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Synthesis and Reactivity of [Tp′(CO)(PhC≡CMe)W═NPh]$^+$ (Tp′ = Hydridotris(3,5-dimethylpyrazolyl)borate)

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The tungsten(IV) nitrene complex [Tp′(CO)(PhC≡CMe)W═NPh]$^+$ (cation of **1**; Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) has been prepared by oxidation of the amido complex Tp′(CO)(PhC≡CMe)W(NHPh) (**2**) with elemental iodine in the presence of triethylamine. Oxidation in the absence of base also forms the aniline complex [Tp′(CO)(PhC≡CMe)W($\mathrm{NH_2Ph}$)]$^+$ (**3**), which has been independently synthesized. Reaction of **1** with 1 equiv of $\mathrm{KBH_4}$ adds hydride to the nitrene ligand to give the amido complex **2**. Reaction of **1** with Li[$\mathrm{HBEt_3}$] forms the formyl adduct Tp′(NPh)(PhC≡CMe)W(η^1-C(O)H) (**4**) as an intermediate, which ultimately yields the hydride complex Tp′(NPh)(PhC≡CMe)W(H) (**5**) with loss of CO. The hydride complex is also formed from reaction of **1** with 10 equiv of $\mathrm{KBH_4}$. Addition of acid to the hydride complex **5** protonates the nitrene nitrogen to form [Tp′(H)(PhC≡CMe)W(NHPh)][$\mathrm{BAr'_4}$] (**6**). Both **5** and **6** exhibit surprisingly low-field hydride resonances in the ^{1}H NMR (13.5 and 20.6 ppm, respectively). Addition of methylmagnesium bromide to the nitrene complex leads to the methyl acyl intermediate Tp′(NPh)(PhC≡CMe)W(η^1-C(O)Me) (**7**), which readily adds a proton and cyclizes to [Tp′(NHPh)$\overline{\mathrm{W(C(Ph)C(Me)C(O)}}$-Me][$\mathrm{BAr'_4}$] (**8**). Reaction of **1** with phenyllithium forms the phenyl acyl complex Tp′(NPh)(PhC≡CMe)W(η^1-C(O)Ph) (**9**). X-ray crystal structures have been determined for **1** and **8**. The ring in complex **8** exhibits a structure similar to a folded envelope, with the flap containing the $\mathrm{C_\alpha}$, W, and O atoms. The ring is bonded in an η^4 fashion to the metal center.

Introduction

Many transition-metal nitrene (or imido) complexes are high-oxidation-state compounds with fairly unreactive nitrene units (M═NR),[1] but reactive nitrene adducts are proposed as intermediates in several important reactions.[2−4] Nitrene ligands exhibit two geometries: linear and bent. The ligand can bend to localize one lone pair on nitrogen in order to minimize donation of the lone pair to the metal center. This makes the nitrene a 2-electron donor in the neutral counting formalism. When linear, the nitrene fragment is aligned to allow π overlap of both nitrogen perpendicular p orbitals with d orbitals at the metal center, and this corresponds to 4-electron donation in the neutral formalism. There are examples, however, of tantalum[5] and osmium[6] complexes with linear nitrene units in which counting the lone pair on nitrogen would formally result in a 20-electron complex. Delocalization of π-donor ligand electrons is highly variable, and electron counting is more complex than for π-acid ligands.[7]

Nucleophilic reactivity at nitrogen, while more prevalent for bent nitrenes, has been observed for both bonding modes.[8−10] Nucleophilic nitrenes of zirconium have been used as reagents for the hydroamination of alkynes[11] and in imine−azide metathesis reactions.[12] Tantalum and chromium complexes with nucleophilic nitrene fragments react with free aldehydes and ketones to form organic imines.[13] Increased nucleophilicity of the bent nitrene is observed for the molybdenum species $\mathrm{Mo(NPh)_2(Et_2dtc)_2}$ ($\mathrm{Et_2dtc}$ = *N*,*N*′-diethyldithiocarbamate), containing one linear and one bent nitrene unit. Acid selectively protonates only one of the nitrene ligands, presumably the bent nitrene.[14,15]

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Nitrenes that exhibit electrophilic behavior at nitrogen are rare relative to nucleophilic nitrenes, and they are generally bound to electron-deficient metal centers.[16] Many electrophilic nitrene complexes can be trapped by phosphines. The heteroatom-stabilized electrophilic nitrene in $(CO)_4W({=}NNMe_2)$ adds (diphenylphosphino)methane to form a metallacyclic phosphinimine.[17] The putative electrophilic nitrene intermediate formed from the reaction of *fac*-$Mo(PPh_3)(CO)_3(MeCN)_2$ with 8-azidoquinoline reacts with triphenylphosphine.[18] Ambiphilic character has been observed for the nitrene in $(CO)_5W({=}NPh)$, which forms the phosphinimine ylide $[(CO)_5W(N(PPh_3)(Ph)]$[19] upon reaction with triphenylphosphine and also reacts with a variety of aldehydes, ketones, and thioketones to form imines.[20]

The role of electrophilic nitrenes as nitrene transfer reagents is an important aspect of their reactivity. Amination of olefins is believed to proceed through four-membered metallacyclic intermediates formed from a [2 + 2] addition reaction. β-Amino alcohols form from transfer of a nitrene and an oxo unit from $Os(O)_3(N^tBu)$ to olefins, while selective transfer of both nitrene units from $Os(O)_2(N^tBu)_2$ forms 1,2-diamines.[21] Many nitrene fragments have been shown to transfer to phosphine to produce free phosphine imides.[22] Stoichiometric transfer of (*p*-tolylsulfonyl)nitrene (NTs) to phosphine has been observed from $Mo(O)(Et_2dtc)_2(NTs)$. For $Mo(Et_2dtc)_2(NTs)_2$, catalytic nitrene transfer to PPh_2Me has been accomplished using Ph_3SbNTs or (PhMeS)NTs as nitrene sources.[23] Copper catalysts[24] and iron and manganese porphyrin systems[25] have been effective for aziridination of olefins using PhI═NTs as a nitrene source. The existence of a Cu(diimine)(NTs) intermediate has been confirmed by Jacobsen and co-workers.[26] Enantioselective aziridination of styrene has been achieved using a copper catalyst with chiral bis(oxazoline) species[27] or benzylidene derivatives of 1,2-diaminocyclohexane as ligands.[28]

While nitrene complexes that contain an ancillary two-electron-donor alkyne[29] or carbon monoxide[29a,30] ligand in the coordination sphere are common, examples of well-characterized, electrophilic complexes with two such π-acids are rare. Schrock and co-workers have isolated the rhenium bis(alkyne) complex $Re(NAr)(RC{\equiv}CR)_2Cl$ ($Ar = 2{,}6\text{-}C_6H_3\text{-}{}^iPr_2$, $R = Me_3CCH_2$) with a bent nitrene unit which exhibits nucleophilic behavior.[31] $Tp'W(CO)_2(NHR)$ is a precursor to both anionic ($R = Ph, CH_2Ph, H$) and cationic ($R = Ts, {}^tBu, Ph, {}^nBu, CH_2Ph, H, CPh_3$) nitrene complexes (Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate).[22c,24c,32] Anionic nitrene complexes $[Tp'W(CO)_2(NR)]^-$ can be synthesized by deprotonation of the appropriate amido complex with ^tBuLi or LDA, and these anions are susceptible to protonation or alkylation at nitrogen. Cationic nitrene adducts $[Tp'W(CO)_2(NR)]^+$ are prepared by the reaction of the amido complex with $[Ph_3C][PF_6]$. For Ts, Ph, and ^tBu derivatives, iodine can also be used as an oxidant to form nitrene ligands. These cationic nitrene complexes are characterized by an electron-deficient metal center. Addition of $LiBH_4$ to $[Tp'W(CO)_2(NR)]^+$ ($R = Ts, Ph, {}^tBu$)[24c,32b] forms the amido complex through net hydride addition to the nitrene nitrogen via a formyl intermediate.[32c]

In this paper we report the synthesis and characterization of an electron-deficient nitrene complex that exhibits electrophilic reactivity at both the nitrene nitrogen and the carbonyl carbon. $[Tp'(CO)(PhC{\equiv}CMe)W{=}NPh][BAr'_4]$ is formed in high yields from oxidation of the amido complex $Tp'(CO)(PhC{\equiv}CMe)W(NHPh)$ with iodine in the presence of triethylamine. Formation of the amido complex by hydride addition to the nitrene fragment is presented, and reactivity of the carbonyl ligand to add nucleophiles is also discussed.

Results and Discussion

Synthesis and Characterization of $[Tp'(CO)(PhC{\equiv}CMe)W{=}NPh]^+$ (Cation of 1), $Tp'(CO)(PhC{\equiv}$

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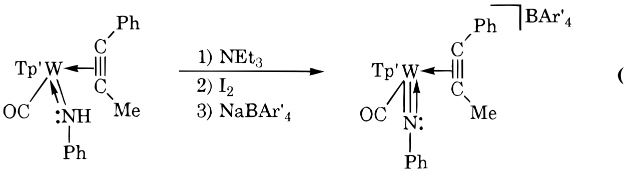
Table 1. Selected Spectroscopic Data for $[Tp'(CO)(PhC{\equiv}CMe)W{=}NPh][BAr'_4]$ (1), $Tp'(CO)(PhC{\equiv}CMe)W(NHPh)$ (2), and $[Tp'(CO)(PhC{\equiv}CMe)W(NH_2Ph)][BAr'_4]$ (3)

		^{1}H NMR[a] (ppm)		^{13}C NMR[a] (ppm)		
complex	IR ν_{CO} (cm^{-1}, KBr)	NH_xPh[b]	PhC≡C*Me*	*C*O	*ipso* NH$_x$*Ph*[b]	PhC_1≡C_2Me
1	2087		3.67	205.2 ($^1J_{W-C}$ = 122 Hz)	154.9 ($^2J_{W-C}$ = 32 Hz)	C_1 = 138.0, C_2 = 141.1
2	1859	7.83 (br)	3.48	238.2 ($^1J_{W-C}$ = 160 Hz)	158.8	C_1 = 181.3, C_2 = 178.3
3	1927	5.44, 4.75 (d, $^2J_{H-H}$ = 13 Hz)	3.10	229.3 ($^1J_{W-C}$ = 150 Hz)	143.3	C_1 = 214.9, C_2 = 216.4

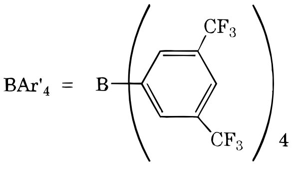
[a] ^{1}H NMR and ^{13}C NMR spectra recorded in CD_2Cl_2. [b] $x = 0-2$.

CMe)W(NHPh) (2), and [Tp′(CO)(PhC≡CMe)W-(NH$_2$Ph)]$^+$ (Cation of 3). The nitrene complex $[Tp'(CO)(PhC{\equiv}CMe)W{=}NPh][BAr'_4]$ (**1**) was synthesized by oxidation of the amido complex Tp′(CO)(PhC≡CMe)W-(NHPh) (**2**) with 1 equiv of iodine in the presence of triethylamine (eq 1). A color change from purple to orange was observed. The net reaction corresponds to removal of hydride from the neutral amido ligand of complex **2**, but the reaction can be better visualized as removal of two electrons by oxidation with iodine and removal of a proton with triethylamine. Counterion exchange of $[BAr'_4]^-$ for $[I]^-$ (BAr′$_4$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate)[33] 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/pentane gave air-stable, dark orange crystals of **1** in 79% yield. Counterion exchange was necessary in order to obtain pure material by chromatography and recrystallization procedures. Similar oxidations of amido complexes containing a β-hydrogen form coordinated imine complexes of the type $[Tp'(CO)(PhC{\equiv}CMe)W(NH{=}CRR')]^+$.[34a]



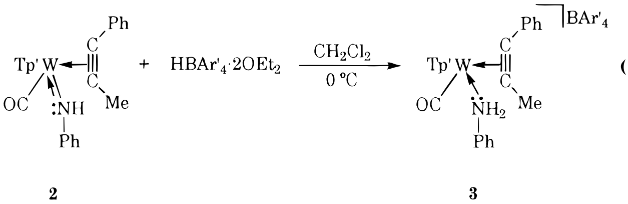
(1)

2 **1**



Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate

Oxidation in the absence of base forms the nitrene complex in a 1:1 ratio with the aniline adduct $[Tp'(CO)(PhC{\equiv}CMe)W(NH_2Ph)]^+$ (cation of **3**). The aniline complex can be synthesized independently by protonation of the amido complex **2** with $HBAr'_4{\cdot}2OEt_2$ in CH_2Cl_2 at 0 °C (eq 2) to produce ink blue crystals of **3** in 61% yield following chromatography and recrystallization from CH_2Cl_2/hexanes.



(2)

2 **3**

The amido complex Tp′(CO)(PhC≡CMe)W(NHPh) (**2**) was prepared according to a literature procedure.[34b] Following chromatography and recrystallization from CH_2Cl_2/MeOH, purple crystals of **2** are isolated in 79% yield.

All complexes have been characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Selected spectroscopic data for complexes **1**−**3** are given in Table 1. The nitrene complex $[Tp'(CO)(PhC{\equiv}CMe)W{=}NPh][BAr'_4]$ (**1**) is characterized by a high-frequency CO stretch at 2087 cm^{-1} in the IR, an increase of approximately 230 cm^{-1} relative to the precursor amido complex, reflecting the decrease in electron density upon oxidation of the metal center. The average frequency of the two carbonyl ligands in $[Tp'W(CO)_2(NPh)]^+$ is 2042 cm^{-1}; thus, the frequency of 2087 cm^{-1} observed here suggests that substitution of an alkyne for one CO ligand actually decreases the electron density at the metal relative to $[Tp'W(CO)_2(NPh)]^+$. The ^{13}C NMR displays a terminal CO resonance at 205 ppm with tungsten coupling of 122 Hz. The *ipso* carbon of the NPh ligand resonates at 155 ppm with two-bond tungsten coupling of 32 Hz, indicative of sp hybridization at nitrogen.[29b,32,35] The nitrene fragment donates four electrons to the metal center in the neutral counting formalism and six electrons as the NPh^{2-} dianion. The alkyne carbons resonate near 141 and 138 ppm in the ^{13}C NMR.

The amido complex Tp′(CO)(PhC≡CMe)W(NHPh) (**2**) is characterized by a CO stretch at 1859 cm^{-1}. The ^{1}H NMR displays a singlet for the amido proton at 7.8 ppm that is broad due to the adjacent quadrupolar nitrogen. The terminal CO resonates at 238 ppm in the ^{13}C NMR with tungsten coupling of 160 Hz. The alkyne carbons appear at 181 and 178 ppm, indicative of a “three-electron” donor alkyne; the alkyne $\pi_\perp$ orbital competes with the filled nitrogen p orbital for donation into the lone vacant metal dπ orbital in this complex.

The CO stretch at 1927 cm^{-1} for $[Tp'(CO)(PhC{\equiv}CMe)W(NH_2Ph)][BAr'_4]$ (**3**) is compatible with other complexes of this type.[34,36] The amine hydrogens are diastereotopic due to the chiral metal center, and they resonate as doublets at 5.4 and 4.8 ppm with a geminal coupling constant of 13 Hz. In the ^{13}C NMR, the CO resonates at 229 ppm with tungsten coupling of 150 Hz. The alkyne carbons appear at 216 and 215 ppm, in the range for a four-electron-donor alkyne.[37]

X-ray Structure for [Tp′(CO)(PhC≡CMe)W=NPh]-[BAr′$_4$] (1). An ORTEP diagram of **1** is shown in Figure 1. Selected bond distances and angles are given in Table 2, and data collection parameters are shown in

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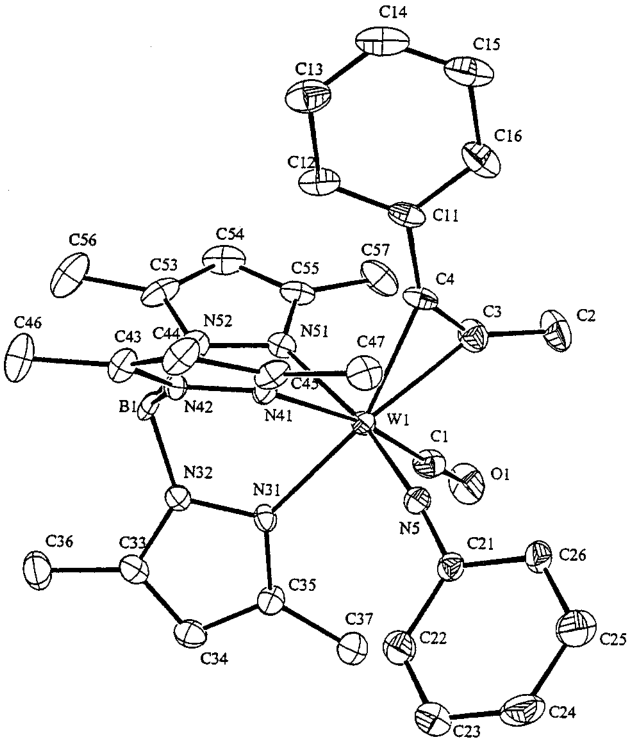


Figure 1. ORTEP diagram of [Tp′(CO)(PhC≡CMe)W=NPh][BAr′$_4$] (**1**).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for [Tp′(CO)(PhC≡CMe)W=NPh][BAr′$_4$] (1)

W(1)−C(1)	2.049(20)	C(2)−C(3)	1.50(3)
W(1)−C(3)	2.180(20)	C(4)−C(11)	1.451(24)
W(1)−C(4)	2.137(17)	C(1)−O(1)	1.16(3)
W(1)−N(5)	1.789(14)	W(1)−N(51)	2.258(14)
N(5)−C(21)	1.371(21)	W(1)−N(41)	2.193(14)
C(3)−C(4)	1.29(3)	W(1)−N(31)	2.225(13)

W(1)−N(5)−C(21)	174.0(12)	W(1)−C(3)−C(2)	143.3(15)
W(1)−C(1)−O(1)	178.0(17)	W(1)−C(3)−C(4)	70.8(12)
C(1)−W(1)−C(3)	71.7(8)	W(1)−C(4)−C(3)	74.5(12)
C(1)−W(1)−C(4)	104.7(7)	W(1)−C(4)−C(11)	143.0(13)
C(1)−W(1)−N(5)	93.4(7)	C(3)−W(1)−N(51)	93.2(6)
C(3)−W(1)−C(4)	34.6(7)	C(3)−W(1)−N(41)	18.9(6)
C(3)−W(1)−N(5)	96.6(7)	C(3)−W(1)−N(31)	156.9(6)
C(4)−W(1)−N(5)	105.2(5)	C(3)−C(4)−C(11)	142.1(18)
N(5)−W(1)−C(3)	96.6(7)	C(4)−W(1)−N(51)	83.3(6)
N(5)−W(1)−C(4)	105.2(6)	C(4)−W(1)−N(41)	85.1(6)
C(2)−C(3)−C(4)	145.7(19)	C(4)−W(1)−N(31)	158.9(6)
N(5)−C(21)−C(22)	121.5(16)	N(5)−C(21)−C(26)	118.6(15)

Table 3. The Tp′ ligand occupies three facial coordination sites of this octahedral complex. The alkyne ligand lies parallel to the metal carbonyl axis, allowing both of these π-acid ligands to accept back-bonding from the lone filled d_{yz} orbital on tungsten. The alkyne $\pi_{\perp}$ orbital competes with one of the filled nitrogen p orbitals for donation into the vacant metal d_{xy} orbital. The second filled p orbital on nitrogen donates into the metal d_{xz} orbital. A schematic of the metal-ligand π interactions for **1** is shown in Figure 2.

Long W−C bond distances of 2.180 and 2.137 Å indicate that the alkyne ligand is effectively limited to a two-electron-donor role, consistent with the upfield alkyne carbon resonances observed in the ^{13}C NMR.[28b,c,e] The W−N distance of 1.789(14) Å is consistent with a strong tungsten−nitrogen multiple bond[8a,29,32a,38] (cf. the W−N distance of 1.770(14) Å found for the linear four-electron-donor nitrene in [WCl$_2$(NPh)(PhC≡CPh)(PMe$_3$)$_2$][29b]). The shortening of the W−N bond relative to amido complexes of this type (ca. 0.2 Å) may explain the decreased bond order of the metal−alkyne interaction.[34a] Consistent with the tungsten coupling observed in the ^{13}C NMR, the nitrene fragment is nearly linear with a W−N(5)−C(21) bond angle of 174.0(12)°.

Table 3. Crystallographic Data Collection Parameters for [Tp′(CO)(PhC≡CMe)W=NPh)][BAr′$_4$] (1) and [Tp′(NHPh)W(C(Ph)C(Me)C(O)Me)][BAr′4] (8)

	Crystal Data	
complex	**1**	**8**
mol formula	$WC_{63}H_{47}N_7B_2F_{24}O$	$WC_{64}H_{50}N_7B_2F_{24}O$
fw	1579.53	1594.56
cryst dimens, mm	0.35 × 0.35 × 0.30	0.50 × 0.35 × 0.10
space group	*C*2/*c*	$P\bar{1}$
Cell parameters		
a, Å	37.4856(19)	13.4669(19)
b, Å	10.1207(3)	16.3744(24)
c, Å	35.5258(22)	16.9962(23)
α, deg		89.717(13)
β, deg	94.737(6)	76.429(13)
γ, deg		66.321(12)
V, Å^3	13407(11)	3319.7(8)
Z	8	2
calcd density, Mg/m^3	1.565	1.595
	Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
monochromator	graphite	graphite
linear abs coeff, mm^{-1}	1.87	1.89
scan type	ω	ω
2θ limit, deg	46	50
h,*k*,*l* ranges	−41 to +40, 0−11, 0−39	−14 to +16, 0−19, −20 to +20
total no. of rflns	9321	11 687
no. of data with $I > 2.5\sigma(I)$	6959	8811
R, %	4.8	6.8
R_w, %	5.9	8.3
GOF	1.86	2.37
no. of params	884	892
Maximum shift/esd	0.056	0.003

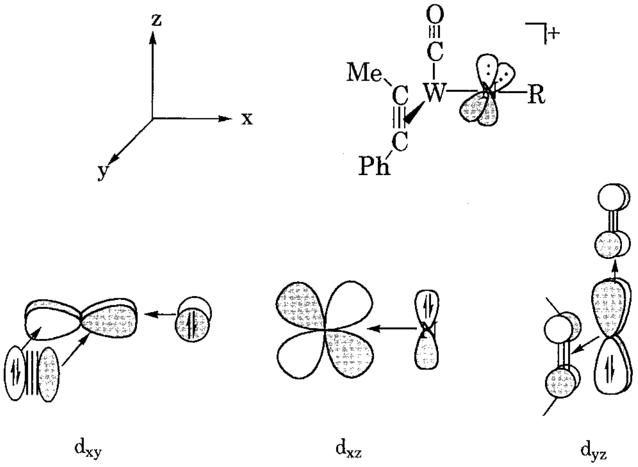
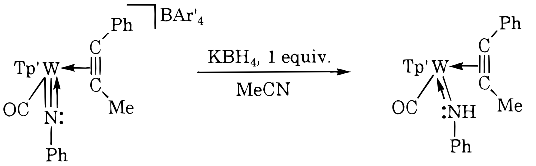


Figure 2. Schematic drawing of the metal dπ–ligand orbital interactions for [Tp′(CO)(PhC≡CMe)W=NPh][BAr′$_4$] (**1**).

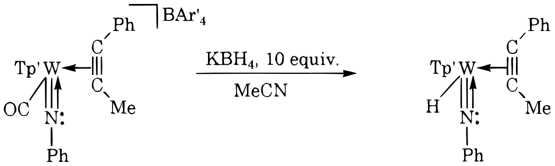
Reaction of [Tp′(CO)(PhC≡CMe)W=NPh][BAr′$_4$] (1) with KBH$_4$. The electrophilicity of the nitrene complex is confirmed by the addition of hydride to complex **1** to form the amido complex Tp′(CO)(PhC≡CMe)W(NHPh) (**2**). An acetonitrile solution of **1** added to 1 equiv of KBH$_4$ at room temperature forms **2** in high yields as monitored by NMR (eq 3). The isolated yield is 61%.



(3)

1 2

Addition of a large excess of KBH$_4$ to [Tp′(CO)(PhC≡CMe)W=NPh][BAr′$_4$] (**1**) in acetonitrile at room temperature leads to precipitation of a yellow, air-stable solid (eq 4). This product was identified by NMR as the hydride complex Tp′(NPh)(PhC≡CMe)W(H) (**5**). Recrystallization from CH$_2$Cl$_2$/hexanes allows isolation of **5** in 68% yield.

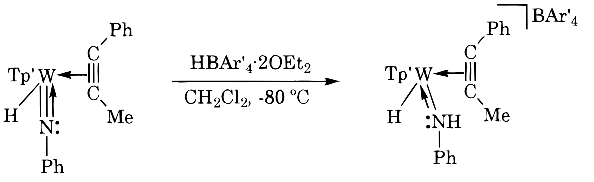


(4)

1 5

In the ^{1}H NMR, the hydride peak appears at 13.5 ppm with one-bond tungsten coupling of 106 Hz. Hydride shifts downfield of 10 ppm are rare, and an explanation for their unusual spectroscopic properties remains elusive.[39,40] Similar downfield shifts are observed for the hydride in Tp′(CO)(RC≡CMe)W(H) (R = Me, Ph), resonating near 10 ppm with a tungsten coupling constant of 116 Hz.[40a] Tantalum hydride complexes containing ancillary aryl oxide and phosphine ligands exhibit hydride shifts in the 10–20 ppm region, and the position of the resonance is sensitive to the relative basicity of the phosphine ligand.[41] The ^{13}C NMR indicates that the linear nitrene unit is still intact; the *ipso* carbon of the NPh group resonates at 176 ppm with $^2J_{W-C}$ = 30 Hz. Loss of CO allows the alkyne ligand to bind more tightly to tungsten, reflected in the shift of the alkyne carbon resonances to 162 and 158 ppm.

The hydride in Tp′(NPh)(PhC≡CMe)W(H) (**5**) is not susceptible to deprotonation; a d_8-THF solution of **5** does not react with ^{n}BuLi, as determined by NMR. Addition of HBAr′$_4$·2OEt$_2$ to the hydride complex forms the cationic hydride amido complex [Tp′(PhC≡CMe)(H)W(NHPh)][BAr′$_4$] (**6**), which exists as two isomers in a 5:1 ratio at −80 °C (eq 5). Presumably, the two isomers are due to restricted rotation about the W–N multiple bond which results from donation from the nitrogen p orbital into an empty metal dπ orbital.[32] When the mixture is warmed to room temperature, the isomer ratio decreases to 1:1; decomposition prevents isolation. The hydride resonance in **6** is shifted to unusually low field (21 ppm, $^1J_{W-H}$ = 105 Hz). The amido proton appears at 11 ppm as a broad singlet. In the ^{13}C NMR, the alkyne carbons resonate near 259 and 240 ppm, downfield of the normal range for four-electron-donor alkynes.[37b]



(5)

5 6

Reaction of [Tp′(CO)(PhC≡CMe)W=NPh][BAr′$_4$] (1) with MeMgBr. Addition of MeMgBr to a CH$_2$Cl$_2$ solution of **1** at room temperature results in an immediate color change from orange to yellow, with slow conversion to dark red-orange over 24 h. The final product, formed from net addition of Me$^-$ to the carbonyl carbon and protonation (presumably from trace water) at the nitrene nitrogen was characterized as the cationic metallacycle [Tp′(NHPh)W(C(Ph)C(Me)C(O)Me][BAr′$_4$] (**8**). Complex **8** can be isolated as air-stable, dark orange crystals in 89% yield after chromatography and recrystallization. The yellow intermediate was determined to

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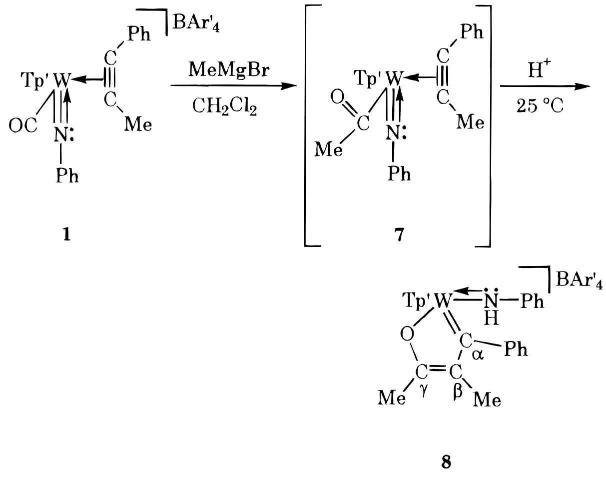
Table 4. Selected Spectroscopic Data for Tp′(NPh)(PhC≡CMe)W(η^1-C(O)H) (4), Tp′(NPh)(PhC≡CMe)W(η^1-C(O)Me) (7), and Tp′(NPh)(PhC≡CMe)W(η^1-C(O)Ph) (9)

	^{1}H NMR[a] (ppm)		^{13}C NMR[a,b] (ppm)		
complex	C(O)*R* (R = H, Me)	PhC≡C*Me*	*C*(O)R (R = H, Me, Ph)	*ipso* NPh	Ph*C*$_1$≡*C*$_2$Me
4	17.1 ($^2J_{W-H}$ = 19 Hz)	3.26	291.8 ($^1J_{C-H}$ = 126 Hz)	163.3 ($^2J_{W-C}$ = 24 Hz)	C$_1$ = 156.6, C$_2$ = 156.4
7	3.22	3.15	325.7 (br)	155.3 ($^2J_{W-C}$ = 36 Hz)	C$_1$ = 153.2, C$_2$ = 154.4
9		c	301.3 (br)	155.2 ($^2J_{W-C}$ = 36 Hz)	C$_1$ = 157.9, C$_2$ = 155.6

[a] ^{1}H NMR and ^{13}C NMR spectra recorded in CD$_2$Cl$_2$. [b] ^{13}C NMR recorded at 253 K for **4**, 273 K for **7**, and 238 K for **9**. [c] Indistinguishable from Tp′ methyls.

be the methyl acyl species Tp′(NPh)(PhC≡CMe)W(η^1-C(O)Me) (**7**) (eq 6).



(6)

The metallacycle complex **8** is characterized in the ^{1}H NMR by the broad amido proton peak at 7.8 ppm. The metallacycle methyl groups are indistinguishable from the Tp′ methyl groups, resonating between 3.3 and 0.9 ppm. Similar to other metallacycles of this type,[42] the carbene-like C$_\alpha$ appears downfield at 237 ppm with tungsten coupling of 76 Hz. The ketonic C$_\gamma$ and the *ipso* carbon of the C$_\alpha$ phenyl group are indistinguishable at 148 and 135 ppm with $^2J_{W-C}$ = 10 and 12 Hz, respectively. The interior olefinic C$_\beta$ of the ring resonates at 87 ppm.

X-ray crystallography was used to determine the solid-state structure of [Tp′(NHPh)W(C(Ph)C(Me)C(O)-Me][BAr′$_4$] (**8**). An ORTEP diagram for **8** is shown in Figure 3, selected bond distances and angles are given in Table 5, and data collection parameters are given in Table 3. Solid-state structures of metallacycles bound to the [Tp′(CO)$_2$M] metal fragment (M = Mo, W) show a planar ring that lies on the mirror plane of the molecule, with the oxygen atom proximal to two pyrazole rings and C$_\gamma$ located between the two CO ligands.[42] In our cationic complex containing the same metallacycle linkage, the ring binds to tungsten through all four ring atoms, in a manner reminiscent of an η^4-butadiene unit. Similar structures have been determined for carbon-, nitrogen-, and oxygen-containing metallacycles of niobium[43] and tantalum.[44] Specifically, the isoelectronic "oxaniobacyclopentatriene" Tp′(CH$_3$O)Nb(C(Ph)C-(Me)C(Me)O) exhibits a remarkable resemblance to **8** in the solid state.[43c] The W−C$_\alpha$ distance of 1.944(10) Å is consistent with a carbene-type double bond,[45,46] and the W−O(1) distance of 2.005(7) Å reflects covalent single-bond character.[47] The distances from tungsten to the interior C$_\beta$ and C$_\gamma$ carbons are 2.347(10) and 2.385(12) Å, respectively. The amido ligand bends away from the metallacycle with a W−N(7)−C(21) angle of 135.6(7)°.

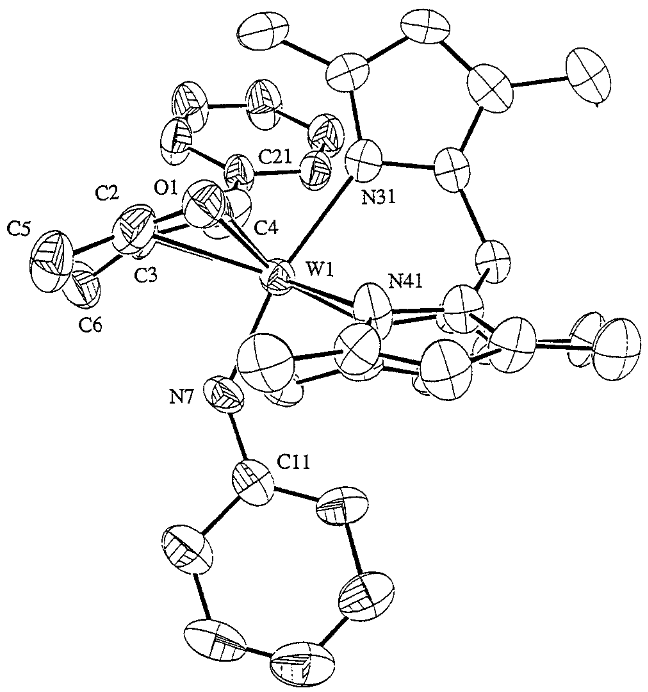


Figure 3. ORTEP diagram of [Tp′(NHPh)W(C(Ph)C(Me)-C(O)Me][BAr′$_4$] (**8**).

Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for [Tp′(NHPh)W(C(Ph)C(Me)C(O)Me)][BAr′$_4$] (8)

W(1)−O(1)	2.005(7)	C(4)−C(11)	1.425(16)
W(1)−C(2)	2.385(12)	C(2)−C(5)	1.467(19)
W(1)−C(3)	2.347(10)	C(3)−O(6)	1.533(17)
W(1)−C(4)	1.944(10)	C(2)−O(1)	1.302(16)
W(1)−N(7)	1.970(8)	W(1)−N(51)	2.150(8)
N(7)−C(21)	1.429(14)	W(1)−N(41)	2.207(8)
C(2)−C(3)	1.481(19)	W(1)−N(31)	2.202(8)
C(3)−C(4)	1.482(18)		
W(1)−N(7)−C(21)	135.6(7)	W(1)−C(3)−C(2)	73.2(7)
W(1)−O(1)−C(2)	89.7(7)	O(1)−C(2)−C(3)	117.8(11)
W(1)−C(4)−C(3)	85.4(7)	O(1)−C(2)−C(5)	121.0(13)
W(1)−C(4)−C(11)	147.1(10)	C(2)−C(3)−C(6)	122.0(10)
C(2)−C(3)−C(4)	166.6(10)	C(4)−C(3)−C(6)	120.0(11)
C(3)−C(2)−C(5)	120.5(12)	C(3)−C(4)−C(11)	127.0(9)
O(1)−W(1)−N(51)	166.2(3)	N(7)−W(1)−N(51)	90.6(3)
O(1)−W(1)−N(41)	90.7(3)	N(7)−W(1)−N(41)	90.1(4)
O(1)−W(1)−N(31)	84.8(3)	N(7)−W(1)−N(31)	166.4(3)
C(4)−W(1)−N(51)	91.8(4)	N(7)−C(21)−C(22)	123.5(6)
C(4)−W(1)−N(41)	159.4(5)	N(5)−C(21)−C(26)	117.1(10)
C(4)−W(1)−N(31)	81.6(4)		

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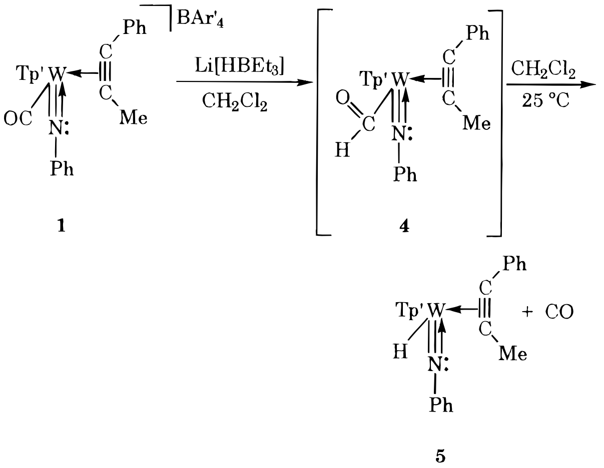
Many metallacycles similar to **8** are formed from alkyne insertion into a metal–acyl bond.[42–44,48] Initial formation of the methyl acyl complex Tp′(NPh)(PhC≡CMe)W(η^1-C(O)Me) (**7**) prior to cyclization to form **8** was confirmed by NMR spectroscopy. Selected spectroscopic data for **7** are given in Table 4. The acyl methyl and the alkyne methyl are indistinguishable at 3.22 and 3.15 ppm in the ^{1}H NMR. Consistent with η^1 bonding, the acyl carbon appears at 326 ppm in the ^{13}C NMR spectrum.[45]

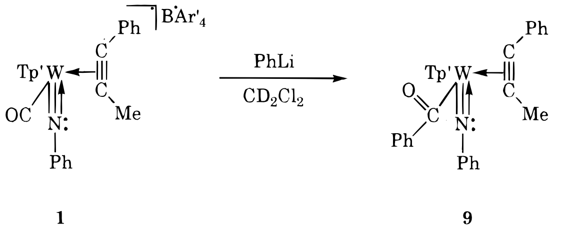
Decarbonylation of transition-metal formyl complexes to form hydride complexes is known.[49] Could a formyl complex similar to **7** lie along the reaction pathway to form the hydride complex Tp′(NPh)(PhC≡CMe)W(H) (**5**)? Indeed, formation of a formyl intermediate, Tp′(NPh)(PhC≡CMe)W(η^1-C(O)H) (**4**), was confirmed by NMR spectroscopy. Reaction of **1** with Li[HBEt$_3$] in CD$_2$Cl$_2$ at room temperature results in a color change from orange to yellow, marking formation of **4** (eq 7).



(7)

Selected spectroscopic data for **4** are shown in Table 4. The signature of the formyl ligand is a proton resonance at 17 ppm with two-bond tungsten coupling of 19 Hz. The formyl carbon appears as a doublet at 292 ppm with $^1J_{C-H}$ = 126 Hz, indicative of a η^1 bonding mode.[32c,39] A $^1J_{W-C}$ coupling constant of 100 Hz is observed. The formyl complex is stable for several days at −30 °C. At room temperature, **4** loses carbon monoxide and converts to the tungsten hydride complex Tp′(NPh)(PhC≡CMe)W(H) (**5**).

Reaction of [Tp′(CO)(PhC≡CMe)W=NPh][BAr′$_4$] (1) with PhLi. Reaction of [Tp′(CO)(PhC≡CMe)W=NPh][BAr′$_4$] (**1**) with 2 equiv of PhLi in CD$_2$Cl$_2$ leads to a color change from orange to yellow as the phenyl acyl complex Tp′(NPh)(PhC≡CMe)W(η^1-C(O)Ph) (**9**) forms (eq 8). Formation of **9** was confirmed by ^{1}H and ^{13}C NMR spectroscopy, and selected spectroscopic data are presented in Table 4. As in the η^1-formyl complex (**4**), the acyl carbon peak appears well downfield (301 ppm). Decomposition of Tp′(NPh)(PhC≡CMe)W(η^1-C(O)Ph) (**9**) precludes isolation.



(8)

Summary

Oxidation of the amido complex Tp′(CO)(PhC≡CMe)W(NHPh) (**2**) with I$_2$ in the presence of NEt$_3$ followed by counterion exchange forms the nitrene complex [Tp′(CO)(PhC≡CMe)W(=NPh)][BAr′$_4$] (**1**) quantitatively. The presence of two π-acids in the coordination sphere (PhC≡CMe and CO) and the cationic charge make this complex electron deficient. The electrophilic nature of the nitrene fragment is confirmed by net addition of hydride to form the amido complex. Addition of nucleophiles (Li[HBEt$_3$], MeMgBr, and PhLi) to the carbonyl ligand forms the neutral formyl, methyl acyl, and phenyl acyl complexes Tp′(NPh)(PhC≡CMe)W(η^1-C(O)R) (R = H (**4**), Me (**7**), Ph (**9**)), which have been observed spectroscopically. Each of these three acyl adducts decomposes at room temperature. The formyl complex **4** is simply an isomer of amido complex **2**. The related formyl complex [Tp′(NPh)(CO)W(η^1-C(O)H)] has been observed spectroscopically, and migration of the hydride ligand between the two carbonyls has been confirmed by low-temperature NMR. Above −30 °C, the hydride migrates to the nitrene ligand to form the amido complex Tp′(CO)$_2$W(NHPh).[32c] For our formyl complex Tp′(NPh)(PhC≡CMe)W(η^1-C(O)H) (**4**), conversion to the hydride complex Tp′(H)(PhC≡CMe)W(=NPh) (**5**) with loss of CO is observed. It is unclear why replacement of one CO with alkyne favors loss of CO rather than amido formation. Also of interest is that addition of KBH$_4$ adds hydride to the nitrene nitrogen to form Tp′(CO)(PhC≡CMe)W(NHPh), but when acyls are formed by addition of nucleophiles to the carbonyl of [Tp′(CO)(PhC≡CMe)W(=NPh)][BAr′$_4$] (**1**), the nitrene nitrogen is easily protonated. The electrophilic behavior of the nitrene ligand in the cationic nitrene complex **1** and the nucleophilic behavior of the nitrene ligand in the neutral complexes of the type [Tp′(R)(PhC≡CMe)W(=NPh)] (R = H, C(O)Me), imply that the reactivity of the nitrene ligand is tightly linked to properties of the ancillary ligands.

Experimental Section

Materials and Methods. Reactions were performed under a dry nitrogen atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF), hexanes, and diethyl ether (Et$_2$O) were distilled from sodium benzophenone ketyl. Dichloromethane was distilled from P$_2$O$_5$. Acetonitrile was distilled

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from calcium hydride. All other solvents were purged with nitrogen and used without further purification. $NaBAr'_4$ and $HBAr'_4{\cdot}2OEt_2$ (BAr'_4 = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) were prepared according to literature procedures.[32a] Metal complexes which were used as reagents, Tp′W(CO)(PhC≡CMe)OTf (OTf = CF_3SO_3) and $[Tp'W(CO)_2(PhC{\equiv}CMe)][OTf]$, were synthesized according to literature procedures.[33b] All other reagents were obtained from commercial sources and used without further purification.

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker WM 250 (250 MHz), a Bruker AMX 300 (300 MHz), or a Varian XL 400 (400 MHz) spectrometer. Infrared spectra were collected on a Mattson Polaris FT-IR spectrometer. Analyses were conducted by Atlantic Microlab of Norcross, GA.

[Tp′(CO)(PhC≡CMe)W═NPh][BAr′$_4$] (1). To a stirred solution of 1.58 g (2.20 mmol) of Tp′(CO)(PhC≡CMe)W(NHPh) (**2**) in 40 mL of CH_2Cl_2 was added 338 μL of NEt_3 (2.42 mmol) followed by 615 mg (2.42 mmol) of I_2. A color change from purple to dark orange was observed within 5 min. The solution was stirred for 15 min. A solution of 1.95 g (2.20 mmol) of $NaBAr'_4$ in 10 mL of Et_2O was then added. Formation of a white precipitate (NaI) was observed. The orange solution was filtered away from the white solid, and solvent was removed *in vacuo*. Chromatography on silica gel (Aldrich, 200−400 mesh, deactivated) yielded an orange band which was eluted with 50/50 CH_2Cl_2/hexanes. Recrystallization from CH_2Cl_2 and pentane produced dark orange crystals in 79% yield (2.75 g, 1.74 mmol). IR (KBr): $\nu_{C\equiv O}$ 2087 cm^{-1}. ^1H NMR (CD_2Cl_2; δ, ppm): 7.76 (s, br, 8H, *o*-H of BAr'_4), 7.60 (s, br, 4H, *p*-H of BAr'_4), 7.40−6.40 (m, 10H, N*Ph*, C≡C*Ph*), 6.17, 5.84, 5.76 (each s, 3H, Tp′ C−*H*), 3.67 (s, 3H, C≡C*Me*), 2.54, 2.50, 2.47, 2.42, 1.82, 1.33 (each s, 18H, Tp′ C−*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; δ, ppm): 205.2 ($^1J_{W-C}$ = 122 Hz, *C*O), 162.1 (q, $^1J_{B-C}$ = 50 Hz, *ipso* of BAr'_4), 154.9 ($^2J_{W-C}$ = 32 Hz, *ipso* of N*Ph*), 155.8, 153.4, 153.3, 147.9, 147.3, 147.1 (Tp′ *C*−Me), 141.1 ($^1J_{W-C}$ = 15 Hz, C≡*C*Me), 138.0 ($^1J_{W-C}$ = 32 Hz, C≡*C*Ph), 135.2 (br, *o* of BAr'_4), 132.6 (*ipso* of C≡C*Ph*), 131.9 (*p* of C≡C*Ph*), 129.5 (*p* of N*Ph*), 129.2 (q of q, $^2J_{C-F}$ = 28 Hz, $^4J_{C-F}$ = 4 Hz, *m* of BAr'_4), 129.9, 129.6, 129.1, 127.1 (*o*, *m* of N*Ph*, C≡C*Ph*), 124.9 (q, $^1J_{C-F}$ = 270 Hz, *C*F_3 of BAr'_4), 117.9 (septet, $^3J_{C-F}$ = 4 Hz, *p* of BAr'_4), 109.6, 109.0, 108.9 (Tp′ *C*−H), 19.5 (C≡C*Me*), 16.0, 15.5, 14.8, 12.9, 12.8, 12.7 (Tp′ C−*Me*). Anal. Calcd for $WC_{52}H_{47}N_7B_2F_{24}O$: C, 47.90; H, 3.00; N, 6.21. Found: C, 48.04; H, 3.03; N, 6.22.

Tp′(CO)(PhC≡CMe)W(NHPh) (2). A solution of $[Tp'W(CO)_2(PhC{\equiv}CMe)][OTf]$ (4.52 g, 5.64 mmol) in 250 mL of THF was refluxed for 1 h. The formation of Tp′W(CO)(PhC≡CMe)(OTf) was monitored by IR in the CO region. To this solution was added NH_2Ph (2.5 mL, 28 mmol, 5.0 equiv) and NEt_3 (2.3 mL, 16 mmol, 2.9 equiv), and heating was continued for 48 h. A color change from blue to purple was observed. Solvent removal by rotary evaporation left a purple solid, which was chromatographed on alumina (Fisher, 80−200 mesh, deactivated). A purple band was eluted with a 50/50 mixture of CH_2Cl_2 and hexanes. Recrystallization from CH_2Cl_2/MeOH produced dark purple crystals in 79% yield (3.2 g, 4.5 mmol). IR (KBr): $\nu_{C\equiv O}$ 1859 cm^{-1}. ^1H NMR (CD_2Cl_2; δ, ppm): 7.83 (s, 1H, N*H*Ph), 7.20−6.40 (m, 10H, NH*Ph*, C≡C*Ph*), 5.92, 5.81, 5.67 (each a s, 3H, Tp′ C−*H*), 3.48 (s, 3H, C≡C*Me*), 2.60, 2.46, 2.37, 2.36, 1.65, 1.54 (each a s, 18H, Tp′ C−*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; δ, ppm): 238.2 ($^1J_{W-C}$ = 160 Hz, *C*O), 181.3 ($^1J_{W-C}$ = 48 Hz, C≡*C*Ph), 178.3 ($^1J_{W-C}$ = 10 Hz, C≡*C*Me), 158.8 (*ipso* of NH*Ph*), 154.4, 152.0, 151.1, 145.0, 144.8, 144.6 (Tp′ *C*−Me), 137.6 (*ipso* of C≡C*Ph*), 128.9, 128.6, 128.3, 119.6 (*o*, *m* of NH*Ph*, C≡C*Ph*), 127.1, 118.7 (*p* of NH*Ph*, C≡C*Ph*), 108.6, 107.4, 106.9 (Tp′ *C*−H), 19.3 (C≡C*Me*), 15.7, 15.5, 14.0, 12.9, 12.8 (1:1:1:2:1, Tp′ C−*Me*). Anal. Calcd for $WC_{21}H_{36}N_7OB{\cdot}CH_2Cl_2$: C, 47.91; H, 4.77; N, 12.22. Found: C, 48.28; H, 4.86; N, 12.47.

[Tp′(CO)(PhC≡CMe)W(NH$_2$Ph)][BAr′$_4$] (3). A solution of Tp′(CO)(PhC≡CMe)W(NHPh) (**2**; 122 mg, 0.170 mmol) in 20 mL of CH_2Cl_2 at 0 °C was stirred during the addition of 172 mg (0.170 mmol) of $HBAr'_4{\cdot}2Et_2O$ in 5 mL of CH_2Cl_2. A color change from purple to blue occurred immediately. The solvent was removed *in vacuo* to leave a blue oil. Recrystallization from CH_2Cl_2/hexanes produced blue crystals in 61% yield (160 mg, 0.10 mmol). IR (KBr): $\nu_{C\equiv O}$ 1927 cm^{-1}. ^1H NMR (CD_2Cl_2; δ, ppm): 7.76 (s, br, 8H, *o*-H of BAr'_4), 7.60 (s, br, 4H, *p*-H of BAr'_4), 7.50−6.60 (m, 10H, NH_2*Ph*, C≡C*Ph*), 6.15, 6.06, 5.78 (each s, 3H, Tp′ C−*H*), 5.44, 4.75 (d, $^2J_{H-H}$ = 13 Hz, 2H, N*H*$_2$Ph), 3.10 (s, 3H, C≡C*Me*), 2.90, 2.60, 2.53, 2.46, 1.81, 1.23 (each a s, 18H, Tp′ C−*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; δ, ppm): 229.3 ($^1J_{W-C}$ = 150 Hz, *C*O), 214.9 ($^1J_{W-C}$ = 53 Hz, C≡*C*Ph), 216.4 ($^1J_{W-C}$ = 15 Hz, C≡*C*Me), 162.2 (q, $^1J_{B-C}$ = 50 Hz, *ipso* of BAr'_4), 153.3, 151.7, 151.4, 148.8, 148.5, 147.1 (Tp′ *C*−Me), 143.3 (*ipso* of NH_2*Ph*), 136.4 (*ipso* of C≡C*Ph*), 135.2 (br, *o* of BAr'_4), 131.2, 127.8 (*p* of NH_2*Ph*, C≡C*Ph*), 129.3 (q of q, $^2J_{C-F}$ = 31 Hz, $^4J_{C-F}$ = 3 Hz, *m* of BAr'_4), 130.4, 129.6, 129.5, 120.2 (*o*, *m* of NH_2*Ph*, C≡C*Ph*), 125.0 (q, $^1J_{C-F}$ = 271 Hz, *C*F_3 of BAr'_4), 117.9 (septet, $^3J_{C-F}$ = 4 Hz, *p* of BAr'_4), 109.9, 109.8, 108.3 (Tp′ *C*−H), 22.3 (C≡C*Me*), 16.6, 16.0, 15.1, 13.0, 12.9, 12.8 (Tp′ C−*Me*). Anal. Calcd for $C_{52}H_{49}N_7WB_2F_{24}O$: C, 47.84; H, 3.12; N, 6.20. Found: C, 47.93; H, 3.14; N, 6.14.

Tp′(NPh)(PhC≡CMe)W(η^1-C(O)H) (4). Into a dry NMR tube was weighed 95 mg (0.06 mmol) of [Tp′(CO)(PhC≡CMe)W═NPh][BAr′$_4$] (**1**), and the tube was then purged with N_2. The sample was dissolved in 1.5 mL of CD_2Cl_2, and 80 μL (1.3 equiv) of potassium tri-*sec*-butylborohydride (1.0 M in THF) was added at room temperature. A color change from orange to yellow was observed. ^1H NMR showed quantitative conversion to **4**. After several hours at room temperature in solution complex **4** converts to Tp′(NPh)(PhC≡CMe)W(H) (**5**). Data for **4**: ^1H NMR (CD_2Cl_2; δ, ppm): 17.1 (s, $^2J_{W-H}$ = 19 Hz, 1H, C(O)*H*), 7.24−6.48 (m, 10H, N*Ph*, C≡C*Ph*), 5.95, 5.85, 5.62 (each s, 3H, Tp′ C−*H*), 3.26 (s, 3H, C≡C*Me*), 2.50, 2.46, 2.41, 2.22, 1.56, 1.48 (each s, 18H, Tp′ C−*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 253 K; δ, ppm): 291.8 ($^1J_{W-C}$ = 100 Hz, $^1J_{C-H}$ = 126 Hz, C(O)H), 163.6 ($^2J_{W-C}$ = 24 Hz, *ipso* of N*Ph*), 156.6 ($^1J_{W-C}$ = 36 Hz, C≡*C*Ph), 156.4 ($^1J_{W-C}$ = 10 Hz, C≡*C*Me), 154.3, 153.2, 152.2, 145.6, 145.5, 144.1 (Tp′ *C*−Me), 138.8 (*ipso* of C≡C*Ph*), 129.1, 128.7, 128.4, 123.9 (*o*, *m* of N*Ph*, C≡C*Ph*), 127.3, 125.1 (*p* of N*Ph*, C≡C*Ph*) 108.1, 107.8, 107.7 (Tp′ *C*−H), 16.7 (C≡C*Me*), 15.1, 14.8, 14.7, 12.9, 12.8 (1:1:1:1:2, Tp′ C−*Me*).

Tp′(NPh)(PhC≡CMe)W(H) (5). A solution of 657 mg (0.416 mmol) of [Tp′(CO)(PhC≡CMe)W═NPh][BAr′$_4$] (**1**) in 30 mL of acetonitrile was added to 120 mg (2.22 mmol, 5.3 equiv) of KBH_4 with stirring at room temperature. An orange supernatant was filtered away from the resulting yellow precipitate, and the solid was dried. The product was extracted into 30 mL of CH_2Cl_2, and the volume was then reduced to 5 mL *in vacuo*. Upon precipitation of a yellow solid, 5 mL of hexanes was added. The orange supernatant was filtered away, and the product was isolated in 60% yield (170 mg, 0.247 mmol). ^1H NMR (CD_2Cl_2; δ, ppm): 13.5 (s, $^1J_{W-H}$ = 106 Hz, 1H, W*H*), 7.13−6.60 (m, 10H, N*Ph*, C≡C*Ph*), 5.92, 5.90, 5.53 (each s, 3H, Tp′ C−*H*), 3.62 (s, 3H, C≡C*Me*), 2.56, 2.44, 2.42, 2.33, 1.74, 1.73 (each s, 18H, Tp′ C−*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2; δ, ppm): 176.3 ($^2J_{W-C}$ = 30 Hz, *ipso* of N*Ph*), 162.2 ($^1J_{W-C}$ = 30 Hz, C≡*C*Ph), 157.7 (C≡*C*Me), 153.5, 153.2, 150.9, 144.6, 144.1, 142.9 (Tp′ *C*−Me), 140.8 (*ipso* of C≡C*Ph*), 129.0, 128.0, 127.8, 122.5 (*o*, *m* of N*Ph*, C≡C*Ph*), 126.0, 122.2 (*p* of N*Ph*, C≡C*Ph*), 107.0, 106.2, 105.6 (Tp′ *C*−H), 25.5 (C≡C*Me*), 16.4, 15.3, 14.8, 12.4, 12.3, 12.2 (Tp′ C−*Me*). Anal. Calcd for $WC_{20}H_{36}N_7BO$: C, 52.27; H, 5.26; N, 14.22. Found: C, 52.20; H, 5.30; N, 14.22.

[Tp′(PhC≡CMe)(H)W(NHPh)][BAr′$_4$] (6). Addition of a CD_2Cl_2 solution of Tp′(NPh)(PhC≡CMe)W(H) (**5**; 12 mg, 0.02 mmol) to an NMR tube containing $HBAr'_4{\cdot}2Et_2O$ (17 mg, 0.02 mmol) at −80 °C showed quantitative formation of **6** as determined by NMR. Complex **6** is observed as two isomers in a 5:1 ratio at −80 °C and decomposes upon warming to room temperature. Data for the minor isomer are given in parentheses. ^1H NMR (CD_2Cl_2; δ, ppm): 20.6 (21.5) (s, $^1J_{W-H}$ = 105 Hz, 1H, W*H*), 10.8 (br, s, 1H, N*H*Ph), 7.76 (s, br, 8H, *o*-H of

BAr′$_4$), 7.60 (s, br, 4H, *p*-H of BAr′$_4$), 7.50−6.60 (m, 10H, NH*Ph*, C≡C*Ph*), 6.20, 6.02, 5.61 (6.04, 5.85, 5.62) (each s, 3H, Tp′ C-*H*), 4.04 (4.40) (s, 3H, C≡C*Me*), 2.62, 2.54, 2.45, 2.31 (2.32), 1.45 (1.31), 1.17 (1.20) (each s, 18H, Tp′ C—*Me*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$; δ, ppm): 258.8 ($^1J_{\mathrm{W-C}} = 22$ Hz, C≡*C*Me), 240.0 ($^1J_{\mathrm{W-C}} = 44$ Hz, C≡*C*Ph), 162.5 (q, $^1J_{\mathrm{B-C}} = 49$ Hz, *ipso* of BAr′$_4$), 155.0, 154.0, 150.8, 148.0, 147.5, 147.4, 146.1 (154.8, 153.5, 150.7, 148.3, 148.1, 146.4) (*ipso* of NH*Ph*, Tp′ *C*—Me), 136.0 (*ipso* of C≡C*Ph*), 134.3 (br, *o* of BAr′$_4$), 133.6 (*p* of C≡*C*Ph) 129.5, 129.4 (*o*, *m* of NH*Ph*, C≡*C*Ph), 120.1 (*p* of NH*Ph*), 128.3 (q of q, $^2J_{\mathrm{C-F}} = 31$ Hz, $^4J_{\mathrm{C-F}} = 3$ Hz, *m* of BAr′$_4$), 124.1 (q, $^1J_{\mathrm{C-F}} = 271$ Hz, *C*F$_3$ of BAr′$_4$), 117.2 (septet, $^3J_{\mathrm{C-F}} = 4$ Hz, *p* of BAr′$_4$), 109.1, 108.8, 107.4 (109.2, 108.6, 107.6) (Tp′ *C*—H), 27.1 (C≡C*Me*), 17.5, 14.9, 14.5, 12.7, 12.6, 12.5 (Tp′ C—*Me*).

Tp′(NPh)(PhC≡CMe)W(η^1-C(O)Me) (7). Into a dry NMR tube was weighed 107 mg (0.068 mmol) of [Tp′(CO)(PhC≡CMe)W=NPh][BAr′$_4$] (**1**), and the tube was then purged with N$_2$. The sample was dissolved in 1.5 mL of CD$_2$Cl$_2$, and 45 μL (3 equiv) of MeMgBr (3.0 M in Et$_2$O) was added at room temperature. A color change from orange to golden yellow was observed. ^{1}H NMR showed quantitative conversion to **7**. While this complex is stable in solution at −30 °C for several days, at room temperature complex **7** adds a proton and converts to the cationic metallacycle **8**. IR (CH$_2$Cl$_2$): $\nu_{\mathrm{C=O}}$ 1630 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$; δ, ppm): 7.30−6.30 (m, 10H, N*Ph*, C≡C*Ph*), 6.04, 5.74, 5.68 (each s, 3H, Tp′ C—*H*), 3.22, 3.15 (s, 3H, C≡C*Me*, C(O)*Me*), 2.49, 2.45, 2.41, 2.36, 1.55, 1.38 (each s, 18H, Tp′ C—*Me*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 273 K) δ (ppm): 325.7 (**C**(O)Me), 155.3 ($^2J_{\mathrm{W-C}} = 36$ Hz, *ipso* of N*Ph*), 154.6, 152.5, 151.9, 145.8, 145.4, 143.8 (Tp′ *C*—Me), 153.2 ($^1J_{\mathrm{W-C}} = 37$ Hz, C≡*C*Ph), 154.4 (C≡*C*Me), 137.8 (*ipso* of C≡C*Ph*), 128.9, 128.8, 128.5, 125.5 (*o*, *m* of N*Ph*, C≡C*Ph*), 127.5, 127.2 (*p* of N*Ph*, C≡C*Ph*), 108.1 (3, Tp′ *C*—H), 52.0 (C(O)*Me*), 20.2 (C≡C*Me*), 16.4, 15.7, 14.7, 13.0, 12.7 (1:1:1:1:2, Tp′ C—*Me*).

[Tp′(NHPh)W(C(Ph)C(Me)C(O)Me)][BAr′4] (8). To a stirred solution of 290 mg (0.18 mmol) of [Tp′(CO)(PhC≡CMe)W=NPh][BAr′$_4$] (**1**) in 10 mL of CH$_2$Cl$_2$ was added 120 μL (2 equiv, 3 M in Et$_2$O) of MeMgBr dropwise. A color change from orange to golden yellow was observed. When the mixture was stirred for 48 h, a second color change to dark red-orange was observed. The solution was filtered away from a white precipitate, and solvent was removed *in vacuo*. The product was chromatographed on silica, and a red-orange band was eluted with 50/50 CH$_2$Cl$_2$/hexanes. Recrystallization from CH$_2$Cl$_2$ and hexanes produced red-orange crystals in 89% yield (269 mg, 0.16 mmol). ^{1}H NMR (CD$_2$Cl$_2$; δ, ppm): 7.82 (br, s, 1H, N*H*Ph), 7.76 (s, br, 8H, *o*-H of BAr′$_4$), 7.60 (s, br, 4H, *p*-H of BAr′$_4$), 7.40−5.70 (m, 10H, NH*Ph*, =C*Ph*), 6.16, 5.87, 5.61 (each s, 3H, Tp′ C—*H*), 3.28, 2.81, 2.71, 2.54, 2.43, 1.73, 1.56, 0.92 (each s, 24H,W=C(Ph)C(*Me*)=C(*Me*)O, Tp′ C—*Me*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$; δ, ppm): 236.5 ($^1J_{\mathrm{W-C}} = 76$ Hz, W=*C*(Ph)C(Me)=C(Me)O), 162.1 (q, $^1J_{\mathrm{B-C}} = 49$ Hz, *ipso* of BAr′$_4$), 160.1 (*ipso* of NH*Ph*), 152.7, 152.3, 151.6, 148.9, 148.0, 147.0 (Tp′ *C*—Me), 147.9 ($^2J_{\mathrm{W-C}} = 10$ Hz), 134.6 ($^2J_{\mathrm{W-C}} = 12$ Hz) (W=C(Ph)C(Me)=*C*(Me)O, *ipso* of =C*Ph*), 135.1 (br, *o* of BAr′$_4$), 133.0 (br), 129.2, 128.4, 121.1 (*o*, *m* of NH*Ph*, =C*Ph*), 132.2, 126.7 (*p* of NH*Ph*, =C*Ph*), 129.2 (q of q, $^2J_{\mathrm{C-F}} = 31$ Hz, $^4J_{\mathrm{C-F}} = 3$ Hz, *m* of BAr′$_4$), 124.9 (q, $^1J_{\mathrm{C-F}} = 271$ Hz, *C*F$_3$ of BAr′$_4$), 117.8 (septet, $^3J_{\mathrm{C-F}} = 4$ Hz, *p* of BAr′$_4$), 109.9, 109.3, 108.9 (Tp′ *C*—H), 87.4 ($^2J_{\mathrm{W-C}} = 8$ Hz, (W=C(Ph)*C*(Me)=C(Me)O), 16.7, 15.9, 15.1, 13.5, 13.2, 12.9, 12.5, 11.0 (W=C(Ph)C(*Me*)=C(*Me*)O, Tp′ C—*Me*). Anal. Calcd for $C_{53}H_{51}N_7WB_2F_{24}O$: C, 48.18; H, 3.22; N, 6.14. Found: C, 48.24; H, 3.26; N, 6.09.

Tp′(NPh)(PhC≡CMe)W(η^1-C(O)Ph) (9). Into a dry NMR tube was weighed 97 mg (0.06 mmol) of [Tp′(CO)(PhC≡CMe)W=NPh][BAr′$_4$] (**1**), and then the tube was purged with N$_2$. Dissolution in CD$_2$Cl$_2$ was followed by addition of 2.1 equiv of PhLi (1.8 M in cyclohexane/Et$_2$O, 0.07 mL, 0.13 mmol) at room temperature. A color change from orange to dark gold was observed upon shaking. NMR spectroscopy confirmed quantitative conversion to Tp′(NPh)(PhC≡CMe)W(η^1-C(O)Ph) (**9**). Repeated efforts to isolate the neutral product were thwarted by decompostion during workup. ^{1}H NMR (CD$_2$Cl$_2$; δ, ppm): 7.70−6.20 (m, 15H, C(O)*Ph*, N*Ph*, C≡C*Ph*), 6.04, 5.82 (br), 5.74 (each s, 3H, Tp′ C-*H*), 2.61 (br), 2.54, 2.51 (br), 2.50, 1.94, 1.54 (br), 1.34 (each s, 21H, C≡C*Me*, Tp′ C—*Me*). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 238 K) δ (ppm): 301.3 (br, *C*(O)Ph), 157.9, 155.6 (C≡*C*Ph, C≡*C*Me), 155.2 ($^2J_{\mathrm{W-C}} = 36$ Hz, *ipso* of N*Ph*), 153.9, 152.6, 151.1, 145.1, 144.6, 143.9 (Tp′ *C*—Me), 150.3 (*ipso* of C(O)*Ph*), 138.2 (*ipso* of C≡C*Ph*), 128.9, 128.7, 128.6, 128.3, 125.2 (1:1:2:1:1, *o*, *m* of C*Ph*O, N*Ph*, C≡C*Ph*), 132.4, 127.4, 127.1 (*p* of C*Ph*O, N*Ph*, C≡C*Ph*), 107.8, 107.7 (2:1 Tp′ *C*—H), 19.7 (C≡C*Me*), 16.5, 15.2, 14.5, 14.2, 12.9, 12.7 (Tp′ C—*Me*).

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 of data collection and refinement are presented in Table 3.

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Supporting Information Available: Listings of anisotropic thermal factors, all bond distances and angles, and atomic positional parameters and labeled figures for **1** and **8** (18 pages). Ordering information is given on any current masthead page.

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