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Optical Resolution and Reactivity of Chiral Tungsten Alkyne Complexes

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Abstract: Displacement of a carbonyl ligand from a cationic dicarbonyltungsten complex, $[Tp'W(CO)_2(PhC{\equiv}CMe)][X]$ (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate; X = BF_4^-, PF_6^-, and OTf^-), by the counterion is effected by allowing the complex to reflux in THF. Substitution of the triflate ligand in $Tp'(CO)(PhC{\equiv}CMe)WOTf$ (= [W]-OTf) with (*S*)-(−)-α-methylbenzylamine yields a pair of tungsten amido diastereomers [W]-NHR*, **5**-(*RS*) and **5**-(*SS*), which are separable by crystallization. Protonation of each tungsten amido diastereomer yields optically pure cationic tungsten amine complexes. Acidification of the optically pure tungsten amine diastereomers, **6**-(*RS*) and **6**-(*SS*), in the presence of acetonitrile yields enantiomerically pure $[W]\text{-}N{\equiv}CMe^+$ complexes, (−)-**7** and (+)-**7**. Displacement of the resolving amine in **6**-(*RS*) and **6**-(*SS*) by iodide yields optically pure [W]-I, (+)-**8** and (−)-**8**. An X-ray structure of **6**-(*RS*)-$\{[W]\text{-}NH_2R^*\}\{BF_4\}$ (space group $P2_12_12_1$, a = 16.130 (2) Å, b = 16.576 (4) Å, c = 15.256 (3) Å, Z = 4, R = 0.044, R_w = 0.063) establishes the absolute configuration of the complex.

Introduction

Optical resolution of chiral transition metal complexes is a prerequisite if these compounds are to be useful in asymmetric organic syntheses. The resolution of an optically active organotransition metal complex, $[CpMn(CO)(NO)(PPh_3)][PF_6]$, by Brunner's group in 1969 led the way for a variety of resolution schemes for other organometallic complexes involving iron, titanium, and chromium complexes.[1]

Liebeskind[2] and Davies[3] have succeeded in elaborating η^1-acyl groups with the chiral iron system $CpFe(CO)(PR_3)L^+$. These acyl elaborations are characterized by high enantioselectivity. Brookhart[4] has achieved enantioselective formation of cyclopropanes by reacting an optically pure iron carbene complex, $[Cp(CO)(PR_3)Fe{=}CHR]^+$, with olefins. Gladysz[5] has synthesized a variety of optically active rhenium complexes of the type $Cp(NO)(PR_3)ReL$ which are capable of transferring the metal-centered chirality to a new ligand-based chiral center. High enantioselectivity also characterizes the transfer of a crotyl group to benzaldehyde in Faller's chiral molybdenum complex, (neomenthylcyclopentadienyl)Mo(NO)(Cl)(π-crotyl), to yield homoallylic alcohols.[6] The chiral fragment $Tp'Mo(CO)(P(OPh)_3)^+$ (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate; Scheme I) has been shown to effect diastereoselective η^2-acyl ligand elaboration reactions.[7]

Stepwise reduction of acetonitrile bound to tungsten to form ethylamine has been reported.[8] A series of H^-/H^+ additions to

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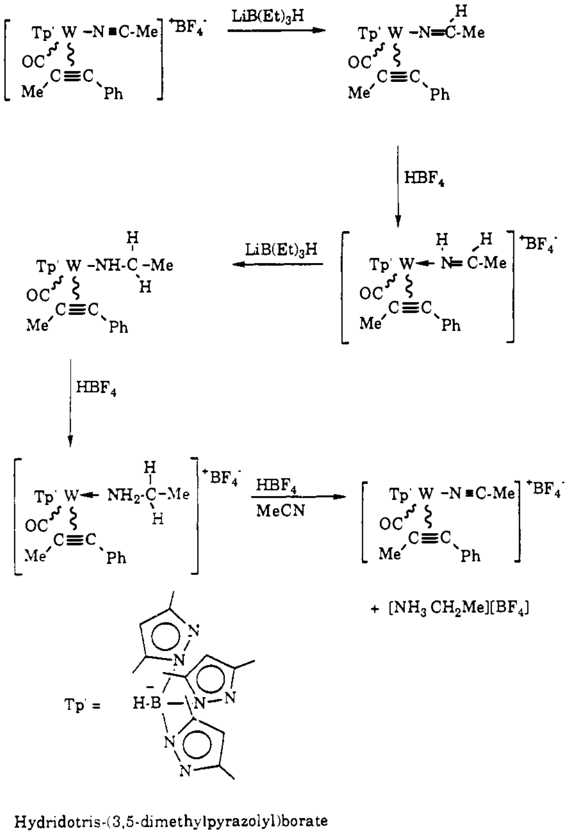
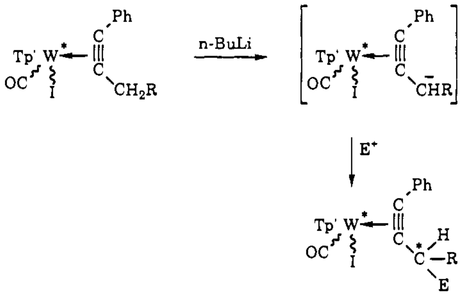
Scheme I



Scheme II

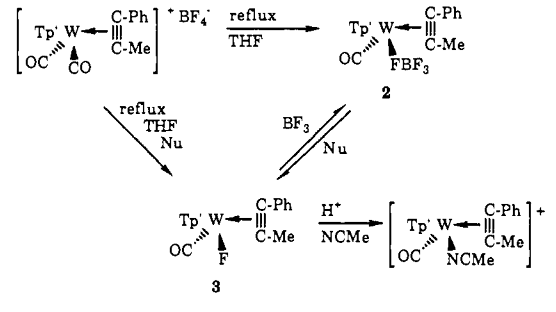


the nitrogen–carbon triple bond of coordinated acetonitrile in $[Tp'(CO)(PhC{\equiv}CMe)WN{\equiv}CMe][BF_4]$ gives isolable products throughout the addition sequence. Protonation of the resulting amine complex in acetonitrile cleaves the amine ligand from tungsten, and solvent coordinates to reform the starting cationic tungsten acetonitrile reagent (Scheme I). Nucleophilic addition of CN^- to C_α of the imine ligand was found to be diastereoselective.[9] Resolution of enantiomers of the tungsten acetonitrile complex should provide a route to enantioselective reactions at the acetonitrile ligand.

Resolution of the neutral $Tp'(CO)(I)W(PhC{\equiv}CMe)$ would also be important since diastereoselective reactions at the alkyne propargyl site have previously been observed. The tungsten-bound alkyne has acidic propargylic protons which can be removed to form metal-coordinated propargyl anions. Electrophilic additions at the propargyl site have proven to be highly diastereoselective (Scheme II).[10]

Syntheses of transition metal complexes with weakly coordinating anions such as BF_4^-, PF_6^-, and $CF_3SO_3^-$ are important in organometallic chemistry.[11] These complexes are valuable from a synthetic viewpoint as flexible precursors to numerous substitution products. Since they are often in equilibrium with their coordinatively unsaturated counterparts, compounds such as $CpM(CO)_2LX$ (M = Mo, W; X = FBF_3, FPF_5, O_3SCF_3) and $CpMo(NO)_2LX$[11] are reactive toward substitutions.

Scheme III



Nu = amines, phosphines, alkoxides or hydroxide.

Gladysz resolved the rhenium complex $[Cp(PR_3)(NO)ReCO][BF_4]$ via an optically pure amine adduct which results from amine attack at the carbonyl ligand to form a pair of separable rhenium carbamoyl diastereomers.[12] The synthesis of rhenium amine complexes was recently accomplished by Gladysz and co-workers[13] by substitution of the triflate ligand in $Cp(NO)(PR_3)ReOTf$ by amines. The triflate ligand in the rhenium system is easily displaced by other ligands at room temperature.

We now report the following: (1) a simple and convenient resolution of $Tp'W(CO)(PhC{\equiv}CMe)(NHR^*)$ which provides a vehicle to access multigram quantities of enantiomerically pure $Tp'W(CO)(PhC{\equiv}CMe)L^{n+}$ (L = $N{\equiv}CMe$, $n = 1$; L = I, $n = 0$); (2) the reactivity of enantiomerically pure $Tp'W(CO)(PhC{\equiv}CMe)(N{\equiv}CMe)^+$ at the acetonitrile ligand; and (3) the X-ray structure of a single diastereomer, $Tp'W(CO)(PhC{\equiv}CMe)(NH_2R^*)^+$, which allows the assignment of absolute configuration in this complex.

Results and Discussion

Synthesis and Characterization of $Tp'(CO)(PhC{\equiv}CMe)WX$ (X = FBF_3, F, OTf, O_3SR). Displacement of a labile CO ligand from the cationic $[Tp'(CO)_2W(PhC{\equiv}CMe)][BF_4]$ dicarbonyltungsten complex is accomplished by heating the complex in boiling THF. In the absence of other nucleophiles, the BF_4^- counterion enters the coordination sphere to fill the empty coordination site and forms a neutral product, $Tp'(CO)(PhC{\equiv}CMe)WFBF_3$ (**2**), in 23% yield. This product is characterized by a carbonyl stretching frequency in the infrared at 1917 cm^{-1}.

Efforts to displace BF_4^- with other ligands such as amines (NH_2Ph), phosphines (PPh_3), alkoxides (NaOEt), and hydroxide (KOH) were unsuccessful. Instead we observed the formation of a tungsten fluoride derivative, $Tp'(CO)(PhC{\equiv}CMe)WF$ (**3**). Presumably the nucleophiles either attack the boron atom and cleave the boron–fluoride bond or trap free boron trifluoride (Scheme III). The fluoride complex has a single carbonyl stretching frequency at 1876 cm^{-1} in the infrared spectrum. A ^{19}F NMR spectrum displayed a singlet at −38.9 ppm with a one-bond tungsten coupling of 27 Hz (^{183}W 14%, $I = {}^1/_2$), a value that lies within the range (12–84 Hz) of reported tungsten–fluorine coupling constants.[14] The [W]-FBF_3 (**2**) and [W]-F (**3**) ([W] = $Tp'W(CO)(PhC{\equiv}CMe)W$) equilibrium is driven toward the latter by nucleophiles, while BF_3 addition reforms **2**. ^1H and ^{13}C NMR spectra reveal that both of these complexes are chiral at metal as the Tp′ ligand displays three separate signals for the three pyrazole protons and six signals for the pyrazole methyl groups.

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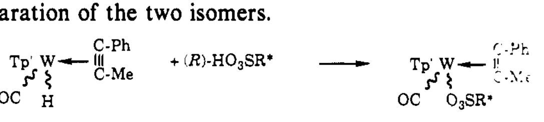
Direct substitution of a carbonyl ligand in $[Tp'W(CO)_2(PhC{\equiv}CMe)][BF_4]$ by amines (NH_2Ph), phosphines (PPh_3), and hydroxide (KOH) was attempted by allowing the complex and the nucleophile to reflux in THF. Simple substitution products were not observed; instead, coordination of the BF_4^- anion to the metal is favored. Nucleophilic cleavage of the boron–fluorine bond then leads to formation of the fluoride complex **3**. The fluoride ligand is easily displaced from the coordination sphere upon protonation in acetonitrile to yield $[Tp'W(CO)(PhC{\equiv}CMe)(N{\equiv}CMe)]^+$ (Scheme III).

Similar behavior is observed when PF_6^- is used as the counterion in the reaction mixture. The [W]-FPF_5 complex is formed when the dicarbonyl species is heated in THF, and attempts to substitute PF_6^- with other ligands resulted in the formation of [W]-F (**3**). The formation of [W]-F evident here is reminiscent of reactions observed in other metal complexes.[15] The zirconocene complex $[Cp_2Zr(Me)(NCMe)][PF_6]$, for example, decomposes instantaneously in THF to the neutral fluoride $Cp_2Zr(Me)F$ via F^- abstraction from PF_6^-.[16]

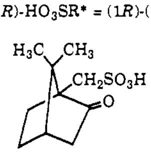
Substituted derivatives of $[Tp'W(CO)_2(PhC{\equiv}CMe)]^+$ can be accessed, however, by starting with the triflate counterion, $O_3SCF_3^-$, in the reaction instead of BF_4^- or PF_6^-. The tungsten dicarbonyl complex $[Tp'(CO)_2W(PhC{\equiv}CMe)][OTf]$ can be heated in solution to form the [W]-OTf complex (**1**) in 85% yield. The [W]-OTf complex is characterized by a strong carbonyl stretching band at 1917 cm^{-1}. Triflate-containing compounds typically exhibit absorptions between 900 and 1400 cm^{-1} in the IR spectrum.[17] Covalently bound triflates have their highest frequency OTf band near 1365–1395 cm^{-1}, while ionic triflates are characterized by absorptions at 1270–1280 cm^{-1}. The $[Tp'(CO)_2W(PhC{\equiv}CMe)][OTf]$ dicarbonyl reagent displays a series of bands in the triflate region with the highest at 1270 cm^{-1}, as expected for an ionic triflate. The monocarbonyl [W]-OTf product shows IR bands in the range appropriate for covalently bound triflate. ^1H and ^{13}C NMR spectra of the [W]-OTf product reveal a compound with C_1 symmetry. The carbon of the triflate appears as a quartet at 118 ppm with a characteristically large $^1J_{CF}$ carbon–fluorine coupling of 316 Hz.

A pair of tungsten sulfonate diastereomers was synthesized by adding (1*R*)-(−)-10-camphorsulfonic acid ($HOSO_2R^*$) to a methylene chloride solution of $Tp'(CO)(PhC{\equiv}CMe)WH$[18] (eq 1). Gas evolution was observed as the product formed, and the carbonyl stretching frequency of the [W]-H reagent at 1876 cm^{-1} decreased in intensity as the carbonyl absorption of the product [W]-OSO_2R^* at 1910 cm^{-1} grew. ^1H and ^{13}C NMR data show the presence of a 1:1 mixture of diastereomers [**4**-(*RR*), **4**-(*SR*)] for this sulfonate compound. Neither chromatography nor recrystallization techniques were successful in achieving efficient separation of the two isomers.



Eq. 1

(*R*)-HO_3SR^* = (1*R*)-(-)-10-camphorsulfonic acid



Synthesis, Characterization, and Separation of a Pair of Tungsten Amido Diastereomers, Tp'(CO)(PhC≡CMe)W-NHR*. An excess of optically pure (*S*)-(−)-α-methylbenzylamine was added to a refluxing THF solution of the [W]-OTf complex, and a pair of neutral tungsten amido diastereomers, **5**-(*RS*) and **5**-(*SS*) (this nomenclature refers to the configuration at metal first and to the configuration at ligand second), formed (Scheme IV). The mixture was purified by alumina column chromatography, but no separation of diastereomers was effected. A single recrystallization from CH_2Cl_2/hexane gave (1) an insoluble fraction corresponding to approximately a 35:1 (*RS*:*SS*) enriched mixture and (2) a soluble portion which provides a 5:1 (*SS*:*RS*) ratio of diastereomers upon isolation. The major isomer in the insoluble fraction, **5**-(*RS*), can be obtained pure as assessed by ^1H NMR after several recrystallizations. (This product was determined to be the R_WS_N diastereomer by a crystal structure of the protonated product; vide infra.)

Scheme IV

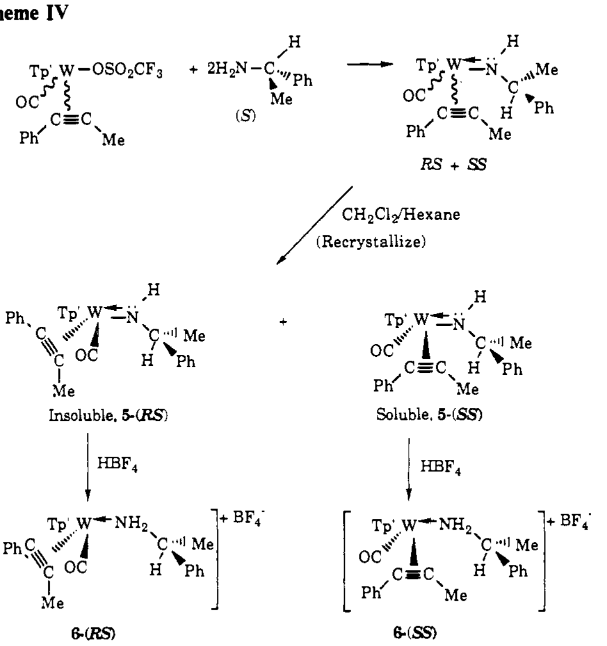


Table I. Optical Rotations of Chiral Tungsten Alkyne Complexes

complex	$[\alpha]^{25}_{589}$, deg	*c* (CH_2Cl_2), g/mL
(−)-**5**-(*RS*)	−870	1.23×10^{-3}
(+)-**5**-(*SS*)	+710	1.26×10^{-3}
(−)-**6**-(*RS*)	−890	2.9×10^{-4}
(+)-**6**-(*SS*)	+990	2.5×10^{-4}
(−)-**7**	−880	3.0×10^{-4}
(+)-**7**	+870	3.4×10^{-4}
(+)-**8**	+340	4.4×10^{-4}
(−)-**8**	−340	4.2×10^{-4}

Both isomers were independently characterized by IR and NMR spectroscopy. Surprisingly, the carbonyl stretching bands for the two diastereomers differ by 6 cm^{-1} (*RS* ν_{CO} = 1846 cm^{-1}; *SS* ν_{CO} = 1852 cm^{-1}). The ^1H and ^{13}C NMR spectra for the two isomers also differ significantly. The ^1H NMR methyl signal of the coordinated amide appears as a doublet at 0.85 ppm for the *RS* diastereomer, and it is shifted downfield to 1.26 ppm for the *SS* diastereomer. The alkyne methyl group appears at 3.18 and 2.90 ppm for **5**-(*RS*) and **5**-(*SS*), respectively. Optical rotations were found to be $[\alpha]^{25}_{589}$ = −870° [**5**-(*RS*)] and +710° [**5**-(*SS*)] for the two diastereomers (optical rotations of all of the resolved complexes described here are summarized in Table I). As one might expect, the two optical rotations are opposite in sign, but the magnitudes are unequal for these diastereomers which are both *S* at carbon.

Both isomers can be protonated to obtain pure cationic tungsten amine compounds which are also distinguishable by IR and NMR spectroscopy (Scheme IV). The carbonyl stretching frequencies of the cationic *RS* and *SS* complexes are 1916 and 1903 cm^{-1}, respectively. ^1H NMR spectra display a resolving amine methyl doublet at 1.10 and 1.72 ppm for the two isomers. The amine hydrogens are diastereotopic. Accordingly, two separate signals are seen in the NMR spectra for the two protons on nitrogen in

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Table II. Crystallographic Data Collection Parameters for (−)-(R_WS_N)-[Tp′W(CO)(PhC≡CMe)NH$_2$C*H(Me)(Ph)][BF$_4$] [(−)-**6**-(*RS*)]

molecular formula	$WC_{33}H_{41}B_2F_4N_7O$
formula weight, g/mol	833.19
crystal dimensions, mm	0.30 × 0.30 × 0.20
space group	$P2_12_12_1$
cell parameters	
a, Å	16.130 (2)
b, Å	16.576 (4)
c, Å	15.256 (3)
V, Å^3	4079 (1)
Z	4
density$_{calcd}$, g/cm^3	1.357
Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo Kα (0.709 30)
monochromator	graphite
linear abs coeff, cm^{-1}	29.4
scan type	$\theta/2\theta$
2θ limit	49.9°
h, *k*, *l* ranges	0–19, 0–19, 0–18
total no. of reflections	3993
data with $I > 2.5\sigma(I)$	2631
R, %	4.4
R_w, %	6.3
GOF	1.39
no. of parameters	433
largest parameter shift	0.675

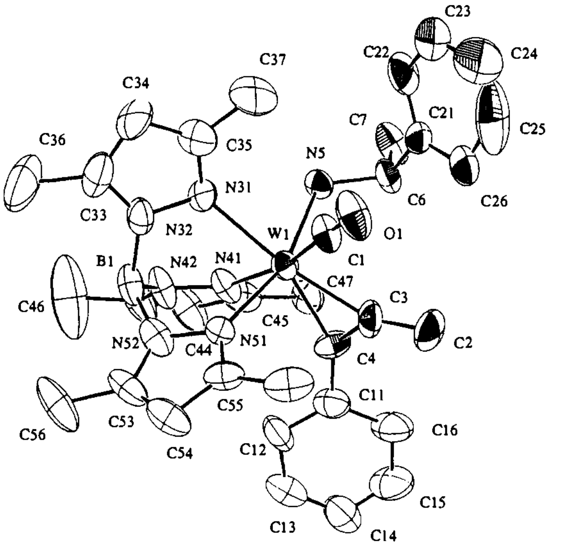


Figure 1. ORTEP diagram showing complete atomic number scheme for (−)-(R_WS_N)-[Tp′W(CO)(PhC≡CMe)NH$_2$C*HMePh][BF$_4$] [(−)-**6**-(*RS*)].

each complex. For the *RS* diastereomer the two primary amine hydrogens appear at 3.95 and 3.15 ppm ($\Delta\delta$ 0.80 ppm). The *SS* diastereomer has amine protons which appear at 3.98 and 3.40 ppm ($\Delta\delta$ 0.58 ppm). The alkyne methyl signal offers a convenient probe to assess diastereomeric purity; the singlet methyl resonances for the *RS* and *SS* compounds appear at 3.84 and 3.45 ppm, respectively.

X-ray crystallographic data for the tetrafluoroborate salt of the optically pure cationic complex **6**-(*RS*) were collected under the conditions described in Table II. Figure 1 shows the crystal structure of **6**-(*RS*) which was used in the determination of the absolute configuration at metal according to the Baird/Sloan modification of the Cahn–Ingold–Prelog priority rules.[19] This crystal structure of **6**-(*RS*) reveals an octahedral coordination sphere. Selected bond distances and angles are reported in Tables III and IV, respectively. The geometrical features of the metal alkyne fragment are typical of group VI d^4 alkyne complexes;[20] the alkyne is parallel to the metal carbonyl axis for well-known electronic reasons. This alkyne orientation maximizes the interactions between metal dπ and filled and empty ligand π orbitals; the π donor orbital of the alkyne donates electron density to the empty dπ orbital of tungsten while the CO ligand can interact with both filled dπ orbitals of the metal.

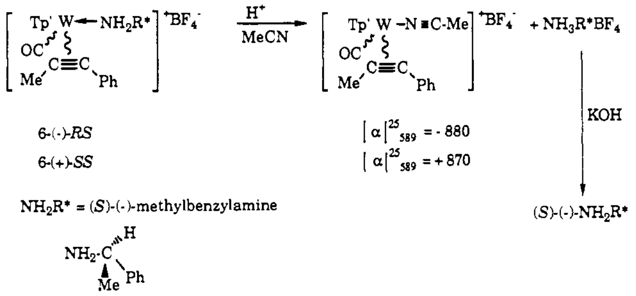
Table III. Selected Bond Distances (Å) for (−)-(R_WS_N)-[Tp′W(CO)(PhC≡CMe)NH$_2$C*H(Me)(Ph)][BF$_4$] [(−)-**6**-(*RS*)]

W(1)–C(1)	1.92 (2)	C(1)–O(1)	1.16 (2)
W(1)–C(3)	2.11 (2)	C(2)–C(3)	1.47 (3)
W(1)–C(4)	2.02 (2)	C(3)–C(4)	1.43 (3)
W(1)–N(5)	2.24 (1)	C(4)–C(11)	1.44 (2)
W(1)–N(31)	2.25 (1)	N(5)–C(6)	1.52 (2)
W(1)–N(41)	2.24 (1)	C(6)–C(7)	1.50 (3)
W(1)–N(51)	2.15 (1)	C(6)–C(21)	1.48 (3)

Table IV. Selected Bond Angles (deg) for (−)-(R_WS_N)-[Tp′W(CO)(PhC≡CMe)NH$_2$C*H(Me)(Ph)][BF$_4$] [(−)-**6**-(*RS*)]

C(1)–W(1)–C(3)	69.2 (8)	N(5)–W(1)–N(31)	83.3 (5)
C(1)–W(1)–C(4)	109.3 (8)	N(5)–W(1)–N(41)	81.8 (5)
C(1)–W(1)–N(5)	94.4 (6)	N(5)–W(1)–N(51)	160.4 (5)
C(1)–W(1)–N(31)	87.2 (7)	N(31)–W(1)–N(41)	82.9 (5)
C(1)–W(1)–N(41)	169.7 (7)	N(31)–W(1)–N(51)	80.0 (5)
C(1)–W(1)–N(51)	94.8 (6)	N(41)–W(1)–N(51)	86.1 (5)
C(3)–W(1)–C(4)	40.5 (8)	W(1)–C(1)–O(1)	178 (2)
C(3)–W(1)–N(5)	103.1 (6)	W(1)–C(3)–C(2)	151 (2)
C(3)–W(1)–N(31)	155.8 (7)	W(1)–C(3)–C(4)	66.2 (9)
C(3)–W(1)–N(41)	120.9 (7)	C(2)–C(3)–C(4)	143 (2)
C(3)–W(1)–N(51)	96.4 (6)	W(1)–C(4)–C(3)	73.3 (9)
C(4)–W(1)–N(5)	105.1 (6)	W(1)–C(4)–C(11)	150 (2)
C(4)–W(1)–N(31)	160.4 (6)	C(3)–C(4)–C(11)	135 (2)
C(4)–W(1)–N(41)	80.9 (7)	W(1)–N(5)–C(6)	122 (1)
C(4)–W(1)–N(51)	88.0 (6)		

Scheme V



The tungsten–nitrogen (2.24 (1) Å) and tungsten–carbon (1.92 (2) Å) bond distances to the amine and carbonyl ligands are consistent with values reported in other systems. Values found in the literature for tungsten–amine bonds[21] are in the range 2.24–2.25 Å.

Substitution of the Resolving Amine in 6-(*RS*) and 6-(*SS*) by Acetonitrile and Iodide To Form Optically Active [W]-N≡CMe$^+$ and [W]-I ([W] = Tp′(CO)(PhC≡CMe)W). The resolving amine can be cleaved from the metal upon acidification in acetonitrile to form an optically pure [W]-N≡CMe$^+$ complex (Scheme V). The ammonium salt produced in the reaction is removed from the reaction mixture through a series of water extractions. The amine complex **6**-(*RS*) leads to the formation of a cationic acetonitrile adduct [W]-N≡CMe$^+$ [(−)-**7**], with an optical rotation of −880°, while **6**-(*SS*) gives the enantiomeric (+)-**7** with an opposite rotation of +870° (Table I). Absolute configurations

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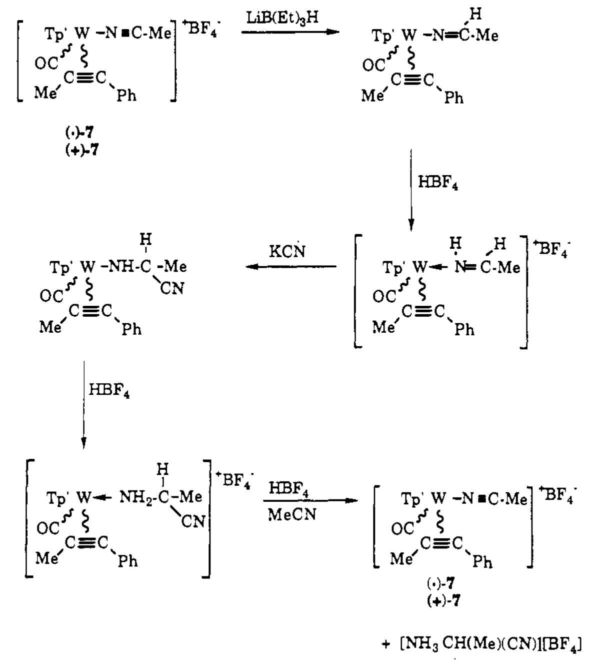
[19] The rank of the ligands is determined by the sum of all atoms of each ligand bound to the metal center. In our cationic tungsten amine complex, **6**-(*RS*), the Tp′, alkyne, amine, and carbonyl ligands are bound to the metal through pseudoatoms of atomic numbers 42 (= 3 × 14N), 24 (= 2 × 12C), 14 (= 1 × 14N), and 12 (= 1 × 12C), respectively. (a) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6599. (b) Sloan, T. *Top. Stereochem.* **1981**, *12*, 1.

[20] Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

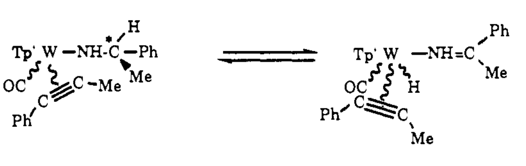
[21] Osterberg, C. E.; Arif, A. M.; Richmond, T. G. *J. Am. Chem. Soc.* **1988**, *110*, 6903.

Scheme VI

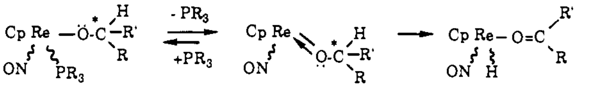


of the enantiomers are not known at this time. Thus, the metal moiety Tp′(CO)(PhC≡CMe)W$^+$ is configurationally robust and undergoes substitution reactions without racemization at tungsten. Geometric integrity appears to be a hallmark for heavy transition metal systems. Cooper[22] recently reported configurational stability throughout tungstenocene [CpCp′W(Me)(N≡CMe)]$^+$ substitution reactions. Acetonitrile is replaced by other ligands with predominant retention of configuration at the metal center.

Recovery of the resolving amine was achieved by deprotonation of the ammonium salt with potassium hydroxide. Diethyl ether extraction of the solution allows isolation of the resolving amine, (*S*)-(−)-α-methylbenzylamine. Measurement of the optical rotation of this isolated amine indicated that no loss of optical purity occurred during the reaction sequence. Why was racemization at carbon of the amine ligand examined? One could imagine an equilibrium between the neutral Tp′(CO)(PhC≡CMe)-WNHCH(Me)(Ph) [**5**-(*RS*) or **5**-(*SS*)] and a putative tungsten imine complex formed by β hydrogen migration to the metal. The imine ligand would be planar and susceptible to racemization at carbon (eq 2). Gladysz and co-workers[23] observe a related epimerization at carbon in rhenium alkoxide compounds. They propose an alkoxide ligand β hydrogen migration to the metal to form a metal hydride ketone complex that leads to racemization at carbon (eq 3). In our system, however, the resolving amine did not racemize; it was recovered without loss of optical purity.



Eq. 2

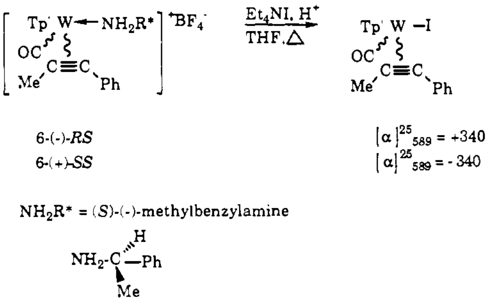


Eq. 3

^{1}H NMR experiments with chiral shift reagents were performed to assess the enantiomeric purity of the [W]-N≡CMe$^+$ enantiomers. The two enantiomers interact differently with the optically pure europium shift reagent (+)-Eu(tfc)$_3$, where tfc is the 3-[(trifluoromethyl)hydroxymethylene]camphorato ligand. When a racemic mixture of [W]-N≡CMe$^+$ complexes is used in this series of experiments, most ^{1}H NMR peaks in the spectrum shift downfield and begin to split into two signals. One of the signals, the acetonitrile methyl group, shifts downfield further and splits more completely than other signals. Base-line resolution of enantiomers was achieved when 4 equiv of (+)-Eu(tfc)$_3$ was added to the racemic CD$_2$Cl$_2$ solution of [W]-N≡CMe$^+$.

The optical purity of (−)-**7** and (+)-**7** was assayed by ^{1}H NMR shift reagent techniques once base-line resolution conditions had been established. A CD$_2$Cl$_2$ solution of (−)-**7** and Eu(tfc)$_3$ was doped with 5% of (+)-**7**. The minor isomers was clearly visible in the spectrum. These results lead us to estimate that 2–3% of one enantiomer could be detected by this NMR shift method in the presence of the other. Since we detect only one enantiomer in the presence of Eu(tfc)$_3$, we believe these products have an ee of at least 95%, and we refer to them as optically pure for discussion purposes.

The Tp′(CO)(PhC≡CMe)WI complex can be obtained by adding tetraethylammonium iodide and fluoboric acid to a refluxing THF solution of the pure tungsten amine diastereomers, either **6**-(*RS*) or **6**-(*SS*) (eq 4). Optical rotations of +340° and −340° were obtained for the resulting iodide complexes (+)-**8** and (−)-**8**, respectively (Table I).



Eq. 4

Reactivity of the [W]-N≡CMe$^+$ Complexes (−)-7 and (+)-7. Stepwise reduction of the acetonitrile ligand in a racemic mixture of [Tp′W(CO)(PhC≡CMe)WN≡CMe][BF$_4$] has been accomplished through a series of H$^-$/H$^+$ additions (Scheme I).[8] The use of a nucleophile other than H$^-$ in the third step generates a chiral carbon. It has been shown that this step is diastereoselective when racemic [W]-N≡CMe$^+$ is used as the starting material and cyanide is employed as the nucleophile.[9] When an enantiomerically pure complex, either (−)-**7** or (+)-**7**, is used in this series of reactions, the attack of CN$^-$ at C$_\alpha$ is diastereoselective. Protonation of the amido complex [W]-NHC*H(CN)(Me) gives a cationic tungsten amine compound. Upon acidification with HBF$_4$ in the presence of acetonitrile, the starting material [W]-N≡CMe$^+$ is regenerated (Scheme VI). Optical rotation measurements and chiral shift reagent ^{1}H NMR experiments indicate that this substitution reaction occurs with retention of configuration at metal, i.e., the same enantiomer is recovered after elaboration and substitution of the acetonitrile ligand. This observation further confirms the remarkable configurational stability of the Tp′(CO)(PhC≡CMe)W$^+$ moiety.

Summary

Diastereomeric amido complexes were synthesized via substitution of the triflate ligand with an optically active amide. Separation of the diastereomeric pair was accomplished by a single recrystallization. Protonation of the diastereomers yields cationic tungsten amine complexes which are also optically active, consistent with the absence of metal–ligand bond cleavage reactions. Displacement of the resolving amine with CH$_3$CN or I$^-$ was accomplished without racemization at the metal center; our system is geometrically robust and retains its configuration at the tungsten center. This sequence of reactions represents a convenient and efficient route to optically pure tungsten alkyne complexes.

Chirality at the metal center here successfully controls the stereochemistry of several ligand-based reactions. Stereoselective alkyne elaborations and acetonitrile reduction reactions are ac-

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[22] McNally, J. P.; Cooper, N. J. *J. Am. Chem. Soc.* **1989**, *111*, 4500.
[23] Saura-Llamas, I.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 2136.

cessible. Cyanide addition at the imine stage followed by protonation of the amido ligand produces a coordinated amine which can be cleaved from the metal center. Isolation of the organic product, an α-amino nitrile, represents a possible route to enantiomerically pure amino acids along the lines of the Strecker synthesis.

Experimental Section

Materials and Methods. Reactions were performed under a dry N_2 atmosphere with standard Schlenk techniques. Tetrahydrofuran (THF), hexanes, and diethyl ether (Et_2O) were distilled from potassium benzophenone ketyl unless otherwise noted. Dichloromethane was distilled from phosphorus pentoxide. All other solvents were purged with nitrogen and used without further purification. Optically pure reagents, (*S*)-(−)-α-methylbenzylamine and (1*R*)-(−)-10-camphorsulfonic acid, were obtained from Aldrich and used without further purification. Metal complexes used as reagents, Tp′W(CO)(PhC≡CMe)H[18] and $[Tp'W(CO)_2(PhC{\equiv}CMe)][X]$ ($X = BF_4$[24] or OTf[25]), were synthesized according to literature procedures.

Infrared spectra were collected on a Mattson Polaris FTIR spectrometer. ^1H and ^{13}C NMR were recorded on a Bruker AC 200 (200 MHz) or a Varian XL 400 (400 MHz) spectrometer. ^{19}F NMR spectra were recorded on a Varian XL 400 (400 MHz) spectrometer, and the chemical shifts are reported in ppm relative to $CFCl_3$. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. UV/vis spectra were recorded on an HP 8451A diode array spectrophotometer. Analyses were conducted by Galbraith Laboratories of Knoxville, TN, Oneida Research Services of Whitesboro, NY, or Atlantic Microlab of Norcross, GA.

Synthesis of Tp′W(CO)(PhC≡CMe)OTf (1). A THF (50 mL) solution of $[Tp'(CO)_2W(PhC{\equiv}CMe)][OTf]$ (0.40 g, 0.50 mmol) was allowed to reflux for 1 h. Gas evolution was observed as the color changed from lime green to blue. The solvent was evaporated to leave an oil, and the product was extracted with diethyl ether. The solvent was removed, and recrystallization from CH_2Cl_2/hexanes produced 0.33 g (85% yield) of product: IR (KBr) ν_{CO} 1917 cm^{-1}; ^1H NMR (CD_2Cl_2) δ (ppm) 7.30–6.64 (m, 5 H, Ph), 5.98, 5.81, 5.75 (each an s, 3 H, Tp′ CH), 3.83 (s, 3 H, PhC≡C*Me*), 2.69, 2.56, 2.43, 1.39, 1.37 (each an s, 3:6:3:3:3 H, Tp′ CMe); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) 229.4 ($^1J_{WC}$ = 153 Hz, CO), 208.7 ($^1J_{WC}$ = 53 Hz, Ph*C*≡CMe), 208.3 ($^1J_{WC}$ = 14 Hz, PhC≡*C*Me), 155.0, 153.8, 151.2, 147.5, 146.7, 145.0 (Tp′ *C*Me), 137.0 (ipso C of Ph), 129.5, 129.4, 128.7 (Ph), 118.6 (q, $^1J_{CF}$ = 316 Hz, O_3SCF_3), 108.4, 108.2, 107.7 (Tp′ CH), 22.7 (PhC≡C*Me*), 16.1, 15.2, 13.4, 13.0, 12.9, 12.7 (Tp′ C*Me*). Anal. Calcd: C, 40.34; H, 3.91; N, 10.86. Found: C, 40.25; H, 3.92; N, 10.76.

Synthesis of Tp′W(CO)(PhC≡CMe)FBF$_3$ (2). A THF (100 mL) solution of $[Tp'W(CO)_2(PhC{\equiv}CMe)][BF_4]$ (0.91 g, 1.23 mmol) was heated to reflux for 2 h. The solution color changed from green to blue. The solvent was evaporated to leave a tar, and then the product was extracted with diethy ether. The solvent was removed, and the compound was recrystallized from CH_2Cl_2/hexanes to yield 0.20 g (23% yield) of crystalline material: IR (KBr) ν_{CO} 1917 cm^{-1}; ^1H NMR (CD_2Cl_2) δ (ppm) 7.25–6.61 (m, 5 H, Ph), 6.00, 5.84, 5.76 (each an s, 3 H, Tp′ CH), 3.72 (s, 3 H, PhC≡C*Me*), 2.74, 2.55, 2.52, 2.40, 1.43 (each an s, 3:3:3:3:6 H, Tp′ CMe); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) 229.4 (CO), 206.9, 205.2 (Me*C*≡*C*Ph), 154.9, 152.9, 151.5, 147.5, 146.1, 145.6 (Tp′ *C*Me), 136.9 (ipso C of Ph), 129.3, 129.1, 128.7 (Ph), 108.8, 108.0, 107.7 (Tp′ CH), 22.1 (PhC≡C*Me*), 16.2, 14.9, 13.1, 13.0, 12.8, 12.7 (Tp′ C*Me*). Anal. Calcd: C, 42.13; H, 4.26; N, 11.81. Found: C, 41.99; H, 4.44; N, 11.59.

Synthesis of Tp′W(CO)(PhC≡CMe)F (3). To a wet THF (100 mL) solution of $[Tp'(CO)_2W(PhC{\equiv}CMe)][BF_4]$ (0.80 g, 1.08 mmol) was added 2 equiv of KOH (0.12 g, 2.14 mmol). The solution was heated at reflux for 24 h. The volume was then reduced to 50 mL and poured through a Celite column. The solvent was removed, and the residue was recrystallized from CH_2Cl_2/hexanes to give 0.22 g (32% yield) of green crystalline product: IR (KBr) ν_{CO} 1876 cm^{-1}; ^1H NMR (CD_2Cl_2) δ (ppm) 7.24–6.65 (m, 5 H, Ph), 5.90, 5.76, 5.71 (each an s, 3 H, Tp′ CH), 3.62 (s, 3 H, *Me*C≡CPh), 2.72, 2.50, 2.48, 2.37, 1.49, 1.46 (each an s, 18 H, Tp′ CMe); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) 239.5 (CO), 198.9, 198.1 (Ph*C*≡*C*Me), 153.0, 152.3, 151.0, 146.5, 145.1, 144.2, 136.8 (Tp′ *C*Me, ipso C of Ph), 129.2, 128.6, 128.4 (Ph), 107.8, 107.4 (Tp′ CH), 21.5 (PhC≡C*Me*), 16.3, 14.8, 13.1, 13.0, 12.9, 12.6 (Tp′ C*Me*); ^{19}F NMR (CD_2Cl_2) δ (ppm) −38.9 ($^1J_{FW}$ = 27 Hz). Anal. Calcd: C, 46.62; H, 4.70; N, 13.05. Found: C, 46.23; H, 4.80; N, 12.98.

Synthesis of (R_WR_C)- and (S_WR_C)-Tp′W(CO)(PhC≡CMe)O$_3$SR* [4-(*RR*), 4-(*SR*)] (O$_3$SR* = (1*R*)-(−)-10-Camphorsulfonate). A solution of (1*R*)-(−)-10-camphorsulfonic acid (0.24 g, 1.03 mmol) in CH_2Cl_2 (50 mL) was added to a CH_2Cl_2 (50 mL) solution of Tp′W(CO)(PhC≡CMe)H (0.64 g, 1.02 mmol). Immediately the color changed from purple to aqua-blue. Gas evolution from the solution was observed while the mixture was stirred for 30 min. The volume of the solution was reduced by solvent evaporation before the product was chromatographed on alumina with CH_2Cl_2 as eluent. The aqua-blue band was collected. Solvent removal gave 0.63 g (87% yield) of a 1:1 mixture of diastereomers. Neither chromatography nor recrystallization from CH_2Cl_2/hexanes was effective for efficient separation of the two isomers: IR (KBr) ν_{CO} 1910, $\nu_{C=O}$ 1730 cm^{-1}; (^1H and ^{13}C NMR signals for the two diastereomers differ where noted in parentheses) ^1H NMR (CD_2Cl_2) δ (ppm) 7.24–6.62 (m, 5 H, Ph), 5.95 (5.94), 5.80, 5.73 (each an s, 3 H, Tp′ CH), 3.75 (3.74) (s, 3 H, PhC≡C*Me*), 3.12, 2.92 (each a d, 2 H, $^2J_{HH}$ = 14.6 Hz, OSO$_2$C*H*$_2$R), 2.81 (2.77), 2.54 (2.53), 2.52, 2.40, 1.49 (1.46), 1.42 (each an s, 18 H, Tp′ CMe), 1.04 (0.99), 0.72 (0.71) (each an s, 6 H, camphor Me), 2.25, 1.99, 1.83, 1.55, 1.34 (each an m, 7 H, remaining camphor H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) 231.9 (231.8) (CO), 215.3 (215.2) (camphor C=O), 206.2 (206.0), 205.2 (205.0) (Ph*C*≡*C*Me), 154.8 (154.6), 153.5, 151.1, 146.9, 146.2, 144.7 (Tp′ *C*Me), 137.3 (ipso C of Ph), 129.2, 128.9, 128.7, 128.6 (Ph), 108.4, 108.0, 107.5 (Tp′ CH), 58.5, (58.4), 47.9, 47.0, 43.1, 42.9, 15.5, 14.0 (camphor signals), 27.2 (PhC≡C*Me*), 25.0, 22.4, 20.2, 19.9, 16.1, 13.0, 12.9, 12.8 (Tp′ C*Me*, camphor Me). Anal. Calcd: C, 49.10; H, 5.31; N, 9.82. Found: C, 48.88; H, 5.29; N, 9.75.

Synthesis of (−)-(R_WS_N)- and (+)-(S_WS_N)-Tp′W(CO)(PhC≡CMe)(NHR*) [(−)-5-(*RS*), (+)-5-(*SS*)] (R* = (*S*)-(−)-α-Methylbenzyl). A solution of $[Tp'W(CO)_2(PhC{\equiv}CMe)][OTf]$ (0.21 g, 0.26 mmol) in THF (75 mL) was heated to reflux for 1 h. Carbon monoxide loss accompanied the formation of Tp′W(CO)(PhC≡CMe)OTf. To this solution was added (*S*)-(−)-α-methylbenzylamine (0.1 mL, 0.78 mmol). The solution was heated at reflux for 24 h. The solvent was removed by rotary evaporation to leave a dark orange-brown oil. The residue was taken up in a minimum amount of toluene and chromatographed on alumina. The orange product was eluted with a mixture of hexanes and toluene progressing to pure toluene, and it was identified as a 1:1 mixture of two diastereomers. The orange band was collected, and the solvent was removed to yield 0.17 g (87% yield) of solid material. The product was characterized as a 1:1 mixture of (−)-**5**-(*RS*) and (+)-**5**-(*SS*) by ^1H NMR spectra (see data below for each of the pure diastereomers): UV/vis (CH_2Cl_2) λ_{max} = 626 nm (ε = 105 M^{-1} cm^{-1}).

Separation of the Diastereomers (−)-(R_WS_N)- and (+)-(S_WS_N)-Tp′W(CO)(PhC≡CMe)NHR* (R* = (*S*)-(−)-α-Methylbenzyl) [(−)-5-(*RS*), (+)-5-(*SS*)]. The 1:1 mixture of diastereomers (−)-(*RS*) and (+)-(*SS*) (1.21 g, 1.62 mmol) formed as described above was separated by fractional crystallization from CH_2Cl_2/hexanes (~4 mL/40 mL) after 8 h at −35 °C. The first fraction (0.47 g, 39% of the 1:1 mixture of diastereomers) was the (−)-**5**-(*RS*) diastereomer in a >35:1 isomer ratio. The second isomer remained in solution and was isolated by evaporation (1:5 isomer ratio). (−)-**5**-(*RS*) was recrystallized from CH_2Cl_2/hexanes several times until a constant optical rotation was reached. (+)-**5**-(*SS*) could not be crystallized, but a pure sample was obtained by deprotonating pure (+)-**6**-(*SS*). Each enantiomer was characterized independently by IR and ^1H and ^{13}C NMR spectroscopy and elemental analysis.

(−)-(R_WS_N)-Tp′W(CO)(PhC≡CMe)NHR* [(−)-5-(*RS*)]: IR (KBr) ν_{CO} 1846 cm^{-1}; ^1H NMR (CD_2Cl_2) δ (ppm) 7.20–6.22 (m, 11 H, MeC≡C*Ph*, NHCHMe*Ph*), 5.73, 5.64, 5.50 (each an s, 3 H, Tp′ CH), 5.37 (dq, 1 H, $^3J_{NHCH}$ = 10.2 Hz, $^3J_{MeCH}$ = 6.8 Hz, NHC*H*MePh), 3.18 (s, 3 H, *Me*C≡CPh), 2.44, 2.42, 2.30, 2.22, 1.58, 1.54 (each an s, 18 H, Tp′ C*Me*), 0.85 (d, 3 H, $^3J_{MeCH}$ = 6.8 Hz, NHCH*Me*Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) 237.4 ($^1J_{WC}$ = 166 Hz, CO), 170.4 ($^1J_{WC}$ = 49 Hz, MeC≡*C*Ph), 167.0 (PhC≡*C*Me), 153.1, 151.0, 150.4, 149.9, 144.2, 144.1, 137.6 (Tp′ *C*Me, 2 ipso C of 2 Ph), 128.3, 128.2, 127.9, 126.1, 126.0, 125.5 (2 Ph), 108.2, 106.7, 106.1 (Tp′ CH), 72.6 (NH*C*HMePh), 26.2 (PhC≡C*Me*), 18.3, 15.7, 15.4, 14.5, 12.7, 12.6, 12.5 (Tp′ C*Me*, NHCHPh*Me*); $[\alpha]^{25}_{589}$ = −870° (c = 1.23 × 10^{-3} g/mL in CH_2Cl_2). Anal. Calcd: C, 53.18; H, 5.42; N, 13.16. Found: C, 53.04; H, 5.37, N, 12.58.

(+)-(S_WS_N)-Tp′W(CO)(PhC≡CMe)NHR* [(+)-5-(*SS*)]: IR (KBr) ν_{CO} 1852 cm^{-1}; ^1H NMR (CD_2Cl_2) δ (ppm) 7.34–6.15 (m, 11 H, MeC≡C*Ph*, NHCHMe*Ph*), 5.94, 5.89, 5.58 (each an s, 3 H, Tp′ CH), 5.56 (dq, 1 H, $^3J_{NHCH}$ = 8.8 Hz, $^3J_{MeCH}$ = 6.8 Hz, NHCMePh*H*), 2.90 (s, 3 H, PhC≡C*Me*), 2.58, 2.42, 2.39, 2.31, 1.78, 1.51 (each an s, 18 H, Tp′ CMe), 1.26 (d, 3 H, $^3J_{MeCH}$ = 6.8 Hz, NHCHPh*Me*); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) 237.1 ($^1J_{WC}$ = 165 Hz, CO), 171.5 ($^1J_{WC}$ = 49 Hz, MeC≡*C*Ph), 170.2 (PhC≡*C*Me), 153.8, 151.6, 150.8, 149.6, 144.6, 144.5, 144.4, 138.2 (Tp′ *C*Me, 2 ipso C of 2 Ph), 128.3, 128.2, 128.1,

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[24] Feng, S. G.; Gamble, A. S.; Philipp, C. C.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 3504.

[25] The procedure for the synthesis of this compound is the same as that for the BF_4^- salt; AgOTf was used rather than $AgBF_4$ in the reaction.

126.8, 126.2, 126.0 (2 Ph), 108.5, 107.4, 106.4 (Tp′ CH), 71.5 (NH*C*HMePh), 28.7 (PhC≡C*Me*), 17.1, 15.7, 15.1, 13.1, 13.0, 12.9 (Tp′ C*Me*, NHCHPh*Me*); $[\alpha]^{25}_{589}$ = +710° ($c = 1.26 \times 10^{-3}$ g/mL in CH_2Cl_2). Anal. Calcd: C, 53.18; H, 5.42; N, 13.16. Found: C, 53.29; H, 5.45; N, 13.01.

Synthesis of (−)-(R_WS_N)-[Tp′W(CO)(PhC≡CMe)NH_2R^*][BF_4] [(−)-6-(*RS*)] (R^* = (*S*)-(−)-*α*-Methylbenzyl). A solution of (−)-(R_WS_N)-Tp′W(CO)(PhC≡CMe)NHR* (0.41 g, 0.55 mmol) in a 1:4 mixture of CH_2Cl_2/Et_2O (75 mL) was cooled to −78 °C in a dry ice/isopropyl alcohol bath. To this solution was added $HBF_4\cdot OMe_2$ (0.05 mL, 0.48 mmol) dropwise with stirring. The color of the solution changed from orange to blue over a 5-min period. Precipitation of blue crystals was observed. Isolation of the crystalline material yielded 0.40 g (87% yield) of the desired product. Successive recrystallizations from CH_2Cl_2/Et_2O were performed until a constant optical rotation was reached. Data for (−)-**6**-(*RS*): UV/vis (CH_2Cl_2) λ_{max} = 606 nm (ϵ = 470 M^{-1} cm^{-1}); IR (KBr) ν_{CO} 1916 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ (ppm) 7.47–6.74 (m, 10 H, 2 Ph), 6.05, 5.99, 5.78 (each an s, 3 H, Tp′ CH), 4.27 (dq, 1 H, $^3J_{CHNH}$ = 9 Hz, $^3J_{CHMe}$ = 6.8 Hz, NH_2C*H*MePh), 3.95 (dd, 1 H, $^2J_{HNH}$ = 12.8 Hz, $^3J_{NHCH}$ = 9 Hz, HN*H*CHMePh), 3.84 (s, 3 H, PhC≡C*Me*), 3.15 (d, 1 H, $^2J_{HNH}$ = 12.8 Hz, *H*NHCHMePh), 2.58, 2.50, 2.47, 2.39, 1.70, 1.34 (each an s, 18 H, Tp′ CMe), 1.10 (d, 3 H, $^3J_{CHNH}$ = 6.8 Hz); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) 229.6 ($^1J_{WC}$ = 148 Hz, CO), 216.8 ($^1J_{WC}$ = 53 Hz, MeC≡*C*Ph), 214.1 ($^1J_{WC}$ = 15 Hz, Me*C*≡CPh), 153.0, 151.5, 151.0, 147.9, 147.8, 146.5 (Tp′ *C*Me), 141.9, 136.0 (2 ipso C of 2 Ph), 130.8, 129.7, 129.4, 129.2, 126.0 (2 Ph), 109.5, 109.2, 107.9 (Tp′ CH), 63.7 (NH_2*C*HMePh), 23.4 (*Me*C≡CPh), 22.2, 15.9, 15.8, 14.4, 12.8, 12.6 (Tp′ C*Me*, NH_2CH*Me*Ph); $[\alpha]^{25}_{589}$ = −890° ($c = 2.9 \times 10^{-4}$ g/mL in CH_2Cl_2). Anal. Calcd: C, 45.96; H, 4.84; N, 11.20. Found: C, 46.10; H, 4.88; N, 11.05. Percentages are based on $WC_{33}H_{41}N_7OB_2F_4\cdot 0.5CH_2Cl_2$ (as determined by ^{1}H NMR).

Synthesis of (+)-(S_WS_N)-[Tp′W(CO)(PhC≡CMe)NH_2R^*][BF_4] [(+)-6-(*SS*)] (R^* = (*S*)-(−)-*α*-Methylbenzyl). The procedure for the protonation of (+)-(S_WS_N)-Tp′W(CO)(PhC≡CMe)NHR* (0.40 g, 0.54 mmol) with $HBF_4\cdot OMe_2$ (0.05 mL, 0.48 mmol) was the same as that described above, and it yielded 0.40 g (89% yield) of blue crystalline material. Multiple CH_2Cl_2/Et_2O recrystallizations of the product led to a constant optical rotation: IR (KBr) ν_{CO} 1903 cm^{-1}; ^{1}H NMR (CD_2Cl_2) δ (ppm) 7.42–6.54 (m, 10 H, 2 Ph), 6.14, 5.94, 5.76 (each an s, 3 H, Tp′ CH), 3.98 (dd, 1 H, $^2J_{HNH}$ = 13.4 Hz, $^3J_{NHCH}$ = 6 Hz, HN*H*CHMePh), 3.77 (m, 1 H, NH_2C*H*MePh), 3.45 (s, 3 H, *Me*C≡CPh), 3.40 (dd, 1 H, $^2J_{HNH}$ = 13.4 Hz, $^3J_{NHCH}$ = 6 Hz, *H*NHCHMePh), 2.88, 2.56, 2.50, 2.44, 1.41, 1.30 (each an s, 18 H, Tp′ CMe), 1.72 (d, 3 H, $^3J_{MeCH}$ = 6.4 Hz, NH_2CH*Me*Ph); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) 230.5 ($^1J_{WC}$ = 149 Hz, CO), 216.4 ($^1J_{WC}$ = 53 Hz, MeC≡*C*Ph), 214.6 ($^1J_{WC}$ = 15 Hz, Me*C*≡CPh), 153.4, 151.9, 151.3, 148.1, 147.8, 146.5 (Tp′ *C*Me), 141.3, 136.4 (2 ipso C of 2 Ph), 130.6, 129.7, 129.3, 129.2, 126.1 (2 Ph), 109.6, 109.5, 108.1 (Tp′ *C*H), 63.4 (NH_2*C*HMePh), 25.1 (*Me*C≡CPh), 22.9, 16.1, 16.0, 14.6, 13.0, 12.9, 12.8 (Tp′ C*Me*, NH_2CH*Me*Ph); $[\alpha]^{25}_{589}$ = +990° ($c = 2.5 \times 10^{-4}$ g/mL in CH_2Cl_2). Anal. Calcd: C, 47.58; H, 4.97; N, 11.77. Found: C, 47.30; H, 4.88; N, 11.65.

Synthesis of (−)-[Tp′W(CO)(PhC≡CMe)(N≡CMe)][BF_4] [(−)-7]. To a CH_3CN solution (30 mL) of (−)-**6**-(*RS*) (1.00 g, 1.20 mmol) was added a CH_3CN solution (20 mL) of $HBF_4\cdot OMe_2$ (0.12 mL, 1.20 mmol). The color of the mixture changed from blue to aqua-blue as it was heated for 10 min. The solvent was stripped off, and the residue was taken up in 20 mL of CH_2Cl_2. The solution was extracted with five 20-mL portions of water to remove ammonium salts. The CH_2Cl_2 layer was dried over $MgSO_4$ and then filtered. Recrystallization from CH_2Cl_2/Et_2O gave 0.72 g (80%) of crystalline product: $[\alpha]^{25}_{589}$ = −880° ($c = 3.0 \times 10^{-4}$ g/mL in CH_2Cl_2); UV/vis (CH_2Cl_2, measured with a racemic mixture of [Tp′W(CO)(PhC≡CMe)N≡CMe][BF_4] λ_{max} = 652 nm (ϵ = 360 M^{-1} cm^{-1}).

Synthesis of (+)-[Tp′W(CO)(PhC≡CMe)(N≡CMe)][BF_4] [(+)-7]. The procedure for the protonation of (+)-**6**-(*SS*) (1.00 g, 1.20 mmol) with $HBF_4\cdot OMe_2$ (0.12 mL, 1.20 mmol) was the same as that described above, and the result was 0.71 g of crystalline product (79% yield): $[\alpha]^{25}_{589}$ = +870° ($c = 3.4 \times 10^{-4}$ g/mL in CH_2Cl_2).

^{1}H NMR Shift Experiments on [Tp′W(CO)(PhC≡CMe)-(N≡CMe)][BF_4] [(+)-7]. A sample of racemic tungsten acetonitrile complex, **7** (14 mg), was dissolved in CD_2Cl_2 (0.8 mL), and its ^{1}H NMR spectrum was recorded at room temperature. Addition of (+)-Eu(tfc)$_3$ to the solution resulted in broadening of the signals. The acetonitrile CH_3 resonance shifted downfield upon addition of further quantities of the chiral shift reagent. As the amount of Eu(tfc)$_3$ increased, the acetonitrile CH_3 peak split into two separate signals. Complete separation was achieved when 67 mg of Eu(tfc)$_3$ had been added (Eu:W = 4 mol ratio). Other resonances shifted downfield less and split less. These shift experiments were also performed for the enantiomerically pure acetonitrile complexes to determine enantiomeric purity.

Synthesis of (+)-Tp′W(CO)(PhC≡CMe)I [(+)-8]. A THF (50 mL) solution of (−)-**6**-(*RS*) (0.40 g, 0.48 mmol), $HBF_4\cdot OMe_2$ (0.05 mL, 0.48 mmol), and tetraethylammonium iodide (0.18 g, 0.70 mmol) was heated to reflux for 3 h. The solvent was removed by rotary evaporation to leave a green tar. The residue was taken up in a minimum amount of CH_2Cl_2 and chromatographed on alumina. A green band was eluted with CH_2Cl_2. Recrystallization from CH_2Cl_2/hexanes yielded 0.23 g (65% yield) of crystalline product: $[\alpha]^{25}_{589}$ = +340° ($c = 4.4 \times 10^{-4}$ g/mL in CH_2Cl_2); UV/vis (CH_2Cl_2, for both (+)-**8** and (−)-**8**) λ_{max} = 674 nm (ϵ = 320 M^{-1} cm^{-1}).

Synthesis of (−)-Tp′W(CO)(PhC≡CMe)I [(−)-8]. The procedure above was repeated using the other reagent diastereomer, (+)-**6**-(*SS*). Recrystallization from CH_2Cl_2/hexanes gave 0.23 g (65% yield) of green crystalline material: $[\alpha]^{25}_{589}$ = −340° ($c = 4.2 \times 10^{-4}$ g/mL in CH_2Cl_2).

X-ray Structure of (−)-(R_WS_N)-[Tp′W(CO)(PhC≡CMe)NH_2R^*]-[BF_4] [(−)-6-(*RS*)] (R^* = (*S*)-(−)-*α*-Methylbenzyl). Crystals of (−)-**6**-(*RS*) were grown from methylene chloride/hexane. The crystal studied was orthorhombic with space group $P2_12_12_1$ and unit cell dimensions a = 16.130 (2) Å, b = 16.576 (4) Å, c = 15.256 (2) Å, V = 4079 (1) Å^3, Z = 4, D_{calcd} = 1.357 g cm^{-3}, λ(Mo Kα) = 0.709 30 Å, μ = 2.94 mm^{-1}, and $F(000)$ = 1660. The data were collected on an Enraf-Nonius CAD-4 automated diffractometer using the $\theta/2\theta$ scan mode. Details are presented in Table **II**. Of the 3993 reflections monitored, 2631 reflections with $I > 2.5\sigma(I)$ were used in the structure solution. Final agreement indices of R = 4.4% and R_w = 6.3% resulted with hydrogens placed in the calculated positions; all other atoms were refined anisotropically. An ORTEP diagram is shown in Figure 1.

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Supplementary Material Available: Tables of atomic positions, thermal parameters, and complete bond distances and angles, an ORTEP diagram, and a labeled figure (8 pages); tables of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.