Reactivity Relationships between Chiral Cyclic Amido and Imine Tungsten(II) Complexes

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Reaction of [Tp′W(CO)$_2$(PhC≡CMe)][OTf] (**1**) (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) with excess pyrrolidine affords the chiral tungsten(II) amido complex Tp′W(CO)(PhC≡CMe)(NCH$_2$CH$_2$-CH$_2$CH$_2$) (**2a**). The corresponding η^1-imine complex [Tp′W(CO)(PhC≡CMe)(N=CHCH$_2$CH$_2$CH$_2$)][BAr′$_4$] (**3a**) is prepared by oxidation of amido complex **2a** with elemental iodine in the presence of base. The 2-methyl-1-pyrroline complex [Tp′W(CO)(PhC≡CMe)(N=CMeCH$_2$CH$_2$CH$_2$)][BAr′$_4$] (**3b**) is synthesized directly by 2-methyl-1-pyrroline addition to the labile tungsten complex **1**. Only one pair of enantiomers (S_WR_C/R_WS_C) of 2-methylpyrrolidine amido complex Tp′W(CO)(PhC≡CMe)(NCHMeCH$_2$CH$_2$CH$_2$) (**2b**) is detected when **2b** is prepared by direct reaction of tungsten complex **1** with deprotonated 2-methylpyrrolidine. An alternative route to this amido complex is available through addition of MeMgBr to cationic imine complex **3a**. In this case the same diastereomer predominates as in the ligand substitution route to **2b**. The opposite diastereomer, S_WS_C/R_WR_C, is obtained as the major product of hydride addition to the cationic 2-methyl-1-pyrroline complex **3b**. Deuteride addition to imine complex **3a** yields the amido complex **2a**-d_1 with a high diastereoselectivity ratio as determined by ^{2}H NMR. Protonation of amido complex **2a** using [H(OEt$_2$)$_2$][BAr′$_4$] gives the cationic pyrrolidine complex [Tp′W(CO)(PhC≡CMe)(NHCH$_2$CH$_2$CH$_2$CH$_2$)][BAr′$_4$] (**4a**).

Introduction

Pyrrolidine and its derivatives are useful starting materials in the preparation of various biologically and pharmaceutically important molecules.[1−3] Successful strategies for enantioselective synthesis of pyrrolidine derivatives include α-alkylation of pyrrolidine-containing moieties.[4−7] Elworthy and Meyers achieved high enantioselectivity in the formation of 2-methyl-Boc-pyrrolidine (Boc = *tert*-butoxycarbonyl) by Sn−Li exchange of enantio-enriched α-tributylstannane using ^{n}BuLi with subsequent methylation of the lithio carbanion.[8] *N*-Boc-protected 2-methylpyrrolidine has been synthesized in up to 95% enantiomeric excess by Kerrick and Beak via asymmetric deprotonation of Boc-pyrrolidine using *sec*-butyllithium/(−)-sparteine followed by reaction with an electrophilic methyl reagent.[9] Enantioselective synthesis of 2-methylpyrrolidine has been accomplished via hydroamination/cyclization of aminoalkenes using organolanthanide catalysts.[10−15]

Diastereoselective conversion of imines to form amido ligands has been reported,[16−20] and transition metal-catalyzed nucleophile addition to activated imines has been accomplished.[21−23] Acyclic imine and amido complexes are found as intermediates in the reduction of coordinated acetonitrile to ethylamine,[24] and various *N*-protio amido complexes undergo hydride abstraction with iodine as the oxidant in the presence of base to yield the

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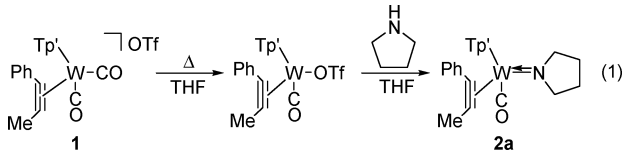
analogous *N*-protio, cationic, imine complexes.[25] Reduction of imines can occur stereoselectively, but the ratio of stereoisomers often correlates directly to the *E*/*Z* ratio of the starting amine.[26,27] Nucleophile addition is complicated with coordinated, *N*-protio-substituted imines as the substrate, since deprotonation of the imine nitrogen becomes a competing reaction.[28−31]

To address the issue of unwanted deprotonation at nitrogen, we sought to utilize secondary amine precursors. Our initial target was a cyclic imine complex based on pyrrolidine. Chiral transition metal amine, amido, and imine complexes containing pyrrolidine-derived ligands are known,[32] and nucleophile addition to a rhenium indolenine complex has been accomplished with high diastereoselectivity.[33] Cyclic imine complexes have two potential advantages as substrates: (1) they are not subject to *E*/*Z* isomer options; (2) they have *N*-alkyl substituents rather than hydrogen so that deprotonation at nitrogen is not an option.

In this paper we report the synthesis of chiral tungsten amido complexes of the type Tp′W(CO)(PhC≡CMe)(NCHRCH$_2$CH$_2$CH$_2$) (**2a**,**b**) (R = H, Me) derived from pyrrolidine. The corresponding imine complexes [Tp′W(CO)(PhCCMe)(N=CRCH$_2$CH$_2$CH$_2$)][X] (**3a**,**b**) (R/X = H/BAr′$_4$, Me/OTf) are synthesized by either net hydride abstraction from the parent amido complex (**2a**) or direct reaction of the deprotonated ligand with the precursor tungsten triflate complex [Tp′W(CO)$_2$(PhC≡CMe)][OTf] (**1**). The pyrrolidine amido complex **2a** may be protonated to form the corresponding cationic cyclic amine complex (**4a**). Studies of the diastereoselectivity of nucleophile addition to the imine complex are accessible with this chiral tungsten system.

Results and Discussion

Pyrrolidine Amido Complex 2a. The amido complex Tp′(CO)(PhC≡CMe)(NCH$_2$CH$_2$CH$_2$CH$_2$) (**2a**), derived from pyrrolidine, was synthesized by heating a THF solution of pyrrolidine and previously prepared Tp′W(CO)(PhC≡CMe)(OTf) at reflux for 14 h (eq 1).[25,34,35] Removal of salts followed by recrystallization from a CH_2Cl_2 solution layered with CH_3OH gave water-sensitive green crystals of amido complex **2a**.



The CO stretching frequency of amido complex **2a** at 1839 cm^{-1} in the IR spectrum is lower than the CO frequency of related acyclic [NHR]$^-$ amido complexes by about 10−20 cm^{-1}, presumably due to stronger electron donation from the cyclic dialkyl amido ligand. The alkyne carbons appear at 169.8 and 167.1 ppm in the ^{13}C NMR spectrum in accord with competition between the amido nitrogen lone pair and the alkyne $\pi_\perp$ electron pair for donation into the lone vacant metal dπ orbital in this W(II) d^4 complex. The result is reminiscent of a "three-electron" donor alkyne.[24,25,36,37] The ^{1}H NMR spectrum of **2a** displays eight distinct multiplets corresponding to the eight diastereotopic hydrogens of the cyclic amido ligand bound to the chiral metal center.

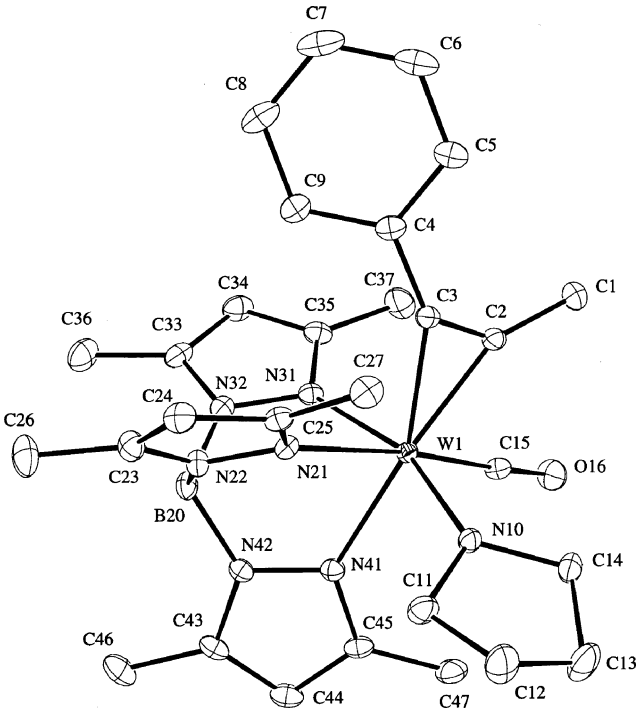


Figure 1. ORTEP diagram of Tp′W(CO)(PhC≡CMe)(NCH$_2$CH$_2$CH$_2$CH$_2$) (**2a**).

An ORTEP diagram of the tungsten amido complex **2a** is shown in Figure 1. For all the structures reported herein, crystallographic data collection parameters are shown in Table 1, and selected bond distances and angles are listed in Table 2. The plane of the amido ligand is oriented approximately parallel (20.8°) to the W−CO axis, compatible with allowing nitrogen to donate its remaining lone pair of electrons into the single empty tungsten dπ orbital. The C≡C axis of the alkyne ligand is also aligned nearly parallel (8.0°) to the W−CO axis, as is typical for group VI d^4 alkyne complexes.[38] This alignment optimizes both π-donation from $\pi_\perp$ and π-acceptance into $\pi_\parallel$* of the alkyne ligand with the appropriate tungsten dπ orbitals. The short tungsten−amido W−N(10) bond distance of 1.999(2) Å reflects some multiple-bond character due to π-donation from the amido nitrogen to the metal; this distance is slightly longer than the distance of 1.941(10) Å found for the related acyclic primary amido complex, Tp′W(CO)(PhC≡CMe)(NHCHMeEt).[25] The distances from the amido nitrogen, N(10), to the α carbons, C(11) and C(14), are 1.481(4) and 1.486(4)

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Table 1. Crystallographic Data

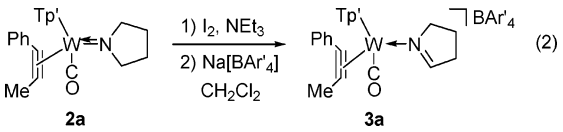
	2a	S_WR_C/R_WS_C-**2b**	**3a**	**3b**
formula	$C_{29}H_{38}BN_7OW$	$C_{30}H_{40}BN_7OW\cdot0.5C_5H_{12}$	$C_{61}H_{49}B_2F_{24}N_7OW$	$C_{62}H_{51}B_2F_{24}N_7OW$
mol wt	695.32	745.42	1557.52	1571.57
cryst syst	orthorhombic	triclinic	triclinic	monoclinic
space group	*Pbca*	$P\bar{1}$	$P\bar{1}$	$P2/c$
a, Å	16.0892(3)	10.9323(5)	12.4266(4)	14.288(3)
b, Å	18.4560(4)	16.8686(7)	16.0186(5)	12.824(3)
c, Å	20.1698(4)	18.2165(8)	17.8952(6)	35.951(7)
α, deg	90	79.961(1)	91.195(2)	90
β, deg	90	81.853(1)	102.850(2)	92.968(12)
γ, deg	90	89.124(1)	107.838(2)	90
V, Å^3	5989.27(21)	3274.38(25)	3290.76(18)	6578(2)
Z	8	2	2	4
calcd density, g/mL	1.542	1.512	1.572	1.587
F(000)	2780.99	1506.54	1544.28	3120
temp, K	173	173	173	173
2*θ* range, deg	5−60	5−56	5−50	1.87−27.00
μ, mm^{-1}	3.90	3.57	1.87	1.871
total no. of rflns	136 549	42 189	46 746	35 574
total no. of unique rflns	8724	15 819	11 608	14 306
R_{merge}	0.044	0.035	0.049	0.0398
R_f, %	0.027	0.031	0.058	0.0433
R_w, %	0.024	0.035	0.060	0.0963
GoF	1.5512	1.2848	1.8488	1.037
residual density, e/Å^{-3}	−0.850 to 1.860	−0.840−1.590	−1.740−1.940	−1.101 − 3.924

Table 2. Selected Bond Distances (Å) and Angles (deg) of Amido (2a, 2b) and Imine (3a, 3b) Ligands

	2a	**2b**	**3a**	**3b**
W−N	1.999(2)	2.010(3)	2.135(7)	2.179(3)
N═C			1.280(14)	1.286(6)
N−C	1.481(4)	1.480(5)	1.490(10)	1.519(5)
	1.486(4)	1.485(5)		
OC−W−N−C	20.8(3)	22.73(3)	57.5(7)	51.0(3)

Å, respectively. These distances are similar to the N−C distance found in Tp′W(CO)(PhC≡CMe)(NHCHMeEt),[25] and all of these C−N distances are compatible with simple N−C single bonds.

1-Pyrroline Complex 3a. Oxidation of **2a** with 1 equiv of I_2 in the presence of NEt_3 followed by counterion exchange using Na[BAr′$_4$] (BAr′$_4$ = tetrakis[3,5-bis(trifuoromethyl)-phenyl]borate) yields the chiral cyclic imine complex [Tp′W(CO)(PhC≡CMe)(N═CHCH$_2$CH$_2$CH$_2$)][BAr′$_4$] (**3a**) (eq 2). Purification by alumina chromatography followed by recrystallization from a CH_2Cl_2 solution layered with hexanes gave air-stable dark blue crystals of **3a** in 61% yield.



(2)

The IR stretching frequency of **3a** is 1910 cm^{-1}, a large increase from the 1839 cm^{-1} stretching frequency in reagent **2a**, but 10−30 cm^{-1} lower than comparable values for acyclic imine complexes [Tp′W(CO)(PhC≡CMe)(NH═CRR′][BAr′$_4$].[25] In the ^{1}H NMR spectrum of **3a** the imine proton on the α carbon resonates at 6.50 ppm, which is close to the value of 6.66 ppm found for the C_α proton of the imine ligand in [Tp′W(CO)-(PhC≡CMe)(NH═C*H*CHMePh][BAr′$_4$].[25] The alkyne methyl protons resonate at 3.86 ppm in the ^{1}H NMR spectrum, as is typical for a cationic imine complex containing a four-electron donor alkyne.[25]

An ORTEP diagram of 1-pyrroline complex **3a** is shown in Figure 2. The tungsten−imine W−N(12) bond distance of 2.135(7) Å is consistent with a single W−N dative bond. Note that conversion of the amido precursor to the cationic imine removes the multiple W−N bond character and the metal−

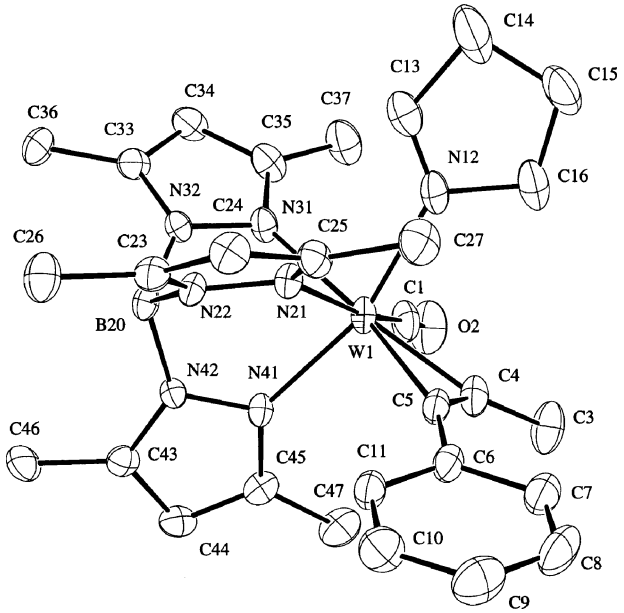
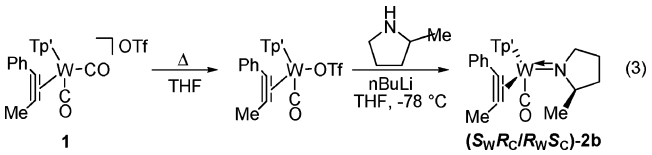


Figure 2. ORTEP diagram of [Tp′W(CO)(PhC≡CMe)(N═CHCH$_2$-CH$_2$CH$_2$)][BAr′$_4$] (**3a**).

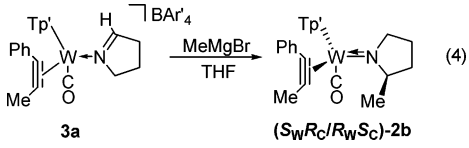
ligand separation increases by 0.14 Å. The N(12)−C(13) bond distance of 1.280(14) Å clearly identifies the N═C linkage, while the distance from N(12) to C(16), 1.490(10) Å, is over 0.20 Å longer and is close to that of the N−C single bonds found in pyrrolidine amido complex **2a**. Clearly there is no disorder between C(13) and C(16) in the structure of imine complex **3a**. The tungsten−alkyne bond distances of 2.063(8) and 2.031(7) Å are consistent with a four-electron donor alkyne. The imine double bond is proximal to two pyrazole rings, adopting a geometry dramatically different from the one found for [Tp′W(CO)(PhC≡CMe)(NH═CMeEt)][BAr′$_4$], where the double bond is oriented between the CO and alkyne ligands. The plane containing the 1-pyrroline ligand is almost perpendicular to the W−CO bond, distinctly different from the ring orientation in the amido complex **2a**. The 1-pyrroline nitrogen is simply a two-electron donor in **3a**, and presumably the ligand can rotate easily in order to reside in the least sterically hindered configuration.

2-Methylpyrrolidine Amido Complex 2b. Refluxing tungsten complex **1** with free 2-methylpyrrolidine in THF failed to yield the 2-methylpyrrolidine amido complex Tp′W(CO)(PhC≡CMe)(NCHMeCH$_2$CH$_2$CH$_2$) (**2b**). Addition of ^{n}BuLi at −78 °C followed by warming to room temperature and stirring for 1.5 h resulted in formation of the target amido complex **2b** (eq 3). This ligand substitution route provides a >95:5 mixture of diastereomers as determined by ^{1}H NMR spectra of the crude product.



(3)

An alternative route to amido complex **2b** involves addition of a nucleophilic methyl reagent, such as MeMgBr, to a THF solution of imine complex **3a** (eq 4). Removal of salts followed by recrystallization from a concentrated pentane solution yielded dark red crystals of **2b**. Reduction of the cationic imine complex decreases the CO stretching frequency from 1910 cm^{-1} in **3a** to 1847 cm^{-1} (KBr) for amido complex **2b**. This CO stretching frequency is slightly higher than that of the unsubstituted cyclic amido complex **2a**, ν_{CO} = 1839 cm^{-1}. The methyl substituent provides a more sterically congested amido ring environment, perhaps causing the tungsten−amido nitrogen distance to lengthen slightly, thus providing less electron density to the tungsten center and subsequently decreasing the π* CO occupation from the d^4 W(II) center and making the CO stretch higher than that observed for the unsubstituted amido complex **2a**. Amido complex **2b** has two stereogenic centers, the metal center and the amido α-carbon; however, the ^{1}H NMR spectrum of the reaction mixture displays only one diastereomer (S_WR_C/R_WS_C) (greater than 95:5 ratio) when synthesized from the imine by the nucleophilic addition route in eq 4. Chirality at tungsten was assigned by treating Tp′ as an η^3 ligand and using the Baird/Sloan modification of the Cahn−Ingold−Prelog priority rules.[39,40] The α-carbon-bound proton of the amido ligand emerges as a multiplet at 4.96 ppm in the ^{1}H NMR spectrum of **2b**, while the cyclic amido methyl signal appears as a clean doublet at 0.58 ppm.



(4)

As in amido complex **2a**, the alkyne carbons resonate between 167 and 172 ppm in the ^{13}C NMR spectrum of **2b**. This upfield shift relative to the alkyne carbons in imine complex **3a** (212−216 ppm) reflects a change from a four-electron donor alkyne to competitive donation relative to the amido ligand. A qualitative molecular orbital scheme for the competition between amido and alkyne is given in Figure 3.

The crystal structure of **2b** contains two molecules in the unit cell, one of which is shown as an ORTEP diagram in Figure 4. Qualitative analysis of the crystal structures of imine complex **3a** and amido complex **2b** indicates that rotation of the imine ring followed by nucleophilic attack on the side closest to the alkyne would yield the single diastereomer obtained. If nucleophilic attack at the imine carbon were to occur with the imine double bond located between two of the Tp′ pyrazolyl rings, as in the solid-state structure, it is not obvious that there would be significant differentiation between the two faces. The W−N(3) distance of 2.010(3) Å in the crystal structure of amido complex **2b** is only slightly longer than the distance seen for amido complex **2a**, 1.999(2) Å. The N(3)−C(4) and N(3)−C(7) bond distances are 1.480(5) and 1.486(5) Å, respectively, and the N(3)−C(7)−C(8) angle is 110.5(3)°.

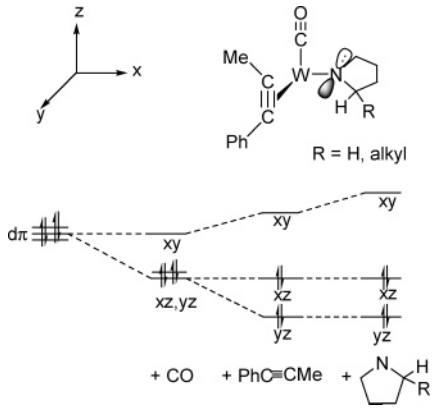


Figure 3. Qualitative molecular orbital scheme for Tp′W(CO)(PhC≡CMe)(NCHRCH$_2$CH$_2$CH$_2$) (**2a**,**b**).

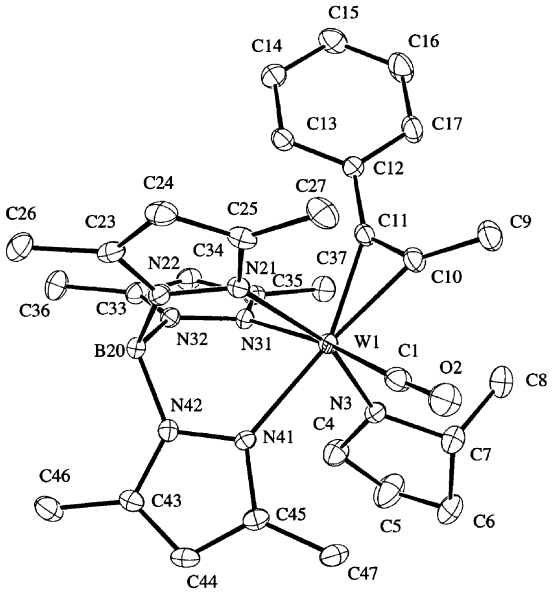


Figure 4. ORTEP diagram of (S_WR_C)-Tp′W(CO)(PhC≡CMe)(NCHMeCH$_2$CH$_2$CH$_2$) (**2b**).

2-Methyl-1-pyrroline Complex 3b. Heating a THF solution of **1** with 2-methyl-1-pyrroline at reflux overnight resulted in no change in the IR spectrum. Addition of ^{n}BuLi to deprotonate the 2-methyl-1-pyrroline substrate results in the formation of the cyclic imine complex [Tp′W(CO)(PhC≡CMe)(N=CMeCH$_2$CH$_2$CH$_2$)][OTf] (**3b**) by alumina chromatography (eq 5). Blue crystals were obtained from a CH_2Cl_2 solution layered with Et_2O. X-ray-quality crystals were obtained by adding Na[BAr′$_4$] to a CH_2Cl_2 solution of **3b** followed by recrystallization from a CH_2Cl_2 solution layered with hexanes to yield the [BAr′$_4$]$^-$ salt of cationic imine complex **3b**. The CO stretching frequency of 2-methyl-1-pyrroline complex **3b** matches that of 1-pyrroline complex **3a**, ν_{CO} = 1910 cm^{-1}. The alkyne methyl group appears at 3.85 ppm in the ^{1}H NMR spectrum of imine complex

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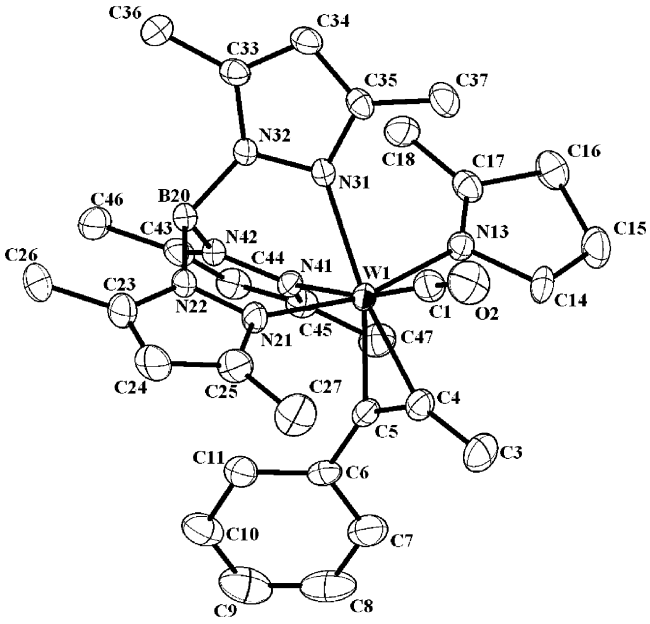
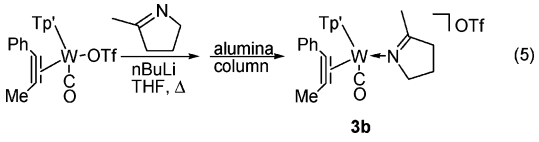


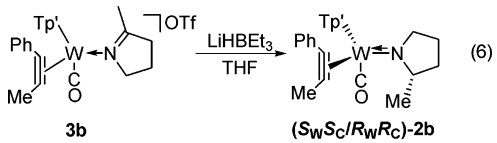
Figure 5. ORTEP diagram of [Tp′W(CO)(PhC≡CMe)(N=CMeCH$_2$CH$_2$CH$_2$)][BAr′4] (**3b**).

3b, similar to that of cationic 1-pyrroline complex **3a**, while the imine methyl signal appears at 0.82 ppm. The carbonyl carbon resonates near 229 ppm in the ^{13}C NMR. The imine carbon peak appears at 191 ppm, consistent with σ-bound imines. The alkyne carbon resonances are in the range 212−214 ppm, indicating a four-electron donor alkyne.

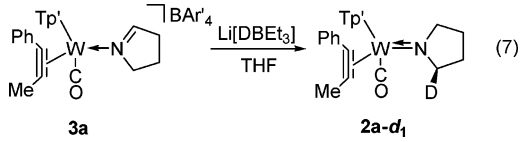


An ORTEP diagram of the [BAr′$_4$]$^-$ salt of 2-methyl-1-pyrroline complex **3b** is presented in Figure 5. The short metal−alkyne distances of 2.016(4) and 2.064(4) Å are consistent with the ^{13}C NMR data for this cationic imine complex, denoting a tightly bound four-electron donor alkyne.[38] The tungsten−imine dative bond, W−N(13), is 2.179(3) Å, slightly longer than the 2.135 Å in the unsubstituted case. The N(13)−C(17) bond distance of 1.286(6) Å is close to the distance found for the N=C bond of 1-pyrroline complex **3a**, 1.280(14) Å. As in imine complex **3a**, the imine double bond and, therefore, the imine methyl substituent of 2-methyl-1-pyrroline complex **3b** are both proximal to two pyrazolyl rings.

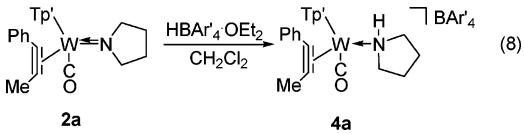
Another route to amido complex **2b** may be realized by addition of Li[HBEt$_3$] to a THF solution of imine complex **3b** (eq 6). Following hydride addition and extraction with pentane, amido complex **2b** is obtained in a 2.5:1 diastereomer ratio as assessed by ^{1}H NMR. Importantly, the predominant diastereomer is the opposite diastereomer (S_WS_C/R_WR_C) of the product formed by methyl addition.



Deuteride Addition to 3a. Reaction of imine complex **3a** with Li[DBEt$_3$] in THF results in formation of amido complex **2a**-d_1 as assessed by IR and ^{1}H NMR spectroscopy (eq 7). Due to the complexity of the NMR signals for the diastereotopic methylene protons, the diastereoselectivity of the deuteride addition is difficult to assess by ^{1}H NMR spectroscopy. ^{2}H NMR spectroscopy is a good alternative for the characterization of the product formed. Although the signal-to-noise level is too high for quantitative analysis, only two signals are observed in the ^{2}H NMR spectrum (3.67 and 2.58 ppm), and these correspond to two diastereotopic protons in the ^{1}H NMR spectrum. Analysis of the COSY NMR spectrum of amido complex **2a** indicates the signal at 3.67 ppm is coupled to resonances at 4.73, 1.68, and 1.42 ppm, while the signal at 2.59 ppm is coupled to multiplets at 3.39 and 1.30 ppm. If deuteride addition occurred on both faces of the 1-pyrroline ring, the two signals observed in the ^{2}H NMR of **2a**-d_1 would be coupled to the same hydrogens. It appears that there is high diastereoselectivity in the addition of deuteride to imine complex **3a**.



Amine Complex 4a. Protonation of the amido complex **2a** with [H(OEt$_2$)$_2$][BAr′$_4$] in CH_2Cl_2 yields the pyrrolidine complex [Tp′W(CO)(PhC≡CMe)(NHCH$_2$CH$_2$CH$_2$CH$_2$)][BAr′$_4$] (**4a**) (eq 8). Purification by alumina chromatography followed by recrystallization from CH_2Cl_2/hexanes produced blue crystals. Protonation of amido complex **2a** increases the CO stretch from 1839 cm^{-1} to 1904 cm^{-1} in the IR spectrum of amine complex **4a**. This is consistent with the increase seen in the protonation of acyclic amido complexes Tp′W(CO)(PhC≡CMe)(NHCHRR′) (R/R′ = Me/Et, Ph/Ph, H/CMePh). A set of eight distinguishable diastereotopic ring protons is found in the ^{1}H NMR of amine complex **4a**. The amine proton is located at 3.39 ppm. The carbonyl carbon resonance is found at 230 ppm in the ^{13}C NMR spectrum, and the alkyne carbons are displayed at 211 and 213 ppm, compatible with a four-electron donor alkyne.[25,38,41]



Summary

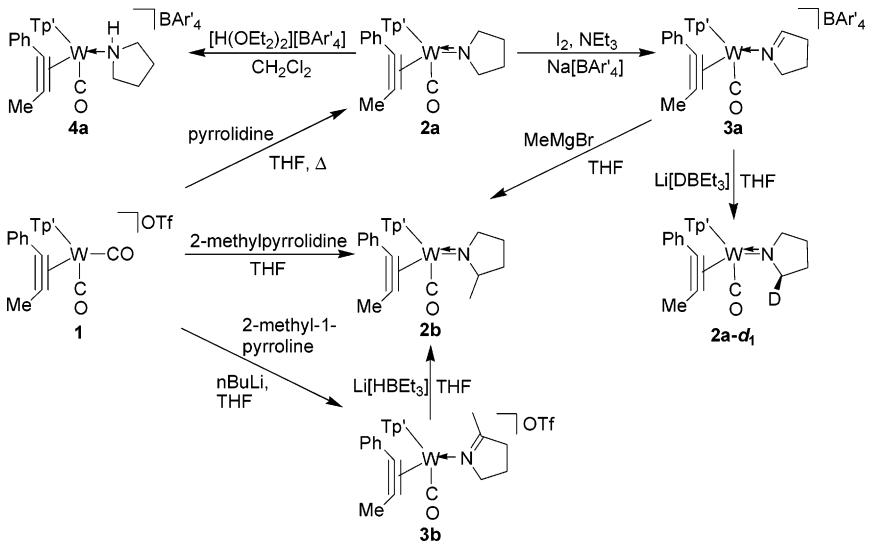
Cyclic amido (**2**) and imine (**3**) complexes of tungsten(II) have been synthesized and structurally characterized. Oxidation of amido complex **2a** with I_2 in the presence of NEt_3 forms 1-pyrroline complex **3a**. Addition of MeMgBr to **3a** occurs with high diastereoselectivity. 2-Methylpyrrolidine complex **2b** was characterized by X-ray crystallography. The second diastereomer (S_WS_C/R_WR_C) of 2-methylpyrrolidine amido complex **2b** can be synthesized by hydride addition to 2-methyl-1-pyrroline complex **3b**. Deuteride addition to **3a** results in the formation of **2a**-d_1. Complex **2a** may also be protonated to form a cationic cyclic pyrrolidine complex, **4a**. The synthetic relationships among these complexes are summarized in Scheme 1.

Experimental Section

General Procedures. Reactions were carried out under a nitrogen atmosphere using Schlenk techniques. Methylene chloride, diethyl

(41) Feng, S. G.; Philipp, C. C.; Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 3504.

Scheme 1



ether, toluene, pentane, and hexanes were purified by passage through a column of activated alumina. Tetrahydrofuran was distilled under nitrogen from sodium and benzophenone. CD_2Cl_2 was distilled from CaH_2 and degassed by several freeze, pump, thaw cycles. [Tp′W(CO)$_2$(PhC≡CMe)][OTf] (**1**),[34,41] Na[BAr′$_4$],[42] and [H(OEt$_2$)$_2$][BAr′$_4$][42] were synthesized according to literature procedures.

NMR spectra were obtained using a Bruker AMX300, DRX400, or AMX400. 2D spectra were recorded on the Bruker AMX400. Elemental analyses were obtained from Altantic Microlabs, Norcross, GA.

Tp′W(CO)(PhC≡CMe)(NCH$_2$CH$_2$CH$_2$CH$_2$) (2a). [Tp′W(CO)$_2$(PhC≡CMe)][OTf] (**1**) (0.751 g, 0.936 mmol) was dissolved in THF to form a green solution, which was heated at reflux for 1 h. After 1 h the solution had turned blue, and 2.5 mL (4.8 mmol) of pyrrolidine was added. The solution was heated at reflux overnight. The solvent was then removed by rotary evaporation, and the greenish oil that remained was purified on an alumina column with 1:1 hexanes/CH_2Cl_2 as the eluent. A purple band was collected after adding THF to the column. Solvent was removed by rotary evaporation, and the residue was recrystallized from CH_2Cl_2/MeOH to produce green needles (0.0476 g, 7% yield). The procedure for purifying the product has been difficult to reproduce due to the sensitivity of the product in the presence of water. A better method is to dissolve the reaction residue in CH_2Cl_2 and add hexanes to precipitate the ammonium triflate salt. Cannula filtration and removal of solvent yields the product as a powder that is clean by ^{1}H NMR spectroscopy (66% yield). IR (KBr): ν_{CO} 1839 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.03, 6.98 (m, 3H, *m*,*p*-Ph), 6.30 (d, 2H, *o*-Ph), 5.88, 5.73, 5.58 (s, 3H, Tp′-C*H*), 4.73, 3.67 (m, 2H, NC*H*$_2$CH$_2$-CH$_2$CH$_2$), 3.39, 2.59 (m, 2H, NCH$_2$CH$_2$CH$_2$C*H*$_2$), 1.68, 1.42 (m, 2H, NCH$_2$C*H*$_2$CH$_2$CH$_2$), 1.68, 1.30 (m, 2H, NCH$_2$CH$_2$C*H*$_2$CH$_2$), 3.17 (s, 3H, PhC≡CC*H*$_3$), 2.63, 2.53, 2.40, 2.37, 1.58, 1.36 (s, 18H, Tp′-C*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 237.1 (*C*O), 169.8 (Ph*C*≡CMe), 167.1 (PhC≡*C*Me), 153.4, 152.6, 151.1, 144.4, 144.3, 143.6 (Tp′-*C*Me), 138.6 (*ipso*-Ph), 128.6, 128.0 (*o*,*m*-Ph), 126.0 (*p*-Ph), 107.4, 107.2, 106.4 (Tp′-*C*H), 70.2, 58.7 (NCH$_2$CH$_2$CH$_2$*C*H$_2$), 28.5, 27.5 (NCH$_2$*C*H$_2$CH$_2$CH$_2$), 18.0 (PhC≡C*Me*), 15.5, 15.43, 15.36, 12.94, 12.90, 12.8 (Tp′-*C*H$_3$). Anal. Calcd for $C_{29}H_{38}N_7OBW\cdot 1/2C_5H_{12}$: C, 51.73; H, 6.06; N, 13.41. Found: C, 51.82; H, 6.01; N, 13.13.

(42) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920.

[Tp′W(CO)(PhC≡CMe)(N=CHCH$_2$CH$_2$CH$_2$)][BAr′$_4$] (3a). Tp′W(CO)(PhC≡CMe)(NCH$_2$CH$_2$CH$_2$CH$_2$) (**2a**) (0.110 g, 0.158 mmol) was dissolved in CH_2Cl_2 (20 mL). Iodine (0.043 g, 0.169 mmol) and NEt_3 (22 μL, 0.158 mmol) were added, and the reaction was allowed to stir for 1 h. A solution of Na[BAr′$_4$] (0.143 g, 0.161 mmol) in Et_2O (10 mL) was cannula transferred into the reaction, and a white precipitate formed. The solution was cannula filtered, and solvent was removed from the aqua green filtrate by rotary evaporation. The residue was purified on an alumina column using 1:1 CH_2Cl_2/hexanes as the first eluent, and then neat CH_2Cl_2 was used after the product was loaded onto the column. The blue band was collected, solvent was removed by rotary evaporation, and the residue was recrystallized from CH_2Cl_2/hexanes (0.150 g, 61% yield). IR (KBr): ν_{CO} 1910 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.33 (m, 3H, *m*,*p*-Ph), 6.76 (m, 2H, *o*-Ph), 6.50 (br t, $^3J_{HH}$ = 1.5 Hz, 1H, N=C*H*), 6.03, 5.93, 5.79 (s, 3H, Tp′-C*H*), 4.32, 3.08 (m, 2H, N=CHC*H*$_2$CH$_2$CH$_2$), 2.94, 2.63 (m, 2H, N=CHCH$_2$CH$_2$C*H*$_2$), 2.05, 1.85 (m, 2H, N=CHCH$_2$C*H*$_2$CH$_2$), 3.86 (s, 3H, PhC≡CC*H*$_3$), 2.58, 2.52, 2.43, 2.32, 1.32, 1.05 (s, 18H, Tp′-C*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 228.6 (*C*O), 215.6 (Ph*C*≡CMe), 212.6 (PhC≡*C*Me), 177.7 (N=*C*HCH$_2$CH$_2$CH$_2$), 153.6, 152.6, 151.2, 148.1, 148.0, 146.6 (Tp′-*C*Me), 136.1 (*ipso*-Ph), 131.3 (*p*-Ph), 129.9, 129.4 (*o*,*m*-Ph), 109.54, 109.45, 108.3 (Tp′-*C*H), 69.2, 37.6, 21.8 (N=CH*C*H$_2$*C*H$_2$CH$_2$), 23.2 (PhC≡C*C*H$_3$), 16.1, 15.6, 13.9, 12.9 (×2), 12.8 (Tp′-*C*H$_3$). Anal. Calcd for $C_{61}H_{49}N_7OB_2F_{24}W$: C, 47.04; H, 3.17; N, 6.30. Found: C, 47.18; H, 3.15; N, 6.33.

Tp′W(CO)(PhC≡CMe)(NCHMeCH$_2$CH$_2$CH$_2$) (S_WR_C/R_WS_C-2b). Method A. [Tp′W(CO)$_2$(PhC≡CMe)][OTf] (**1**) (0.5230 g, 0.652 mmol) was dissolved in THF and was heated at reflux for 1.5 h. 2-Methylpyrrolidine (0.2 mL, 1.96 mmol) was added, and the solution was heated overnight. No change was observed by IR spectroscopy, so more 2-methylpyrrolidine (0.2 mL, 1.96 mmol) was added. After 1.5 h, no change was seen by IR spectroscopy. Triethylamine (0.15 mL, 1.1 mmol) was then added, but the added base did not induce a reaction. The reaction was then cooled to −78 °C, and ^{n}BuLi was added to deprotonate the 2-methylpyrrolidine. The solution was warmed to room temperature and stirred for 1.5 h. Solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 (3 mL), and pentane (30 mL) was added. The solution was cannula filtered, and solvent was removed in vacuo. The product was recrystallized by slow evaporation of a solution in pentane (0.313 g, 65% yield).

Method B. 1-Pyrroline complex **3a** (59.2 mg, 0.38 mmol) was dissolved in THF (4 mL). An excess of MeMgBr (0.5 mL, 3 M in Et_2O) was added. The solution turned from blue to wine red. Solvent was removed in vacuo, and the residue was dissolved in CH_2Cl_2 (0.7 mL). Hexanes (10 mL) was added, a white precipitate formed, and the solution was cannula filtered. Solvent was again removed in vacuo, and the residue was dissolved in CH_2Cl_2 and layered with hexanes. More salts precipitated, and the solution was cannula-filtered once more. Solvent was removed in vacuo, and crystals were grown in a concentrated pentane solution in the freezer (0.020 g, 71% yield). IR (KBr): ν_{CO} 1847 cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 7.05, 6.99 (m, 3H, *m*,*p*-Ph), 6.26 (d, 2H, *o*-Ph), 5.86, 5.74, 5.55 (s, 3H, Tp′-C*H*), 4.96 (m, 1H, NC*H*MeCH$_2$CH$_2$CH$_2$), 3.36, 2.70 (m, 2H, NCHMeCH$_2$CH$_2$C*H*$_2$), 2.01, 1.2 (m, 2H, NCHMeC*H*$_2$CH$_2$CH$_2$), 1.3, 1.1 (m, 2H, NCHMeCH$_2$C*H*$_2$CH$_2$), 3.19 (s, 3H, PhC≡CC*H*$_3$), 2.64, 2.53, 2.37, 2.36, 1.60, 1.40 (s, 18H, Tp′-C*H*$_3$), 0.58 (d, $^3J_{HH}$ = 6.4 Hz, 3H, NCH*Me*CH$_2$CH$_2$CH$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 236.3 (*C*O), 171.6, 168.1 (Ph*C*≡*C*CH$_3$), 153.3, 152.7, 151.1, 144.32, 144.28, 143.5 (Tp′-*C*Me), 138.8 (*ipso*-Ph), 128.3, 128.0 (*o*,*m*-Ph), 126.0 (*p*-Ph), 107.5, 107.1, 106.3 (Tp′-*C*H), 75.4, 58.0 (N*C*HMeCH$_2$CH$_2$*C*H$_2$), 35.3, 26.7, 23.9 (NCH*Me**C*H$_2$*C*H$_2$*C*H$_2$), 18.7 (PhC≡C*C*H$_3$), 15.8, 15.53, 15.51, 12.94, 12.87, 12.85 (Tp′-*C*H$_3$). Anal. Calcd for $C_{30}H_{40}N_7OBW\cdot 1/2C_5H_{12}$: C, 52.37; H, 6.22; N, 13.15. Found: C, 52.84; H, 6.38; N, 12.90.

Tp′W(CO)(PhC≡CMe)(NCHMeCH$_2$CH$_2$CH$_2$) (S_WS_C/R_WR_C-2b). Imine complex **3b** (74.2 mg, 0.0838 mmol) was dissolved in THF (10 mL). LiHBEt$_3$ (0.30 mL, 1.0 M) was added, and the solution turned green. Solvent was removed in vacuo. The product was extracted from the residue with pentane. Solvent was again removed in vacuo, and a ^1H NMR spectrum was obtained of the residue (2.5:1 dr) (0.0154 g, 25% yield). IR (THF): ν_{CO} 1850 cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 7.04, 6.98 (m, 3H, *m*,*p*-Ph), 6.23 (d, 2H, *o*-Ph), 5.87, 5.75, 5.54 (s, 3H, Tp′-C*H*), 4.91 (m, 1H, NC*H*MeCH$_2$CH$_2$CH$_2$), 4.04, 4.01, 3.59, 2.38, 1.58, 1.15 (m, 6H, NCHMeC*H*$_2$C*H*$_2$C*H*$_2$), 3.12 (s, 3H, PhC≡CC*H*$_3$), 2.78, 2.54, 2.38, 2.37, 1.51, 1.38 (s, 18H, Tp′-C*H*$_3$), 0.05 (d, $^3J_{HH}$ = 6.8 Hz, 3H, NCH*Me*CH$_2$CH$_2$CH$_2$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 237.4 (*C*O), 170.6, 166.3 (Ph*C*≡*C*CH$_3$), 152.6, 152.4, 151.6, 144.7, 144.4, 143.4 (Tp′-*C*Me), 138.7 (*ipso*-Ph), 128.6, 128.0 (*o*,*m*-Ph), 125.9 (*p*-Ph), 107.5, 106.8, 106.5 (Tp′-*C*H), 74.6, 56.7 (N*C*HMeCH$_2$CH$_2$*C*H$_2$), 34.1, 25.2, 22.2 (NCH*Me**C*H$_2$*C*H$_2$*C*H$_2$), 17.8 (PhC≡C*C*H$_3$), 16.5, 15.5, 15.4, 13.1, 13.0, 12.9 (Tp′-*C*H$_3$).

[Tp′W(CO)(PhC≡CMe)(N=CMeCH$_2$CH$_2$CH$_2$)][OTf] (3b). [Tp′W(CO)$_2$(PhC≡CMe)][OTf] (**1**) (0.2151 g, 0.268 mmol) was dissolved in THF (15 mL) and heated at reflux for 1 h. 2-Methyl-1-pyrroline (50 μL, 0.53 mmol) was added, and the reaction was heated overnight at reflux. No reaction was observed by IR spectroscopy. The reaction was then cooled to room temperature, and ^{n}BuLi (0.12 mL, 2.4 M) was added. The solution turned from blue to bright green. Solvent was removed in vacuo, and the residue was purified on alumina with a series of eluents: CH_2Cl_2, THF (1 mL), CH_2Cl_2, MeOH (1 mL), and CH_2Cl_2. The fraction collected after the addition of methanol contained the desired blue product, which was recrystallized from CH_2Cl_2/Et_2O (0.043 g, 18% yield). IR (KBr): ν_{CO} 1910 cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 7.32, 6.76 (m, 5H, *Ph*C≡CMe), 6.05, 5.92, 5.78 (s, 3H, Tp′-C*H*), 4.4, 3.0 (m, 2H, N=CMeC*H*$_2$CH$_2$CH$_2$), 2.9, 2.6 (m, 2H, N=CMeCH$_2$CH$_2$C*H*$_2$), 2.0, 1.8 (m, 2H, N=CMeCH$_2$C*H*$_2$CH$_2$), 3.85 (s, 3H, PhC≡C*Me*), 2.60, 2.52, 2.46, 2.39, 1.35, 1.12 (s, 18H, Tp′-C*H*$_3$), 0.82 (N=C*Me*CH$_2$CH$_2$CH$_2$). ^{13}C NMR (CD_2Cl_2, δ): 229.1 (*C*O), 214.1, 211.7 (Ph*C*≡*C*Me), 190.7 (N=*C*MeCH$_2$CH$_2$CH$_2$), 154.1, 153.4, 151.1, 147.9, 147.6, 146.4 (Tp′-*C*Me), 136.2, 130.8, 129.4, 129.2 (*Ph*C≡CMe), 109.1, 108.9, 108.1 (Tp′-*C*H), 72.1, 41.5 (two pyrroline *C*H$_2$'s), 22.9, 22.3 (PhC≡C*Me*, pyrroline *C*H$_2$), 17.3, 16.1, 15.6, 14.0, 13.0 (×2), 12.8 (Tp′-C*H*$_3$, N=C*Me*CH$_2$CH$_2$CH$_2$). Anal. Calcd for $C_{31}H_{39}N_7O_4SF_3BW$: C, 43.43; H, 4.58; N, 11.44. Found: C, 43.63; H, 4.71; N, 11.36.

[Tp′W(CO)(PhC≡CMe)(NHCH$_2$CH$_2$CH$_2$CH$_2$)][BAr′$_4$] (4a). Pyrrolidine complex **2a** (59.0 mg, 0.085 mmol) and [H·(OEt$_2$)$_2$][BAr′$_4$] (75.0 mg, 0.087 mmol) were combined and dissolved in 10 mL of CH_2Cl_2. After 20 min the solvent was reduced to 2 mL by evaporation under vacuum. Pentane (40 mL) was added, and the solution was stirred. Solvent was filtered away from the light blue solid that formed, and the solid was washed with pentane (2 × 20 mL). Crystals were obtained from CH_2Cl_2/hexanes (0.074 g, 55% yield). IR (KBr): ν_{CO} 1904 cm^{-1}. ^1H NMR (CD_2Cl_2, δ): 7.31 (m, 3H, *m*,*p*-Ph), 6.69 (m, 2H, *o*-Ph), 6.10, 5.98, 5.74 (s, 3H, Tp′-C*H*), 3.79 (s, 3H, PhC≡CC*H*$_3$), 3.39 (m, 1H, N*H*CH$_2$CH$_2$CH$_2$CH$_2$), 3.55, 2.93 (m, 2H, NHC*H*$_2$CH$_2$CH$_2$CH$_2$), 2.39, 2.02 (m, 2H, NHCH$_2$CH$_2$CH$_2$C*H*$_2$), 1.93, 1.67 (m, 2H, NHCH$_2$C*H*$_2$CH$_2$CH$_2$), 1.75, 1.49 (m, 2H, NHCH$_2$CH$_2$C*H*$_2$CH$_2$), 2.71, 2.60, 2.51, 2.45, 1.49, 1.23 (s, 18H, Tp′C*H*$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, δ): 230.2 (*C*O), 212.8 (Ph*C*≡CMe), 210.5 (PhC≡*C*Me), 161.9, 161.0, 154.1, 151.9, 151.0, 146.7 (Tp′*C*Me), 135.9 (*ipso*-Ph), 129.0 (*o*,*m*-Ph), 126.8 (*p*-Ph), 110.2, 108.2, 108.0 (Tp′*C*H), 79.3, 72.0 (NH*C*H$_2$-CH$_2$CH$_2$*C*H$_2$), 23.1, 21.5 (NHCH$_2$*C*H$_2$*C*H$_2$*C*H$_2$), 15.9, 14.3 (×2), 13.2, 13.1, 13.0 (Tp′*C*H$_3$). Anal. Calcd for $C_{61}H_{51}N_7OF_{24}B_2W$: C, 46.98; H, 3.30; N, 6.29. Found: C, 47.11; H, 3.23; N, 6.24.

Tp′W(CO)(PhC≡CMe)(NCHDCH$_2$CH$_2$CH$_2$) (2a-d_1). 1-Pyrroline complex **3a** (47.5 mg, 0.031 mmol) was dissolved in THF (4 mL). Li[DBEt$_3$] (31 μL, 1 M in THF) was added, and the solution turned from blue to reddish-purple. Solvent was removed in vacuo. The green residue was dissolved in CH_2Cl_2 (1 mL) and cannula transferred to an NMR tube under nitrogen. A ^2H NMR spectrum was obtained to determine the ratio of diastereomers. In a separate experiment, the ^1H NMR spectrum was obtained in CD_2Cl_2 and compared to complex **2** to confirm the identity of the product. IR (THF): ν_{CO} 1848 cm^{-1}. ^2H NMR (CH_2Cl_2, δ): 3.67, 2.58 (each a s).

X-ray Crystallography. Single crystals of compounds **2a**, S_WR_C/R_WS_C-**2b**, and **3a** were each mounted on a glass wand and coated with epoxy in order to collect structural data. Diffraction data were collected on a Bruker SMART diffractometer using ω-scan mode for complexes **2a**, S_WR_C/R_WS_C-**2b**, and **3a**. A single crystal of complex **3b** was mounted on a MiTeGen MicroMount and coated in a drop of oil to collect structural data. Diffraction data were collected on a Bruker SMART APEX-II diffractometer using ω-scan mode for complex **3b**.

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Supporting Information Available: Crystallographic information files (CIFs) for compounds **2a**, (S_WR_C/R_WS_C)-**2b**, **3a**, and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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