The similar coupling patterns exhibited by the pairs of ^1H NMR resonances at δ = 5.2 and 8.6 and δ = 5.5 and 5.6 suggest that these pairs occupy chemically similar environments in the flyover unit (Figure 6e), but a heteronuclear correlation spectroscopy experiment suggested otherwise. Proton resonances at δ = 5.5 and 8.6 correlated with the carbon resonances at δ = 172.5 and 202.0, respectively, which are σ-bonded to one of the tungsten atoms. The connectivity of the four protons was revealed through a 1D NOE multiplet difference experiment. The irradiation of the flyover protons exhibited the following major NOE effects (Figure 6): δ = 8.6 showed an NOE to δ = 5.6, δ = 5.6 showed NOE's to both δ = 8.6 and 5.2, δ = 5.2 showed NOE's to both δ = 5.6 and 5.5, and δ = 5.5 showed an NOE to δ = 5.2. These relationships unequivocally establish the connectivity as that shown in Figure 6. Additionally, the irradiation of the resonance at δ = 5.6 developed a substantial NOE at a doublet arising from a Me_2BINO proton at δ = 6.6.

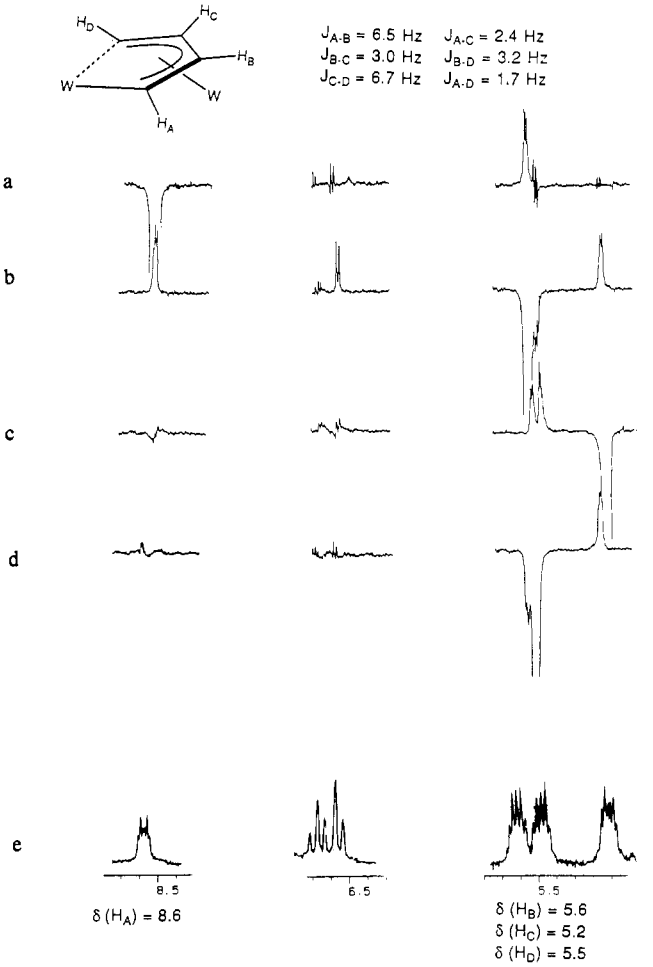
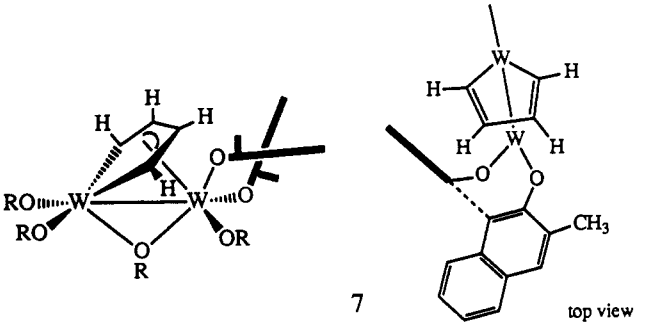


Figure 6. 1D NOE difference spectra (a, irradiate 8.6 ppm; b, irradiate 5.6 ppm; c, irradiate 5.2 ppm; d, irradiate 5.5 ppm), assignments for ^1H NMR resonances (e), and H–H coupling constants for flyover protons in **7** (500 MHz, toluene-d_8, 20 °C).



The proximity of the flyover proton resonating at δ = 5.6 and the Me_2BINO doublet at δ = 6.6, as deduced from the NOE difference experiment, in concert with the strong shielding of the proton whose resonance appears at δ = 5.5, are two key elements in assigning a probable structure to this complex. Only four protons on the Me_2BINO ligand, those in the 5,5′- and 8,8′-positions, appear as doublets. One of these protons must resonate at δ = 6.6 and lie in close proximity to the 3-position flyover unit. Several structures locating a 1-position flyover proton directly in the shielding cone of one of the naphthalene rings are possible, including those containing bridging Me_2BINO groups. However, molecular models of these complexes suggest that the conformer represented by **7** is the most likely structure, as it alone both accounts for the shielding of the 1-position proton and orients the

(41) Chisholm, M. H.; Eichhorn, B. W.; Folting, K.; Huffman, J. C. *Organometallics* **1989**, *8*, 49, 67, 80.
(42) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Rothwell, I. P. *J. Am. Chem. Soc.* **1982**, *104*, 4389.
(43) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. *Organometallics* **1983**, *2*, 1340.

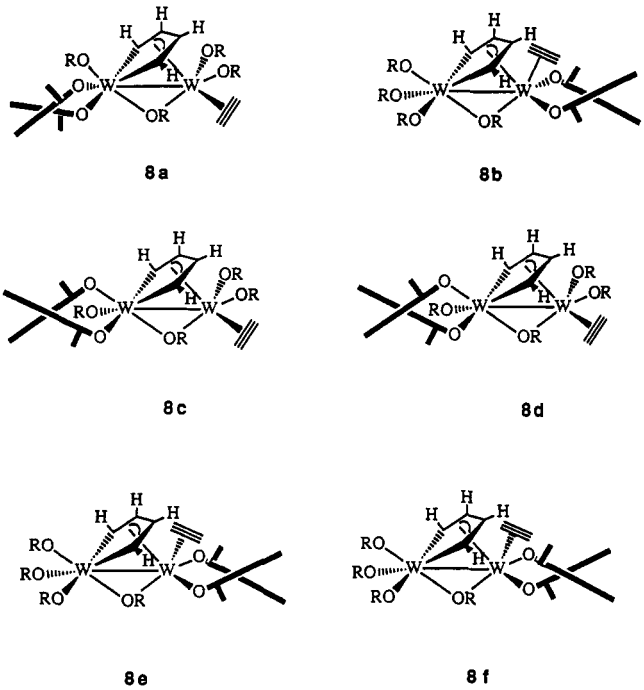


Figure 7. Six of the ten possible structural isomers of $(\eta^2\text{-}C_2H_2)(\eta^4,\mu_2\text{-}C_4H_4)(Me_2BINO)W_2(O\text{-}t\text{-}Bu)_4$ (**8**).

3-position flyover proton toward an 8-position proton on the Me_2-BINO group.

When **2** reacts with greater than 6 equiv of acetylene, a new adduct containing a flyover fragment and an additional terminal acetylene ligand, $(\eta^2\text{-}C_2H_2)(\mu_2,\eta^4\text{-}C_4H_4)(Me_2BINO)W_2(O\text{-}t\text{-}Bu)_2$ (**8**), is formed (eq 7). None of the flyover protons in this

$$\underset{\mathbf{2}}{(Me_2BINO)W_2(O\text{-}t\text{-}Bu)_4} + 3C_2H_2 \longrightarrow \underset{\mathbf{8}}{(\eta^2\text{-}C_2H_2)(\mu_2\text{-}C_4H_4)(Me_2BINO)W_2(O\text{-}t\text{-}Bu)_4} \quad (7)$$

complex experience a strong anisotropic shift. The terminal acetylene appears at $\delta = 11.29$ and exhibits tungsten satellites ($J_{W\text{-}H} = 9.7$ Hz). This resonance freezes out into two chemical environments at −53 °C ($\Delta G^{\ddagger} = 11.4$ kcal/mol). Using the skeletal arrangement of other structurally-defined tris(acetylene) complexes of $W_2(O\text{-}t\text{-}Bu)_6$ as a basis,[3] simple molecular models of the ten possible isomers of the complex can be constructed. Severe steric interactions between the naphthalene rings and at least one of the *t*-BuO ligands in the four isomers containing bridging binaphtholate ligands effectively eliminate these structures from consideration. Of the remaining six isomers (Figure 7), most can be excluded on steric grounds. In **8a** and **8b**, steric interactions between the bridging *t*-BuO ligand and the binaphtholate disfavor these diastereomeric structures. Structures **8c** and **8d** experience similar interactions, in this case between the terminal *t*-BuO and the binaphtholate ligand bound to the same tungsten center. The orientation of the 3-substituent of one of the naphthalene rings toward a β-hydrogen of the tungstapentadiene ring in structure **8f** would render it slightly destabilized relative to structure **8e**. Consequently, structure **8e** appears to be the most likely structure of the tris(acetylene) product. The similarity of the Me_2BINO coordination modes in structures **7** and **8e** suggests that *t*-BuO migration and acetylene coordination occur during the formation of complex **8e** from an intermediate such as **7**. It follows that the Me_2BINO ligand must have changed its orientation during the ligand rearrangement process, as evidenced by the lack of a large shielding effect of one of the flyover protons in **8e**.

Compound **3** is also reactive toward acetylene. Regardless of the reaction stoichiometry, a tris(acetylene) complex, **9**, results

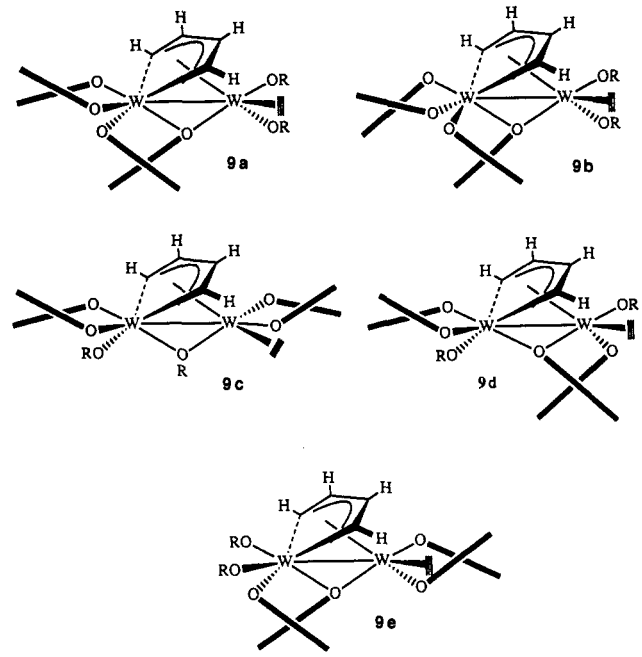


Figure 8. Possible structural forms of $(\eta^2\text{-}C_2H_2)(\eta^4,\mu_2\text{-}C_4H_4)(BINO)_2W_2(O\text{-}t\text{-}Bu)_2$ (**9**).

when **3** reacts with acetylene (eq 8). Resonances that are

$$\underset{\mathbf{3}}{anti\text{-}(R,S)\text{-}(BINO)_2W_2(O\text{-}t\text{-}Bu)} \longrightarrow \underset{\mathbf{9}}{(\eta^2\text{-}C_2H_2)(\mu_2\text{-}C_4H_4)(BINO)_2W_2(O\text{-}t\text{-}Bu)_2} \quad (8)$$
$$+ 3\,C_2H_2$$

characteristic of $\mu_2,\eta^4\text{-}C_4H_4$ and $\eta^2\text{-}C_2H_2$ units are observed in the ^1H and ^{13}C NMR spectra of this compound. These spectroscopic studies also reveal that the products exist as a mixture of two isomers in a ratio of 2:1. The presence of the chiral BINO ligands in the coordination spheres of the tungsten centers readily explains the formation of these diastereomeric complexes. If we make the assumption that these acetylene complexes retain the same binaphtholate ligands as in the parent molecule **3** (i.e., one (*R*)- and one (*S*)-BINO), sixteen structures are possible, twelve of which contain bridging binaphtholate groups. Representatives of the structural types of these isomers can be found in Figure 8. While bridging BINO groups are disfavored in structures such as **8**, the presence of only two *t*-BuO ligands in compound **9** relieves steric congestion and permits such bridging structures. In contrast, isomers containing a bridging *t*-BuO group, such as **9c**, require a terminal BINO and a *t*-BuO ligand to bind to the same tungsten center, an arrangement disfavored on steric grounds. This interaction also excludes structures such as **9d** from consideration. In structure **9e**, interactions between one of the bridging BINO rings with the *t*-BuO ligands would be greater than in the case of compounds such as **2**, because the BINO ligand is skewed toward one metal center, creating a sterically disfavored arrangement. The remaining structures, **9a** and **9b**, could exist in two forms which differ in the chirality of the bridging and terminal BINO groups. Interactions of one naphthalene ring of the bridging BINO with a terminal *t*-BuO disfavor one member of each of these pairs. On the basis of solely steric considerations, compounds **9a** and **9b**, as illustrated, are the most probable structures for these two diastereomeric reaction products.

The major and minor isomer structures could be assigned on the basis of ^1H NMR spectroscopic data of the product mixture. At room temperature, the terminal acetylenes are involved in a dynamic exchange process, producing two singlets that show no evidence of exchange, as would be expected were the isomers

interconverting on the NMR time scale. At −50 °C, the static η^2-C_2H_2 units exhibit resonances with significantly different chemical shifts (δ = 11.59 and 10.96 for the major product and 11.32 and 10.76 for the minor isomer). The upfield shift of a flyover proton in the minor isomer is reminiscent of that observed previously for **8**. This similarity allows us to suggest that the major isomer is **9a** and the minor isomer is **9b**. To the best of our knowledge, these acetylene complexes are the first examples of diastereomeric complexes derived from the $W_2(OR)_6$ template.

Conclusions

Alcoholysis reactions between homoleptic ditungsten alkoxides and binaphthols allow for the ready formation of chiral ditungsten complexes, with the chiral diol preferring to adopt a bridging bonding mode, as illustrated in the structure of **2**. The nonstatistical distributions of products observed in such reactions appear to be thermodynamically controlled, as evidenced by exchange reactions involving optically pure isomers. The extent of substitution of the W_2(O-*t*-Bu)$_6$ core, as well as the relative orientations of the binaphtholate ligands, is dictated predominantly by the stereochemistry of the bidentate alcohol and the relative stability of the gauche and anti isomers. These complexes still retain the reactivity of the W–W triple bond toward acetylenes, although the increased steric demands of the chelating ligands limit this reactivity to ethyne. The chiral binaphtholate ligand influences the overall structure of such products, producing the first known diastereomeric complexes based on the $W_2(OR)_6$ template.

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. HMQC and modified 1D NOE difference[44] spectra were recorded on a Bruker AM 500-MHz spectrometer. UV–vis spectra were recorded on a Hewlett Packard 8450A spectrometer. Circular dichroism spectra were recorded on a AVIV Model 60DS spectrometer, and optical rotations were determined using a Perkin-Elmer Model 241 polarimeter. Molecular modeling calculations were performed using the SYBYL 5.4 Molecular Modeling package on a VAX 9000-210 computer, with a dummy atom used to model the tungsten center. Energies of the structures were minimized to relieve severe steric interactions, and final bond distances and angles were within acceptable ranges. 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) and (*R*)-(+)-1,1′-bi-2-naphthol (Aldrich) were used as received. 3,3′-Disubstituted-1,1′-bi-2-naphthols (methyl,[45] phenyl[29b]) were prepared by slight alterations of literature methods, and W_2(O-*t*-Bu)$_6$ was prepared as described by Chisholm.[46]

(BINO)W$_2$(O-*t*-Bu)$_4$ (1). W_2(O-*t*-Bu)$_6$ (0.70 g, 0.87 mmol) in a small Schlenk flask (25 mL) was dissolved in toluene (12 mL) followed by slow addition of racemic 1,1′-bi-2-naphthol (0.25 g, 0.87 mmol). The solution was stirred for 16 h, and the solvent was removed in vacuo. Addition of hexanes (10 mL) followed by filtration left a yellow powder of (BINO)$_2$W$_2$(O-*t*-Bu)$_2$ and a red solution. Drastic reduction of the solution volume and refrigeration at −20 °C overnight yielded red crystals (0.05 g, 6% yield). ^{1}H NMR data (benzene-d_6, 20 °C): δ = 7.88 (2H, d, J = 9.0 Hz, NAP), 7.76 (2H, d, J = 5.1 Hz, NAP), 7.73 (2H, d, J = 5.4 Hz NAP), 7.41 (2H, d, J = 8.7 Hz, NAP), 7.13 (2H, t, J = 8.7 Hz, NAP), 6.96 (2H, t, J = 7.3 Hz, NAP), 1.84 (18H, s, OC(C*H*$_3$)$_3$), 0.69 (18H, s, OC(C*H*$_3$)$_3$). ^{13}C NMR data (benzene-d_6, 20 °C): δ = 167.5 (NAP $C_{2,2'}$), 136.5, 131.0, 128.8, 127.2, 126.8, 124.5, 123.1, 122.0 (NAP), 83.7, 75.5 (O*C*(CH$_3$)$_3$), 33.1, 32.3 (OC(*C*H$_3$)$_3$). Anal. Calcd: C, 45.76; H, 5.08. Found: C, 45.38; H, 5.17.

(Me$_2$BINO)W$_2$(O-*t*-Bu)$_4$ (2). W_2(O-*t*-Bu)$_6$ (1.28 g, 1.6 mmol) in a small Schlenk flask (25 mL) was dissolved in toluene (12 mL) followed by slow addition of racemic 3,3′-dimethyl-1,1′-bi-2-naphthol (0.50 g, 2.6 mmol). The solution was stirred for 16 h, and 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 orange crystals (0.85 g, 55% yield). ^{1}H NMR data (benzene-d_6, 20 °C): δ = 7.83 (2H, s, NAP), 7.79, 7.38 (2H, d, J = 8.3 Hz, NAP), 2.88 (6H, s, Me), 1.75, 0.67 (18H, s, OC(C*H*$_3$)$_3$). ^{13}C NMR data (benzene-d_6, 20 °C): δ = 167.1 (NAP $C_{2,2'}$), 134.0, 130.8, 130.4, 128.9, 127.1, 176.4, 125.6, 124.2, 121.6 (NAP), 83.6, 75.2 (O*C*(CH$_3$)$_3$), 35.6, 32.3 (OC-(*C*H$_3$)$_3$), 18.8 (Me). Anal. Calcd: C, 46.91; H, 5.43. Found: C, 47.16; H, 5.37.

(*R*,*S*)-(BINO)$_2$W$_2$(O-*t*-Bu)$_2$ (3). W_2(O-*t*-Bu)$_6$ (0.70 g, 0.87 mmol) in a small Schlenk flask (25 mL) was dissolved in toluene (12 mL) followed by slow addition of racemic 1,1′-bi-2-naphthol (0.50 g, 1.7 mmol). The solution was stirred for 12 h with the precipitation of a yellow powder after about 45 min. The solution was removed by syringe. The yellow powder was washed with cold toluene and dried in vacuo (0.47 g, 50% yield). ^{1}H NMR data (benzene-d_6, 20 °C): δ = 7.91 (4H, d, J = 9.9 Hz, NAP), 7.81 (4H, d, J = 9.6 Hz, NAP), 7.71 (4H, d, J = 7.8 Hz, NAP), 7.31 (4H, d, J = 7.2 Hz, NAP), 7.08 (4H, t, J = 5.7 Hz, NAP), 6.91 (4H, t, J = 6.3 Hz, NAP), 0.13 (18H, s, OC(C*H*$_3$)$_3$). ^{13}C NMR data (benzene-d_6, 20 °C): δ = 168.2 (NAP $C_{2,2'}$), 135.2, 131.0, 129.6, 126.9, 126.3, 124.4, 122.0, 121.0, 110.4 (NAP), 76.1 (O*C*(CH$_3$)$_3$), 31.8 (OC(*C*H$_3$)$_3$). Anal. Calcd: C, 53.06; H, 4.27. Found: C, 52.68; H, 3.67.

(*R*,*R*,*R*)-(BINO)$_3$W$_2$ (4). In a Schlenk flask (25 mL), W_2(O-*t*-Bu)$_6$ (0.374 g, 0.463 mmol) was dissolved in toluene (10 mL), followed by slow addition of (*R*)-binaphthol (0.400 g, 1.397 mmol). The solution was stirred for 20 h; then the solvent was removed in vacuo. The resulting brown powder was washed with hexane and dried in vacuo. Dichloromethane was added to precipitate a yellow powder (18% yield). ^{1}H NMR data (benzene-d_6, 20 °C): δ = 7.85, 7.08 (d, 1H, J = 8.3 Hz: H(3,4)), 7.56, 6.18 (d, 1H, J = 8.7 Hz: H(8,5)), 7.21, 6.90 (5, 1H, J = 9.0 Hz: H(6,7)). ^{13}C NMR data (benzene-d_6, 20 °C): δ = 166.4 (C(2)), 135.4 (C(1)), 130.9 (C(10)), 128.0, 124.8 (C(7,8)), 127.1, 127.0 (C(4,6)), 121.4 (C(9)), 121.3 (C(5)).

(*R*,*R*)-(BINO)$_2$W$_2$(O-*t*-Bu)$_2$ (6). W_2(O-*t*-Bu)$_6$ (0.70 g, 0.87 mmol) in a small Schlenk flask (25 mL) was dissolved in toluene (12 mL) followed by slow addition of (*R*)-binaphthol (0.50 g, 1.7 mmol). The solution was stirred for 16 h, and 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 a yellow powder (0.51 g, 54% yield). ^{1}H NMR data (benzene-d_6, 20 °C): δ = 7.94 (2H, d, J = 7.8 Hz, NAP), 7.82 (2H, d, J = 8.8 Hz, NAP), 7.71 (2H, d, J = 7.9 Hz, NAP), 7.49 (2H, d, J = 8.8 Hz, NAP), 7.34 (2H, d, J = 8.3 Hz, NAP), 7.24 (2H, t, J = 7.5 Hz, NAP), 7.15–6.96 (8H, m, NAP), 6.83 (2H, t, J = 6.6 Hz, NAP), 6.69 (2H, d, J = 8.8 Hz, NAP), 0.97 (18H, s, OC-(C*H*$_3$)$_3$). ^{13}C NMR data (toluene-d_8, 20 °C): δ = 167.8, 167.2 (NAP $C_{2,2'}$), 135.6, 135.4, 131.0, 130.6, 129.9, 128.2, 127.1, 126.9, 126.8, 126.7, 124.5, 123.4, 122.3, 121.5, 121.4, 121.0 (NAP), 80.4 (O*C*(CH$_3$)$_3$), 32.5 (OC(*C*H$_3$)$_3$). Anal. Calcd: C, 53.06; H, 4.27. Found: C, 53.66; H, 4.09.

(Me$_2$BINO)W$_2$(μ_2-C$_4$H$_4$)(O-*t*-Bu)$_4$ (7). (Me$_2$BINO)W$_2$(O-*t*-Bu)$_4$ (0.78 g, 0.80 mmol) in a small Schlenk flask (50 mL) was dissolved in toluene (20 mL). The solution was cooled to 77 K, and 2 equiv of acetylene was introduced into the frozen solution. The reaction mixture was warmed to room temperature and filtered, and 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 a red powder (0.33 g, 40% yield). ^{1}H NMR data (benzene-d_6, 20 °C): δ = 8.62 (1H, m, WC*H*), 7.73 (2H, d, J = 7.8 Hz, NAP), 7.54 (2H, s, NAP), 7.28 (2H, d, J = 7.8 Hz, NAP), 7.01 (2H, t, J = 8.7 Hz, NAP), 6.92–6.81 (6H, m, NAP), 6.73–6.63 (4H, m, NAP), 6.12 (2H, s, NAP), 5.64 (1H, m, WCHC*H*), 5.58 (1H, m, WCHC*H*), 5.22 (1H, m, WC*H*), 2.63 (3H, s, Me), 1.91 (9H, s OC(C*H*$_3$)$_3$), 1.64 (s, 3H, Me), 1.52 (s, 9H, OC(C*H*$_3$)$_3$), 1.50 (s, 9H, OC(C*H*$_3$)$_3$), 1.29 (s, 9H, OC(C*H*$_3$)$_3$). ^{13}C NMR data (toluene-d_8, 20 °C); δ = 202.0 (W*C*H, J = 68 Hz) 183.4 (NAP C_2 or $C_{2'}$), 172.5 (W*C*H, J = 82 Hz), 140.5 (NAP C_2 or $C_{2'}$), 139.0, 138.3, 132.3, 130.6, 129.9, 129.7, 128.7, 127.8, 127.3, 127.0, 125.7, 125.4, 125.1, 123.3, 122.6, 117.7, 116.6, 89.3 (WCH*C*H*C*HCH or NAP), 85.3, 83.7,

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82.1, 81.3 ($OC(CH_3)_3$), 32.2, 31.5, 31.3, 30.9 ($OC(CH_3)_3$), 18.7, 17.9 (Me). Anal. Calcd: C, 49.23; H, 5.51. Found: C, 50.00; H, 5.67.

$(Me_2BINO)W_2(\mu_2\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)(O\text{-}t\text{-}Bu)_4$ (8). $(Me_2BINO)W_2(O\text{-}t\text{-}Bu)_4$ (0.78 g, 0.80 mmol) in a small Schlenk flask (50 mL) was dissolved in toluene (20 mL). The solution was cooled to 77 K, and 6 equiv of acetylene was introduced into the frozen solution. The reaction mixture was warmed to room temperature and filtered, and 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 red microcrystals (0.33 g, 40% yield). ^{1}H NMR data (benzene-d_6, 20 °C): δ = 11.29 (2H, s, J_{W-H} = 9.7 Hz, W(η^2-*H*CC*H*)), 9.97–9.94 (1H, m, WC*H*), 8.71–8.66 (1H, m, WC*H*), 7.82–7.80 (3H, m, NAP), 7.60 (1H, s, NAP), 7.53 (1H, d, J = 8.3 Hz, NAP), 7.22–7.21 (3H, m, NAP), 7.16–7.12 (1H, m, WCHC*H*), 6.94 (1H, t, J = 7.3 Hz, NAP), 6.90 (1H, t, J = 7.1 Hz, NAP), 6.64–6.60 (1H, m, WCHC*H*), 2.80 (3H, s, Me), 1.59 (3H, s, Me), 1.48 (9H, s, $OC(CH_3)_3$), 1.32 (9H, s, $OC(CH_3)_3$), 1.30 (9H, s, $OC(CH_3)_3$), 1.20 (9H, s, $OC(CH_3)_3$). [^{1}H NMR data (partial) (toluene-d_8, −61 °C): δ = 11.48 (1H, s, W η^2-*H*CCH)), 10.85 (1H, s, W(η^2-HCC*H*)).] ^{13}C NMR (benzene-d_6, 20 °C): δ = 193.5 (W*C*H, J_{W-C} = 69 Hz), 193.1 (W*C*H, J_{W-C} = 75 Hz), 190.8 (W(η^2-H*C*CH), broad), 166.7, 164.0, 149.8, 133.9, 133.7, 131.4, 130.8, 129.1, 128.5, 128.3, 127.8, 127.4, 127.2, 126.6, 124.8, 124.7, 123.8, 123.5, 123.0, 122.1, 120.3, 117.6 (WCH*C*H*C*HCH or NAP), 93.0, 84.5, 82.9, 82.4 ($OC(CH_3)_3$), 31.7, 31.4, 31.2, 31.0 ($OC(CH_3)_3$), 23.0, 17.5 (Me). [^{13}C NMR data (partial) (toluene-d_8, −61 °C): δ = 194.7 (W(η^2-HC*C*H)), 193.3, 191.5 (W*C*H), 186.7 (W(η^2-HC*C*H)).] Anal. Calcd for $(\mu\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)(Me_2BINO)W_2(O\text{-}t\text{-}Bu)_4 \cdot {}^1/_3$(toluene): C, 51.46; H, 5.66. Found: C, 51.30; H, 5.45.

$(BINO)_2W_2(\mu_2\text{-}C_4H_4)(\eta^2\text{-}C_2H_2)(O\text{-}t\text{-}Bu)_2$ (9). (*R*,*S*)-$(BINO)_2W_2(O\text{-}t\text{-}Bu)_2$ (0.039 g, 0.036 mmol) was dissolved in toluene-d_8 (0.6 mL), and the solution was placed in an NMR tube. The solution was cooled to 77 K, and 6 equiv of acetylene was introduced into the frozen solution. The NMR tube was sealed and the solution warmed to room temperature. As the tube warmed, the solution became dark brown and insoluble poly(acetylene) was formed. ^{1}H NMR spectroscopy revealed that two diastereomers had formed in a ratio of approximately 2:1. Major isomer: ^{1}H NMR data (partial)(toluene-d_8, −50 °C) δ = 11.5, 10.9 (1H, s, η^2-*H*CC*H*), 9.8, 9.2 (1H, m, WC*H*), 0.94, 0.58 (9H, s, $OC(CH_3)_3$); ^{13}C NMR data (partial) (toluene-d_8, 20 °C) δ = 194.8, 173.8 (η^2-H*C*CH), 204.3, 189.5 (W*C*H), 87.3, 87.0 ($OC(CH_3)_3$), 30.5, 29.5 ($OC(CH_3)_3$). Minor isomer: ^{1}H NMR data (partial) (toluene-d_8, −50 °C) δ = 11.3, 10.7 (1H, s, η^2-*H*CC*H*), 10.2, 8.1 (1H, m, WC*H*), 1.09, 1.03 (9H, s, $OC(CH_3)_3$); ^{13}C NMR data (partial) (toluene-d_8, 20 °C) 193.5, 179.1 (η^2-H*C*CH), 198.1, 187.1 (W*C*H), 86.8, 85.9 ($OC(CH_3)_3$), 30.6, 29.7 ($OC(CH_3)_3$).

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