Diastereoselective Hydride Addition to [Tp′W(CO)(PhCCMe)(NH=CRR′)][BAr′$_4$]: Effects of Equilibrium and Kinetic Acidity

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A series of alkyl and aryl amido, imine, azavinylidene, and amine complexes containing the [Tp′W(CO)(PhCCMe)]$^+$ fragment have been synthesized. Reaction of Na[HBEt$_3$] with an *E*/*Z* mixture of [Tp′W(CO)(PhCCMe)(NH=CMeEt)][BAr′$_4$] results in hydride addition at the imine carbon to form the amido complex with high diastereoselectivity. This high diastereoselectivity reflects differentiation between methyl and ethyl groups on the substrate imine carbon. A competing reaction forms an azavinylidene complex as a minor product via deprotonation of the coordinated imine ligand in the reagent. The ratio of amido to azavinylidene products tracks the *E* to *Z* isomer ratio and suggests that different reaction pathways characterize these two isomers. Relative pK_a's of the various imine and amine complexes have been measured in THF, and kinetic acidity measurements of related imine complexes have been used to help understand these results.

Introduction

Stereoselective reduction of an unsaturated bond usually requires that one isomer (*E*/*Z*) of the reagent predominates and that reduction occurs at only one face of the substrate. Examples where the *E*/*Z* ratio has no impact on the stereoselectivity of the reaction are rare.[1,2] Many reactions that involve stereoselection rely on steric differences between large and small groups to differentiate two stereofaces of the substrate. Few reactions successfully discriminate between methyl and ethyl groups.[3−6]

Many methods for stereoselectively converting imines to amines have been developed.[7−11] Examples of stoichiometric, diastereoselective nucleophile addition to coordinated imine complexes have been reported. Gladysz has effectively utilized electrophilic CpRe(NO)(PPh$_3$)(imine)$^+$ complexes to add nucleophiles diastereoselectively to coordinated imines (eq 1).[12−20] The

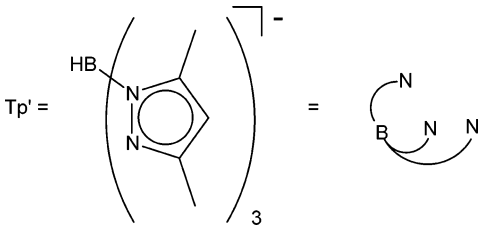

Figure 1. Tp′ = hydrido tris(3,5-dimethylpyrazolyl)borate.

enantiomers of this rhenium system have been resolved, so a single amine enantiomer can be synthesized.[14] Restriction of reagent *E*/*Z* imine isomers via chelation in Boncella's orthometalated *N*-phenylbenzaldimine complex allows nucleophiles to add to form a 98:2 diastereomer ratio of amido products (eq 2).[21] Imines bound to the arene in chiral (η^6-arene)Cr(CO)$_3$ complexes also undergo stereoselective nucleophilic addition at the imine carbon.[22,23]

Acetonitrile coordinated to [Tp′W(CO)(PhCCMe)]$^+$ can be reduced by sequential hydride and proton additions to give an ethylamine complex [Tp′ = hydrido tris(3,5-dimethylpyrazolyl)borate, see Figure 1],[24] and stepwise

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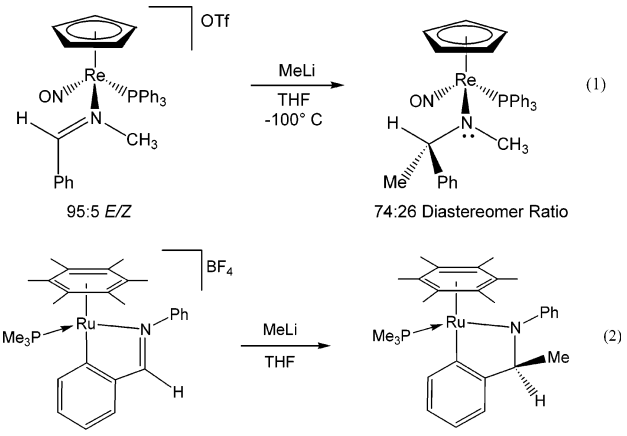


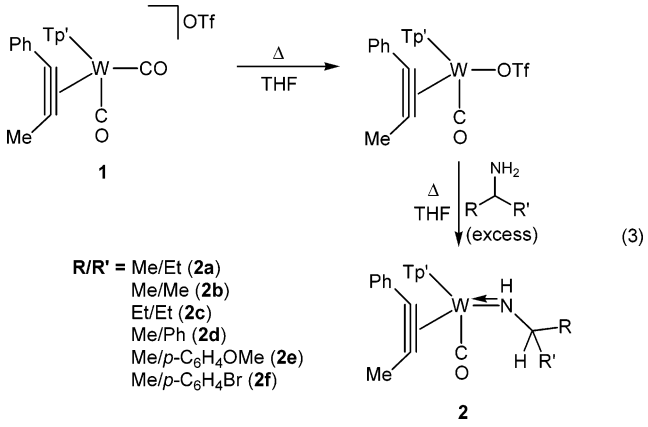
oxidation of coordinated benzylamine to benzonitrile has also been described (Scheme 1).[25] Addition of CN^- to the imine carbon in [Tp′W(CO)(PhCCMe)(NH=CHMe)][BF_4], which exists as the *E* isomer, occurs diastereoselectively.[24] Enantiomers of the Tp′W(CO)(PhCCMe)$^+$ fragment are available since derivative complexes have been resolved by fractional crystallization.[26]

Hydride addition to [Tp′W(CO)(PhCCMe)(NH=CMeEt)][BAr′$_4$] (**3a**) (BAr′$_4$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) occurs with high diastereoselectivity to yield an amido complex through *E*/*Z* isomer reactivity differences.[27] Effective differentiation between methyl and ethyl groups on the prochiral imine carbon is a distinguishing feature of this system. Here we report both kinetic and thermodynamic acidity studies as well as structural and mechanistic details for the reactions of the *E* and *Z* isomers of complex **3a**.

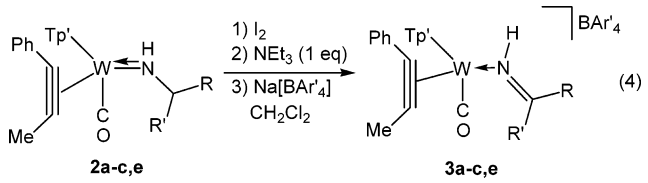
Results and Discussion

The sythesis of amido, imine, azavinylidene, and amine complexes has previously been reported. Complexes **2**−**5a**, **2**−**4b**, **2**−**4c**, and **2**−**5d** have been described.[27,28] Complexes **5b**,**c** and **2**−**5e**,**f** are reported here for the first time.

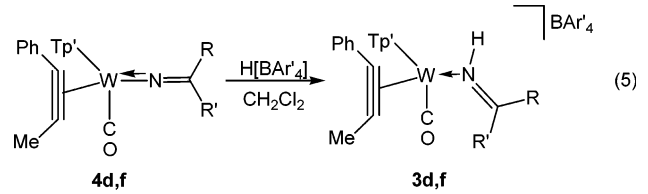
Synthesis of Amido Complexes Tp′W(CO)(PhCCMe)(NHCHRR′) (2a−f). Heating [Tp′W(CO)$_2$(PhCCMe)][OTf] (**1**) in THF at reflux for 1 h leads to the loss of one CO ligand and coordination of the triflate counterion. Addition of a primary amine, NH_2CHRR', and continued heating for 1 to 2 days, depending on the amine, displaces the coordinated triflate and forms neutral amido complexes **2a**−**f** (eq 3).[28] This synthetic route allows the isolation of a variety of alkyl and aryl amido complexes.



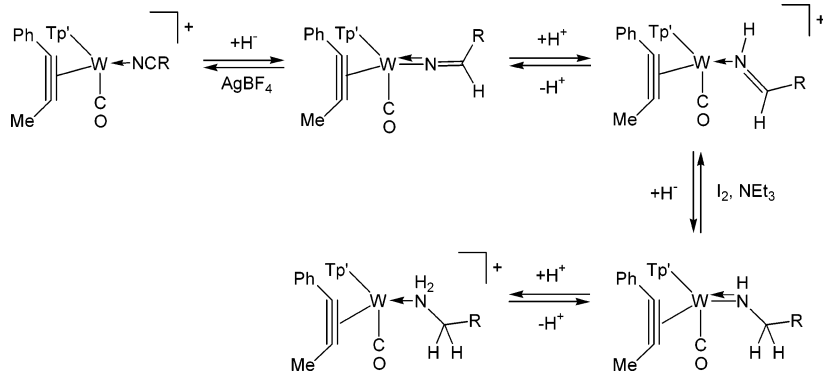
Synthesis of Imine Complexes [Tp′W(CO)(PhCCMe)(NH=CRR′)][BAr′$_4$] (3a−c,e). Oxidation of electron-rich amido complexes **2a**−**c**,**e** (R/R′ = Me/Et, **2a**; Me/Me, **2b**; Et/Et, **2c**; Me/*p*-C_6H_4OMe, **2e**) by I_2 in the presence of NEt_3 in CH_2Cl_2 yields the imine complexes [Tp′W(CO)(PhCCMe)(NH=CRR′)][I] via net hydride removal. Anion exchange is effected by cannula transferring a diethyl ether solution of Na[BAr′$_4$] into the reaction mixture (eq 4).



Since oxidation of amido complexes **2d**,**f** (R/R′ = Me/Ph, **2d**; Me/*p*-C_6H_4Br, **2f**) by I_2 in the presence of base led to the isolation of azavinylidene complexes **4d**,**f** (see below), imine complexes **3d**,**f** were synthesized by protonation of the azavinylidene complexes **4d**,**f** by H[BAr′$_4$] (eq 5).



Scheme 1

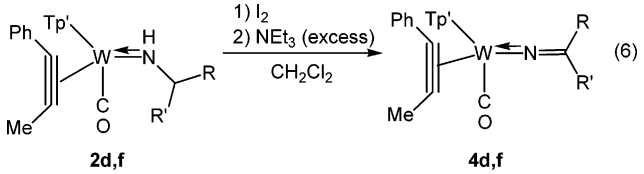


E and *Z* isomers of imine complex **3a** (R/R′ = Me/Et) exist in a 75:25 ratio as determined by ^{1}H NMR spectroscopy; these isomers do not interconvert at 100 °C on the NMR time scale in C_6D_5Br, indicating a $\Delta G^{\ddagger}$ of >18 kcal/mol.[28] NMR spectra for the two isomers were assigned by a combination of COSY and NOESY techniques. In contrast, only the *E* isomer is observed for complexes **3d**−**f** (R/R′ = Me/Ph, **3d**; Me/*p*-C_6H_4OMe, **3e**; Me/*p*-C_6H_4Br, **3f**).

Recrystallization of imine complex **3a** by slow diffusion of hexanes into a CH_2Cl_2 solution of the imine yields a 75:25 *E*/*Z* ratio of isomers. Addition of THF to the CH_2Cl_2/hexanes solvent system provides a method of enriching the solid in the *E* isomer. Slow diffusion of hexanes into a solution of the imine complex in 3:2:1 hexanes/CH_2Cl_2/THF allows for a range of *E*/*Z* ratios from 80:20 to 93:7 to be obtained in 91% yield. Isomerization of the imine ligand may be promoted by THF since deprotonation at nitrogen to form azavinylidene complex **4a** followed by reprotonation of the opposite nitrogen face will interconvert *E* and *Z* isomers (vide infra).

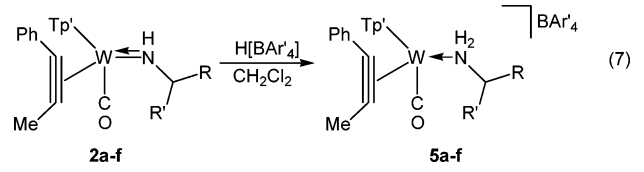
Synthesis of Azavinylidene Complexes Tp′W(CO)(PhCCMe)(=N=CRR′) (4a−f). For imine complexes **3a**−**c**,**e** (R/R′ = Me/Et, **3a**; Me/Me, **3b**; Et/Et, **3c**; Me/*p*-C_6H_4OMe, **3e**) that were isolated cleanly from the amido oxidation reaction above, the corresponding azavinylidene complexes **4a**−**c**,**e** were synthesized by simple deprotonation of the imine complex by using KH as the base.

Oxidation of electron-poor amido complexes **2d**,**f** (R/R′ = Me/Ph, **2d**; Me/*p*-C_6H_4Br, **2f**) with I_2 and 1 equiv of NEt_3 led to the formation of a mixture of imine and azavinylidene complexes.[28] Rather than isolate the imine complexes, excess NEt_3 was added to deprotonate the imine ligand, and neutral azavinylidene complexes **4d**,**f** (eq 6) were isolated.



(6)

Synthesis of Amine Complexes [Tp′W(CO)(PhCCMe)(NH$_2$CHRR′)][BAr′$_4$] (5a−f). Amine complexes were synthesized by protonation of the corresponding amido complexes **2a**−**f** by H[BAr′$_4$] in CH_2Cl_2 (eq 7).



(7)

Variable-Temperature NMR Studies. Perhaps surprisingly, both the *E* and *Z* isomers of imine complex **3a** show broad signals for the imine alkyl groups cis to tungsten, whether CH_3 or CH_2CH_3. The *E* isomer has a broad methyl singlet at 2.05 ppm, and the *Z* isomer has a broad methyl triplet at 1.06 ppm. Since the *E* and *Z* isomers do not interconvert on the NMR time scale, some other more facile dynamic process must be occurring within each isomer independently to account for the broad signals. Hindered rotation around the W−N imine bond can account for this observation; each imine isomer apparently has one W−N conformation with the NH pointed between the pyrazole rings and another conformation with the NH pointed between the CO and alkyne ligands (Scheme 2, see NOESY data below). The broad signals for the methyl group of the *E* isomer and the ethyl group of the *Z* isomer reflect large chemical shift differences for that group in the two conformers due to anisotropic diamagnetic shielding by the pyrazole rings. The minor conformation would shift the alkyl methyl groups upfield when they lie between the pyrazole rings. Interconversion of these two conformers is rapid at room temperature, but since coalescence depends on the chemical shift differential, each of the signals can sharpen into one signal at different temperatures, and the result is selective broadening of a few signals. Signals for the minor conformations could not be identified even at low temperature since the majority of the sample exists in the conformation with the NH's directed toward the pyrazole rings of Tp′. The methyl singlet at 2.05 ppm for the *E* isomer broadens from 260 to 315 K and begins to sharpen again above 315 K at 1.90 ppm. This indicates that the minor rotamer's methyl signal lies upfield from 1.90 ppm, as expected. The $\Delta G^{\ddagger}$ for W−N rotation from the major rotamer to the minor rotamer for the *E* isomer was calculated from line broadening of the methyl singlet at 2.05 ppm and determined to be 15 kcal/mol at 296 K.

NOESY of [Tp′W(CO)(PhCCMe)(NH=CMeEt)][BAr′$_4$] (3a). In the original report describing [Tp′W(CO)(PhCCMe)(NH=CMeEt)][BAr′$_4$] (**3a**), an observed $^4J_{HH}$ coupling of 1 Hz in one CH_3 signal of the minor species led to its incorrect assignment as being trans to the NH proton in the *E* isomer.[28] Using NOESY correlations between the NH proton and the methyl and ethyl groups of the imine ligand, the *E* isomer has now been assigned as the major species. Intuitively, the *E* isomer should be favored on the basis of steric factors. In both isomers, the NH protons, which appear at 8.92 ppm, show strong NOE correlations to Tp′ methyl groups at 1.21 and 2.47 ppm, indicating that these imine protons lie between two pyrazole rings. The X-ray structure of the imine complex also reveals the NH proton situated between two pyrazole rings.[28] The NH proton also correlates to the methyl triplet of the major isomer at 0.92 ppm and the 1 Hz methyl doublet of the minor isomer at 2.22 ppm. Other NOE correlations are schematically depicted in Figure 2. This system shows

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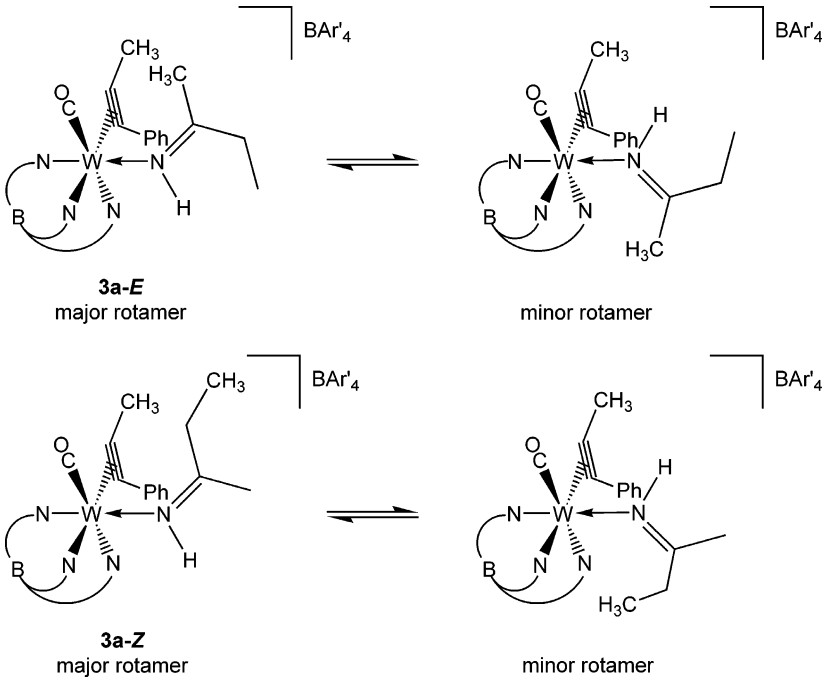
Scheme 2



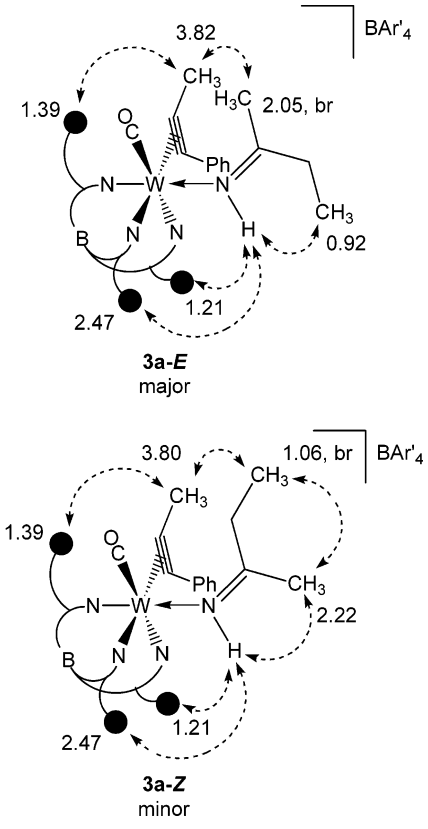


Figure 2. NOE correlations (dashed arrows) in the *E* and *Z* isomers of imine complex **3a**. The three Tp′ methyl groups that are directed toward the three ancillary ligands are depicted as black circles. ^{1}H NMR chemical shifts are given in ppm.

the value of the Tp′ methyl groups as NOE reporter sites for determining the orientation of ancillary ligands.[29,30]

NOESY of Tp′W(CO)(PhCCMe)(=N=CMeEt) (4a). Azavinylidene complex **4a** exists as two rotamers in a 75:25 ratio. The azavinylidene plane is oriented perpendicular to the W−CO axis so it can donate its lone pair into the empty dπ orbital on tungsten; this places the ethyl group proximal to the alkyne ligand in one rotamer (**prox-4a**) and distal to the alkyne in the other (**dis-4a**).[31] In the NOESY spectrum, the major rotamer displayed a correlation between the methyl triplet of the azavinylidene ethyl group at 0.67 ppm and the alkyne methyl singlet at 3.07 ppm. This suggests that **prox-4a** is the major rotamer and **dis-4a** is the minor rotamer (Figure 3). Note that the orientation of the ethyl group proximal to the alkyne methyl in the major azavinylidene isomer is opposite the orientation in the imine major isomer.

Isomerization of *E* and *Z* [Tp′W(CO)(PhCCMe)(NH=CMeEt)][BAr′$_4$] (3a). Imine complex **3a** that had been enriched in the *E* isomer by careful recrystallization was isomerized to a 75:25 *E*/*Z* distribution of isomers immediately in CD_2Cl_2 upon addition of 5 mol % NEt_3. The 75:25 *E*/*Z* ratio is the thermodynamic ratio. A ^{1}H NMR spectrum of 90:10 *E*/*Z* ratio imine complex showed isomerization to a 60:40 *E*/*Z* ratio upon dissolution in THF-d_8.

Hydride Addition to [Tp′W(CO)(PhCCMe)(NH=CMeEt)][BAr′$_4$] (3a). In an NMR tube, Na[HBEt$_3$] was added to an 80:20 mixture of *E*/*Z* imine isomers of

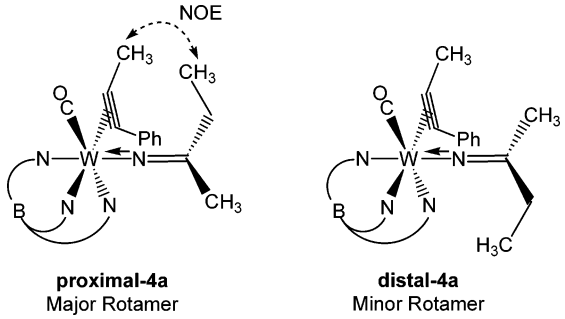


Figure 3. Major and minor W−N rotamers as determined by NOESY for azavinylidene complex **4a**.

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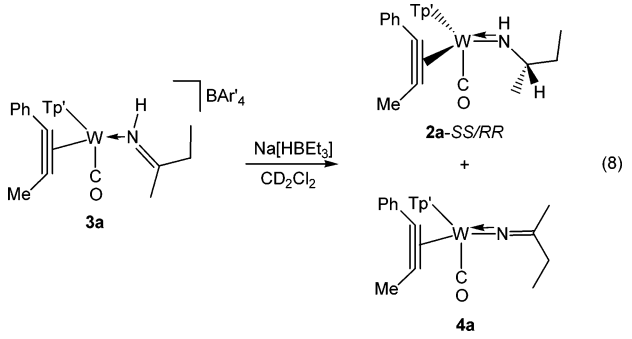
Table 1. Diastereoselectivity and Amido to Azavinylidene Ratios for Different *E/Z* Ratios of the Starting Imine Reagent

imine complex **3a** *E/Z*	amido complex **2a**		azavinylidene complex **4a**				
	2a-*SS/RR* maj. diast.	**2a-*SR/RS*** min. diast.	**prox-4a** maj. rot.	**dis-4a** min. rot.	maj. products:min. products[a]	**3a-*E*** add.:depr.[b]	**3a-*Z*** add.:depr.[c]
80:20	70	5	13	12	83:17	5:1	0.4:1
80:20	71	6	12	11	83:17	6:1	0.5:1
83:17	71	4	17	7	88:11	4:1	0.6:1
93:7	78	3	13	5	91:8	6:1	0.6:1

[a] **2a-*SS/RR***, **prox-4a**:**2a-*SR/RS***, **dis-4a**. [b] **2a-*SS/RR***:**prox-4a**. [c] **2a-*SR/RS***:**dis-4a**.

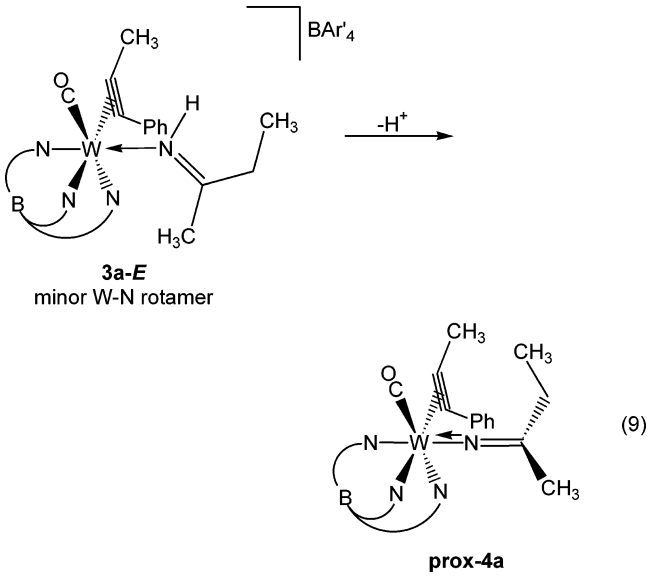
complex **3a** in CD_2Cl_2. ^1H NMR spectroscopy showed an unexpected 93:7 diastereomer ratio (*SS/RR*:*SR/RS*, vide infra) of amido complex **2a** (eq 8). This ratio is surprisingly high in view of the low *E/Z* ratio of the coordinated imine reagent. Azavinylidene complex **4a** was also observed as a product from deprotonation of imine complex **3a** (76:24 addition to deprotonation, Table 1).



The effect of the *E/Z* ratio on diastereoselectivity was probed from the nonequilibrium ratio of *E/Z* imine complex isomers (93:7 *E/Z*). Na[$HBEt_3$] was added to a solution of 93:7 *E*/*Z* isomer mixture of imine complex **3a** in an NMR tube. Slightly higher diastereoselectivity was observed, 96:4, but less azavinylidene complex was formed from deprotonation (81:18 addition to deprotonation, Table 1).

The two rotamers of the azavinylidene complex do not interconvert on the time scale of these experiments. It appears that formation of the azavinylidene ligand via deprotonation of the imine ligand occurs diastereoselectively. That is, ratios of products suggest that deprotonation of the *E* isomer of imine complex **3a** leads to a single rotamer of azavinylidene complex **4a**; the *Z* isomer of imine complex **3a** leads to the other. The ratio of the sum of the major diastereomer (**2a-*SS/RR***) plus the major rotamer (**prox-4a**) to the sum of the minor diastereomer (**2a-*SR/RS***) plus the minor rotamer (**dis-4a**) is approximately equal to the *E/Z* ratio of the starting imine complex regardless of the starting *E/Z* ratio (Table 1). This suggests that the *E* isomer can add hydride to form **2a-*SS/RR*** or be deprotonated to form **prox-4a**. Since both hydride addition and imine deprotonation form distinct products from each imine isomer, the ratio of addition to deprotonation for the *E* isomer can be calculated to be about 5:1 (**2a-*SS/RR***:**prox-4a**), so addition of hydride is favored by a $\Delta\Delta G^{\ddagger}$ of roughly 1 kcal/mol. In contrast, the ratio of addition to deprotonation for the *Z* isomer is approximately 0.5:1 (**2a-*SR/RS***:**dis-4a**), so deprotonation is favored by a $\Delta\Delta G^{\ddagger}$ of about 0.5 kcal/mol.

The orientation of the azavinylidene rotamers has been determined by NOESY. Assignment of the azavinylidene products formed in the reaction reveals that the major azavinylidene rotamer, **prox-4a**, described above results from deprotonation of the *E* isomer of imine complex **3a**. Structural similarity between the minor W−N rotamer of **3a-*E*** and the major azavinylidene rotamer, **prox-4a**, suggests that deprotonation of the imine complex occurs from the minor W−N rotamer (eq 9). Deprotonation of the minor W−N rotamer of **3a-*Z*** would form the other azavinylidene rotamer, **dis-4a**. Molecular models suggest that the NH proton would be more accessible in the minor rotamer, where it is not in the cleft between two pyrazole rings.



The symmetrical imine complex **3b** (R/R′ = Me/Me) reacts with hydride to lead to an 80:20 ratio of addition to deprotonation, while addition of hydride to imine complex **3c** (R/R′ = Et/Et) displays a 30:70 ratio of addition to deprotonation. The barrier to deprotonation as well as the barrier for hydride addition to the imine carbon are affected by the imine substituents. Diethyl substitution at the imine carbon sufficiently slows down hydride addition so that deprotonation dominates despite **3c**'s low kinetic acidity (see below). Even though all of these reactions occur in a matter of seconds, the reaction of hydride with **3c** is noticeably slower than with **3b**.

Relative pK_a Measurements. Proton transfer between acids and bases in organic solvents is important for understanding reaction pathways. Work in this area

(30) Pregosin, P. S.; Macchioni, A.; Templeton, J. L.; White, P. S.; Feng, S. G. *Magn. Reson. Chem.* **1994**, *32*, 415−421.
(31) Feng, S. G.; White, P. S.; Templeton, J. L. *Organometallics* **1993**, *12*, 2131−2139.

Table 2. Relative pK_a's for Imine and Amine Complexes

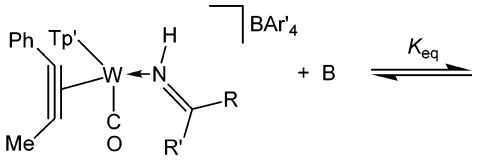
R/R′	ΔpK_a (NEt_3)	ΔpK_a (4-MeOpy)	standardized scale $[HNEt_3]^+ \equiv 0$
Me/Me imine (**3b**)	1.58(4)		1.58(4)
Me/Et imine (**3a**)	0.88(6)		0.88(6)
Me/Me amine (**5b**)	0.63(4)		0.63(4)
Me/Et amine (**5a**)	0.38(13)		0.38(13)
Et/Et imine (**3c**)	0.23(5)		0.23(5)
Et/Et amine (**5c**)	−0.02(2)		−0.02(2)
Me/*p*-C_6H_4OMe amine (**5e**)	−0.13(7)		−0.13(7)
Me/Ph amine (**5d**)	−0.71(14)		−0.71(14)
Me/*p*-C_6H_4Br amine (**5f**)	−1.41(14)		−1.41(14)
Me/*p*-C_6H_4OMe imine (**3e**)	−1.78(4)	1.29(9)	−1.78(10)
Me/Ph imine (**3d**)		0.65(2)	−2.42(10)
Me/*p*-C_6H_4Br imine (**3f**)		−0.52(4)	−3.59(11)

has often used DMSO[32] or acetonitrile solvents;[33] less studied are relative pK_a's in THF.[34−37] Measurements in THF are complicated by its low dielectric constant, which prevents dissociation of ion pairs. Measured acid/base values in THF have been termed pK_{ip} to reflect ion pair phenomenon (eq 10a).[37] This equation describes the reaction between a neutral acid and a neutral base. The reaction of a cationic acid and a neutral base shown in eq 10b more closely describes our cationic imine and amine complexes.[36]

$$A^-H^+ + B \overset{K_{ip}}{\rightleftharpoons} BH^+A^- \overset{K_{diss}}{\rightleftharpoons} BH^+ + A^- \quad (10a)$$

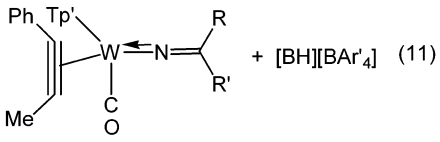
$$HB_1{}^+A^- + B_2 \overset{K_{diss}}{\rightleftharpoons} HB_1{}^+ + A^- + B_2 \overset{K}{\rightleftharpoons} B_1 + A^- + HB_2{}^+ \overset{1/K_{diss}}{\rightleftharpoons} B_1 + HB_2{}^+A^- \quad (10b)$$

Relative pK_a's were measured in THF by monitoring the intense CO stretch of cationic and neutral complexes in the IR spectrum. Each imine or amine complex was dissolved in THF, and base, either triethylamine or 4-methoxypyridine, was added. The ratio of the two CO absorbances was measured for either the imine/azavinylidene (eq 11) or the amine/amido (eq 12) pairs. From this ratio and the relative molar absorptivities, the equilibrium constant, K_{eq} (eq 13), was obtained and can be used to calculate a ΔpK_a for the acidic imine or amine complexes relative to $[HNEt_3]^+$, selected as the standard acid. The relative pK_a's for complexes **3a**−**c**,**e** and **5a**−**f** were measured using NEt_3. The acidities of complexes **3d**−**f** were measured using 4-methoxypyridine. The two scales were linked by matching measurements with both bases for complex **3e**, and $[HNEt_3]^+/NEt_3$ was defined as the standard with a pK_a of 0. Table 2 shows the ΔpK_a's for the tungsten imine and amine complexes reported here, where the equilibrium constant for reaction 11 would be $10^{-\Delta pK_a}$ for B = NEt_3. A positive ΔpK_a reflects limited proton transfer to NEt_3, while a negative ΔpK_a reflects a strongly acidic imine or amine complex.



3

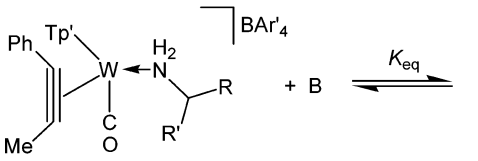
$\nu_{CO} \approx 1920\ cm^{-1}$



(11)

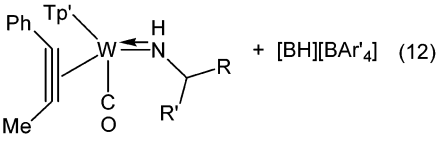
4

$\nu_{CO} \approx 1890\ cm^{-1}$



5

$\nu_{CO} \approx 1920\ cm^{-1}$



(12)

2

$\nu_{CO} \approx 1860\ cm^{-1}$

$$K_{eq} = \frac{[\mathbf{4}]\,[[BH][BAr'_4]]}{[\mathbf{3}]\,[B]} \qquad K_{eq} = \frac{[\mathbf{2}]\,[[BH][BAr'_4]]}{[\mathbf{5}]\,[B]} \quad (13)$$

The acidity of imine and amine complexes increases in the same order, (least acidic) Me/Me < Me/Et < Et/Et < Me/*p*-C_6H_4OMe < Me/Ph < Me/*p*-C_6H_4Br (most acidic), but the imine pK_a's span a range of about 5 orders of magnitude, while the amine complexes span only about 2 orders of magnitude. For the aliphatic imines the diethyl derivative (**3c**, $\Delta pK_a = 0.23$) is more than an order of magnitude more acidic than the dimethyl analogue (**3b**, $\Delta pK_a = 1.58$), a result that is difficult to reconcile with electronic properties. The larger imine complex **3c** (R/R′ = Et/Et) is more acidic than the smaller dialkyl analogues, probably due to a relief of steric strain in the tungsten complex upon deprotonation to form the linear azavinylidene complex.

Separate pK_a values for the *E* and *Z* isomers of **3a** could not be obtained due to rapid isomerization of the imine double bond in the presence of base. Relative pK_a measurements of related imine complexes were used to probe factors influencing the acidity of these isomers. [Tp′W(CO)(PhCCMe)(NH=CMe_2)][BAr′$_4$] (**3b**) with two methyl groups, and of course a methyl group cis to tungsten, is less acidic than the methyl/ethyl imine complex **3a** (R/R′ = Me/Et). The dimethyl imine complex **3b** may approximate the *E* isomer of complex **3a** in acid/base behavior because they both have a methyl group cis to tungsten. Correspondingly, the diethyl imine

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(33) Kaljurand, I.; Rodima, T.; Leito, I.; Koppel, I. A.; Schwesinger, R. *J. Org. Chem.* **2000**, *65*, 6202−6208.
(34) Abdur-Rashid, K.; Fong, T. P.; Greaves, B.; Gusev, D. G.; Hinman, J. G.; Landau, S. E.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2000**, *122*, 9155−9171.
(35) Fraser, R. R.; Bresse, M.; Chuaqui-Offermanns, N.; Houk, K. N.; Rondan, N. G. *Can. J. Chem.* **1983**, *61*, 2729−2734.
(36) Rodima, T.; Kaljurand, I.; Pihl, A.; Mäemets, V.; Leito, I.; Koppel, I. A. *J. Org. Chem.* **2002**, *67*, 1873−1881.
(37) Streitwieser, A.; Kim, Y. J. *J. Am. Chem. Soc.* **2000**, *122*, 11783−11786.

Table 3. Proton Transfer Rate Constants (in $M^{-1}s^{-1}$)

R/R′	k_1 (k_{-1})	k_2	k_{-2}
Me/Me (**3b**)	4600 ± 2000	(39 ± 10) × 10^4	(20 ± 4) × 10^4
Et/Et (**3c**)	470 ± 300	(1.8 ± 0.2) × 10^4	(0.61 ± 0.1) × 10^4

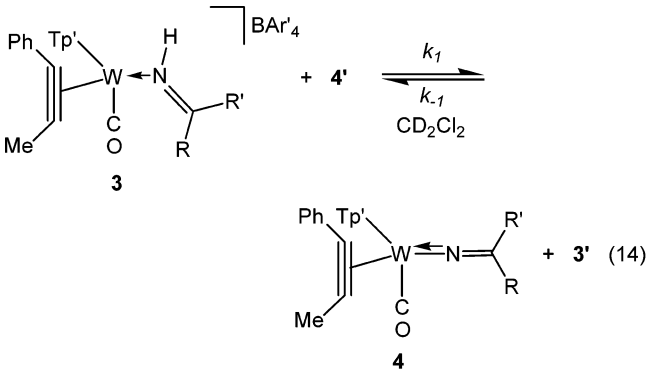
complex [Tp′W(CO)(PhCCMe)(NH=CEt$_2$)][BAr′$_4$] (**3c**) is more acidic than methyl/ethyl imine complex **3a**. This complex, with an ethyl group cis to tungsten, may approximate the acidity of the *Z* isomer of imine complex **3a**. Note that the relative pK_a of imine complex **3a** reflects an average of the pK_a's of both the *E* and *Z* isomers.

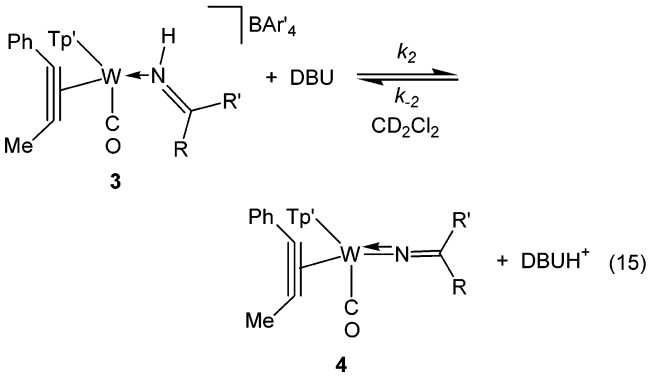
All of the aromatic imine complexes are more acidic than the aliphatic complexes. Substitution at the para position reveals a clear electronic influence on their acidity. The electron-withdrawing bromo-substituted imine complex **3f** is the most acidic, while the electron-donating methoxy-substituted imine complex **3e** is the least acidic of the three aromatic imine complexes. The aromatic amine complexes follow a similar trend, although the variation in acidity is less pronounced. Deprotonation of an amine complex to form an amido complex leads to little relief of steric strain, and since there is no conjugation between the phenyl group and the nitrogen in the amine/amido pairs, electronic influences are muted in the amine/amido acid/base pairs.[38−40]

Kinetic Acidity Measurements. The difference in reactivity between the *E* and *Z* isomers of imine complex **3a** in the presence of Na[HBEt$_3$] is surely a kinetic phenomenon. Direct assessment of the kinetic acidity of each of these *E*/*Z* isomers proved to be elusive since fast isomerization of the *E* and *Z* isomers in the presence of base makes it difficult to separate their reactivity. Kinetic acidity measurements of the symmetrically substituted imine complexes **3b** and **3c** were used to probe germane features of these complexes.

Self-exchange proton transfer rates were measured between imine complexes and the corresponding aza-vinylidene complexes using ^{1}H NMR line shape analysis (eq 14).[41,42] The proton transfer rate between each imine complex and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was also measured (eq 15). The self-exchange rate was too slow to contribute to the observed proton transfer rate with DBU, so k_1 (due to self-exchange) was ignored in the calculation of k_2 (due to DBU). Rate constants for eqs 14 and 15 are shown in Table 3.

The proton transfer rate constant (k_2) for imine complex **3c**, with an ethyl group cis to the imine proton, is 20 times slower than for imine complex **3b**, with a methyl group cis to the imine proton. The difference in rates can be attributed to steric crowding of the imine proton by the ethyl group. This result provides a plausible explanation for the reactivity observed for the *E* and *Z* isomers of imine complex **3a**. The *Z* isomer has a methyl group cis to the imine proton and would be susceptible to rapid deprotonation. The *E* isomer has





an ethyl group cis to the imine proton, which would impede deprotonation and thus allow hydride addition to dominate. This difference in *E*/*Z* reactivity coupled with high facial selectivity for hydride addition to the *E* isomer can explain the observed diastereoselectivity.

Kinetic versus Thermodynamic Acidity. The kinetic acidities for imine complexes **3b** and **3c** are juxtaposed with the equilibrium acidity data. In other words, complex **3b** has a lower equilibrium acidity but a higher kinetic acidity than complex **3c**. This is contrary to the Brønsted catalysis law, which states that equilibrium acidity should be proportional to kinetic acidity.[43] There are, however, numerous examples of systems with a negative Brønsted coefficient.[44−47]

In this system, the negative Brønsted coefficient results from the alkyl substituents on the imine carbon. The thermodynamic acidity is governed by the substituent cis to tungsten, with larger substituents resulting in a more acidic imine proton through release of steric strain upon deprotonation. Kinetic acidity is controlled by the substituent trans to tungsten, with larger groups blocking access to the imine proton and decreasing the rate of proton transfer. This results in a need for different model complexes to estimate the thermodynamic and kinetic acidities of the *E* and *Z* isomers of complex **3a** (Table 4). Note that the *E* isomer is expected to have both a lower thermodynamic and kinetic acidity than the *Z* isomer due to unsymmetrical substitution at the imine carbon.

Mechanism for Diastereoselectivity. To probe why hydride addition occurs with such high diastereo-

(38) Another possibility is that the acidity of the bulky complexes is due to steric hindrance inhibiting effective solvation.
(39) Brown, H. C.; Kanner, B. *J. Am. Chem. Soc.* **1966**, *88*, 986−992.
(40) Condon, F. E. *J. Am. Chem. Soc.* **1965**, *87*, 4494−4496.
(41) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945−3953.
(42) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255−1263.
(43) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper & Row: New York, 1987.
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(47) Bernasconi, C. F.; Sun, W.; Garcia-Río, L.; Yan, K.; Kittredge, K. *J. Am. Chem. Soc.* **1997**, *119*, 5583−5590.

Table 4. Comparison of Model Complexes Used for Kinetic and Thermodynamic Acidity

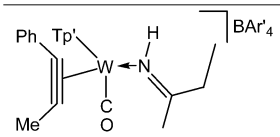
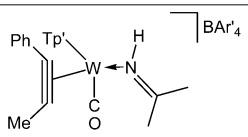
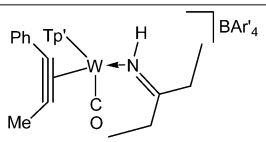
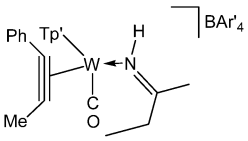
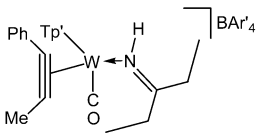
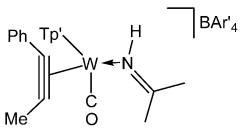
Methyl/Ethyl Imine Complex **3a**	Model for Thermodynamic Acidity	Model for Kinetic Acidity
 **3a-*E***	 **3b**	 **3c**
	$\Delta pK_a = 1.58$	$k_2 = 1.8 \times 10^4\ M^{-1}s^{-1}$
 **3a-*Z***	 **3c**	 **3b**
	$\Delta pK_a = 0.23$	$k_2 = 39 \times 10^4\ M^{-1}s^{-1}$

Table 5. Selected Bond Distances (Å) and Angles (deg) for Tp′W(CO)(PhCCMe)(NH$_2$CHMeEt)][BAr′$_4$] (5a)

W1−N3	2.204(4)	W1−N3−C4	125.5(4)
N3−C4	1.494(8)	N3−C4−C5	113.8(7)
W1−C10	2.005(5)	N3−C4−C6	111.6(7)
W1−C9	2.025(5)	C4−C5−C6	113.2(9)
W1−N21	2.219(4)	C1−W1−N41	166.51(19)
W1−N31	2.149(4)	N3−W1−N31	158.75(15)
W1−N41	2.233(4)		

Table 6. Crystallographic Data Collection Parameters for 5a

formula	$WC_{61}H_{53}B_2F_{24}N_7O$
mol wt	1561.55
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	12.3978(5)
b, Å	15.9301(7)
c, Å	17.9054(7)
α, deg	90.020(1)
β, deg	75.844(1)
γ, deg	72.9054(7)
V, Å^3	3261.47(23)
Z	2
calcd density, g/mL	1.590
F(000)	1552.28
cryst dimens, mm	0.25 × 0.25 × 0.20
temp, °C	−100
radiation (*λ*,Å)	Mo Kα, 0.71073
2*θ* range, deg	5−56
μ, mm^{-1}	1.89
scan mode	*ω*
total no. of rflns	27 407
total no. of unique rflns	11 477
R_{merge}	0.030
($I > 2.5\sigma(I)$)	10103
R_F, %	0.042
R_w, %	0.051
GoF	2.0406
max Δ/*σ*	0.004
residual density, e/Å^3	−1.210 to 1.170

selectivity, identification of the amido diastereomer formed upon hydride addition was pursued. Hydride reduction of imine complex **3a** on a preparatory scale yields amido complex **2a**. Chromatography on alumina protonates the amido complex to form amine complex **5a**, [Tp′W(CO)(PhCCMe)(NH$_2$CHMeEt)][BAr′$_4$]. Neither stereocenter (W or C) is involved in protonation at nitrogen. Recrystallization using CH_2Cl_2 and hexanes resulted in X-ray quality crystals of one diastereomer of amine complex **5a**, and an X-ray structure revealed that the *SS* enantiomer was obtained. An ORTEP of [Tp′W(CO)(PhCCMe)(NH$_2$CHMeEt)][BAr′$_4$] (**5a**) is shown in Figure 4. Selected bond distances and angles are shown in Table 5, and crystallographic data collection parameters are shown in Table 6. 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.[48,49] ^{1}H NMR spectroscopy of *the single crystal actually used* in the X-ray data collection and analysis confirmed it to be the major diastereomer.

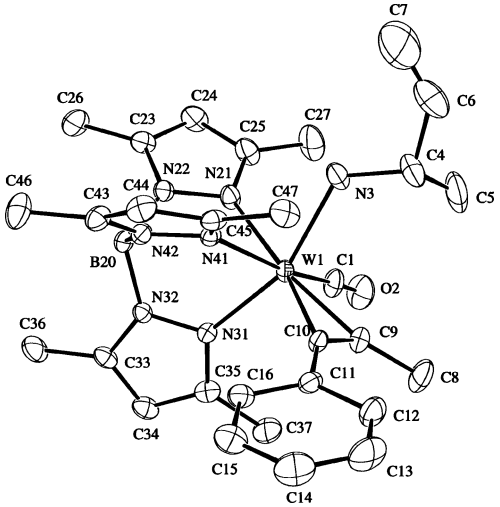


Figure 4. ORTEP of (*SS*)-[Tp′W(CO)(PhCCMe)(NH$_2$-CHMeEt)][BAr′$_4$] (**5a**).

In order for hydride addition to form the *SS*/*RR* pair of enantiomers from the *E* isomer of the imine ligand, hydride must attack along the tungsten−alkyne axis in the major W−N conformation with the NH between the pyrazole rings. The preference for this direction of attack may result from a steric interaction between the imine methyl and alkyne methyl groups. This interaction would cause the W−N bond to rotate such that one face of the imine ligand is blocked by a Tp′ methyl group. Figure 5 shows the orientation of the imine ligand and the direction of hydride addition required for formation of the diastereomer that predominates. For the minor

(48) Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1−36.
(49) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598−9599.

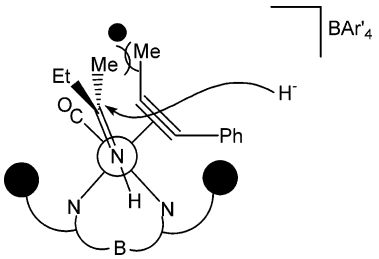


Figure 5. Newman-type projection along the imine−tungsten axis of imine complex **3a** showing the direction of hydride addition to give the *SS* diastereomer.

W−N conformation of the *E* isomer, the imine carbon would be embedded in Tp′ shrubbery.

Conclusion

Hydride addition to an *N*-protio imine complex (**3a**) occurs with high diastereoselectivity to form a primary amido complex (**2a**). The reaction of imine complex **3a** with hydride is under kinetic control. The *E* isomer undergoes mostly hydride addition to give amido complex **2a-*SS*/*RR***, while the *Z* isomer is mostly deprotonated to form azavinylidene complex **dis-4a**. This difference in reactivity leads to effective differentiation between methyl and ethyl groups despite the low *E*/*Z* ratio in the reagent imine complex.

The kinetic acidities of the *E* and *Z* isomers can be explained using imine complexes **3b**,**c** as models. Alkyl substituents cis to the imine proton affect the kinetic acidity. An ethyl group blocks access to the proton and decreases the rate of proton transfer. If the substituent cis to the imine proton is a methyl group, proton transfer becomes more rapid. These data suggest that the *Z* isomer of complex **3a** is more kinetically acidic than the *E* isomer.

The equilibrium acidity of the alkyl imine complexes (**3a**−**c**) appears to be dominated by a steric interaction due to the substituent cis to the tungsten complex. Relief of this unfavorable steric interaction upon deprotonation suggests that the *Z* isomer of **3a** would have a greater acidity. For the aryl imine complexes (**3d**−**f**), the acidity is dominated by the electronic influence of the aryl ring. Electron-donating substituents decrease the acidity, while electron-withdrawing groups increase the acidity. Both electronic and steric factors are less pronounced in the acidity of the amine complexes (**5a**−**f**).

Experimental Section

General Procedures. Reactions were carried out under a nitrogen atmosphere using Schlenk techniques. Methylene chloride, diethyl ether, 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, DBU, NEt_3, and 4-methoxypyridine were distilled from CaH_2 and degassed by several freeze, pump, thaw cycles. [Tp′W(CO)$_2$(PhCCMe)][OTf] (**1**),[26,50] Tp′W(CO)(PhCCMe)(NHCHMeEt) (**2a**), [Tp′W(CO)(PhCCMe)(NH=CMeEt)][BAr′$_4$] (**3a**), Tp′W(CO)(PhCCMe)(=N=CMeEt) (**4a**), [Tp′W(CO)(PhCCMe)(NH=CMePh)][BAr′$_4$] (**3d**), [Tp′W(CO)(PhCCMe)(NH$_2$CHMeEt)][BAr′$_4$] (**5a**),[28] Tp′W(CO)(PhCCMe)(NHCHMePh) (**2d**), [Tp′W(CO)(PhCCMe)(NH$_2$CHMePh)][BAr′$_4$] (**5d**),[26] Na[BAr′$_4$], and H(OEt$_2$)$_2$[BAr′$_4$] were synthesized according to literature procedures.[51]

NMR spectra were obtained using a Bruker AMX300, DRX400, AMX400, or Avance 500 spectrometer. 2D spectra were recorded on the Bruker AMX400 or Avance 500 spectrometer. NMR spectra of single X-ray crystals were obtained on a Bruker Avance 500 spectrometer using a 3 mm probe.

Representative [BAr′$_4$]$^-$ NMR Data. ^{1}H NMR data for the [BAr′$_4$]$^-$ counterion are reported separately for simplicity. ^{1}H NMR (CD_2Cl_2, δ): 7.72 (br, 8H, *o*-Ar′), 7.56 (br, 4H, *p*-Ar′). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 162.2 (q, $^1J_{BC}$ = 50 Hz, *ipso* of Ar′), 135.2 (br, *o*-Ar′), 129.3 (q of q, $^2J_{CF}$ = 31 Hz, $^4J_{CF}$ = 3 Hz, *m*-Ar′), 125.0 (q, $^1J_{CF}$ = 272 Hz, *C*F$_3$), 117.9 (septet, $^3J_{CF}$ = 4 Hz, *p*-Ar′).

Tp′W(CO)(PhCCMe)(NHCHMe$_2$) (2b). [Tp′W(CO)$_2$(PhCCMe)][OTf] (1.98 g, 2.5 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 4.5 mL (53 mmol) of isopropylamine was added. The solution temperature was maintained at 40 °C overnight. The solvent was then removed by rotary evaporation, and the orange oil was purified on an alumina column with CH_2Cl_2 as the eluent. The lone orange band was collected, and the solvent was removed by rotary evaporation. The residual orange oil was dissolved in pentane and sonicated to give an orange powder (1.33 g, 76% yield). The product was recrystallized from a concentrated hexanes solution. IR (KBr): ν_{CO} = 1856 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.03, 6.30 (m, 5H, Ph), 5.86, 5.82, 5.57 (s, 3H, Tp′-C*H*), 4.46 (d of septets, $^3J_{HH}$ = 7 Hz, 10 Hz, 1H, NHC*H*Me$_2$), 3.19 (s, 3H, *Me*C≡CPh), 2.76, 2.54, 2.39, 2.35, 1.60, 1.59 (s, 18H, Tp′-C*H*$_3$), 0.96, 0.62 (d, $^3J_{HH}$ = 7 Hz, 6H, NHCH*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 237.9 (*C*O), 169.6 (MeC≡*C*Ph), 166.6 (Me*C*≡CPh), 153.4, 151.5, 150.6, 144.50, 144.46, 144.41 (Tp′-*C*Me), 137.9 (*ipso* Ph), 128.4, 128.1 (*o*,*m* Ph), 126.3 (*p* Ph), 108.4, 107.1, 106.3 (Tp′-*C*H), 64.1 (NH*C*HMe$_2$), 27.5, 26.0 (NHCH(*C*H$_3$)$_2$), 18.4 (*Me*C≡CPh), 15.7, 15.6, 14.8, 12.94, 12.92, 12.8 (Tp′-*C*H$_3$). Anal. Calcd for $C_{28}H_{38}N_7OBW\cdot C_3H_7$: C, 51.26; H, 6.24; N, 13.50. Found: C, 51.23; H, 6.29; N, 13.25.

Tp′W(CO)(PhCCMe)(NHCHEt$_2$) (2c). [Tp′W(CO)$_2$(PhCCMe)][OTf] (1.86 g, 2.3 mmol) was dissolved in THF to form a green solution, which was heated at reflux for 1 h. 3-Aminopentane (NH$_2$CHEt$_2$) (0.8 mL, 6.9 mmol) was added, and the reaction was heated at reflux for 2 days. The solvent was removed by rotary evaporation. The residual oil was then purified on an alumina column with CH_2Cl_2 as the eluent. The orange band was collected, and the solvent was removed. The remaining orange oil was dissolved in hexanes and sonicated to produce an orange powder (1.38 g, 83% yield). IR (KBr): ν_{CO} = 1856 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.03, 6.27 (m, 5H, Ph), 5.85, 5.82, 5.56 (s, 3H, Tp′-C*H*), 4.11 (m, 1H, NH$_2$C*H*Et$_2$), 3.13 (s, 3H, *Me*C≡CPh), 2.80, 2.54, 2.38, 2.35 (s, 12H, Tp′-C*H*$_3$), 1.60 (s, 6H, Tp′-C*H*$_3$), 1.19 (m, 3H, C*H*$_2$CH$_3$, CH*H*CH$_3$), 1.00 (m, 1H, C*H*HCH$_3$), 0.77 (t, $^3J_{HH}$ = 8 Hz, 3H, CH$_2$C*H*$_3$), 0.57 (t, $^3J_{HH}$ = 8 Hz, 3H, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 237.9 (*C*O), 169.2 (MeC≡*C*Ph), 166.1 (Me*C*≡CPh), 153.4, 151.4, 150.5, 144.5, 144.29, 144.26 (Tp′-*C*Me), 138.0 (*ipso* Ph), 128.3, 128.1 (*o*,*m* Ph), 126.2 (*p* Ph), 108.4, 107.2, 106.2 (Tp′-*C*H), 73.7 (NH$_2$*C*HEt$_2$), 30.5, 29.7 (*C*H$_2$CH$_3$), 18.1 (*Me*C≡CPh), 16.1, 15.7, 14.6, 13.0, 12.9, 12.8 (Tp′-*C*H$_3$), 10.4, 9.8 (CH$_2$*C*H$_3$). Anal. Calcd for $C_{30}H_{42}N_7OBW$: C, 50.65; H, 5.95; N, 13.78. Found: C, 50.79; H, 6.06; N, 13.78.

Tp′W(CO)(PhCCMe)(NHCHMe(*p*-C$_6$H$_4$OMe)) (2e). Tp′W(CO)$_2$(PhCCMe)[OTf] (1.88 g, 2.3 mmol) was dissolved in THF to form a green solution, which was heated at reflux for 1 h. 4-Methoxy-α-methylbenzylamine [NH$_2$CHMe(*p*-C$_6$H$_4$OMe)] (0.10 g, 6.6 mmol) was added, and the reaction was heated at reflux overnight. By IR spectroscopy, the reaction was still incomplete so more amine was added (0.37 g), and the reaction was heated

(50) Feng, S. G.; Philipp, C. C.; Gamble, A. S.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 3504−3512.

(51) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics* **1992**, *11*, 3920−3922.

at reflux for 4 h. The solvent was then removed by rotary evaporation, and the orange oil was purified on an alumina column with CH_2Cl_2 as the eluent. The orange band was collected, and the solvent was removed by rotary evaporation. Dissolution of the residual oil in hexanes and removal of solvent gave an orange powder (0.95 g, 52% yield). Crystals were obtained by slow diffusion of methanol into a CH_2Cl_2 solution of the amido complex. IR (KBr): $\nu_{CO} = 1850$ cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.1−6.7, 6.18 (6.33) (m, 9H, Ar-*H*), 5.90, 5.85, 5.55 (5.82, 5.74, 5.59) (s, 3H, Tp′-C*H*), 5.49 (5.41) (m, 1H, C*H*), 3.82 (3.72) (s, 3H, OCH_3), 2.86 (3.26) (s, 3H, *Me*C≡CPh), 2.55, 2.39, 2.36 (x2), 1.72, 1.49 (2.55, 2.53, 2.39, 2.31, 1.66, 1.63) (s, 18H, Tp′-CH_3), 1.20 (0.92) (d, $^3J_{HH} = 7$ Hz, 3H, CHCH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 237.7, 237.2 (*C*O), 171.2, 170.4, 169.9, 167.1 (Me*C*≡*C*Ph), 153.7, 153.3, 151.5, 151.2, 150.7, 150.6, 144.6, 144.5, 144.4 (×2), 142.5, 141.9 (Tp′-*C*Me), 158.4, 158.3, 138.2, 137.9, 126.3, 126.2 (*ipso* Ar), 128.4, 128.2, 128.1, 128.08, 127.6, 126.7, 113.8, 113.6 (*o*,*m*,*p* Ar), 108.5, 108.4, 107.4, 107.0, 106.3, 106.2 (Tp′-*C*H), 72.1, 70.8 (NH*C*HMeAr), 55.7, 55.5 (OCH$_3$), 30.1, 28.7 (NHCH*Me*Ar), 18.5, 17.2 (*Me*C≡CPh), 16.0, 15.7 (×2), 15.6, 15.0, 14.8, 13.0, 12.93, 12.91, 12.86, 12.80 (×2) (Tp′-*C*H$_3$). Anal. Calcd for $C_{34}H_{42}N_7O_2BW$: C, 52.67; H, 5.46; N, 12.64. Found: C, 52.39; H, 5.38; N, 12.66.

Tp′W(CO)(PhCCMe)(NHCHMe(*p*-C$_6$H$_4$Br)) (2f). [Tp′W(CO)$_2$(PhCCMe)][OTf] (1.88 g, 2.3 mmol) was dissolved in THF to form a green solution that was heated at reflux for 1 h. 4-Bromo-α-methylbenzylamine [NH$_2$CHMe(*p*-C$_6$H$_4$Br)] (1.6 mL, 11.2 mmol) was added to the reaction, and it was heated at reflux overnight. The solvent was then removed by rotary evaporation, and the orange oil was purified on an alumina column with CH_2Cl_2 as the eluent. The orange band was collected, and the solvent was removed to give an orange oil. The oil was dissolved in hexanes and sonicated to give an orange powder (1.63 g, 83% yield). IR (KBr): $\nu_{CO} = 1854$ cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.40, 6.83 (7.32) (d, 4H, C$_6H_4$Br), 7.04, 6.19 (6.33) (m, 5H, Ph), 5.91, 5.86, 5.55 (5.83, 5.75, 5.59) (s, 3H, Tp′-C*H*), 5.51 (dq, $^3J_{HH} = 7$ Hz, 8 Hz, 1H, NHC*H*MeAr) (5.43) (dq, $^3J_{HH} = 7$ Hz, 10 Hz, 1H, NHC*H*MeAr), 2.85 (3.27) (s, 3H, *Me*C≡CPh), 2.55, 2.39, 2.37, 2.36, 1.72, 1.49 (2.54, 2.48, 2.40, 2.32, 1.65, 1.62) (s, 18H, Tp′-CH_3), 1.21 (0.92) (d, $^3J_{HH} = 7$ Hz, 3H, NHCH*Me*Ar). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 236.9 (237.5) (*C*O), 172.1 (171.2) (MeC≡*C*Ph), 170.3 (167.8) (Me*C*≡CPh), 153.7 (153.2) (*ipso* C$_6$H$_4$Br), 151.5, 150.8, 148.9, 144.64, 144.56, 144.5 (151.2, 150.7, 149.3, 144.5) (Tp′-*C*Me), 138.0 (137.8) (*ipso* Ph), 131.2, 128.8, 128.20, 128.16 (131.5, 128.4, 128.14, 127.7) (*o*,*m* Ph, C$_6$H$_4$Br), 126.3 (126.4) (*p* Ph), 119.4 (119.7) (*ipso* C$_6$H$_4$Br), 108.5, 107.4, 106.4 (108.4, 107.0, 106.3) (Tp′-*C*H), 70.8 (72.3) (NH*C*HMeAr), 28.5 (26.1) (NHCH*Me*Ar), 17.2 (18.6) (*Me*C≡CPh), 15.68, 15.65, 15.0, 13.0, 12.9, 12.8 (16.0, 15.6, 14.7, 12.85) (Tp′-*C*H$_3$). Anal. Calcd for $C_{33}H_{39}N_7OBrBW \cdot C_3H_7$: C, 49.85; H, 5.35; N, 11.30. Found: C, 49.98; H, 5.24; N, 11.24.

[Tp′W(CO)(PhCCMe)(NH=CMe$_2$)][BAr′$_4$] (3b). Tp′W(CO)(PhCCMe)(NHCHMe$_2$) **(2b)** (0.77 g, 1.1 mmol) was dissolved in CH_2Cl_2. Iodine (0.28 g, 1.1 mmol) and NEt_3 (0.15 mL, 1.1 mmol) were added, and the solution was allowed to stir for 2 h. A solution of Na[BAr′$_4$] (0.98 g, 1.1 mmol) in Et_2O was prepared and cannula transferred into the reaction vessel. A white precipitate formed. The solution was cannula filtered away from the solid, and the solvent was removed from the filtrate by rotary evaporation. The residual blue oil was purified on an alumina column using 1:1 CH_2Cl_2/hexanes. The solvent mixture for elution was gradually changed to pure CH_2Cl_2. The blue band was collected, solvent was removed, and the blue oil was recrystallized from CH_2Cl_2/hexanes (1.02 g, 60% yield). IR (KBr): $\nu_{CO} = 1924$ cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 8.99 (br, 1H, N*H*), 7.31, 6.71 (m, 5H, Ph), 6.01, 5.95, 5.79 (s, 3H, Tp′-C*H*), 3.81 (s, 3H, PhC≡CCH_3), 2.58, 2.51, 2.44, 2.42, 1.39, 1.24 (s, 18H, Tp′-CH_3), 2.25 (d, $^3J_{HH} = 2$ Hz, 3H, NH=CMeCH_3), 2.09 (br, 3H, NH=CH_3Me). ^{13}C{^{1}H} NMR (CD_2Cl_2, 263K, δ): 229.1 (CO), 215.8 (PhC≡CMe), 212.9 (PhC≡*C*Me), 190.4 (NH=*C*Me$_2$), 153.1, 152.1, 151.1, 147.6, 147.4, 146.3 (Tp′-*C*Me), 135.5 (*ipso* Ph), 130.7 (*p* Ph), 129.3, 129.0 (*o*,*m* Ph), 109.0, 108.5, 107.9 (Tp′-*C*H), 31.1, 27.1 (NH=C*Me$_2$*), 23.1 (PhC≡C*Me*), 16.0, 15.3, 13.7, 12.9, 12.7, 12.6 (Tp′-*C*H$_3$). Anal. Calcd for $C_{60}H_{49}N_7OF_{24}B_2W$: C, 46.63; H, 3.20; N, 6.34. Found: C, 46.50; H, 3.33; N, 7.03.

[Tp′W(CO)(PhCCMe)(NH=CEt$_2$)][BAr′$_4$] (3c). Tp′W(CO)(PhCCMe)(NHCHEt$_2$) (**2c**) (0.55 g, 0.77 mmol) was dissolved in CH_2Cl_2. Iodine (0.20 g, 0.77 mmol) and NEt_3 (0.11 mL, 0.77 mmol) were added, and the solution was allowed to stir for 2 h. A solution of Na[BAr′$_4$] (0.68 g, 0.77 mmol) in Et_2O was prepared and cannula transferred into the reaction vessel. A white precipitate formed. The solution was cannula filtered, and the solvent was removed by rotary evaporation. The residual blue oil was purified on an alumina column using 1:1 CH_2Cl_2/hexanes as the eluent. The solvent was gradually changed to pure CH_2Cl_2. The blue band was collected, the solvent was removed, and the blue oil was recrystallized from CH_2Cl_2/hexanes (0.62 g, 51% yield). IR (KBr): $\nu_{CO} = 1920$, 1927 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 8.84 (br, 1H, N*H*), 7.31, 6.70 (m, 5H, Ph), 6.02, 5.95, 5.79 (s, 3H, Tp′-C*H*), 3.80 (s, 3H, PhC≡CCH_3), 2.58, 2.52, 2.42, 2.40, 1.40, 1.19 (s, 18H, Tp′-CH_3), 2.55 (m, 1H, C*H*HCH$_3$), 2.45 (m, 2H, C*H*HCH$_3$, CH*H*CH$_3$), 2.15 (m, 1H, CH*H*CH$_3$), 1.03 (br t, $^3J_{HH} = 8$ Hz, 3H, CH$_2$CH_3), 0.87 (t, $^3J_{HH} = 8$ Hz, 3H, CH$_2$CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 260 K, δ): 228.8 (*C*O), 216.3 (Ph*C*≡CMe), 213.2 (PhC≡*C*Me), 196.6 (NH=*C*Et$_2$), 152.9, 152.2, 151.3, 147.63, 147.57, 146.4 (Tp′-*C*Me), 135.6 (*ipso* Ph), 130.8 (*p* Ph), 129.2, 129.1 (*o*,*m* Ph), 109.1, 108.6, 108.0 (Tp′-*C*H), 33.0, 32.4 (*C*H$_2$CH$_3$), 23.1 (PhC≡C*C*H$_3$), 16.1, 15.4, 13.9, 12.9, 12.8, 12.7 (Tp′-*C*H$_3$), 10.0, 9.1 (CH$_2$*C*H$_3$). Anal. Calcd for $C_{62}H_{53}N_7OF_{24}B_2W$: C, 47.32; H, 3.39; N, 6.23. Found: C, 47.35; H, 3.37; N, 6.36.

[Tp′W(CO)(PhCCMe)(NH=CMe(*p*-C$_6$H$_4$OMe))][BAr′$_4$] (3e). Tp′W(CO)(PhCCMe)(NHCHMe(C$_6$H$_4$OMe)) (**2e**) (0.46 g, 0.59 mmol) was dissolved in CH_2Cl_2. Iodine (0.15 g, 0.60 mmol) and NEt_3 (82 μL, 0.59 mmol) were added, and the reaction was allowed to stir for 2 h. The solvent was then removed by rotary evaporation to give a green oil, which was purified on an alumina column with 1:1 CH_2Cl_2/hexanes as the eluent. The solvent was gradually changed to pure CH_2Cl_2. The green band was collected and recrystallized from CH_2Cl_2/hexanes (0.51 g, 53% yield). IR (KBr): $\nu_{CO} = 1918$ cm^{-1}. ^{1}H NMR (CD_2Cl_2, 271 K, δ): 9.16 (s, 1H, N*H*), 7.28 (m, 5H, C$_6H_4$OMe, Ph), 6.88 (d, 2H, C$_6H_4$OMe), 6.71 (m, 2H, Ph), 5.99, 5.92, 5.80 (s, 3H, Tp′-C*H*), 3.86 (s, 3H, PhC≡CCH_3), 3.78 (s, 3H, OCH_3), 2.57, 2.51, 2.41, 2.39, 1.42, 1.13 (s, 18H, Tp′-CH_3), 2.45 (NH=C*Me*Ar). ^{13}C NMR (CD_2Cl_2, 271 K, δ): 229.2 (*C*O), 215.4 (Ph*C*≡CMe), 212.9 (PhC≡*C*Me), 182.3 (NH=*C*MeAr), 153.2, 152.3, 151.4, 147.63, 147.55, 146.4 (Tp′-*C*Me), 164.4, 135.7, 130.7, 126.9 (*ipso*, *p* C$_6$H$_4$OMe, Ph), 129.4, 129.1, 128.9, 115.1 (*o*,*m* C$_6$H$_4$OMe, Ph), 109.2, 108.7, 108.1 (Tp′-*C*H), 56.0 (OCH$_3$), 24.6 (NH=C*Me*Ar), 23.2 (PhC≡C*C*H$_3$), 16.1, 15.3, 13.7, 13.0, 12.8, 12.7 (Tp′-*C*H$_3$). Anal. Calcd for $C_{66}H_{53}N_7O_2B_2F_{24}W$: C, 48.41; H, 3.26; N, 5.99. Found: C, 48.54; H, 3.25; N, 6.04.

[Tp′W(CO)(PhCCMe)(NH=CMe(*p*-C$_6$H$_4$Br))][BAr′$_4$] (3f). Tp′W(CO)(PhCCMe)(=N=CMe(C$_6$H$_4$Br)) (**4f**) (0.11 g, 0.13 mmol) was dissolved in CH_2Cl_2 to give an orange solution. In the drybox, H[BAr′$_4$] (0.13 g, 0.13 mmol) was weighed into another flask. The H[BAr′$_4$] was put on the Schlenk line, cooled to 0 °C, and dissolved in CH_2Cl_2. The H[BAr′$_4$] solution was then cannula transferred to the azavinylidene complex solution, which turned blue. The solvent was removed in vacuo, and the blue oil was recrystallized using CH_2Cl_2/hexanes (0.18 g, 77% yield). IR (KBr): $\nu_{CO} = 1918$ cm^{-1}. ^{1}H NMR (CD_2Cl_2, 253 K, δ): 9.38 (s, 1H, N*H*), 7.57, 7.11 (d, 4H, C$_6H_4$Br), 7.28, 6.73 (m, 5H, Ph), 6.01, 5.91, 5.79 (s, 3H, Tp′-C*H*), 3.88 (s, 3H, PhC≡CCH_3), 2.57, 2.50, 2.41, 2.40, 1.39, 1.10 (s, 1:1:1:2:1:1, 21H, Tp′-CH_3, NH=C*Me*Ar). ^{13}C NMR (CD_2Cl_2, 253 K, δ): 228.0 (*C*O), 216.0 (Ph*C*≡CMe), 213.8 (PhC≡*C*Me), 182.5 (NH=*C*MeAr), 152.9, 152.1, 151.2, 147.60, 147.56, 146.4 (Tp′-*C*Me), 135.4, 133.8, 130.8, 128.9 (*ipso*, *p* C$_6$H$_4$Br, Ph), 133.0, 129.3,

129.0, 127.8 (*o,m* C_6H_4Br, Ph), 109.0, 108.7, 108.0 (Tp′-*C*H), 24.9 (NH=C*Me*Ar), 23.4 (PhC≡C*C*H_3), 16.1, 15.3, 13.7, 12.9, 12.8, 12.6 (Tp′-*C*H_3). Anal. Calcd for $C_{65}H_{50}N_7OB_2BrF_{24}W$: C, 46.29; H, 2.99; N, 5.81. Found: C, 46.30; H, 3.03; N, 5.73.

Tp′W(CO)(PhCCMe)(=N=CMe$_2$) (4b). KH (1 g, 30 w/w in mineral oil) was washed three times with 10 mL of pentane and dried in vacuo. A THF solution of imine complex **3b** (0.14 g, 0.09 mmol) was cannula transferred into the flask containing the dry KH. After a few minutes, the blue solution turned orange. The solution was cannula filtered, and the solvent was removed in vacuo. The residual orange oil was dissolved in pentane. This solution was then cannula filtered away from the insoluble salts. The solvent was concentrated in vacuo, and crystals began to grow (0.050 g, 78% yield). IR (KBr): ν_{CO} = 1868 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.06, 6.41 (m, 5H, Ph), 5.89, 5.71, 5.60 (s, 3H, Tp′-C*H*), 3.11 (s, 3H, PhC≡CC*H*$_3$), 2.70, 2.51, 2.40, 2.38, 1.60, 1.49 (s, 18H, Tp′-C*H*$_3$), 1.62, 1.57 (s, 6H, =N=C*Me*$_2$). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 234.0 (*C*O), 159.0, 158.0, 152.1 (=N=*C*Me$_2$, Ph*C*≡*C*Me), 152.5, 152.3, 150.7, 144.6, 144.1, 143.8 (Tp′-*C*Me), 138.0 (*ipso* Ph), 128.6, 128.2 (*o,m* Ph), 126.2 (*p* Ph), 107.2, 106.8, 106.5 (Tp′-*C*H), 22.0, 21.1 (=N=C*Me*$_2$), 17.8 (PhC≡C*C*H$_3$), 16.7, 15.8, 14.6, 12.94, 12.90, 12.8 (Tp′-*C*H$_3$). Satisfactory elemental analysis was not obtained.

Tp′W(CO)(PhCCMe)(=N=CEt$_2$) (4c). KH (1 g, 30 w/w in mineral oil) was washed three times with 10 mL of pentane and dried in vacuo. A THF solution of imine complex **3c** (0.19 g, 0.12 mmol) was cannula transferred into the flask containing the dry KH. After a few minutes, the blue solution turned yellow. The solution was cannula filtered, and the solvent was removed in vacuo. The residual orange oil was dissolved in pentane. This solution was then cannula filtered away from the insoluble salts. The solvent was removed in vacuo. Crystals were grown in a concentrated pentane solution (0.065 g, 75% yield). IR (KBr): ν_{CO} = 1868 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.06, 6.43 (m, 5H, Ph), 5.88, 5.70, 5.60 (s, 3H, Tp′-C*H*), 3.07 (s, 3H, PhC≡CC*H*$_3$), 2.68, 2.50, 2.40, 2.38, 1.60, 1.50 (s, 18H, Tp′-C*H*$_3$), 2.24, 2.08 (dq, 2H, $^3J_{HH}$ = 8 Hz, $^2J_{HH}$ = 17 Hz, C*H*$_2$CH$_3$), 1.90, 1.77 (dq, 2H, $^3J_{HH}$ = 8 Hz, $^2J_{HH}$ = 14 Hz, C*H*$_2$CH$_3$), 0.67, 0.43 (t, 6H, $^3J_{HH}$ = 8 Hz, CH$_2$C*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 234.6 (*C*O), 160.5, 158.8, 158.3 (=N=*C*Et$_2$, Ph*C*≡*C*Me), 152.5, 152.1, 150.5, 144.4, 144.0, 143.6 (Tp′-*C*Me), 138.3 (*ipso* Ph), 128.5, 128.2 (*o,m* Ph), 126.1 (*p* Ph), 107.2, 106.7, 106.5 (Tp′-*C*H), 28.2, 27.1 (*C*H$_2$CH$_3$), 17.6 (PhC≡C*C*H$_3$), 16.8, 15.9, 14.2, 13.0, 12.91, 12.86 (Tp′-*C*H$_3$), 11.6, 10.3 (CH$_2$*C*H$_3$). Satisfactory elemental analysis was not obtained.

Tp′W(CO)(PhCCMe)(=N=CMe(*p*-C$_6$H$_4$OMe)) (4e). KH (1 g, 30 w/w in mineral oil) was washed three times with 10 mL of pentane and dried in vacuo. A THF solution of imine complex **3e** (0.19 g, 0.11 mmol) was cannula transferred to the dry KH. After a few minutes, the green solution had turned orange. The solution was cannula filtered, and solvent was removed in vacuo. The orange oil was dissolved in pentane. This solution was then cannula filtered away from the insoluble salts. The solvent was removed in vacuo to give an orange powder (0.074 g, 87% yield). IR (KBr): ν_{CO} = 1881 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.04, 6.45 (m, 5H, Ph), 6.81 (m, 4H, C$_6$*H*$_4$-OMe), 5.95, 5.64 (m, 1:2H, Tp′-C*H*), 3.78 (3.69) (s, 3H, OMe), 3.26 (3.16) (s, 3H, PhC≡CC*H*$_3$), 2.74, 2.50, 2.41, 2.40, 1.96, 1.67, 1.18 (2.54, 2.44, 2.43, 1.61, 1.47) (s, 21H, Tp′-C*H*$_3$, =N=CC*H*$_3$Ar). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 242.4 (*C*O), 158.7, 158.5, 157.2 (=N=*C*MeAr, Ph*C*≡*C*Me), 152.7, 152.5, 150.8, 144.8, 144.1, 143.8 (Tp′-*C*Me), 137.8, 132.5 (*ipso* Ph), 128.5, 128.2, 126.8, 126.3 (*o,m* Ph), 124.7 (*ipso* Ph), 113.3 (*p* Ph), 107.2, 106.9, 106.7 (Tp′-*C*H), 55.5 (O*C*H$_3$), 18.0 (PhC≡C*C*H$_3$), 16.8, 16.7, 15.9, 14.6, 12.95, 12.9, 12.8 (Tp′-*C*H$_3$, =N=CC*H*$_3$Ar). Satisfactory elemental analysis was not obtained.

Tp′W(CO)(PhCCMe)(=N=CMe(*p*-C$_6$H$_4$Br)) (4f). Tp′W(CO)(PhCCMe)(NHCHMe(*p*-C$_6$H$_4$Br)) (**2f**) (0.30 g, 0.36 mmol) was dissolved in CH_2Cl_2. Iodine (0.092 g, 0.36 mmol) and NEt_3 (50 μL, 0.36 mmol) were added, and the reaction was stirred for 3 h. The IR spectrum then showed a 2:1 ratio of imine complex **3f** to azavinylidene complex **4f**. Four more equivalents of NEt_3 were added to fully deprotonate the imine complex. The solvent was then removed by rotary evaporation, and the residual oil was purified on an alumina column with 1:1 CH_2Cl_2/hexanes. The orange band was collected, and the solvent was removed to give an orange oil. A powder was obtained by sonication of the product in hexanes (0.19 g, 64% yield). Two isomers are observed in the ^{1}H NMR in a 7:1 ratio. IR (KBr): ν_{CO} = 1883 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.36, 6.77 (d, 4H, C$_6$*H*$_4$-Br), 7.06, 6.47 (m, 5H, Ph), 5.96, 5.65, 5.64 (Tp′-C*H*), 3.27 (3.19) (s, 3H, PhC≡CC*H*$_3$), 2.74, 2.50, 2.42, 2.41, 1.67, 1.17 (2.52, 2.44, 2.43, 2.32, 1.61, 1.46) (s, 18H, Tp′-C*H*$_3$), 1.98 (s, 3H, =N=CC*H*$_3$-Ar). ^{13}C{^{1}H} NMR (CD_2Cl_2, δ): 229.9 (*C*O), 158.5 (Ph*C*≡*C*Me), 157.1 (Ph*C*≡*C*Me), 152.8, 152.5, 151.0, 144.9, 144.3, 144.0 (Tp′-*C*Me), 150.1 (=N=*C*MeAr), 139.2, 137.6 (*ipso* C$_6$H$_4$Br, Ph), 130.8, 128.6, 128.3, 127.1 (*o,m* C$_6$H$_4$Br, Ph), 126.5 (*p* Ph), 119.9 (*ipso* C$_6$H$_4$Br) (131.5, 130.7, 128.6, 128.4, 126.9) (minor Ar), 107.3, 107.0, 106.8 (107.2, 106.6) (Tp′-*C*H), 18.0 (PhC≡C*C*H$_3$), 16.8, 15.9, 14.6, 13.0, 12.9, 12.85 (Tp′-*C*H$_3$), 16.3 (=N=C*C*H$_3$-Ar). Anal. Calcd for $C_{33}H_{37}N_7OBrBW\cdot C_3H_7$: C, 49.97; H, 5.12; N, 11.33. Found: C, 49.58; H, 5.04; N, 11.37.

[Tp′W(CO)(PhCCMe)(NH$_2$CHMe$_2$)][BAr′$_4$] (5b). Tp′W(CO)(PhCCMe)(NHCHMe$_2$) (**2b**) (0.17 g, 0.25 mmol) was dissolved in CH_2Cl_2 to give an orange solution. In the drybox, H[BAr′$_4$] (0.23 g, 0.25 mmol) was weighed into another flask. The H[BAr′$_4$] was put on the Schlenk line, cooled to 0 °C, and dissolved in CH_2Cl_2. The H[BAr′$_4$] solution was then cannula transferred to the amido complex solution, which turned blue. The solvent was removed in vacuo, and the blue oil was recrystallized using CH_2Cl_2/hexanes (0.27 g, 72% yield). IR (KBr): ν_{CO} = 1930 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.37, 6.77 (m, 5H, MeC≡C*Ph*), 6.13, 6.05, 5.83 (s, 3H, Tp′-C*H*), 3.83 (s, 3H, *Me*C≡CPh), 2.79, 2.60, 2.54, 2.45, 1.55, 1.36 (s, 18H, Tp′-C*H*$_3$), 3.45 (dd, $^3J_{HH}$ = 5 Hz, $^2J_{HH}$ = 13 Hz, 2H, N*H*$_2$), 2.86 (d of septets, $^3J_{HH}$ = 5 Hz, 6 Hz, 1H, NH$_2$C*H*Me$_2$), 1.45, 0.89 (d, $^3J_{HH}$ = 7 Hz, 6H, NH$_2$CH(C*H*$_3$)$_2$). ^{13}C NMR (CD_2Cl_2, δ): 230.3 (CO), 216.8 (Ph*C*≡CMe), 214.5 (PhC≡*C*Me), 152.8, 151.4, 151.3, 148.4, 148.2, 147.0 (Tp′-*C*Me), 136.1 (*ipso Ph*C≡CMe), 131.2 (*p-Ph*C≡CMe), 129.5, 129.4 (*o,m-Ph*C≡CMe), 109.7, 109.6, 108.3 (Tp′-*C*H), 55.1 (NH$_2$*C*HMe$_2$), 24.7, 23.8 (NH$_2$-CH*Me*$_2$), 23.3 (PhC≡C*Me*), 16.1, 16.0, 14.2, 13.0, 12.9, 12.8 (Tp′-*C*H$_3$). Anal. Calcd for $C_{60}H_{51}N_7OB_2F_{24}W$: C, 46.57; H, 3.32; N, 6.34. Found: C, 46.82; H, 3.40; N, 6.37.

[Tp′W(CO)(PhCCMe)(NH$_2$CHEt$_2$)][BAr′$_4$] (5c). Tp′W(CO)(PhCCMe)(NHCHEt$_2$) (**2c**) (0.15 g, 0.20 mmol) was dissolved in CH_2Cl_2 to give an orange solution. In the drybox, H[BAr′$_4$] (0.19 g, 0.20 mmol) was weighed into another flask. The H[BAr′$_4$] was put on the Schlenk line, cooled to 0 °C, and dissolved in CH_2Cl_2. The H[BAr′$_4$] solution was then cannula transferred to the amido complex solution, which turned blue. The solvent was removed in vacuo, and the blue oil was recrystallized using CH_2Cl_2/hexanes (0.23 g, 75% yield). IR (KBr): ν_{CO} = 1937 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.33, 6.72 (m, 5H, MeC≡C*Ph*), 6.09, 6.00, 5.77 (s, 3H, Tp′-C*H*), 3.77 (s, 3H, *Me*C≡CPh), 2.74, 2.57, 2.50, 2.42, 1.49, 1.32 (s, 18H, Tp′-C*H*$_3$), 3.33 (dd, $^3J_{HH}$ = 7 Hz, $^2J_{HH}$ = 13 Hz, 1H, NH*H*), 2.76 (m, 1H, N*H*H), 2.67 (m, 1H, NH$_2$C*H*Et$_2$), 1.87 (ddq, $^3J_{HH}$ = 4.5 Hz, $^3J_{HH}$ = 8 Hz, $^2J_{HH}$ = 15 Hz, 1H, NH$_2$CH(CH*H*CH$_3$)Et), 1.69 (d of quintets, $^3J_{HH}$ = 7 Hz, $^2J_{HH}$ = 15 Hz, 1H, NH$_2$CH(C*H*HCH$_3$)-Et), 1.03 (dq, $^3J_{HH}$ = 6 Hz, 8 Hz, 2H, NH$_2$CHEt(C*H*$_2$CH$_3$)), 0.89, 0.81 (t, $^3J_{HH}$ = 8 Hz, 6H, CH$_2$C*H*$_3$). ^{13}C NMR (CD_2Cl_2, δ): 230.1 (CO), 216.7 (Ph*C*≡CMe), 214.5 (PhC≡*C*Me), 153.0, 151.5, 151.4, 148.4, 148.2, 147.0 (Tp′-*C*Me), 136.0 (*ipso Ph*C≡CMe), 131.2 (*p-Ph*C≡CMe), 129.4 (*o,m-Ph*C≡CMe), 109.73, 109.67, 108.3 (Tp′-*C*H), 64.0 (NH$_2$*C*HEt$_2$), 26.6, 25.4 (*C*H$_2$CH$_3$), 23.3 (PhC≡C*Me*), 16.2, 16.0, 14.4, 12.98, 12.97, 12.8 (Tp′-*C*H$_3$), 8.6, 8.5 (CH$_2$*C*H$_3$). Anal. Calcd for $C_{62}H_{55}N_7OB_2F_{24}W$: C, 47.26; H, 3.52; N, 6.22. Found: C, 47.04; H, 3.40; N, 6.23.

[Tp′W(CO)(PhCCMe)(NH$_2$CHMe(*p*-C$_6$H$_4$OMe))][BAr′$_4$] (5e). Tp′W(CO)(PhCCMe)(NHCHMe(*p*-C$_6$H$_4$OMe)) (**2e**) (0.1959 g, 0.25 mmol) was dissolved in CH_2Cl_2 to give an orange

solution. In the drybox, H[BAr′$_4$] (0.24 g, 0.25 mmol) was weighed into another flask. The H[BAr′$_4$] was put on the Schlenk line, cooled to 0 °C, and dissolved in CH_2Cl_2. The H[BAr′$_4$] solution was then cannula transferred to the amido complex solution, which turned blue. The solvent was removed in vacuo, and the blue oil was recrystallized using CH_2Cl_2/hexanes (0.31 g, 76% yield). The ratio of diastereomers was observed to be 3.3:1 by ^{1}H NMR. Differences for the minor diastereomer are given in parentheses. IR (KBr): ν_{CO} = 1920 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.35, 6.77 (6.43) (m, 5H, MeC≡C*Ph*), 7.13, 6.92 (6.85) (d, $^3J_{HH}$ = 9 Hz, 4H, C_6H_4OMe), 6.02, 5.97, 5.78 (6.11, 5.92, 5.77) (s, 3H, Tp′−C*H*), 4.37 (3.43) (m, 1H, NH_2C*H*MePhOMe), 3.87 (3.60) (s, 3H, CH_3C≡CPh), 3.77 (3.76) (s, 3H, OCH_3), 3.77 (m, 1H, N*H*H), 2.94 (d, $^3J_{HH}$ = 14 Hz, 1H, NH*H*), 2.55, 2.50, 2.49, 2.37, 1.69, 1.35 (2.87, 2.53, 2.41, 2.12, 1.38, 1.32) (s, 18H, Tp′-CH_3), 1.02 (1.74) (d, $^3J_{HH}$ = 7 Hz, 3H, NH_2CH*Me*PhOMe). ^{13}C NMR (CD_2Cl_2, δ): 230.4 (229.8) (*C*O), 217.2 (216.7) (Ph*C*≡CMe), 214.4 (214.7) (PhC≡*C*Me), 160.8 (*ipso* $MeOC_6H_4$), 153.0, 151.4, 151.3, 148.29, 148.27 (Tp′-*C*Me), 136.0 (*ipso Ph*C≡CMe), 134.0 (*ipso* C_6H_4-OMe), 131.3 (*p-Ph*C≡CMe), 129.5, 129.4 (*o,m-Ph*C≡CMe), 127.1, 115.3 (127.0, 115.2) (*o, m Ph*OMe), 109.8, 109.5, 108.3 (Tp′-*C*H), 63.4 (62.5) (NH_2*C*HMePhOMe), 55.7 (O*Me*), 23.7 (PhC≡C*Me*), 21.8 (23.0) (NH_2CH*Me*PhOMe), 16.0, 16.11 (16.15), 14.7 (14.2), 13.0, 12.9, 12.8 (Tp′-*C*H_3). Anal. Calcd for $C_{66}H_{55}N_7O_2B_2F_{24}W$: C, 48.35; H, 3.38; N, 5.98. Found: C, 47.70; H, 3.38; N, 6.01.

[Tp′W(CO)(PhCCMe)(NH_2CHMe(*p*-C_6H_4Br))][BAr′$_4$] (5f). Tp′W(CO)(PhCCMe)(NHCHMe(*p*-C_6H_4Br)) (**2f**) (0.21 g, 0.25 mmol) was dissolved in CH_2Cl_2 to give an orange solution. In the drybox, H[BAr′$_4$] (0.24 g, 0.25 mmol) was weighed into another flask. The H[BAr′$_4$] was put on the Schlenk line, cooled to 0 °C, and dissolved in CH_2Cl_2. The H[BAr′$_4$] solution was then cannula transferred to the amido complex solution, which turned blue. The solvent was removed in vacuo, and the blue oil was recrystallized using CH_2Cl_2/hexanes (0.34 g, 80% yield). The ratio of diastereomers was observed to be 1.6:1 by ^{1}H NMR. Differences for the minor diastereomer are given in parentheses. IR (KBr): ν_{CO} = 1924 cm^{-1}. ^{1}H NMR (CD_2Cl_2, δ): 7.51, 6.89 (7.57, 7.85) (d, $^3J_{HH}$ = 9 Hz, 4H, C_6H_4Br), 7.35, 6.65 (6.77) (m, 5H, MeC≡C*Ph*), 6.12, 5.93, 5.78 (6.03, 5.98, 5.78) (s, 3H, Tp′-C*H*), 3.40 (4.41) (m, 1H, NH_2C*H*MePhBr), 3.89 (3.78) (m, 1H, N*H*H), (2.97) (d, $^3J_{HH}$ = 14 Hz, 1H, NH*H*), 3.23 (dd, $^3J_{HH}$ = 9 Hz, $^2J_{HH}$ = 13 Hz, 1H, NH*H*), 3.61 (3.87) (s, 3H, CH_3C≡CPh), 2.87, 2.54, 2.49, 2.41, 1.36, 1.32 (2.55, 2.48, 2.37, 1.68, 1.35) (s, 18H, Tp′-CH_3), 1.76 (1.02) (d, $^3J_{HH}$ = 7 Hz, 3H, NH_2CH*Me*PhBr). ^{13}C NMR (CD_2Cl_2, δ): 230.1 (229.6) (CO), 216.9 (Ph*C*≡CMe), 214.7 (PhC≡*C*Me), 152.7, 151.6, 151.4, 148.6, 148.4, 147.0 (152.8, 151.5, 151.2, 158.43, 148.39, 147.1) (Tp′-*C*Me), 140.2 (141.1) (*ipso* C_6H_4Br), 136.0 (135.9) (*ipso Ph*C≡CMe), 133.2, 127.4 (133.3, 127.5) (*C*$_6H_4$Br), 131.2 (131.4) (*p-Ph*C≡CMe), 129.47, 129.37 (129.53) (*o,m Ph*C≡CMe), 123.7 (123.8) (*ipso* BrC_6H_4), 109.79, 109.7, 108.39 (109.84, 109.6, 108.37) (Tp′-*C*H), 62.3 (63.4) (NH_2*C*HMePhBr), 24.3 (21.7) (NH_2CH*Me*PhBr), 23.1 (23.7) (PhC≡C*Me*), 16.2, 16.0, 14.5, 13.0, 13.0, 12.7 (16.1, 16.06, 14.7, 14.2, 12.9, 12.8) (Tp′-*C*H_3). Anal. Calcd for $C_{65}H_{52}N_7OBrB_2F_{24}W$: C, 46.24; H, 3.10; N, 5.81. Found: C, 46.58; H, 3.33; N, 5.70.

[Tp′W(CO)(PhCCMe)(NH=CMeEt)][BAr′$_4$] (3a). Corrected ^{1}H NMR data were determined by gradient NOESY and COSY techniques. Differences for the minor *Z* isomer are listed in parentheses. The *E*/*Z* ratio in CD_2Cl_2 can range from 75:25 to 93:7 depending on the recrystallization method. The *E*/*Z* ratio in THF-d_8 is 60:40. ^{1}H NMR (CD_2Cl_2, 298 K, δ): 8.92 (br, 1H, N*H*), 7.31, 6.71 (m, 5H, Ph), 6.02, 5.95, 5.79 (s, 3H, Tp′-C*H*), 3.82, (3.80) (s, 3H, PhC≡C*Me*), 2.58, 2.51, 2.42, 2.42, 1.39, (1.23), 1.21 (s, 18H, Tp′-CH_3), 2.47 (m, 1H, C*H*HCH$_3$) (2.22) (d, $^4J_{HH}$ = 1 Hz, 3H, NH=C*Me*Et), 2.05 (br, 3H, NH=C*Me*Et), 1.26 (m, 1H, CH*H*CH$_3$), (1.06) (br, 3H, CH$_2$*C*H$_3$), 0.92 (t, $^3J_{HH}$ = 7 Hz, 3H, CH$_2$*C*H$_3$). ^{1}H NMR (THF-d_8, 298 K, δ): 10.07 (10.14) (br, 1H, N*H*), 7.29, 6.75 (m, 5H, Ph), 6.12, 6.03, 5.85 (s, 3H, Tp′-C*H*), 3.86 (3.85) (s, 3H, PhC≡C*Me*), 2.62, 2.53, 2.50, 2.45, (1.44) 1.43, (1.31) 1.30 (s, 18H, Tp′-CH_3), 2.10 (2.28) (s, 3H, NH=C*Me*Et), 2.11, 2.50 (m, 2H, CH_2CH$_3$), 1.04 (1.07) (t, $^3J_{HH}$ = 8 Hz, 3H, CH$_2$CH_3).

***E*-Enriched [Tp′W(CO)(PhCCMe)(NH=CMeEt)][BAr′$_4$] (3a).** Crystals of 75:25 *E*:*Z* imine complex **3a** (0.163 g, 0.105 mmol) were dissolved in a mixture of 3:2:1 hexanes/CH_2Cl_2/THF (1 mL) and layered with hexanes (30 mL). The crystals that formed were enriched in the *E* isomer of imine complex (0.149 g, 0.0953 mmol, 91% yield). A range of *E*/*Z* ratios can be obtained by this method from 80:20 to 93:7.

(*SS*)-[Tp′W(CO)(PhCCMe)(NH_2CHMeEt)][BAr′$_4$] (5a). [Tp′W(CO)(PhCCMe)(NH=CMeEt)][BAr′$_4$] (**3a**) (90:10 *E*/*Z*, 0.11 g, 0.07 mmol) was dissolved in CH_2Cl_2. Li[HBEt$_3$] (0.12 mL, 0.12 mmol) was added to the imine solution, and Tp′W(CO)(PhCCMe)(NHCHMeEt) (**2a**) formed immediately. The orange solution was then purified on an alumina column with 1:1 hexanes/CH_2Cl_2 as the eluent. A blue band of [Tp′W(CO)(PhCCMe)(NH_2CHMeEt)][BAr′$_4$] (**5a**) was collected and recrystallized using CH_2Cl_2/hexanes. The stereochemistry was then determined by X-ray analysis.

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Supporting Information Available: Experimental details for the hydride addition reactions, *E*/*Z* isomerization, and thermodynamic and kinetic acidity measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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