Chemistry Surrounding Chiral Tungsten(II) η^1-Imine Complexes

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Chiral tungsten(II) η^1-imine complexes $[Tp'(CO)(PhC{\equiv}CMe)W(NH{=}CRR')]^+$ (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) have been prepared by oxidation of the corresponding amido complexes Tp′(CO)(PhC≡CMe)W(NHCHRR′) (R/R′ = Ph/Ph, Ph/Me, Me/Et, and H/CHMePh) with elemental iodine. These oxidations also result in formation of amine complexes which have been independently synthesized. Oxidation in the presence of a weak base suppresses amine formation. However, when R = Ph, deprotonation of the imine product forms the neutral azavinylidene complex Tp′(CO)(PhC≡CMe)W(N=CRR′). Protonation of the azavinylidene complex provides a clean route to the desired imine complex. Crystal structures of a representative complex from each category of nitrogen donor ligand have been determined: cationic imine complex $[Tp'(CO)(PhC{\equiv}CMe)W(NH{=}CMeEt)][BAr'_4]$ (**2a**), cationic amine complex $[Tp'(CO)(PhC{\equiv}CMe)W(NH_2CH_2CHMePh)][I_3]$ (**4d**), neutral amido complex Tp′(CO)(PhC≡CMe)W(NHCHMeEt) (**1a**), and neutral azavinylidene complex Tp′(CO)(PhC≡CMe)W(N=CMePh) (**3b**).

Introduction

In contrast to the abundance of amine, nitrile, and chelating imine complexes,[1] there are comparatively few examples of simple imines serving as monodentate ligands. Gladysz and co-workers have synthesized a series of σ-imine complexes of the type $[CpRe(NO)(PPh_3)(NH{=}CRR')][CF_3SO_3]$.[2a,b] Some of these imine complexes were prepared by displacement of triflate by free imine, others by the the addition of nucleophiles to a cationic nitrile complex followed by protonation, and some by reaction of a transition metal ammonia complex with free aldehydes or ketones.[2b]

Imines can also bind in a π fashion to electron-rich metal centers. A variety of η^2-imine complexes of titanium have been synthesized with ancillary aryl oxide ligands.[3] Dehydrogenation of amines to form π-bound imines has been reported in zirconocene[4] and tantalum complexes.[5]

The reactivity of both σ- and π-bound imine complexes is important. Diastereoselective addition of nucleophiles to imines to form amido ligands is known,[6] and transition metal-catalyzed addition of nucleophiles to activated imines has been reported.[7] Catalytic hydrogenation of imines to form amines commonly uses rhodium- and iridium-based catalysts.[8] Catalytic asymmetric hydrogenation of imines has been accomplished with a chiral titanocene catalyst.[9]

Complexes with low molecular weight, N-protio imines have proven difficult to isolate. The dimethyl imine complex $(CO)_5Cr(NH{=}CMe_2)$ was isolated from the reaction of $(CO)_5Cr{=}C(OMe)(Me)$ with $Me_2C{=}NOH$.[10] The chromium and tungsten analogs were prepared by combining $Na_2M_2(CO)_{10}$ (M = Cr, W) with Me_2CBrNO.[11] $W(CO)_5(THF)$ reacts with ketoximes and aldoximes at room temperature to form imine complexes.[12] The benzophenone imine complex has been synthesized by treating the diphenylcarbene complex $(CO)_5M{=}CPh_2$ (M = Cr,W) with trimethylsilyl azide, $Me_3SiN{=}N{=}N$.[13] Cationic ruthenium aldimine complexes of the type $[CpRu(PPh_3)L(NR{=}CHPh)]^+$ (R = H, Me) with SbF_6^- or PF_6^- anions have also been synthesized.[14]

The oxidation of amines to form imines is known with a variety of oxidizing agents.[15] Imine complexes can be formed electrochemically, but further oxidation of the imine products is problematic.[16] Oxidation of primary

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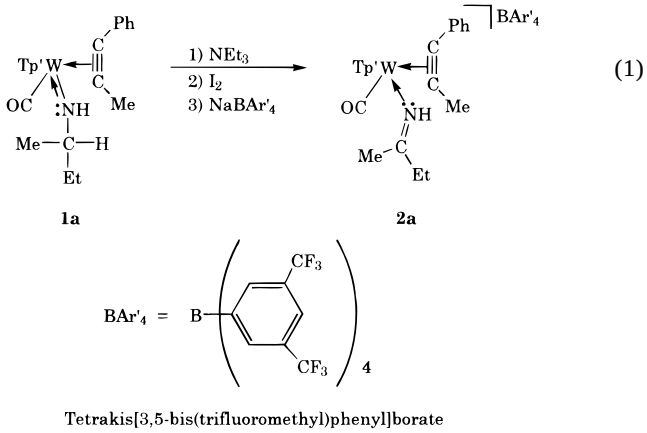
and secondary amines to imines has been achieved using iodosobenzene[17,18] and in low yields with molecular oxygen in the presence of a ruthenium catalyst.[18] Imine complexes have been isolated as intermediates in the reduction of coordinated nitriles.[19,20] The reverse of this sequence, oxidation of coordinated benzylamine to benzonitrile on the $[Tp'W(CO)(PhC{\equiv}CMe)]^+$ fragment (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate), has recently been accomplished.[21]

In this paper we report the synthesis of tungsten imine complexes of the type $[Tp'W(CO)(PhC{\equiv}CMe)(NH{=}CRR')]^+$ by oxidation of the corresponding amido complexes Tp′W(CO)(RC≡CMe)(NHCHRR′) (R/R′ = Ph/Ph, Ph/Me, Me/Et, and H/CHMePh). Our goal was to find a general route to cationic tungsten(II) imine complexes, but our efforts were complicated by the formation of related nitrogen donor ligands. The results reported herein reflect the synthetic complexity of successful routes to d^4 transition metal imine complexes.

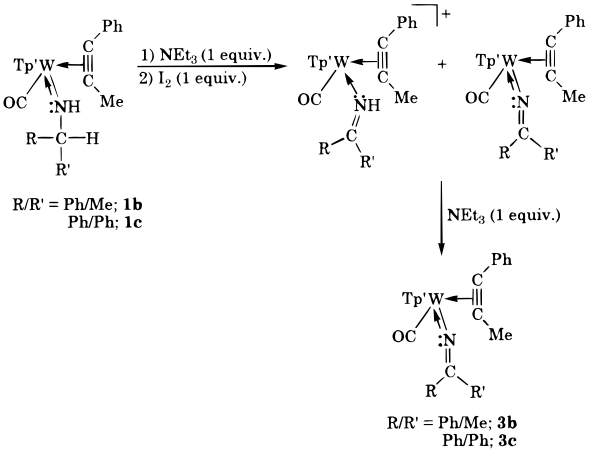
Results and Discussion

Syntheses. The imine complex $[Tp'(CO)(PhC{\equiv}CMe)W(NH{=}CMeEt)]^+$ (**2a**) was synthesized by oxidation of the amido complex Tp′(CO)(PhC≡CMe)W(NHCHMeEt) (**1a**) with 1 equiv of iodine in the presence of NEt_3 (eq 1). Counterion exchange of $[BAr'_4]^-$ for $[I]^-$ (BAr'_4 = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate)[22] was accomplished by adding 1 equiv of $Na[BAr'_4]$ in Et_2O to a CH_2Cl_2 solution of the reaction mixture. Chromatography followed by recrystallization from CH_2Cl_2/hexanes gave air-stable, ink-blue crystals of **2a** in a 74% yield.



(1)

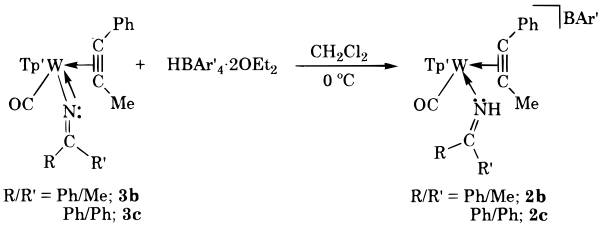
The aryl amido complex Tp′(CO)(PhC≡CMe)W(NHCHRR′) (**1b**, R/R′ = Me/Ph; **1c**, R/R′ = Ph/Ph) reacted with I_2 in the presence of NEt_3 to form a mixture of the imine complex and the neutral azavinylidene complex. Addition of a second equivalent of NEt_3 led to total conversion to the azavinylidene Tp′(CO)(PhC≡CMe)W(N=CRR′) (**3b**, R/R′ = Me/Ph; **3c**, R/R′ = Ph/Ph) (eq 2).



(2)

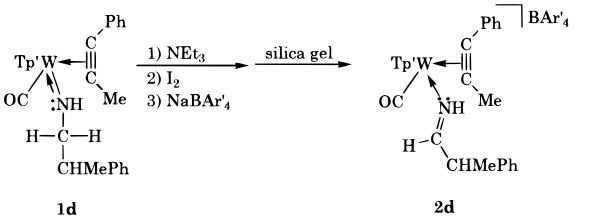
Isolated yields of 92% (**3b**) and 59% (**3c**) of light orange crystals of the azavinylidene products were realized after chromatography and recrystallization (THF/hexanes).

Protonation of the azavinylidene complexes **3b** (R/R′ = Me/Ph) and **3c** (R/R′ = Ph/Ph) occurred quantitatively to form imine complexes. A CH_2Cl_2 solution of the azavinylidene was cooled to 0 °C in an ice bath. A color change from light orange to green accompanied the dropwise addition of 1 equiv of $HBAr'_4{\cdot}2OEt_2$ in CH_2Cl_2 (eq 3). Recrystallization from CH_2Cl_2/hexanes produced green, air-stable crystals of $[Tp'(CO)(PhC{\equiv}CMe)W(NH{=}CRR')][BAr'_4]$ (**2b**, R/R′ = Me/Ph; **2c,** R/R′ = Ph/Ph) in high yields (87−90%).



(3)

The aldimine complex $[Tp'(CO)(PhC{\equiv}CMe)W(NH{=}CHCHMePh)]^+$ (**2d**) formed in a 2:1 ratio with the coordinated amine complex $[Tp'(CO)(PhC{\equiv}CMe)W(NH_2{-}CH_2CHMePh)]^+$ (**4d**) from the reaction of the amido complex Tp′(CO)(PhC≡CMe)W(NHCH$_2$CHMePh) (**1d**) with I_2 in the presence of NEt_3 (eq 4). After counterion exchange (BAr'_4) and chromatography on silica gel, the pure imine complex was isolated as blue crystals (30% yield).



(4)

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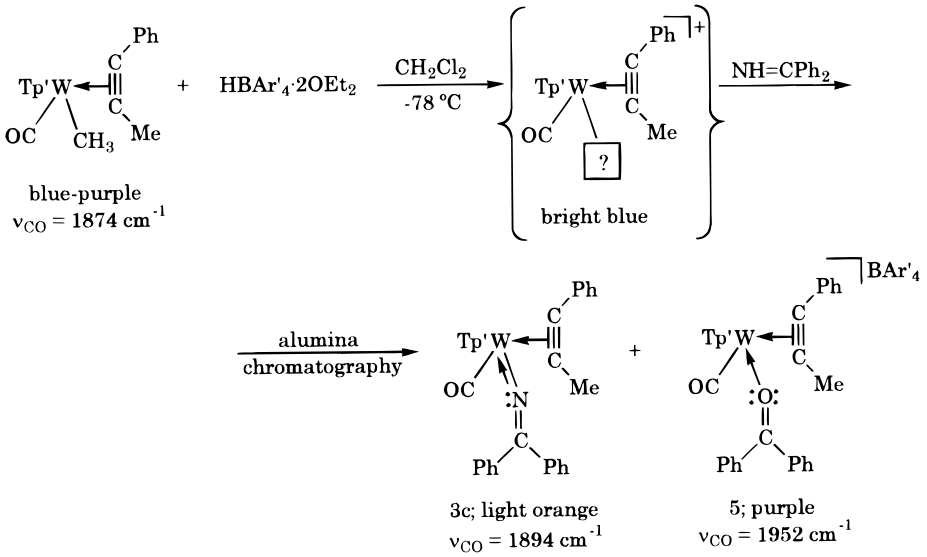
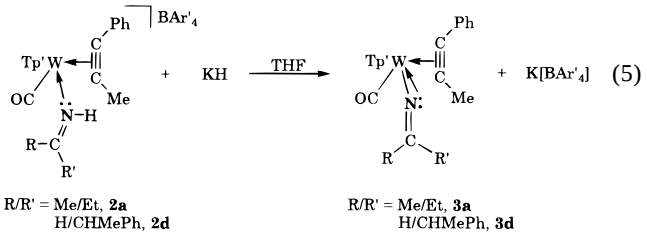
Scheme 1



Addition of $HBAr'_4{\cdot}2OEt_2$ to the methyl complex Tp′(CO)(PhC≡CMe)W(CH_3)[23] followed by addition of the diphenyl imine $NH{=}CPh_2$ at −78 °C produced a brown solution which contained both the imine complex [Tp′(CO)(PhC≡CMe)W($NH{=}CPh_2$)][BAr'_4] (**2c**) and the hydrolysis product [Tp′(CO)(PhC≡CMe)W(η^1-O=CPh_2)][BAr'_4] (**5**). Separation by chromatography on alumina caused deprotonation of the imine adduct to form the neutral azavinylidene complex Tp′(CO)(PhC≡CMe)W(N=CPh_2) (**3c**), which eluted with hexanes (Scheme 1). This product was isolated in 39% yield as a light orange solid. N-Alkyl or N-aryl imines do not add to the [Tp′(CO)(PhC≡CMe)W]$^+$ metal fragment under similar conditions.

The hydrolysis product, the σ-bound benzophenone adduct, was isolated in 4% yield as purple, air-stable crystals. This complex was independently synthesized by protonation of the methyl complex with $HBAr'_4{\cdot}2OEt_2$ in CH_2Cl_2 at −78 °C followed by addition of benzophenone. Isolation of [Tp′(CO)(PhC≡CMe)W(η^1-O=CPh_2)][BAr'_4] (**5**) was achieved in 75% yield.

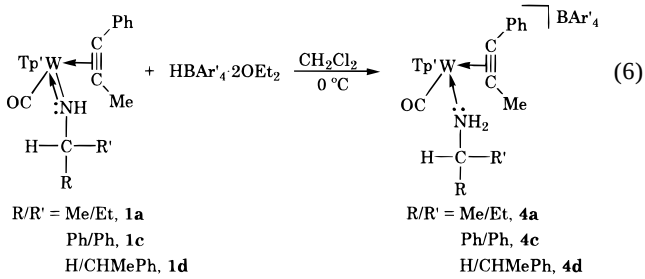
While the aryl imine complexes (**2b**, R/R′ = Me/Ph; **2c**, R/R′ = Ph/Ph) are deprotonated by NEt_3, the imine proton in **2a** (R/R′ = Me/Et) and **2d** (R/R′ = H/CHMePh) requires a stronger base for deprotonation. The azavinylidene complex Tp′(CO)(PhC≡CMe)W(N=CRR′) (**3a**, R/R′ = Me/Et; **3d**, R/R′ = H/CHMePh) was formed when a THF solution of the imine complex was added to excess KH at room temperature (eq 5). A color change



(5)

from blue to orange was observed. The solution was filtered from the unreacted KH and dried to an orange oil. The product was extracted from the K[BAr'_4] precipitate with hexanes and was isolated as an orange solid in yields of 95% for **3a** and 60% for **3d**. These complexes are stable as solids when stored under nitrogen. Addition of ^{n}BuLi to the imine complex led to decomposition rather than deprotonation.

The coordinated amine complexes [Tp′(CO)(PhC≡CMe)W(NH_2CHRR')][BAr'_4] (**4a**, **c**, and **d**) were easily prepared by protonation of the appropriate amido complex with $HBAr'_4{\cdot}2OEt_2$ in CH_2Cl_2 at 0 °C (eq 6). A



(6)

color change from orange to dark blue was observed. Solvent removal followed by recrystallization from CH_2Cl_2/hexanes produced air-stable, ink-blue crystals of the amine complex in yields of 65−70%. These complexes are also formed along with the imine complexes **2a**−**d** during oxidation of the amido complexes **1a**−**d** with I_2 in the *absence* of NEt_3. The synthesis and characterization of [Tp′(CO)(PhC≡CMe)W($NH_2CHMePh$)][BF_4] has been reported previously.[24]

The new amido complexes **1a**, **c**, and **d** were synthesized according to the procedure published previously for the synthesis of Tp′(CO)(PhC≡CMe)W(NHCHMePh) **(1b)**.[24] Addition of 1 equiv of NEt_3 helps facilitate deprotonation, thereby reducing reaction time and improving yields. Reaction times range from 2 h to 2 days. The resulting orange complexes are air-stable in solution for short periods. They were purified by chromatography on alumina and were eluted with CH_2Cl_2. The products were recrystallized from CH_2Cl_2/MeOH, forming dark orange, air-stable crystals of Tp′(CO)(PhC≡CMe)W(NHCHRR′) (**1a**, **c**, and **d**) in yields of 53−70%.

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Table 1. Selected Spectroscopic Data for Imine Complexes [Tp′(CO)(PhC≡CMe)W(NH=CRR′)][BAr′$_4$] (2a−d)

complex (R/R′)	IR ν_{CO} (cm^{-1}, KBr)	^{1}H NMR[a] (ppm) N*H*=CRR′	^{1}H NMR[a] (ppm) NH=C*R*R′ (R = Me or H)	^{13}C NMR[a] (ppm) *C*O	^{13}C NMR[a] (ppm) NH=C*R*R′
2a (Me/Et)[b]	1938	8.94 (8.96)	2.06 (2.22, d, $^4J_{HH}$ = 1.3 Hz)	229.2 (228.9) $^1J_{WC}$ = 147 Hz	193.7 (193.5)
2b (Me/Ph)	1923	9.42	2.48	228.5[c] $^1J_{WC}$ = 150 Hz	184.3[c]
2c (Ph/Ph)	1936	9.81		227.1 $^1J_{WC}$ = 146 Hz	182.0
2d (H/CHMePh)[d]	1936	9.50 (9.51) $^3J_{HH}$ = 21 Hz	6.66 (6.75) dd, $^3J_{HH}$ = 5.3, 21 Hz	227.7 (227.5) $^1J_{WC}$ = 151 Hz	183.1 (182.8)

[a] ^{1}H NMR and ^{13}C NMR spectra recorded in CD_2Cl_2. [b] There are two isomers in a 3:1 ratio; data for the minor isomer are given in parentheses. [c] Recorded at 233 K. [d] There are two diastereomers in a 1:1 ratio; data for the second diastereomer are given in parentheses.

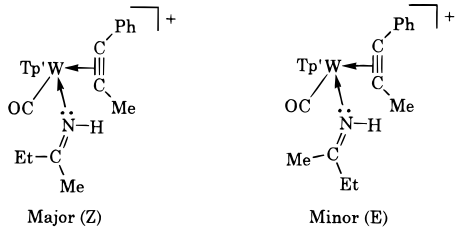

Figure 1. Isomers of [Tp′(CO)(PhC≡CMe)W(NH=CMeEt)][BAr′$_4$] (**2a**).

Characterizaton of Cationic Imine Complexes [Tp′(CO)(PhC≡CMe)W(NH=CRR′)]$^+$ (2a−d). All complexes were characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Selected spectroscopic data for imine complexes **2a**−**d** are summarized in Table 1. The IR spectrum displays a CO stretch of 1923−1938 cm^{-1} for these cationic complexes. In the ^{1}H NMR, the imine proton resonates between 8.9 and 9.8 ppm and is broad due to the adjacent quadrupolar nitrogen. The carbonyl carbon resonates near 228 ppm in the ^{13}C NMR with tungsten coupling of 146−151 Hz. The imine carbon peak appears between 182 and 194 ppm, consistent with σ-bound imines. The alkyne carbon resonances are in the range of 213−217 ppm, indicating a four-electron donor alkyne.[25,26]

The NMR spectrum for [Tp′(CO)(PhC≡CMe)W(NH=CMeEt)][BAr′$_4$] (**2a**) displays two isomers at room temperature with an equilibrium ratio of 2.5:1. The diastereotopic methylene protons of the imine ethyl group resonate as multiplets at 1.22 and 2.49 ppm for the major isomer. For the minor isomer, both methylene protons appear as a multiplet at 2.46 ppm. The ^{1}H NMR signal for the imine methyl group for the major isomer appears at 2.06 ppm as a broad singlet, while the minor isomer peak at 2.22 ppm is a doublet with a four-bond coupling constant of 1.3 Hz. This small 1.3 Hz coupling observed for the minor isomer suggests that the minor isomer has the methyl group *trans* to the imine proton and *cis* to the metal fragment (Figure 1). The two isomers are present in the NMR spectrum up to 100 °C with no broadening detected, corresponding to a minimum barrier to isomer interconversion of 18 kcal/mol. The orientation in the solid state has the ethyl group *trans* to the metal; details of the X-ray diffraction study are presented later.

The room temperature NMR signals for [Tp′(CO)(PhC≡CMe)W(NH=CMePh)][BAr′$_4$] (**2b**) are broad due to fluxionality in the molecule. Low-temperature NMR freezes out *cis*/*trans* isomers with a population ratio of 8:1 at −10 °C. The coalescence point is just below room temperature. Using line broadening, the barrier to conversion from the major isomer to the minor isomer was estimated to be 15.8 kcal/mol, while the barrier in the opposite direction was estimated to be 14.4 kcal/mol. The calculated $\Delta G°$ of 1.4 kcal/mol is roughly compatible with the ground state energy difference of 1.1 kcal/mol observed at −10 °C.

The aldimime complex [Tp′(CO)(PhC≡CMe)W(NH=CHCHMePh)][BAr′$_4$] (**2d**) has two stereogenic centers, the metal and the imine α carbon, and the NMR displays two diastereomers in a 1:1 ratio. Each of the diastereomers displays an imine proton resonance as a doublet near 9.5 ppm with a coupling constant of 21 Hz, a typical value for *trans* H−H coupling across the N=C bond.[20] This places the bulky -CHMePh group *cis* to the imine proton and *trans* to the large metal fragment. The aldimine proton peak appears as a doublet of doublets near 6.7 ppm for the two diastereomers with $^3J_{HH}$ = 5.3 and 21 Hz.

The imine proton in complexes **2a**−**d** exchanges with deuterated water slowly on the NMR time scale, and the time for complete exchange was on the order of minutes.

X-ray Structure for [Tp′(CO)(PhC≡CMe)W(NH=CMeEt)][BAr′$_4$] (2a). An ORTEP diagram for **2a** is shown in Figure 2. Selected bond distances and angles are given in Table 2, and data collection parameters for all complexes are given in Table 3. A comparison of pertinent bond distances and angles for each type of complex is given in Table 4, and general structural information for this complex is typical of all the structures presented in this paper. The Tp′ ligand occupies three coordination sites of the octahedral complex in a facial geometry. The alkyne ligand lies parallel to the metal carbonyl axis, as is common for group VI d^4 alkyne complexes.[26] This orientation maximizes the interaction of the empty metal dπ orbital with the filled alkyne $\pi_\perp$ orbital while allowing the filled dπ metal orbitals to overlap with the empty π* orbitals on CO.

Consistent with the ^{13}C NMR data for these cationic imine complexes, the short alkyne−metal distances of 1.998(13) and 2.034(12) Å denote a tightly-bound four-electron donor alkyne.[25] The sixth coordination site is occupied by the imine ligand. The W−N(5) bond distance of 2.146(9) Å is consistent with a single W−N

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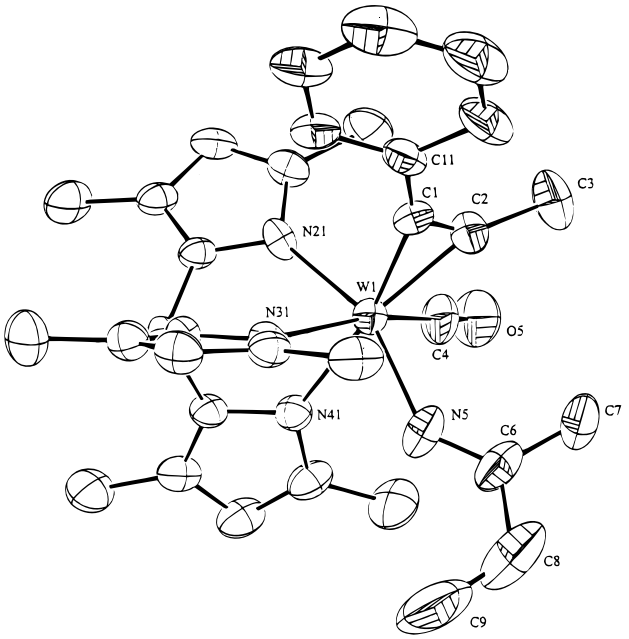

Figure 2. ORTEP diagram of [Tp′(CO)(PhC≡CMe)W(NH=CMeEt)][BAr′$_4$] (**2a**).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for [Tp′(CO)(PhC≡CMe)W(NH=CMeEt)][BAr′$_4$] (2a)

W(1)−C(1)	1.998(13)	C(6)−C(7)	1.487(24)
W(1)−C(4)	1.960(14)	C(6)−C(8)	1.48(3)
W(1)−C(2)	2.034(12)	C(8)−C(9)	1.42(4)
W(1)−N(5)	2.146(9)	C(4)−O(5)	1.138(17)
W(1)−N(41)	2.200(9)	C(1)−C(2)	1.244(20)
W(1)−N(31)	2.259(8)	C(1)−C(11)	1.480(20)
W(1)−N(21)	2.140(8)	C(3)−C(2)	1.550(18)
N(5)−C(6)	1.279(14)		
C(1)−W(1)−C(4)	107.3(6)	N(5)−C(6)−C(7)	120.6(13)
C(2)−W(1)−C(4)	72.3(6)	N(5)−C(6)−C(8)	124.1(16)
C(4)−W(1)−N(5)	96.6(5)	C(7)−C(6)−C(8)	115.3(13)
C(1)−W(1)−C(2)	35.9(6)	C(6)−C(8)−C(9)	117.7(15)
W(1)−C(2)−C(3)	145.1(12)	C(1)−W(1)−N(5)	103.1(4)
W(1)−C(1)−C(11)	149.4(9)	C(2)−W(1)−N(5)	99.5(4)
C(1)−C(2)−C(3)	144.0(14)	C(1)−W(1)−N(41)	164.4(4)
C(2)−C(1)−C(11)	136.5(12)	C(1)−W(1)−N(31)	85.6(4)
W(1)−C(2)−C(1)	70.5(8)	C(1)−W(1)−N(21)	93.3(4)
W(1)−C(1)−C(2)	73.6(9)	C(2)−W(1)−N(41)	159.3(5)
W(1)−N(5)−C(6)	139.9(10)	C(2)−W(1)−N(31)	120.5(5)
W(1)−C(4)−O(5)	176.9(12)	C(2)−W(1)−N(21)	102.5(4)

dative bond.[24] The N(5)−C(6) bond distance of 1.279(14) Å is close to the bond distance of 1.285(10) Å found for [Tp′(CO)(PhC≡CMe)W(NH=CHPh)][BF_4],[21] as well as the N=C bond length of 1.272(5) Å reported by Gladysz and co-workers for [CpRe(NO)(PPh_3)(NMe=CHPh)][OTf].[2a]

Characterization of Neutral Azavinylidene Complexes Tp′(CO)(PhC≡CMe)W(N=CRR′) (3a−d). Selected spectroscopic data for azavinylidene complexes **3a**−**d** are given in Table 5. These neutral complexes display a CO stretch between 1867 and 1894 cm^{-1}. The terminal CO resonance in the ^{13}C NMR spectrum appears near 230 ppm with tungsten coupling of 150−158 Hz. The azavinylidene carbon resonates between 138 and 156 ppm for these complexes, with two-bond tungsten coupling of 21−27 Hz. Coupling constants of 21−28 Hz are typical for these complexes and indicate a fairly linear W−N=C backbone, facilitating donation from the nitrogen p orbital into the empty metal dπ orbital.[20,26] The alkyne carbons for these complexes

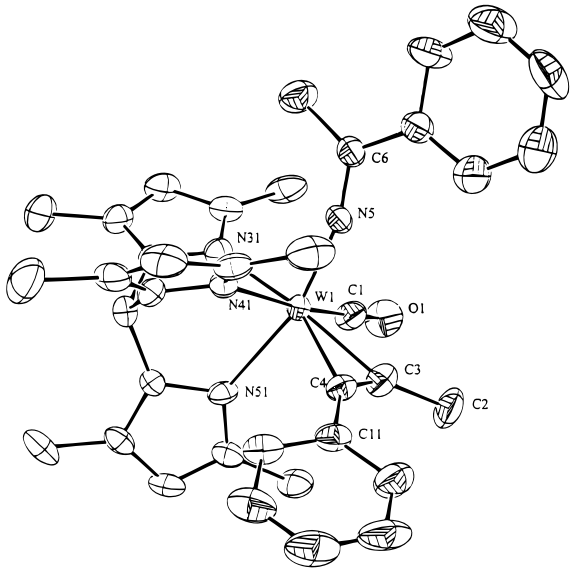

Figure 3. ORTEP diagram of Tp′(CO)(PhC≡CMe)W(N=CMePh) (**3b**).

resonate between 156 and 159 ppm. This upfield shift relative to the alkyne carbons in the imine complexes (213−217 ppm) indicates a change from a four-electron to a "three-electron" donor alkyne. The alkyne $\pi_\perp$ orbital competes with the azavinylidene nitrogen lone pair for donation into the lone vacant metal dπ orbital.[27]

The room temperature ^1H NMR of Tp′(CO)(PhC≡CMe)W(N=CMeEt) (**3a**) displays two isomers in a 3:1 ratio. Since the phenylmethylacetylene ligand routinely populates only one isomer, that with the phenyl near the pyrazole rings,[25] the two isomers are presumably due to the orientation of the azavinylidene fragment. As with the corresponding imine complex, no broadening of NMR signals was observed up to 100 °C, indicating a minimum barrier to isomer interconversion of 20 kcal/mol. The methylene protons of the azavinylidene ethyl group are diastereotopic and resonate as multiplets at 2.14 (major isomer) and 1.85 ppm (minor isomer).

The ^1H NMR spectrum of Tp′(CO)(PhC≡CMe)W(N=CHCHMePh) (**3d**) shows two isomers in a 3:1 ratio, and each isomer exists as two diastereomers. Like **3a**, the complex Tp′(CO)(PhC≡CMe)W(N=CMePh) (**3b**) displays two isomers in the room temperature NMR spectrum, but with a ratio of 7:1. No NMR signal broadening was observed up to 100 °C for this complex, corresponding to a minimum barrier to isomer interconversion of 19 kcal/mol.

An X-ray crystal structure was obtained for azavinylidene complex **3b**, and an ORTEP diagram is shown in Figure 3. Selected structural data are given in Table 4. The W−N(5) bond distance of 1.897(8) Å is considerably shorter than that in the imine complex, reflecting the increased tungsten−nitrogen bond order in these complexes. The N(5)−C(6) distance of 1.288(14) Å is close to the imine double bond distance of 1.279(14) Å. The tungsten−alkyne carbon bond distances of 2.073(9) and 2.093(11) Å are longer than those in the imine complex and reflect the "three-electron" donor role of the alkyne.

The azavinylidene fragment is aligned to allow donation of the lone pair into the lone vacant metal dπ

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Table 3. Crystallographic Data Collection Parameters for Tp′(CO)(PhC≡CMe)W(NHCHMeEt) (1a), [Tp′(CO)(PhC≡CMe)W(NH=CMeEt)][BAr′$_4$] (2a), [Tp′(CO)(PhC≡CMe)W(NH$_2$CH$_2$CHMePh)][I$_3$] (4d), and Tp′(CO)(PhC≡CMe)W(N=CMePh) (3b)

complex	**1a**·CH_2Cl_2	**2a**	**4d**·$^1/_3CH_2Cl_2$	**3b**
molecular formula	$WC_{29}H_{40}N_7BO$	$WC_{61}H_{46}F_{24}N_7B_2O$	$WC_{34}H_{41}N_7BOI_3$	$WC_{33}H_{38}N_7BO$
formula weight, g/mol	755.99	1554.50	1167.42	743.36
crystal dimensions, mm	0.35 × 0.35 × 0.20	0.45 × 0.40 × 0.10	0.40 × 0.25 × 0.12	0.45 × 0.35 × 0.20
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$
a, Å	10.558(6)	12.4254(22)	12.5819(18)	22.9427(24)
b, Å	12.095(6)	16.2607(22)	12.933(3)	10.1386(11)
c, Å	15.359(7)	18.038(3)	15.233(3)	28.810(3)
α, deg	88.23(4)	90.953(13)	65.138(14)	
β, deg	73.50(5)	103.764(14)	88.077(14)	91.328(9)
γ, deg	68.07(4)	107.897(14)	87.179(14)	
volume, Å^3	1738.3(15)	3352.6(9)	2246.1(7)	6699.6(13)
Z	2	2	2	8
density calcd, Mg/m^3	1.444	1.540	1.726	1.474
radiation (wavelength, Å)	Mo Kα (0.709 30)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.709 30)
monochromator	graphite	graphite	graphite	graphite
linear abs coeff, mm^{-1}	3.58	1.87	4.70	3.56
scan type	$\theta/2\theta$ w/profile analysis	$\theta/2\theta$ w/profile analysis	Ω w/profile analysis	Ω w/profile analysis
2θ limit, deg	45	50	45	50
h,k,l ranges	−10/11,0/13,−16/16	−14/13,0/19,−21/21	−13/13,0/13,−14/16	−27/27,0/12,0/34
total no. of reflections	4553	11 785	5866	5897
data with $I > 2.5\sigma(I)$	3885	6624	3217	3904
R, %	5.6	6.2	6.5	4.6
R_w, %	6.7	6.7	7.6	5.6
GOF	2.34	1.82	1.86	1.69
no. of parameters	377	865	436	388
maximum shift/σ	0.039	0.015	0.075	0.000

Table 4. Selected X-ray Crystallographic Data[a] for Tp′(CO)(PhC≡CMe)W(NHCHMeEt) (1a), [Tp′(CO)(PhC≡CMe)W(NH=CMeEt)][BAr′$_4$] (2a), Tp′(CO)(PhC≡CMe)W(N=CMePh) (3b), and [Tp′(CO)(PhC≡CMe)W(NH$_2$CH$_2$CHMePh)][I$_3$] (4d)

complex	W—N (Å)	N⋯C (Å)	W—N=C (deg)	W(Ph)C$_1$C$_2$Me (Å)
1a	1.941(10)	1.461(17)	137.1(10)	C_1, 2.086(11) C_2, 2.082(13)
2a	2.146(9)	1.279(14)	139.9(10)	C_1, 1.998(13) C_2, 2.034(12)
3b	1.897(8)	1.288(14)	165.4(8)	C_1, 2.073(9) C_2, 2.093(11)
4d	2.226(18)	1.44(3)	115.6(15)	C_1, 2.033(19) C_2, 2.07(3)

[a] Bond distances and angles for ancillary ligands in **2a** are given in Table 2, and these are representative of the other structures, too.

orbital. Therefore, the plane of the azavinylidene is perpendicular to the alkyne fragment. The W−N(5)−C(6) framework is only slightly bent (165.4(8)°), compatible with the two-bond tungsten coupling to carbon of 26 Hz. The deviation of the azavinylidene from 180° may be to relieve steric crowding as the fragment bends away from the alkyne. A qualitative orbital scheme for the "three-electron" donor alkyne is given in Figure 4.

Characterization of Cationic Amine Complexes [Tp′(CO)(PhC≡CMe)W(NH$_2$CHRR′)]$^+$ (4a−d). Selected spectroscopic data for complexes **4a**−**d** are given in Table 6. Characterization data for [Tp′(CO)(PhC≡CMe)W(NH$_2$CHMePh)][BF$_4$] have been published previously.[24] Spectroscopic properties of these complexes are compatible with those of other cationic amine complexes of the type [Tp′(CO)(PhC≡CMe)W(NH$_2$CHRR′)]$^+$ (R,R′ = H, alkyl, and aryl).[20,21,24] Protonation increases the frequency of the CO stretch in the IR by 60−80 cm^{-1} relative to the neutral amido complexes. The amine nitrogen hydrogens are diastereotopic due to the chiral metal center, and complexes **4a**, **b**, and **d** (R/R′ = Me/Et, Me/Ph, and H/CHMePh) have a second chiral center at the amine α-carbon. Two diastereomers in a 1:1 ratio are observed in all cases in the NMR. Two-dimensional NMR was required to assign the ^{1}H NMR peaks. The hydrogens on nitrogen are coupled to the hydrogen on the α-carbon with ^3J = 10 Hz, and they are coupled to each other with a two-bond coupling constant of 2.5 Hz.

Table 5. Selected Spectroscopic Data for Azavinylidene Complexes Tp′(CO)(PhC≡CMe)W(N=CRR′) (3a−d)

complex	IR ν_{CO} (cm^{-1}, KBr)	^{1}H NMR[a] (ppm) N=C*R*R′ (R = Me or H)	^{13}C NMR[a] (ppm) *C*O	^{13}C NMR[a] (ppm) N=*C*RR′
3a (Me/Et)[b]	1867	1.52 (1.51)	234.5 (234.3) $^1J_{WC}$ = 158 Hz	138.2 (138.0) $^2J_{WC}$ = 21 Hz
3b (Me/Ph)[c]	1886	*d*	230.6 $^1J_{WC}$ = 157 Hz	151.0 $^2J_{WC}$ = 26 Hz
3c (Ph/Ph)	1894		228.8 $^1J_{WC}$ = 150 Hz	156.8 $^2J_{WC}$ = 27 Hz
3d (H/CHMePh)[e]	1881	6.23 $^3J_{HH}$ = 3 Hz	*f*	*f*

[a] ^{1}H NMR and ^{13}C NMR spectra recorded in CD_2Cl_2. [b] There are two isomers in a 3:1 ratio; data for the minor isomer are given in parentheses. [c] There are two isomers in a 7:1 ratio; data for the minor isomer are given in parentheses. [d] Degenerate with Tp′ methyl groups. [e] There are two diastereomers in a 1:1 ratio; data for the second diastereomer are given in parentheses. [f] The ^{13}C NMR spectrum was not assignable.

Table 6. Selected Spectroscopic Data for Amine Complexes [Tp′(CO)(PhC≡CMe)W(NH$_2$CHRR′)][BAr′$_4$] (4a−d) and Amido Complexes Tp′(CO)(PhC≡CMe)W(NHCHRR′) (1a−d)

		^{1}H NMR[a] (ppm)		^{13}C NMR[a] (ppm)	
complex	IR ν_{CO} (cm^{-1}, KBr)	NH*C*HRR″ or NH$_2$*C*HRR′	NHC*H*RR″ or NH$_2$C*H*RR′	*C*O	NHC*H*RR″ or NH$_2$C*H*RR′
1a (Me/Et)[b]	1847	6.83 (6.70), d, $^3J_{HH}$ = 10 Hz	4.23, m	237.8 (237.9) $^1J_{WC}$ = 168 Hz	69.5 (69.4)
1b (Me/Ph)[b,24]	1846 (1852)	*c*	5.37 (5.56), dq $^3J_{HH}$ = 6.8, 10 (9) Hz	237.4 (237.1) $^1J_{WC}$ = 166 (165) Hz	72.6 (71.5)
1c (Ph/Ph)	1863	6.63 d, $^3J_{HH}$ = 9 Hz	*c*	236.9 $^1J_{WC}$ = 166 Hz	80.8
1d (H/CHMePh)[b]	1847	6.81, m	4.36, m	238.3 (238.2) $^1J_{WC}$ = 168 Hz	73.5 (73.3)
4a (Me/Et)[b]	1928	3.44 (2.75), m 3.35 (1.41), m	2.79 (2.48), m	230.4 (230.1) $^1J_{WC}$ = 152 Hz	60.0 (60.2)
4b (Me/Ph)[b,d,24]	1916 (1903)	3.95, dd, *J* = 13, 9 Hz (3.98, dd, *J* = 13, 6 Hz) 3.15, d, ^2J = 13 Hz (3.40, dd, *J* = 13, 6 Hz)	4.27, dq, *J* = 9, 7 Hz (3.77, m)	229.6 (230.5) $^1J_{WC}$ = 148 (149) Hz	63.7 (63.4)
4c (Ph/Ph)	1923	5.53, dd, *J* = 2.5, 10 Hz 4.48, t, br, *J* = 10 Hz	4.48, t, *J* = 10 Hz	229.3 $^1J_{WC}$ = 149 Hz	72.1
4d (H/CHMePh)[b]	1928	3.36 (2.89), m 2.45 (2.15), m	2.10 (3.20), m	230.3 (229.7) $^1J_{WC}$ = 168 Hz	59.7 (58.7)

[a] ^{1}H NMR and ^{13}C NMR spectra recorded in CD_2Cl_2. [b] There are two diastereomers in a 1:1 ratio; data for the second diastereomer are given in parentheses. [c] Obscured by phenyl peaks. [d] The counterion is BF_4.

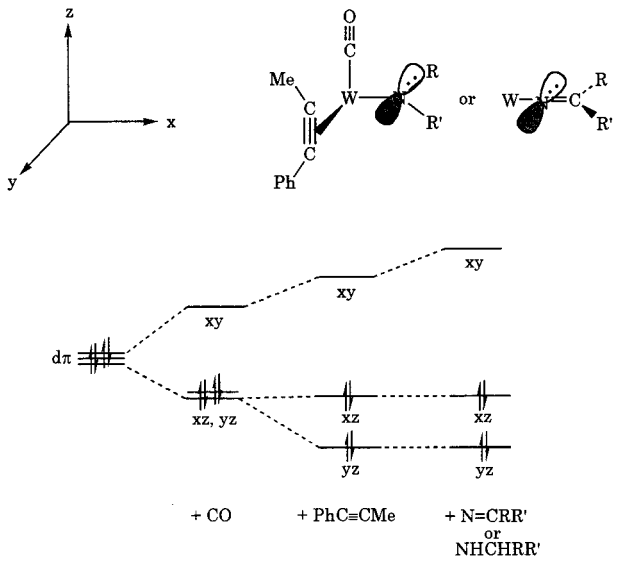

Figure 4. Qualitative molecular orbital scheme for Tp′(CO)(PhC≡CMe)W(NHCHRR′) (**1a**−**d**) and Tp′(CO)(PhC≡CMe)W(N=CRR′) (**3a**−**d**).

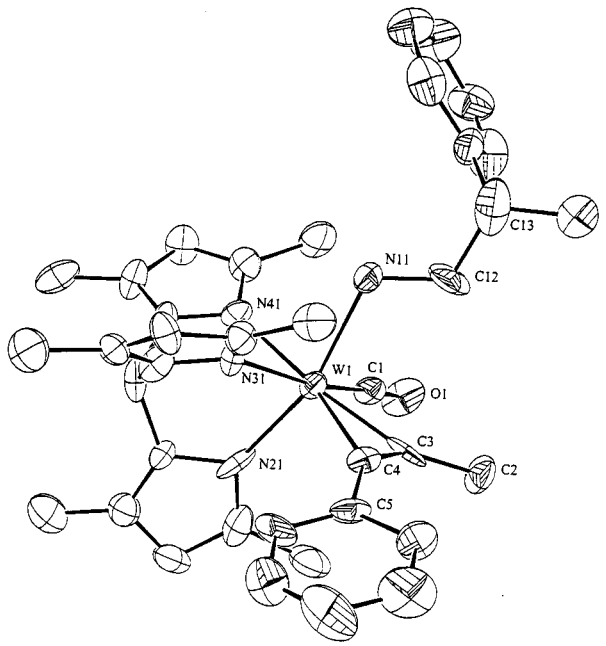

Figure 5. ORTEP diagram of [Tp′(CO)(PhC≡CMe)W(NH$_2$CH$_2$CHMePh)][I$_3$] (**4d**).

The ^{13}C NMR displays the carbonyl carbon resonance near 230 ppm with tungsten coupling of 149−168 Hz. The alkyne carbons are in the range of four-electron donor alkynes, 213−217 ppm. The amine α-carbon is displayed between 58 and 72 ppm for these complexes.

The X-ray crystal structure has been determined for [Tp′(CO)(PhC≡CMe)W(NH$_2$CH$_2$CHMePh)][I$_3$] (**4d**), and the ORTEP is shown in Figure 5. Selected structural data are given in Table 4. The W−N(11) bond distance of 2.226(18) Å is close to the W−N distance of 2.24(1) Å found for (−)-(*RS*)-[Tp′(CO)(PhC≡CMe)W(NH$_2$CHMePh)][BF$_4$].[24] The tungsten−alkyne bond distances of 2.07(3) and 2.03(2) Å are consistent with a four-electron donor alkyne. The N(11)−C(12) amine bond distance of 1.44(3) Å is in the range of other N−C single bonds.

Characterization of Neutral Amido Complexes Tp′(CO)(PhC≡CMe)W(NHCHRR′) (1a−d). Selected spectroscopic data for complexes **1a**−**d** are given in Table 6. Data for Tp′(CO)(PhC≡CMe)W(NHCHMePh) (**1b**) has been published previously.[24] The terminal CO stretch for these complexes ranges from 1847 to 1863 cm^{-1}. Two-dimensional NMR spectroscopy was used to assign the NMR spectra of amido complexes **1a** and **1d**, each of which exists as a 1:1 ratio of diastereomers. In the ^{1}H NMR, the hydrogen bonded to the nitrogen resonates between 6.63 and 6.83 ppm and is split by the hydrogen on the α-carbon with a coupling of 10 Hz.

The ^{13}C NMR spectrum displays the terminal carbonyl carbon near 237 ppm with tungsten coupling of 166−168 Hz. The alkyne carbons are in the range for "three-electron" donor alkynes as was observed for the azavinylidene complexes, resonating between 166 and 172 ppm.

The X-ray crystal structure has been determined for Tp′(CO)(PhC≡CMe)W(NHCHMeEt) **(1a),** and the ORTEP is shown in Figure 6. Selected structural data are given in Table 4. The amido ethyl group is disordered, each with 50% occupancy. The short W−N(2) bond

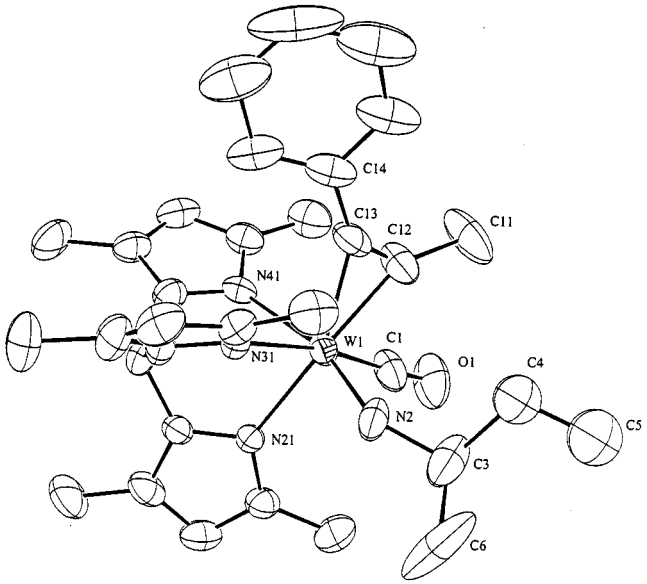

Figure 6. ORTEP diagram of Tp′(CO)(PhC≡CMe)W(NHCHMeEt) (**1a**).

distance of 1.941(10) Å reflects π-donation from the nitrogen to the metal. The alkyne carbon distances of 2.086(11) and 2.082(13) Å are close to the distances found for the azavinylidene complex Tp′(CO)(PhC≡CMe)W(N=CMePh) (**3b**) due to the "three-electron" donor role of the alkyne.

Summary

Oxidation of amido complexes of the type Tp′(CO)(PhC≡CMe)W(NHCHRR′) with I_2, $[Ph_3C][PF_6]$, $AgBF_4$, or $[Cp_2Fe][PF_6]$ forms a mixture of the coordinated imine and amine complexes. Oxidation of Tp′(CO)(PhC≡CMe)W(NHCHMeEt) (**1a**) with I_2 in the presence of weak base suppresses amine formation to cleanly form the coordinated imine complex. Similar results are obtained for **1b** (R/R′ = Me/Ph) and **1c** (R/R′ = Ph/Ph); however, NEt_3 deprotonates the imine complex *in situ* to form the neutral azavinylidene Tp′(CO)(PhC≡CMe)W(N=CRR′) (**3b**,**c**) which can be protonated with $HBAr'_4 \cdot 2OEt_2$ to form the imine complex in high yields. For **1d** (R/R′ = H/CHMePh), NEt_3 does not fully suppress amine formation; however, pure imine complex can be isolated by chromatography on silica gel. Other attempts to synthesize imine complexes in a general way, including addition of free imine to coordinatively-unsaturated metal complexes and condensation of free aldehydes or ketones with the parent amido complex Tp′(CO)(PhC≡CMe)W(NH_2), have been unsuccessful.

Independent synthesis of amine complexes can be achieved by protonation of the appropriate amido complex. Formation of azavinylidene complexes, Tp′(CO)(PhC≡CMe)W(N=CRR′), can be accomplished by deprotonation of imine complexes. The alkyne ligand plays an important role in these reactions, where it serves as a flexible donor of either "three" or "four" electrons, depending on the π-donor properties of the nitrogen ligand.

Experimental Section

Materials and Methods. Reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF), hexanes, and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from P_2O_5. Acetonitrile was distilled from calcium hydride. All other solvents were purged with nitrogen and used without further purification. Benzophenone imine was purchased from Aldrich and was dried over molecular sieves for 24 h prior to use. $NaBAr'_4$ and $HBAr'_4 \cdot 2OEt_2$ (BAr'_4 = tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate) were prepared according to literature procedures.[22] Metal complexes which were used as reagents, Tp′W(CO)(PhC≡CMe)Me, Tp′W(CO)(PhC≡CMe)OTf (OTf = CF_3SO_3), [Tp′$W(CO)_2$(PhC≡CMe)][OTf], and Tp′W(CO)(PhC≡CMe)NHCHMePh (**1b**), were synthesized according to literature procedures.[24] All other reagents were obtained from commercial sources and used without further purification.

^1H NMR and ^{13}C NMR were recorded on a Bruker WM 250 (250 MHz), a Bruker AMX 300 (300 MHz), or a Varian XL 400 (400 MHz) spectrometer. All 2-D NMR were recorded on a Bruker AMX 300 (300 MHz) spectrometer. Infrared spectra were collected on a Mattson Polaris FT-IR spectrometer. Analyses were conducted by Atlantic Microlab of Norcross, GA. Complete spectroscopic data for all complexes are given in the Supporting Information.

Tp′(CO)(PhC≡CMe)W(NHCHMeEt) (1a). A slight modification of the procedure previously reported[24] was used. A solution of [Tp′$W(CO)_2$(PhC≡CMe)][OTf] (2.48 g, 3.1 mmol) in 200 mL of THF was refluxed for 1 h. The formation of Tp′(CO)(PhC≡CMe)W(OTf) by loss of CO was monitored by IR. To this solution was added $NH_2CHMeEt$ (0.95 mL, 9.3 mmol, 3.0 equiv), and heating was continued for 2 days. Solvent removal by rotary evaporation left a dark orange oil. The oil was dissolved in a minimum amount of CH_2Cl_2 and chromatographed on alumina. An orange band was eluted with CH_2Cl_2. The solvent was removed to produce an orange oil, which was recrystallized from CH_2Cl_2/MeOH to produce dark orange crystals in a 54% yield (1.30 g, 1.66 mmol). Anal. Calcd for $C_{29}H_{40}N_7WOB \cdot CH_2Cl_2$: C, 46.07; H, 5.41; N, 12.53. Found: C, 46.72; H, 5.55; N, 12.82.

Tp′(CO)(PhC≡CMe)W(NHCHPh_2) (1c). A solution of [Tp′$W(CO)_2$(PhC≡CMe)][OTf] (4.40 g, 5.49 mmol) in 200 mL of THF was refluxed for 1 h. The formation of Tp′(CO)(PhC≡CMe)W(OTf) by loss of CO was monitored by IR. To this solution were added NH_2CHPh_2 (2.84 mL, 16.5 mmol, 3 equiv) and NEt_3 (1.2 mL, 8.3 mmol, 1.5 equiv), and heating was continued for 2.5 days. The workup procedure was the same as that described for **1a** and resulted in dark orange crystals in a 70% yield (3.11 g, 3.85 mmol). Anal. Calcd for $C_{38}H_{42}N_7WBO$: C, 56.52; H, 5.24; N, 12.14. Found: C, 56.37; H, 5.23; N, 12.23.

Tp′(CO)(PhC≡CMe)W(NHCH_2CHMePh) (1d). A solution of [Tp′$W(CO)_2$(PhC≡CMe)][OTf] (2.71 g, 3.38 mmol) in 200 mL of THF was refluxed for 1 h. The formation of Tp′(CO)(PhC≡CMe)W(OTf) by loss of CO was monitored by IR. To this solution was added $NH_2CH_2CHMePh$ (1.50 mL, 10.1 mmol), and reflux was continued for 2 h. The workup procedure was the same as that described for **1a**. On alumina, the orange product protonates to form a blue band, which elutes in CH_2Cl_2 as an orange solution. Recrystallization from CH_2Cl_2/MeOH resulted in dark orange crystals in a 53% yield (1.35 g, 1.78 mmol). Anal. Calcd for $C_{34}H_{42}N_7WBO$: C, 53.77; H, 5.57; N, 12.91. Found: C, 53.66; H, 5.59; N, 12.90.

[Tp′(CO)(PhC≡CMe)W(NH=CMeEt)][BAr'_4] (2a). To a stirred solution of 0.269 g (0.386 mmol) of Tp′(CO)(PhC≡CMe)W(NHCHMeEt) (**1a**) in 25 mL of CH_2Cl_2 was added 54 μL NEt_3 (0.39 mmol), followed by 101 mg (0.386 mmol) of I_2. A color change from orange to green was observed within 5 min. The solution was stirred for 2 h. A solution of 352 mg (0.398 mmol) of $NaBAr'_4$ in 5 mL of Et_2O was then added. Formation of a white precipitate (NaI) was observed. The green solution was filtered away from the white solid, and solvent was removed *in vacuo*. Chromatography on alumina yielded a blue band, which eluted with a progression from 50/50 CH_2Cl_2/

hexanes to pure CH_2Cl_2. Recrystallization from CH_2Cl_2 and hexanes produced dark blue crystals in a 74% yield (0.446 g, 0.286 mmol. The equilibrium ratio of the isomers was determined to be 2.5:1 by heating a NMR sample of complex **2a** in C_6H_5Br-d_5 at 75 °C for several days. Anal. Calcd for $C_{61}H_{51}N_7WB_2F_{24}O$: C, 46.98; H, 3.29; N, 6.29. Found: C, 47.07; H, 3.35; N, 6.33.

[Tp′(CO)(PhC≡CMe)W(NH═CMePh)][BAr′$_4$] (2b).[28] To a stirred solution of 103 mg (0.139 mmol) of Tp′(CO)-(PhC≡CMe)W(N═CMePh) (**3b**) in 10 mL of CH_2Cl_2 was added 140 mg (0.14 mmol) of HBAr′$_4$·2Et$_2$O in 5 mL of CH_2Cl_2 at 0 °C. An immediate color change from orange to green was observed. The solvent was removed *in vacuo,* and the green residue was recrystallized from CH_2Cl_2/hexanes, producing green crystals in an 87% yield (192 mg, 0.119 mmol). Low-temperature NMR indicated two isomers in an 8:1 ratio. Anal. Calcd for $C_{65}H_{51}N_7WB_2F_{24}O$: C, 48.56; H, 3.20; N, 6.10. Found: C, 48.53; H, 3.25; N, 6.17.

[Tp′(CO)(PhC≡CMe)W(NH═CPh$_2$)][BAr′$_4$] (2c).[28] A solution of Tp′(CO)(PhC≡CMe)W(N═CPh$_2$) (**3c**) (112 mg, 0.139 mmol) in 15 mL of CH_2Cl_2 at 0 °C was stirred during the addition of 142 mg (0.140 mmol) of HBAr′$_4$·2Et$_2$O in 5 mL of CH_2Cl_2. A color change from orange to green occurred immediately. The solvent was removed *in vacuo* to leave a green oil. Recrystallization from CH_2Cl_2/hexanes produced green crystals in a 90% yield (210 mg, 0.126 mmol). Anal. Calcd for $C_{70}H_{53}N_7WB_2F_{24}O$: C, 50.35; H, 3.20; N, 5.87. Found: C, 50.23; H, 3.21; N, 5.93.

[Tp′(CO)(PhC≡CMe)W(NH═CHCHMePh)][BAr′$_4$] (2d). To a stirred solution of 0.390 g (0.513 mmol) of Tp′(CO)-(PhC≡CMe)W(NHCH$_2$CHMePh) (**1d**) in 30 mL of CH_2Cl_2 was added 72 μL of NEt$_3$ (0.51 mmol), followed by 132 mg (0.520 mmol) of I_2. A color change from orange to teal blue was observed within 5 min. The solution was stirred for 2 h. A solution of 460 mg (0.520 mmol) of NaBAr′$_4$ in 5 mL of Et$_2$O was then added. Formation of a white precipitate (NaI) was observed. The teal solution was filtered away from the white solid, and solvent was removed *in vacuo.* Chromatography on silica twice yielded a blue band, which eluted with a progression from 50/50 CH_2Cl_2/hexanes to pure CH_2Cl_2. A blue solid was isolated in a 30% yield (0.249 g, 0.153 mmol). Anal. Calcd for $C_{66}H_{53}N_7WB_2F_{24}O$: C, 48.88; H, 3.29; N, 6.05. Found: C, 48.77; H, 3.33; N, 6.03.

Tp′(CO)(PhC≡CMe)W(N═CMeEt) (3a). A solution of 167 mg (0.107 mmol) of [Tp′(CO)(PhC≡CMe)W(NH═CMeEt)]-[BAr′$_4$] (**2a**) in 25 mL of THF was prepared. This solution was added via cannula to a large excess of KH that had been washed with 2 × 20 mL of hexanes. A color change from blue to orange was observed over a period of 10 min. The orange solution was filtered and dried to an orange oil. Upon dissolution in hexanes, a white precipitate formed. The orange solution was filtered away, and then it was dried *in vacuo* to form an orange solid, which was isolated in a yield of 95% (71 mg, 0.10 mmol). Anal. Calcd for $C_{29}H_{38}N_7WBO$: C, 50.09; H, 5.51; N, 14.10. Found: C, 50.14; H, 5.93; N, 13.04.

Tp′(CO)(PhC≡CMe)W(N═CMePh) (3b). To a solution of 120 mg (0.16 mmol) of Tp′(CO)(PhC≡CMe)W(NHCHMePh) (**1b**) in 25 mL of CH_3CN was added 22 μL (0.16 mmol) of NEt$_3$, followed by 41 mg (0.16 mmol) of I_2. A color change from orange to green was observed. Another equivalent of NEt$_3$ was added, and the solution turned yellow. Solvent was removed *in vacuo* to leave a gold oil. An orange band was eluted from an alumina column with a 50/50 mixture of CH_2Cl_2 and hexanes. The solvent was removed *in vacuo* to produce a bright orange solid in a 92% yield (110 mg, 0.15 mmol). Anal. Calcd for $C_{33}H_{38}N_7WBO$: C, 53.40; H, 5.15; N, 13.19. Found: C, 53.44; H, 5.20; N, 13.22.

(28) Experimental procedures and spectroscopic data for this complex with [I$_3$] and [BF$_4$] counterions are given in the Supporting Information. [Tp′(CO)(PhC≡CMe)W(NH═CMePh)][I$_3$] was first synthesized by Dr. Stacy A. O'Reilly in our group.

Tp′(CO)(PhC≡CMe)W(N═CPh$_2$) (3c). Method A. To a stirred solution of Tp′(CO)(PhC≡CMe)W(CH$_3$) (253 mg, 0.395 mmol) in 20 mL of CH_2Cl_2 was added 404 mg (0.399 mmol) of HBAr′$_4$·2Et$_2$O at −78 °C. A color change from teal to bright blue was observed. To this solution was added NH═CPh$_2$ (150 μL, 0.89 mmol), and a color change to brown was observed within 5 min. The solution was allowed to warm to room temperature, and the solvent was removed *in vacuo* to give a green and purple oil. Chromatography on alumina yielded an orange band, which eluted with a 50/50 mixture of CH_2Cl_2 and hexanes. A purple band which was eluted with CH_2Cl_2 was also collected, and it was the corresponding hydrolysis product Tp′(CO)(PhC≡CMe)W(η^1-O═CPh$_2$][BAr′$_4$] (**5**). Recrystallization of the orange band from THF and hexanes produced orange crystals in a 39% yield (123 mg, 0.153 mmol).

Method B. To a stirring solution of 366 mg (0.453 mmol) of Tp′(CO)(PhC≡CMe)W(NHCHPh$_2$) (**1c**) in 40 mL of acetonitrile was added 65 μL (0.45 mmol) of NEt$_3$, followed by 119 mg (0.455 mmol) of I_2 under positive nitrogen pressure. A color change from orange to brown was observed within 5 min. Addition of another equivalent of NEt$_3$ turned the solution bright orange. The solvent was removed *in vacuo* leave to an orange-brown oil. Chromatography on alumina yielded an orange band, which was eluted with a 50/50 mixture of CH_2Cl_2 and hexanes. The solvent was removed *in vacuo* to produce a bright orange solid in a 59% yield (215 mg, 0.267 mmol). Anal. Calcd for $C_{38}H_{40}N_7WBO$·Et$_2$O: C, 57.35; H, 5.73; N, 11.15. Found: C, 56.96; H, 5.65; N, 11.12.

Tp′(CO)(PhC≡CMe)W(N═CHCHMePh) (3d). A solution of 198 mg (0.122 mmol) of [Tp′(CO)(PhC≡CMe)W(NH═CHC-HMePh)][BAr′$_4$] (**2d**) in 20 mL of THF was prepared. This solution was added via cannula to a large excess of KH that had been washed with 2 × 20 mL of hexanes. A color change from blue to orange was observed over a period of 10 min. The orange solution was filtered and dried to an orange oil. Upon dissolution in hexanes, a white precipitate formed. The orange solution was filtered away, and then it was dried *in vacuo* to form an orange oil. The product was chromatographed on alumina and eluted as an orange band with a 50/50 mixture of CH_2Cl_2/hexanes. Isolation of a dark orange solid was achieved after recrystallization from THF and hexanes in a 60% yield (61 mg, 0.07 mmol). Anal. Calcd for $C_{34}H_{40}N_7$-WBO·THF: C, 55.02; H, 5.83; N, 11.82. Found: C, 54.53; H, 5.70; N, 11.63.

[Tp′(CO)(PhC≡CMe)W(NH$_2$CHMeEt)][BAr′$_4$] (4a). To a solution of 81 mg (0.12 mmol) of Tp′(CO)(PhC≡CMe)W-(NHCHMeEt) (**1a**) in 10 mL of CH_2Cl_2 was added 118 mg (0.116 mmol) of HBAr′$_4$·2Et$_2$O in 5 mL of CH_2Cl_2 at 0 °C. An immediate color change from orange to dark blue was observed. The solvent was removed *in vacuo* to leave a blue oil. Recrystallization from CH_2Cl_2/hexanes produced ink-blue crystals in a 65% yield (118 mg, 0.076 mmol). Anal. Calcd for $C_{61}H_{53}N_7WB_2F_{24}O$: C, 46.92; H, 3.42; N, 6.28. Found: C, 47.00; H, 3.47; N, 6.34.

[Tp′(CO)(PhC≡CMe)W(NH$_2$CHPh$_2$)][BAr′$_4$] (4c). To a solution of 101 mg (0.125 mmol) of Tp′(CO)(PhC≡CMe)W-(NHCHPh$_2$) (**1c**) in 10 mL of CH_2Cl_2 was added 130 mg (0.13 mmol) of HBAr′$_4$·2Et$_2$O in 5 mL of CH_2Cl_2 at 0 °C. An immediate color change from orange to dark blue was observed. The solvent was removed *in vacuo* to leave a blue oil. Recrystallization from CH_2Cl_2/hexanes produced ink-blue crystals in a 70% yield (145 mg, 0.087 mmol). Anal. Calcd for $C_{70}H_{55}N_7WB_2F_{24}O$: C, 50.29; H, 3.32; N, 5.86. Found: C, 50.07; H, 3.50; N, 5.75.

[Tp′(CO)(PhC≡CMe)W(NH$_2$CH$_2$CHMePh)][BAr′$_4$] (4d). To a solution of 89 mg (0.117 mmol) of Tp′(CO)(PhC≡CMe)W-(NHCH$_2$CHMePh) (**1d**) in 10 mL of CH_2Cl_2 was added 119 mg (0.117 mmol) of HBAr′$_4$·2Et$_2$O in 5 mL of CH_2Cl_2 at 0 °C. An immediate color change from orange to dark blue was observed. The solvent was removed *in vacuo* to leave a blue oil. Recrystallization from CH_2Cl_2/hexanes produced ink-blue crystals in a 54% yield (102 mg, 0.063 mmol). Anal. Calcd

for $C_{66}H_{55}N_7WB_2F_{24}O$: C, 48.82; H, 3.41; N, 6.04. Found: C, 48.87; H, 3.47; N, 6.04.

[Tp′(CO)(PhC≡CMe)W(η^1-O=CPh$_2$][BAr′$_4$] (5). To a stirred solution of Tp′(CO)(PhC≡CMe)W(CH_3) (150 mg, 0.234 mmol) in 20 mL of CH_2Cl_2 was added 242 mg (0.239 mmol) of HBAr′$_4$·2Et$_2$O at −78 °C. A color change from purple to blue was observed. To this solution was added O=CPh$_2$ (146 mg, 0.801 mmol, 3.42 equiv) with positive nitrogen flow, and a color change to bright purple was observed within 5 min. The solution was allowed to warm to room temperature, and the solvent was reduced *in vacuo* to ∼3 mL. Addition of 40 mL of hexanes resulted in the precipitation of a purple solid. The colorless supernatant was filtered away, and the product was washed with an additional 20 mL of hexanes. Recrystallization from CH_2Cl_2 and hexanes formed dark purple crystals in a 75% yield (294 mg, 0.176 mmol): IR (KBr) $\nu_{C\equiv O} = 1952$ cm^{-1}; selected $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm) 205.4, 202.7, 201.1 (C≡*C*Ph, C≡*C*Me, O=*C*Ph$_2$). Anal. Calcd for $C_{70}H_{52}N_6WB_2O_2F_{24}$: C, 50.32; H, 3.14; N, 5.03. Found: C, 50.33; H, 3.20; N, 5.09.

X-ray Structure Data Collection: Each crystal was mounted on a glass wand and coated with epoxy. Diffraction data were collected on a Rigaku automated diffractometer. Hydrogens were placed in calculated positions and all other atoms were refined anisotropically. Details are presented in Table 3.

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Supporting Information Available: Listings of anisotropic thermal factors, complete bond distances and angles, and atomic positional parameters and labeled figures for **1a**, **2a**, **3b**, and **4d**, as well as complete IR and NMR data for all complexes (39 pages). Ordering information is given on any current masthead page.

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