

Sequential Chemical Transformations of a Tungsten Carbyne Ligand: Protonation, Alkyne Insertion, Vinylcarbene Formation, and Metallacyclopropene/Metallafuran Isomerization

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Proton addition and phenylacetylene insertion convert carbyne complexes of the type $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{C}-\text{OAr}$ ($\text{Ar} = \text{Ph}$, $p\text{-C}_6\text{H}_4\text{Me}$, $p\text{-C}_6\text{H}_4\text{OMe}$; $\text{Tp}' = \text{hydridotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$) into tungsten η^3 -vinylcarbene complexes of the form $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha, \text{C}_\beta, \text{C}_\gamma)=\text{CPh}-\text{CH}=\text{CH}(\text{O}(p\text{-C}_6\text{H}_4\text{R})))][\text{X}]$ ($\text{R} = \text{H}$, $\text{X} = \text{BF}_4$, **6a**; $\text{R} = \text{Me}$, $\text{X} = \text{BF}_4$, **6b**; $\text{R} = \text{OMe}$, $\text{X} = \text{BF}_4$, **6c**; $\text{R} = \text{H}$, $\text{X} = \text{BAR}'_4$, **6a'**). The intermediate agostic carbene complex $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{H})\text{O}(p\text{-C}_6\text{H}_4\text{OMe})][\text{BAR}'_4]$ (**7**) was characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy. Addition of base to the cationic vinylcarbene complex **6** forms the metallafuran complex $\text{Tp}'(\text{CO})_2\text{W}(\kappa^2\text{-}(\text{C}_\alpha, \text{O})=\text{CPh}-\text{CH}=\text{CH}-\text{O})$ (**9**) as the major product. Although the net reaction corresponds to loss of C_6H_5^+ , mechanistically it is attractive to postulate addition of OH^- to the electron-deficient C_γ site followed by proton removal by base coupled with loss of OPh^- to generate the metallafuran stoichiometry. Isolation of an intermediate metallacyclopropene complex (**10**), possessing an aldehyde substituent on the three-membered ring, which isomerizes to the thermodynamically favored metallafuran complex, is consistent with this mechanism. The vinylcarbyne complex $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{C}-\text{CPh}=\text{CH}(\text{OTol})$ (**11b**) was also recovered from the reaction mixture of complex **6b** and base. Addition of 0.10 equiv of $\text{H}[\text{BF}_4]$ to metallacyclopropene complex **10** resulted in complete conversion of **10** to the metallafuran complex **9** at room temperature. Addition of acid to metallacyclopropene complex **10** at low temperature allowed ^1H NMR characterization of the η^3 -vinylcarbene intermediate $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha, \text{C}_\beta, \text{C}_\gamma)=\text{CPh}-\text{CH}=\text{CH}(\text{OH}))][\text{BF}_4]$ (**17**). Upon addition of $\text{Li}[\text{Et}_3\text{BH}]$ to **6**, double hydride addition and loss of aryloxide occurred at C_γ of the aryloxy-substituted vinylcarbene complex **6** to form the previously reported η^2 -vinyl complex $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-}(\text{C}_\alpha, \text{C}_\beta)\text{CPh}=\text{CH}-\text{CH}_3)$ (**8**). These experiments illustrate reaction routes available to C_3 ligand skeletons derived from carbyne-alkyne coupling. The oxygen of the aryloxy substituent on the original carbyne carbon plays an integral role in this reaction sequence.

Introduction

A rich chemistry has developed from the combination of transition metal carbene complexes¹ with alkynes to form η^3 -vinylcarbene,^{2–4} η^2 -vinyl (metallacyclopropene),^{5,6} and metallafuran^{2,5b,7,8} complexes (Scheme 1). Such complexes are probable intermediates in the construction^{2,9} of important organic frameworks.¹⁰

Addition of electrophiles to carbyne complexes has been used to generate reactive carbene intermediates.¹¹

Geoffroy et al. reported that protonation of the carbyne complex $\text{Cp}(\text{CO})_2\text{W}\equiv\text{C}(\text{Tol})$ with $\text{H}[\text{BF}_4]$ in the presence of $\text{PhC}\equiv\text{CPh}$ resulted in the η^3 -vinylcarbene complex $[\text{Cp}(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha, \text{C}_\beta, \text{C}_\gamma)=\text{CPh}-\text{CPh}=\text{CH}(\text{Tol}))][\text{BF}_4]$ (**1**) (Scheme 2).² Cationic complex **1** underwent CO substi-

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tution with I^- to form the neutral η^3 -vinylcarbene complex $Cp(CO)(I)W(\eta^3-(C_{\alpha}C_{\beta}C_{\gamma})=CPh-CPh=CH(Tol))$ (**2**) (Scheme 3). Hydride addition to the carbene carbon of complex **1** generated a neutral η^3 -allyl complex, $Cp(CO)_2W(\eta^3-(C_{\alpha}C_{\beta}C_{\gamma})CPh(H)CPhCH(Tol))$ (**3**) (Scheme

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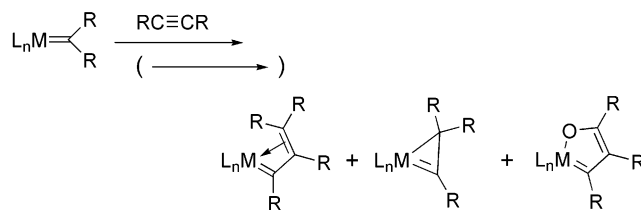
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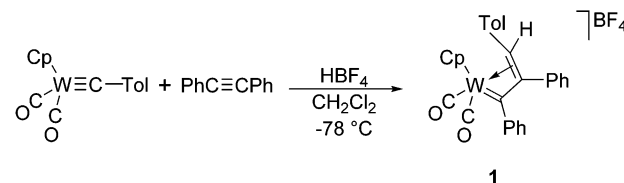
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Scheme 1. η^3 -Vinylcarbene, Metallacyclopropene (η^2 -vinyl), and Metallafuran Ligands from Carbene Complexes and Alkynes^a

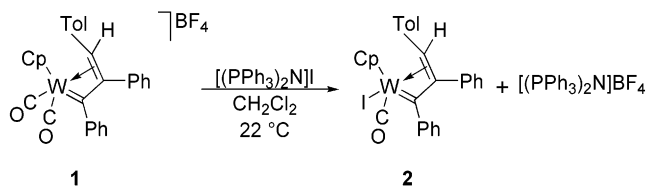


^a Composition of the ligand in the products varies due to additional reactions such as CO insertion and isomerization.

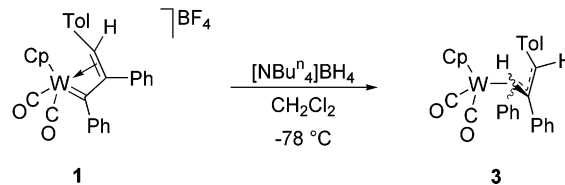
Scheme 2. Synthesis of $[Cp(CO)_2W(\eta^3-(C_{\alpha}C_{\beta}C_{\gamma})=CPh-CPh=CH(Tol))][BF_4]$ (**1**)



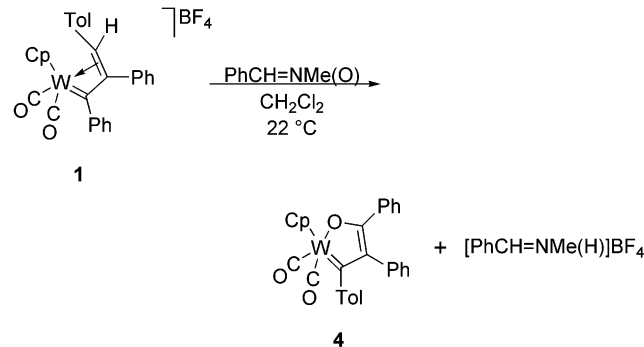
Scheme 3. Synthesis of $Cp(CO)(I)W(\eta^3-(C_{\alpha}C_{\beta}C_{\gamma})=CPh-CPh=CH(Tol))$ (**2**)



Scheme 4. Synthesis of $Cp(CO)_2W(\eta^3-(Ph)HCCPhCH(Tol))$ (**3**)



Scheme 5. Synthesis of $Cp(CO)_2W(\eta^2-(C_{\alpha}O)=CTol-CPh=CPh-O)$ (**4**)



4),² and the metallafuran complex $Cp(CO)_2W(\kappa^2-(C_{\alpha}O)=CTol-CPh=CPh-O)$ (**4**) resulted from oxidation of **1** with the nitron $PhCHC=N(O)Me$, an oxygen transfer reagent (Scheme 5).²

The availability of tungsten carbene complexes with an aryloxy substituent in the $Tp'(CO)_2W=COAr$ family provided an opportunity to compare Cp and Tp' systems and to explore carbene substituent effects on protona-

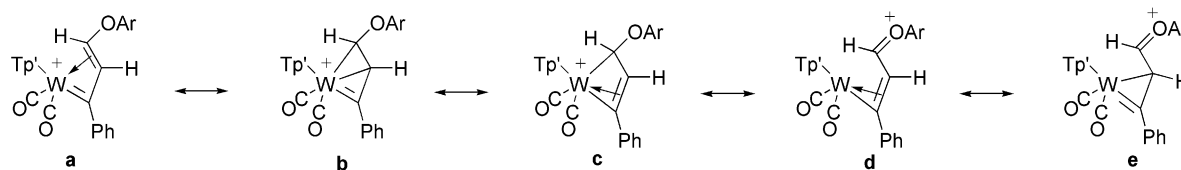


Figure 1. Resonance contributors for the cationic η^3 -vinylcarbene complex **6**.

tion and alkyne insertion reactions. Here we report conversion of $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{COAr}$ to $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha, \text{C}_\beta, \text{C}_\gamma)=\text{CPh}-\text{CH}=\text{CH}-\text{OAr})]^+$ upon addition of acid in the presence of phenylacetylene. The intermediate cationic carbene complex $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{H})\text{O}(\text{p-C}_6\text{H}_4\text{-OMe})]^+$ resulting from protonation of the carbyne complex was characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy. Reactions of the cationic η^3 -vinylcarbene complex with base and with hydride donor reagents have been explored. A significant feature of these Tp' tungsten η^3 -vinylcarbene complexes is that the aryloxy substituent on C_γ promotes reactivity at C_γ instead of C_α as was observed for the η^3 -vinylcarbene complex described by Geoffroy et al.²

Results and Discussion

Synthesis and Characterization of η^3 -Vinylcarbene Complexes: $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha, \text{C}_\beta, \text{C}_\gamma)=\text{CPh}-\text{CH}=\text{CH}-\text{O}(\text{p-C}_6\text{H}_4\text{R}))][\text{BF}_4]$ (**R** = **H** (**6a**), **Me** (**6b**), **OMe** (**6c**)). Complexes possessing η^3 -vinylcarbene ligands have previously been generated by a variety of synthetic pathways^{3a} that include alkylation of an η^3 -acrolein ligand,^{4b,e,j,k} ring-opening of cyclopropenes,^{4f,i} addition of alkyne to a carbene ligand,^{2,4a} addition of an allyl bromide to a carbyne ligand,^{3f,j} and conversion of an η^1 -vinylcarbene ligand to an η^3 -vinylcarbene ligand.^{3c,d} Cyclizations involving Fischer-type carbene complexes and alkynes have been used to synthesize a variety of cyclic and polycyclic compounds.^{9c,10c,d,12} Here we protonated a carbyne ligand to generate a cationic carbene complex that reacts with added alkyne to form an η^3 -vinylcarbene ligand.

A -78°C solution of $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{COPh}$ (**5a**) and excess phenylacetylene in methylene chloride changed from yellow to red upon addition of 1.8 equiv of $\text{H}[\text{BF}_4]$. New carbonyl absorptions at 2050 and 1965 cm^{-1} replaced those of the starting material at 1968 and 1868 cm^{-1} . Precipitation from diethyl ether after filtration through silica resulted in a 30% yield of $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha, \text{C}_\beta, \text{C}_\gamma)=\text{CPh}-\text{CH}=\text{CH}-\text{OPh})][\text{BF}_4]$ (**6a**) (Scheme 6). Analogous reactions with *p*-Me and *p*-OMe aryl substituents on the reagent carbyne complexes produced products **6b** and **6c**, respectively, although in lower yields.

NMR signals from the Tp' ligand revealed that complexes **6a–c** have C_1 symmetry. The C_α carbon of the vinylcarbene ligand appeared near 238 ppm, a chemical shift clearly indicating carbene character, while the second carbon (C_β) appeared near 65 ppm, and the third carbon (C_γ), bound to oxygen, appeared near 150 ppm. In the metallacyclopropene resonance structure (**b** in Figure 1), the sp^3 character of C_β is compatible with the observed chemical shift. Three-bond tungsten–

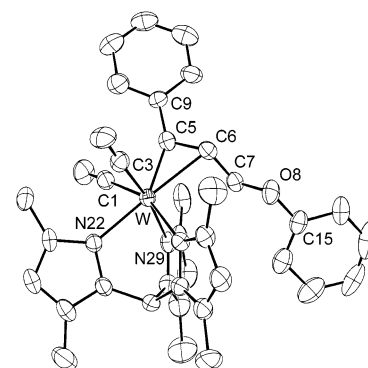
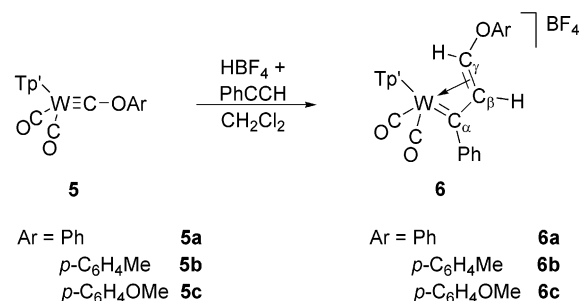


Figure 2. ORTEP representation of **6a'**.

Scheme 6. Synthesis of η^3 -Vinylcarbene Complexes



hydrogen coupling to the proton attached to C_β was observed to be 11 Hz for **6a** and 12 Hz for both **6b** and **6c**. One-bond tungsten–carbon coupling constants to the two distinct carbonyl ligands (214 and 211 ppm) differ significantly from one another at 119 and 166 Hz, respectively, for complex **6b**. The chemical shifts of the C_α , C_β , and C_γ carbons in **6a–c** are similar to those observed for carbon atoms in the cationic η^3 -vinylcarbene complex $[\text{Cp}(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha, \text{C}_\beta, \text{C}_\gamma)=\text{CPh}-\text{CPh}=\text{CH}(\text{Tol}))][\text{BF}_4]$ (**1**).²

Although the BF_4^- salts of **6b** and **6c** were isolated in high purity, satisfactory elemental analysis was not obtained for **6a** as the BF_4^- salt. To isolate pure material $[\text{H}(\text{Et}_2\text{O})_2][\text{BAR}'_4]$ ($\text{Ar}' = 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$) was employed as an alternate proton source to synthesize $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha, \text{C}_\beta, \text{C}_\gamma)=\text{CPh}-\text{CH}=\text{CHOPh})][\text{BAR}'_4]$ (**6a'**). Even with the BAR'_4^- salt **6a'**, repetitive filtering was required before the complex crystallized from diethyl ether and pentane.

Crystals of **6a'** and **6b** suitable for X-ray analysis were isolated, and the geometric parameters of the unusual vinylcarbene ligand were obtained (Figures 2 and 3 and Tables 1 and 2, respectively). Structural data are crucial to the correct formulation of these C_3R_4 fragments. The vinylcarbene ligand in **6** is similar to the coordinated $\text{C}_3\text{Ph}_2\text{HTol}$ fragment in $\text{Cp}(\text{CO})(\text{I})\text{W}(\eta^3\text{-}(\text{C}_\alpha, \text{C}_\beta, \text{C}_\gamma)=\text{CPh}-\text{CPh}=\text{CH}(\text{Tol}))$ (**2**), which was crystallographically characterized.² The tungsten–carbon distances for $\text{W}-\text{C}_\alpha$

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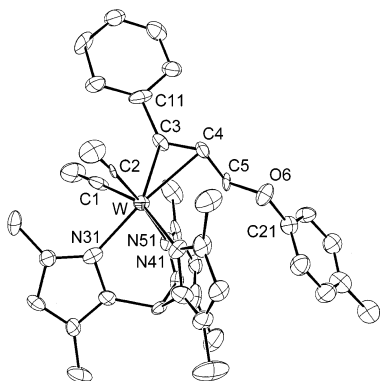


Figure 3. ORTEP representation of **6b**.

Table 1. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha\text{C}_\beta\text{C}_\gamma)=\text{CPh}-\text{CH}=\text{CH}-\text{CHOPh})][\text{BAR}'_4]$ (**6a'**)

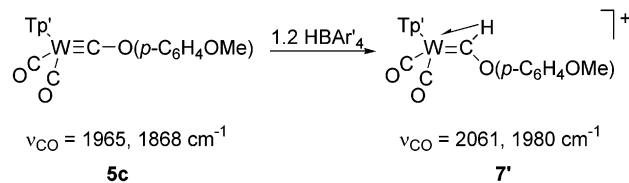
Distances (Å)			
W–C $_\alpha$ (5)	1.97(1)	C $_\alpha$ (5)–C $_\beta$ (6)	1.44(1)
W–C $_\beta$ (6)	2.37(1)	C $_\beta$ (6)–C $_\gamma$ (7)	1.36(1)
W–C $_\gamma$ (7)	2.78(1)	C $_\gamma$ (7)–O(8)	1.32(1)
W–N(22)	2.17(1)	W–C $_{\text{CO}}$ (1)	2.02(1)
W–N(29)	2.22(1)	W–C $_{\text{CO}}$ (3)	1.99(1)
W–N(36)	2.19(1)		
Bond Angles (deg)			
W–C $_\alpha$ (5)–C(9)	150.0(4)	C $_\alpha$ (5)–C $_\beta$ (6)–C $_\gamma$ (7)	123.0(6)
W–C $_\alpha$ (5)–C $_\beta$ (6)	86.4(4)	C $_\beta$ (6)–C $_\gamma$ (7)–O(8)	120.1(6)
W–C $_\beta$ (6)–C $_\alpha$ (5)	56.2(3)	C $_\gamma$ (7)–O(8)–C(15)	118.3(5)
W–C $_\beta$ (6)–C $_\gamma$ (7)	92.0(4)	C $_{\text{CO}}$ (1)–W–C $_{\text{CO}}$ (3)	94.5(3)
C $_\alpha$ (5)–W–N(22)	149.1(2)		
Torsion Angles (deg)			
W–C $_\alpha$ (5)–C $_\beta$ (6)–C $_\gamma$ (7)			67(1)
C $_{\text{CO}}$ (1)–W–C $_\alpha$ (5)–C $_\beta$ (6)			–167(1)
N(29)–W–C $_\beta$ (6)–C $_\gamma$ (7)			–27(1)

Table 2. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha\text{C}_\beta\text{C}_\gamma)=\text{CPh}-\text{CH}=\text{CH}-\text{CHOTol})][\text{BF}_4]$ (**6b**)

Distances (Å)			
W–C $_\alpha$ (3)	2.00(2)	C $_\alpha$ (3)–C $_\beta$ (4)	1.37(4)
W–C $_\beta$ (4)	2.43(2)	C $_\beta$ (4)–C $_\gamma$ (5)	1.30(3)
W–C $_\gamma$ (5)	2.68(2)	C $_\gamma$ (5)–O(6)	1.36(3)
W–N(31)	2.15(2)	W–C $_{\text{CO}}$ (1)	2.02(3)
W–N(41)	2.21(2)	W–C $_{\text{CO}}$ (2)	1.97(3)
W–N(51)	2.26(2)		
Bond Angles (deg)			
W–C $_\alpha$ (3)–C(11)	140(2)	C $_\alpha$ (3)–C $_\beta$ (4)–C $_\gamma$ (5)	122(2)
W–C $_\alpha$ (3)–C $_\beta$ (4)	90(2)	C $_\beta$ (4)–C $_\gamma$ (5)–O(6)	120(2)
W–C $_\beta$ (4)–C $_\alpha$ (3)	55(1)	C $_\gamma$ (5)–O(6)–C(21)	114(2)
W–C $_\beta$ (4)–C $_\gamma$ (5)	86(2)	C $_{\text{CO}}$ (1)–W–C $_{\text{CO}}$ (2)	97(1)
C $_\alpha$ (3)–W–N(31)	154(1)		
Torsion Angles (deg)			
W–C $_\alpha$ (3)–C $_\beta$ (4)–C $_\gamma$ (5)			58(2)
C $_{\text{CO}}$ (1)–W–C $_\alpha$ (3)–C $_\beta$ (4)			–160(2)
N(51)–W–C $_\beta$ (4)–C $_\gamma$ (5)			–30(2)

in the vinylcarbene complexes **6a'**, **6b**, and **2** are similar (W–C $_\alpha$ = 1.97(1) Å, **6a'**; W–C $_\alpha$ = 2.00(2) Å, **6b**; W–C $_\alpha$ = 1.999(7) Å, **2**), but W–C $_\beta$ is significantly longer for **6a'** and **6b** than for **2** (W–C $_\beta$ = 2.37(1) Å, **6a'**; W–C $_\beta$ = 2.43(2) Å, **6b**; W–C $_\beta$ = 2.305(8) Å, **2**). The long W–C $_\gamma$ distances in **6a'** and **6b** of 2.77(1) and 2.68(2) Å, respectively, indicate at most marginal W–C $_\gamma$ bonding when compared to the W–C $_\gamma$ bond length of 2.293(8) Å in **2**. It appears that an important resonance contribution available to the vinylcarbene ligand in **6a'** and **6b** resembles a metallacyclopropene oxonium ligand (Fig-

Scheme 7. Formation of the Cationic Carbene Complex 7'



ure 1, **d** and **e**). An analogous resonance form in **2** is relatively unimportant given the W–C $_\gamma$ proximity.

Monitoring Acid Addition to $\text{Tp}'(\text{CO})_2\text{W}=\text{CO}(p\text{-C}_6\text{H}_4\text{OMe})$: Characterization of a Cationic Carbene Intermediate by IR and NMR Spectroscopy. Cyclizations involving Fischer-type carbene complexes have been shown to be initiated by generation of an unsaturated carbene complex.^{2,13} Typically, this is achieved through ligand dissociation. Geoffroy proposed that the unsaturated carbene complex $[\text{Cp}(\text{CO})_2\text{W}=\text{C}(\text{H})\text{Tol}]^+$ formed from $\text{Cp}(\text{CO})_2\text{W}=\text{C}(\text{Tol})$ and diphenylacetylene in the presence of acid and served as an intermediate in the formation of $[\text{Cp}(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha\text{C}_\beta\text{-C}_\gamma)=\text{CPh}-\text{CPh}=\text{CH}(\text{Tol}))][\text{BF}_4]$ (**1**).² An analogous carbene intermediate in our system has been characterized and converted to an η^3 -vinylcarbene complex upon addition of alkyne, consistent with Geoffroy's proposed mechanism.

Addition of 1.2 equiv of $[\text{H}(\text{Et}_2\text{O})_2][\text{BAR}'_4]$ to a solution of $\text{Tp}'(\text{CO})_2\text{W}=\text{CO}(p\text{-C}_6\text{H}_4\text{OMe})$ in CH_2Cl_2 at -50°C resulted in protonation at the carbyne carbon. In addition to carbyne reagent IR absorbance peaks at 1965 and 1868 cm^{-1} , the acidified solution had additional IR absorbances at 2061 and 1980 cm^{-1} that were assigned to an intermediate cationic carbene complex $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{H})\text{O}(p\text{-C}_6\text{H}_4\text{OMe})][\text{BAR}'_4]$ (**7'**) (Scheme 7). Warming the solution to -10°C resulted in further conversion of starting material to the cationic product.

In a related reaction, complete disappearance of the carbonyl reagent absorptions resulted from addition of 4 equiv of $\text{H}[\text{BF}_4]$ to the starting carbyne complex at -45°C . Seconds after the addition, the only significant absorptions in the carbonyl stretching region of the IR spectrum were due to $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{H})\text{O}(p\text{-C}_6\text{H}_4\text{OMe})][\text{BF}_4]$ (**7**). A similar shift of the carbonyl stretching frequencies was observed during protonation of the carbyne complex $\text{Tp}'(\text{CO})_2\text{W}=\text{CH}$ ($\nu_{\text{CO}} = 1989, 1893 \text{ cm}^{-1}$) to form the isolable cationic methyldene complex $[\text{Tp}'(\text{CO})_2\text{W}=\text{CH}_2][\text{BAR}'_4]$ ($\nu_{\text{CO}} = 2076, 2003 \text{ cm}^{-1}$).¹⁴

The protonation reaction was repeated in CD_2Cl_2 and monitored by NMR spectroscopy. Addition of $[\text{H}(\text{Et}_2\text{O})_2][\text{BAR}'_4]$ to the starting material at -50°C generated the intermediate cationic carbene complex $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{H})\text{O}(p\text{-C}_6\text{H}_4\text{OMe})][\text{BAR}'_4]$. The initial ratio of carbene complex **7'** to carbyne complex **5c** was 1:3 based on integration of the ^1H NMR spectrum. Upon warming to room temperature, the ratio of carbene complex to carbyne complex increased to 2:1. The most salient feature in the ^1H NMR spectrum of the cationic carbene complex **7'** is the agostic proton, bound to the carbene

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carbon, that appears at -0.22 ppm. This upfield resonance, integrating for one proton, exhibits tungsten coupling (14.4% ^{183}W , $^2J_{\text{WH}} = 12$ Hz) and carbon coupling (1.1% ^{13}C , $^1J_{\text{CH}} = 89$ Hz). The NMR characteristics of the proton bound to the carbene carbon in $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{H})\text{O}(\text{p-C}_6\text{H}_4\text{OMe})][\text{BAR}'_4]$ resemble those of the agostic proton in $[\text{Tp}'(\text{CO})_2\text{W}=\text{CH}_2][\text{BAR}'_4]$ (1.38 ppm, $^2J_{\text{WH}} = 22$ Hz, $^1J_{\text{CH}} = 92$ Hz).¹⁴ The use of 4 equiv of $\text{H}[\text{BF}_4]$ to protonate the aryloxycarbene complex in CD_2Cl_2 at -45 °C resulted in a larger proportion of cationic carbene complex **7** (no starting material was observed); however, the reaction was not as clean as the one utilizing $[\text{H}(\text{Et}_2\text{O})_2][\text{BAR}'_4]$.

A gradient HMQC experiment revealed that the agostic proton in the cationic carbene complex $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{H})\text{O}(\text{p-C}_6\text{H}_4\text{OMe})]^+$ is attached to a carbon resonating near 201 ppm in the ^{13}C spectrum, and indeed a doublet in the proton-coupled ^{13}C spectrum of **7** at 201.2 ppm with a $^1J_{\text{CH}}$ coupling constant of 89 Hz confirmed this assignment. The chemical shift found for the carbene carbon in $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{H})\text{O}(\text{p-C}_6\text{H}_4\text{OMe})][\text{BAR}'_4]$ is similar to the chemical shift of 224.8 ppm found for the carbene carbon in $[\text{Tp}'(\text{CO})_2\text{W}=\text{CH}_2][\text{BAR}'_4]$.¹⁴

The unsaturated carbene intermediate **7** is stabilized by donation of electron density from the agostic hydrogen on the carbene carbon. Complexes with an α -agostic carbene ligand are well-known: $[\text{Tp}(\text{P}(\text{OMe})_3)(\text{CO})\text{Mo}=\text{C}(\text{H})\text{Bu}][\text{BF}_4]$,^{11a} $[\text{Tp}'(\text{CO})_2\text{Mo}=\text{C}(\text{H})\text{Fe}(\text{CO})_2\text{Cp}][\text{BF}_4]$,¹⁵ $[\text{Cl}(\text{PMe}_3)_4\text{W}=\text{C}(\text{H})\text{H}][\text{OTf}]$,¹⁶ $[\text{X}(\text{PMe}_3)_2(\text{CO})(\text{NCR})\text{W}=\text{C}(\text{H})\text{R}][\text{Y}]$ ($\text{X} = \text{Cl, I}$; $\text{R} = \text{CMe}_3, \text{C}_6\text{H}_{11}, 2,6\text{-C}_6\text{H}_3\text{Me}_2$; $\text{Y} = \text{OTf, BF}_4$),¹⁷ and $[\text{X}(\text{P}_3)(\text{CO})\text{W}=\text{C}(\text{H})\text{Tol}][\text{BF}_4]$ ($\text{X} = \text{Br, CH}_3$; $\text{P}_3 = \text{PhP}(\text{C}_2\text{H}_4\text{PPh}_2)_2$).¹⁸ A dative bond from a heteroatom substituent is an alternate source of electron density. The thiomethoxy carbene complex $[\text{Tp}(\text{CO})_2\text{W}=\text{C}(\text{SMe})\text{H}][\text{OTf}]$ possesses a sulfur–metal dative bond,¹⁹ and the *o*-anisyl carbene complex $[\text{Tp}(\text{CO})_2\text{W}=\text{C}(2\text{-C}_6\text{H}_4\text{OMe})\text{H}][\text{BF}_4]$ is thought to be stabilized by an oxygen–metal dative bond.²⁰ In our system, an agostic bond is favored over an oxygen–metal dative bond for stabilizing the unsaturated metal center.

Monitoring the Addition of $\text{PhC}\equiv\text{CH}$ to the Cationic Carbene Intermediate $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{H})\text{O}(\text{p-C}_6\text{H}_4\text{OMe})][\text{BF}_4]$ by in Situ IR and NMR Spectroscopy: Alkyne Insertion To Generate the Cationic η^3 -Vinylcarbene Complex $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-C}_\alpha\text{C}_\beta\text{C}_\gamma)=\text{CPh}-\text{CH}=\text{CHO}(\text{p-C}_6\text{H}_4\text{OMe})][\text{BF}_4]$ (6c**).** Addition of 4 equiv of phenylacetylene to the cationic carbene intermediate $[\text{Tp}'(\text{CO})_2\text{W}=\text{C}(\text{H})\text{O}(\text{p-C}_6\text{H}_4\text{OMe})][\text{BF}_4]$ resulted in the formation of the cationic η^3 -vinylcarbene complex $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-C}_\alpha\text{C}_\beta\text{C}_\gamma)=\text{CPh}-\text{CH}=\text{CHO}(\text{p-C}_6\text{H}_4\text{OMe})][\text{BF}_4]$ (**6c**) (Scheme 8). After addition of $\text{PhC}\equiv\text{CH}$ to the CH_2Cl_2 solution at -45 °C the IR spectrum revealed new absorbances ($\nu_{\text{CO}} = 2054$,

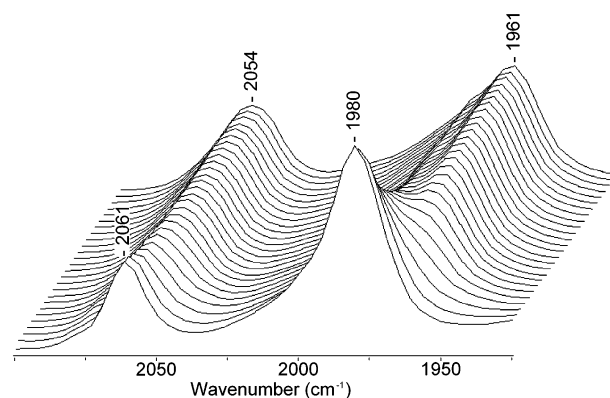


Figure 4. In situ IR spectra obtained during the insertion reaction.

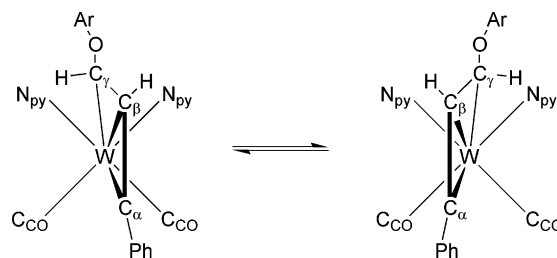
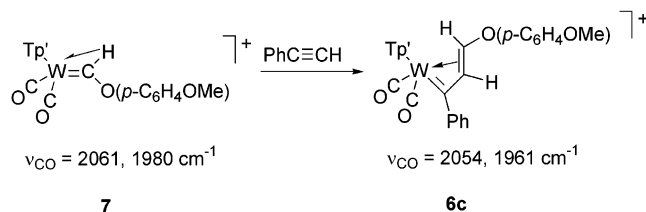


Figure 5. Interconversion of enantiomers through isomerization of the C_3R_4 ligand.

Scheme 8. Formation of η^3 -Vinylcarbene Complex **6c**



1961 cm^{-1}) increasing as the absorptions of the cationic carbene intermediate ($\nu_{\text{CO}} = 2061, 1980\text{ cm}^{-1}$) diminished (Figure 4). Under these conditions, the half-life of the alkyne-insertion reaction was approximately 4 min.

^1H NMR spectroscopy confirmed formation of cationic η^3 -vinylcarbene complex $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-C}_\alpha\text{C}_\beta\text{C}_\gamma)=\text{CPh}-\text{CH}=\text{CHO}(\text{p-C}_6\text{H}_4\text{OMe})][\text{BF}_4]$ (**6c**) after addition of phenylacetylene to a -45 °C CD_2Cl_2 solution of the cationic carbene intermediate generated with $\text{H}[\text{BF}_4]$. Similarly, addition of phenylacetylene to the BAR'_4^- salt of the cationic carbene intermediate cleanly generated the cationic η^3 -vinylcarbene complex **6c**.

Fluxional Behavior of the Cationic η^3 -Vinylcarbene Complexes. Although the proton and carbon resonances of the η^3 -vinylcarbene ligand in **6** were sharp, signals corresponding to two arms of the Tp' ligand were broad at room temperature in the ^1H NMR spectrum. Below 263 K all signals were sharp. Fluxional behavior involving movement of the vinylcarbene ligand, which interconverts enantiomers, can account for this observation (Figure 5). Inversion at C_β and C_γ could occur via a 16-electron intermediate carbene complex resulting from dissociation of the vinyl fragment. One can envision a C_s intermediate as the free vinyl fragment swings through a molecular mirror plane. Coordination

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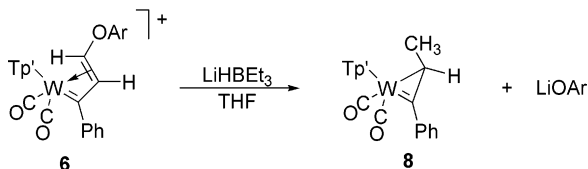
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Scheme 9. The Reaction of 6 with a Hydride Source To Yield 8


dination of the olefin generates distinct enantiomers depending on which face of the olefin binds to the metal. This movement would average the environments of the diastereotopic pyrazolyl rings as well as the two carbonyl ligands. The exchange process leaves the η^3 -vinylcarbene protons in enantiomeric environments, hence causing no change in NMR observables for the vinylcarbene ligands.

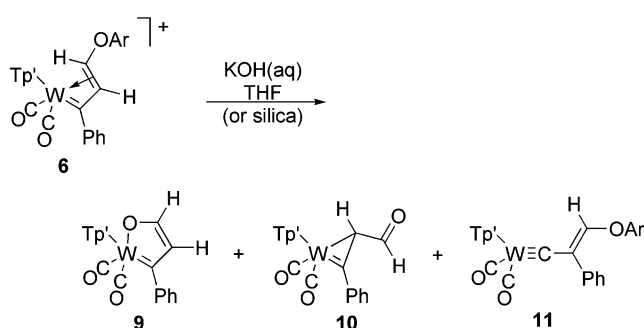
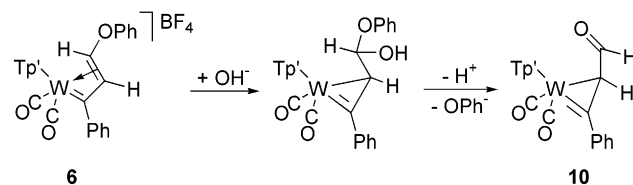
The η^3 -vinylcarbene tungsten complex $[\text{Cp}(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha, \text{C}_\beta, \text{C}_\gamma)=\text{CPh}-\text{CPh}=\text{CH}(\text{ToI}))][\text{BF}_4]$ (**1**) possessed two distinct carbonyl carbon resonances at room temperature.² The stronger interaction of the vinyl group with the tungsten metal center of **1** is evident in the short $\text{W}-\text{C}_\gamma$ distance and results in a static η^3 -vinylcarbene ligand at room temperature in contrast to the behavior of **6**. Fluxional behavior involving dissociation of the vinyl fragment from the η^3 -vinylcarbene chromium complex $(\text{CO})_4\text{Cr}(\eta^3\text{-C}(\text{morpholino})(1\text{-cyclopentenyl}))$ was invoked to explain dynamic behavior.^{3d}

Reactivity of the Cationic η^3 -Vinylcarbene Complexes: $\text{Li}[\text{HBEt}_3]$. Nucleophiles that react with η^3 -vinylcarbene ligands have generally been observed to react at the carbene carbon to form η^3 -allyl complexes.^{3a} We observed that complexes **6a–c** react primarily at the terminal vinyl carbon instead of the carbene carbon.

Reaction of **6b** with $\text{Li}[\text{HBEt}_3]$ as a hydride source led to double hydride addition to C_γ with accompanying loss of OAr^- (Scheme 9). The $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-}(\text{C}_\alpha, \text{C}_\beta)\text{-CPhCHCH}_3)$ (**8**) product was identified by comparison of NMR data to literature values.^{5e} The product of single hydride addition was not observed. Note that, in contrast, hydride addition to the η^3 -vinylcarbene complex $[\text{Cp}(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha, \text{C}_\beta, \text{C}_\gamma)=\text{CPh}-\text{CPh}=\text{CH}(\text{ToI}))][\text{BF}_4]$ (**1**) occurred at C_α to form the neutral η^3 -allyl complex $\text{Cp}(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha, \text{C}_\beta, \text{C}_\gamma)\text{CPh}(\text{H})\text{CPhCH}(\text{ToI}))$ (**3**).² Steric bulk from the pendant methyl groups of the Tp' ligand in **6** may shield C_α from nucleophilic attack.

$[\text{Bu}_4\text{N}][\text{I}]$. Since Geoffroy prepared the neutral cyclopentadienyl vinylcarbene complex **2** by substituting iodide for one of the carbonyl ligands in the cationic dicarbonyl reagent **1**² we attempted a similar transformation. Stirring a solution of the cationic Tp' tungsten vinylcarbene complex **6** and $[\text{Bu}_4\text{N}][\text{I}]$ for days did not result in formation of a neutral monocarbonyl complex.

Silica Chromatography. The presence of an orange paramagnetic material that has broad NMR signals and no carbonyl absorptions complicated purification of **6**. Conversion of cationic complex **6** to neutral products occurred during silica chromatography, and early chromatographic efforts led to isolation of metallafuran complex **9**. More extensive chromatography of the cationic vinylcarbene complex **6** led to the isolation of multiple products. The orange band that eluted first from the silica column was identified as metallafuran complex **9**, and a second orange band was identified as an aryloxy-substituted vinylcarbyne complex (**11a** from

Scheme 10. Products Isolated from the Addition of an OH^- Source to Complex 6

Scheme 11. Possible Reaction Pathway for the Formation of 10


6a', 11b from **6b**). A green band that eluted last was identified as metallacyclopentene aldehyde complex **10** (vide infra).

Aqueous Base. In view of the transformations that were evident during silica chromatography we explored addition of base to the cationic vinylcarbene complex **6b**. Addition of excess aqueous potassium hydroxide to a solution of **6b** in tetrahydrofuran at ambient temperature resulted in formation of approximately a 1:1 mixture of $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-}(\text{C}_\alpha, \text{O})\text{CPhCHCHO})$ (**9**) and $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-}(\text{C}_\alpha, \text{C}_\beta)\text{CPhCHCHO})$ (**10**) (Scheme 10). These products are consistent with initial attack of the hydroxide nucleophile at C_γ of the vinylcarbene ligand. Deprotonation of the resulting neutral species and loss of phenoxide under basic conditions would lead directly to the aldehyde functionality on the metallacyclopentene ligand of **10** (Scheme 11). Cooling the reagents to -30°C resulted in generation of only **10**, which was recovered in 36% yield (based on carbyne complex **5**).

Characterization of the Metallafuran Complex $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-}(\text{C}_\alpha, \text{O})=\text{CPh}-\text{CH}=\text{CH}-\text{O})$ (9**).** Alkyne insertion into a metal–acyl bond is a common route to metallafuran complexes.^{7f} An η^3 -vinylcarbene ligand has been converted into a metallafuran ligand by addition of a nucleophilic oxygen (from a nitrene) to the carbene carbon.² The terminal vinyl carbon in complex **6** reacts more readily with nucleophiles than the carbene carbon, and hydroxide ion reacts at the terminal vinyl carbon to generate the metallafuran complex $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-}(\text{C}_\alpha, \text{O})=\text{CPh}-\text{CH}=\text{CH}-\text{O})$ (**9**).

Metallafuran complex **9** is C_s symmetric on the NMR time scale with a 2:1 pattern observed for the tridentate Tp' ligand rings in the ^1H and ^{13}C NMR spectra of **9**. Thus, the metallafuran ring must effectively lie in the plane of symmetry, bisecting the two carbonyl ligands and two arms of the Tp' ligand. The ring proton on C_γ , next to oxygen, appeared downfield at 8.78 ppm, while the proton on C_β appeared at 7.13 ppm. The proton on C_γ was observed to couple to tungsten with a three-bond coupling constant of 13 Hz. A surprisingly small vicinal coupling of 1 Hz between the C_β and C_γ protons was

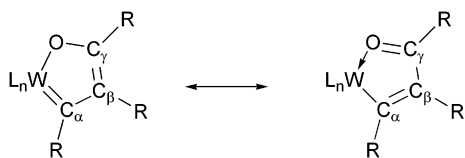


Figure 6. Resonance forms for the metallafuran ligand.

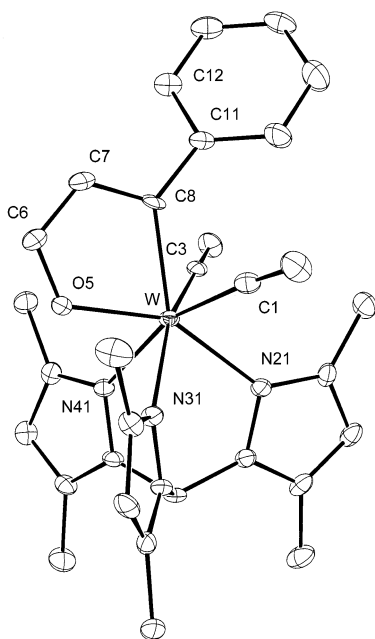


Figure 7. ORTEP representation of **9**.

observed. The carbene carbon, C_{α} , was located at 241.3 ppm ($^1J_{WC} = 29$ Hz), while ring carbons C_{β} and C_{γ} were observed at 124.8 and 172.1 ppm, respectively.

Both the metallafuran resonance form and the resonance form with a C=O fragment coordinated through a dative bond to the metal from oxygen appear to contribute to both Tp' and Cp metallafuran complexes (Figure 6).^{5c}

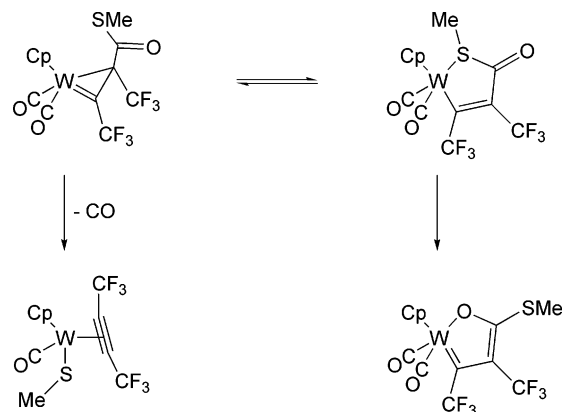
A related metallafuran complex, $Cp(CO)_2W(\kappa^2-(C_{\alpha},O)=CTol-CPh=CPh-O)$ (**4**), was generated by oxidation of vinylcarbene complex **1**.² One similarity between **4** and **9** is reflected in the proximity of the stretching frequencies for the carbonyl ligands in **4** (1965 and 1887 cm^{-1}) and **9** (1964 and 1870 cm^{-1}). The metallafuran ring in complex **4** was oriented perpendicular to the mirror plane of the $Cp(CO)_2W$ fragment, and indeed the same orientation is observed for the metallafuran ring in other cyclopentadienyl derivatives, including $Cp^*(CO)_2W(\kappa^2-(C_{\alpha},O)CMeCMeCMeO)$ ^{7f} (**12**) and $Cp(NO)(I)W(\kappa^2-(C_{\alpha},O)C(^tBu)CHC(CH_2COOEt)O)$ ^{7a} (**13**). Why is the metallafuran orientation orthogonal to the molecular mirror plane in Cp complexes but aligned in the mirror plane in Tp' complexes? The steric bulk of the 3,5-dimethylpyrazolyl rings and the tridentate N_3 donation in **9** favor placement of the metallafuran ring between two arms of the Tp' ligand and thus in the mirror plane of the $Tp'(CO)_2W$ fragment. Other Tp' complexes such as $Tp'(CO)_2W(\kappa^2-(C_{\alpha},O)CHCHCPhO)$ ^{7b} (**14**) and $Tp'(CO)_2W(\kappa^2-(C_{\alpha},O)C(^nBu)CHC(CH=CH(^nBu)O))$ ^{5b} (**15**) also adopt this symmetric orientation.

The structure of $Tp'(CO)_2W(\kappa^2-(C_{\alpha},O)=CPh-CH=CH-O)$ (**9**) was obtained (Figure 7 and Table 3), and the bond distances in the metallafuran ring are similar

Table 3. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for $Tp'(CO)_2W(\kappa^2-(C_{\alpha},O)=CPh-CH=CH-O)$ (**9**)

Distances (Å)			
W-C $_{\alpha}$ (8)	2.16(1)	C $_{\alpha}$ (8)-C $_{\beta}$ (7)	1.41(1)
W-O(5)	2.040(4)	C $_{\beta}$ (7)-C $_{\gamma}$ (6)	1.35(1)
W-N(21)	2.249(4)	C $_{\gamma}$ (6)-O(5)	1.29(1)
W-N(31)	2.226(4)	W-C $_{CO}$ (1)	1.97(1)
W-N(41)	2.24(1)	W-C $_{CO}$ (3)	1.97(1)
Bond Angles (deg)			
W-C $_{\alpha}$ (8)-C $_{\beta}$ (7)	113.1(4)	C $_{\alpha}$ (8)-C $_{\beta}$ (7)-C $_{\gamma}$ (6)	115(1)
W-C $_{\alpha}$ (8)-C(11)	131.6(4)	C $_{\beta}$ (7)-C $_{\gamma}$ (6)-O(5)	117(1)
W-O(5)-C $_{\gamma}$ (6)	120.8(4)	C $_{CO}$ (1)-W-C $_{CO}$ (3)	101.9(2)
N(21)-W-C $_{\alpha}$ (8)	134.6(2)	C $_{CO}$ (1)-W-C $_{\alpha}$ (8)	72.3(2)
N(21)-W-O(5)	151.3(2)	C $_{CO}$ (3)-W-C $_{\alpha}$ (8)	69.4(2)
C $_{CO}$ (1)-W-N(41)	162.0(2)	C $_{CO}$ (3)-W-N(31)	158.6(2)
Torsion Angles (deg)			
W-C $_{\alpha}$ (8)-C(11)-C(12)			136(1)
W-C $_{\alpha}$ (8)-C $_{\beta}$ (7)-C $_{\gamma}$ (6)			-1(1)

Scheme 12. Isomerization of and CO Loss from $Cp(CO)_2W(\eta^2-(C_{\alpha},C_{\beta})CCF_3CCF_3C(O)SMe)$



to those of other Tp tungsten metallafuran complexes ($W-C_{\alpha} = 2.16(1)$ Å, $W-O = 2.040(4)$ Å, $C_{\gamma}-O = 1.29(1)$ Å, **9**; $W-C_{\alpha} = 2.12(1)$ Å, $W-O = 2.03(1)$ Å, $C_{\gamma}-O = 1.33(2)$ Å, **14**; $W-C_{\alpha} = 2.16(1)$ Å, $W-O = 2.044(4)$ Å, $C_{\gamma}-O = 1.32(1)$ Å, **15**) The $W-C_{\alpha}$ distances in Cp tungsten metallafuran complexes are similar to those of the Tp complexes ($W-C_{\alpha} = 2.13(1)$ Å, **4**; $W-C_{\alpha} = 2.14(1)$ Å, **12**; $W-C_{\alpha} = 2.19(1)$ Å, **13**), as are the $W-O$ and $C_{\gamma}-O$ bond distances in the Cp complexes ($W-O = 2.100(3)$ Å, $C_{\gamma}-O = 1.30(1)$ Å, **4**; $W-O = 2.10(1)$ Å, $C_{\gamma}-O = 1.29(2)$ Å, **12**; $W-O = 2.11(1)$ Å, $C_{\gamma}-O = 1.26(2)$ Å, **13**).

Characterization of the Metallacyclopropene Aldehyde Complex $Tp'(CO)_2W(\eta^2-(C_{\alpha},C_{\beta})=CPh-CHCHO)$ (10**).** Few metallacyclopropene (η^2 -vinyl) complexes possess a formyl, acyl, or carboxylate group at C_{β} .^{5a,7f} Those that have been isolated are light- and heat-sensitive intermediates in isomerization reactions (Scheme 12).²¹

The dark green complex $Tp'(CO)_2W(\eta^2-(C_{\alpha},C_{\beta})=CPh-CHCHO)$ (**10**) exhibits metal-CO absorptions at 1980 and 1888 cm^{-1} and an aldehyde CO stretch at 1644 cm^{-1} . The presence of an aldehyde functionality was further supported by resonances observed at 9.08 ppm in the 1H NMR spectrum and 202.5 ppm in the ^{13}C NMR spectrum. The aldehyde proton couples to the C_{β} proton

(21) (a) Davidson, J. L.; Shiralian, M.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1979**, 30. (b) Davidson, J. L. *J. Chem. Soc., Chem. Commun.* **1979**, 597.

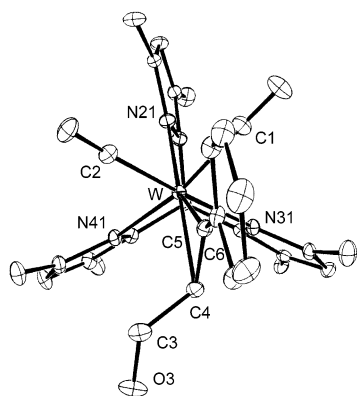


Figure 8. ORTEP representation of **10**.

Table 4. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-C}_\alpha\text{C}_\beta\text{)=CPh-CH=CH-O}$ (**10**)

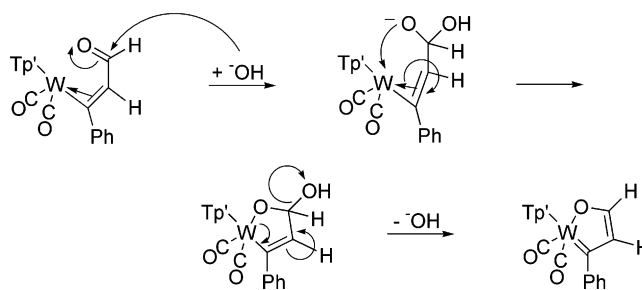
Distances (Å)			
W–C _α (5)	1.99(1)	C _α (5)–C _β (4)	1.45(1)
W–C _β (4)	2.25(1)	C _β (4)–C _γ (3)	1.43(1)
W–C _γ (3)	3.22(1)	C _γ (3)–O(3)	1.23(1)
W–N(21)	2.21(1)	W–C _{CO} (1)	2.00(1)
W–N(31)	2.23(1)	W–C _{CO} (2)	1.99(1)
W–N(41)	2.24(1)		
Bond Angles (deg)			
W–C _α (5)–C(6)	148.4(4)	C _α (5)–C _β (4)–C _γ (3)	119.5(5)
W–C _α (5)–C _β (4)	80.1(3)	C _β (4)–C _γ (3)–O(3)	126.2(5)
W–C _β (4)–C _α (5)	60.5(3)	C _{CO} (1)–W–C _{CO} (2)	90.1(2)
W–C _β (4)–C _γ (3)	120.2(4)	C _α (5)–W–N(21)	155.1(2)
Torsion Angles (deg)			
W–C _α (5)–C _β (4)–C _γ (3)			–110(1)
C _{CO} (1)–W–C _α (5)–C _β (4)			–146(1)
N(31)–W–C _β (4)–C _γ (3)			–131(1)

observed at 3.53 ppm ($^3J_{\text{HH}} = 8$ Hz), and two-bond tungsten–hydrogen coupling of 12 Hz was also observed for the proton on C_β. Tungsten coupling was observed for the carbene carbon C_α (232.3 ppm, $^1J_{\text{WC}} = 34$ Hz), C_β (46.4 ppm, $^1J_{\text{WC}} = 19$ Hz), and the aldehyde carbon C_γ (202.5 ppm, $^2J_{\text{WC}} = 7$ Hz), as well as for the carbonyl ligands (221.7 ppm, $^1J_{\text{WC}} = 164$ Hz; 220.7 ppm, $^1J_{\text{WC}} = 141$ Hz).

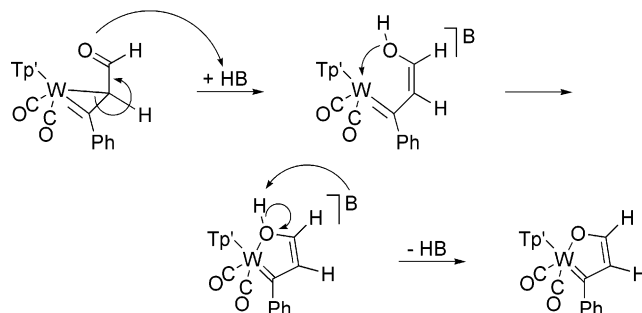
The metallacyclopropene aldehyde formulation was confirmed by an X-ray structure determination (Figure 8 and Table 4). The metallacyclopropene (η^2 -vinyl) ligand here is reminiscent of complexes such as $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-C}_\alpha\text{C}_\beta\text{)CPhCHPh}$ ^{5b,e} (**16**), but in this case an uncoordinated aldehyde functional group is present. Only one isomer was observed for complex **10** even though complex **16** exists as two isomers (55:45 ratio). Chemical shift values and structural parameters for **10** are close to those found for **16**. The W–C_α carbon bond lengths (1.988(5) Å, **10**; 1.990(8) Å, **16**) and the W–C_β bond lengths (2.250(5) Å, **10**; 2.263(8) Å, **16**) of **10** and **16** are virtually identical.

Protonation of the Metallacyclopropene Aldehyde Complex (10): Isomerization from the Metallacyclopropene Aldehyde Complex (10) to the Metallafuran Complex (9). Alkyne insertion into metal–alkyl bonds and nucleophilic addition to coordinated alkynes are the most common routes to metallacyclopropene complexes. Here, electrons on oxygen feed into the C_γ carbon to convert the vinylcarbene ligand into an η^2 -vinyl ligand, an alternative description for metallacyclopropene ligands. Given that the stoichiometry

Scheme 13. Possible Mechanism for Base-Catalyzed Isomerization of **10** to **9**



Scheme 14. Proposed Mechanism for the Acid-Catalyzed Isomerization of **10** to **9**

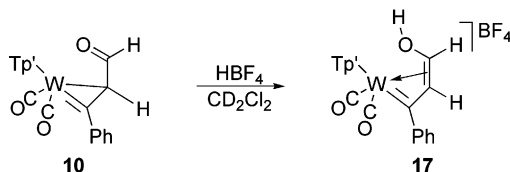


of **9** and **10** is identical, could they interconvert? Since we had originally isolated only the metallafuran complex **9**, and in view of the large number of metallafuran complexes in the literature,^{2,5b,7,8} it seemed likely that the metallafuran complex is the thermodynamically favored product. Could the metallacyclopropene aldehyde be a kinetic product that goes on to form metallafuran?

Indeed, monitoring an NMR sample of recrystallized metallacyclopropene complex **10** revealed slow formation of metallafuran complex **9**. The concentration of **9** increased at the expense of **10** with a half-life of approximately 3 weeks. No other products were evident.

Two distinct pathways were explored as routes to catalyze the isomerization of the metallacyclopropene aldehyde complex to the metallafuran. Hydroxide could conceivably facilitate the conversion of **10** to **9** by attacking at the aldehyde carbon and generating a nucleophilic alkoxide substituent (Scheme 13). Coordination of the anionic oxygen to tungsten and loss of hydroxide would generate the metallafuran species **9**. In fact, only a slight increase in the rate of isomerization of **10** to **9** was observed with the addition of aqueous KOH to a 3:1 CH₂Cl₂:Et₂O solution of **10**. This small increase in the rate of isomerization is consistent with the persistence of **10** in the KOH/H₂O/THF reaction solution described above.

A second possible pathway for catalytic isomerization of the metallacyclopropene aldehyde complex to the metallafuran complex is through protonation (Scheme 14). Coordination of the alcohol oxygen to tungsten followed by deprotonation could lead to catalytic formation of **9**. Indeed addition of a 0.1 equiv of H[BF₄] (in Et₂O) to a CD₂Cl₂ solution of **10** at room temperature resulted in complete conversion to **9** over a period of about 30 min. A ¹H NMR spectrum of the reaction solution about 15 min after addition of acid revealed a

Scheme 15. Formation of η^3 -Vinylcarbene Intermediate 17


transient species in which two arms of the Tp' ligand appeared to be broadened.

Addition of 0.9 equiv of acid to **10** at 183 K allowed ^1H NMR characterization of an intermediate species; it is the protonated complex $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha\text{C}_\beta\text{C}_\gamma)\text{=CPh-CH=CH-OH})][\text{BF}_4]$ (**17**) (Scheme 15). The ^1H NMR spectrum for **17** is similar to the ^1H NMR spectra for the cationic aryloxy-substituted η^3 -vinylcarbene **6**, except that the proton on C_β of **17** appears upfield of the Tp' methine signals while the C_β proton in **6** appears downfield of the Tp' methine signals. The hydroxy proton in complex **17** resonates around 10 ppm.

Davidson observed heat- and light-sensitive metallacyclopentene thiocarboxylate complexes rearrange to metallathiofuranone, metallafuran, and η^2 -alkyne complexes (Scheme 12).^{21b} In the crystal structure of the metallacyclopentene *S*-alkyl thiocarboxylate $\text{Cp}(\text{CO})_2\text{W}(\eta^2\text{-}(\text{C}_\alpha\text{C}_\beta)\text{=C}(\text{CF}_3)\text{-}(\text{CF}_3)\text{C}(\text{O})\text{SMe})$ ^{21a} and in the crystal structure of $\text{Tp}'(\text{CO})_2\text{W}(\eta^2\text{-}(\text{C}_\alpha\text{C}_\beta)\text{=CPh-CHCHO})$ (**10**) the substituent attached to the carbonyl carbon (SMe or H) is pointed toward the Cp or Tp' ligand. Metallacyclopentene species may be persistent intermediates on the way to metallafuran complexes that possess a diminutive substituent on the oxygen-bound carbon. The possibility that metallafuran complexes formed from alkyne insertion into metal-acyl bonds pass through intermediates analogous to metallacyclopentene complex **10** deserves consideration.

Photochemical Isomerization of the Metallafuran Complex (9) to the Metallacyclopentene Aldehyde Complex (10). Having established that metallafuran **9** is the thermodynamically favored isomer, we turned to photolysis as a possible method for converting **9** to the metallacyclopentene isomer **10**. A CD_2Cl_2 solution of the pure metallafuran complex **9** was prepared in an NMR tube and the sample was irradiated with a UV lamp. The photolysis was monitored by ^1H NMR, and after 4 h of irradiation the ratio of metallafuran complex **9** to metallafuran complex **10** was approximately 1:1.

Characterization of the Vinylcarbyne Complexes $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{C-CPh=C(H)OPh}$ (11a**) and $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{C-CPh=C(H)OTol}$ (**11b**).** Vinylcarbyne complexes **11a** and **11b** were isolated as byproducts of the conversion of $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha\text{C}_\beta\text{C}_\gamma)\text{=CPh-CH=CH-OPh})][\text{BAR}'_4]$ (**6a'**) and the tolyl derivative (**6b**) to metallafuran and metallacyclopentene complexes **9** and **10** during chromatography on alumina or silica. CO absorbance peaks consistent with $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CR}$ formulations were observed in the IR spectrum for each complex ($\nu_{\text{CO}} = 1953, 1868\text{ cm}^{-1}$, **11a**; $\nu_{\text{CO}} = 1953, 1870\text{ cm}^{-1}$, **11b**). The vinyl proton was observed at 7.27 ppm for **11a** and at 7.24 ppm for **11b**. The Tp' ^1H and ^{13}C NMR signals from the 3,5-dimethylpyrazolyl rings appear as a 2:1 pattern that reflects the mirror symmetry of the carbyne complex.

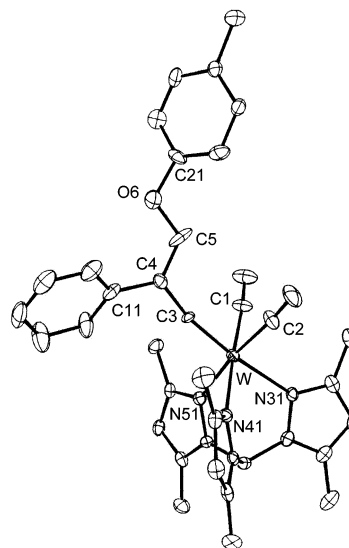


Figure 9. ORTEP representation of **11b**.

Table 5. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{C-CPh=CHOTol}$ (11b**)**

Distances (Å)			
W-C $_{\alpha}$ (3)	1.85(1)	C $_{\alpha}$ (3)-C $_{\beta}$ (4)	1.40(1)
W-N(31)	2.28(1)	C $_{\beta}$ (4)-C $_{\gamma}$ (5)	1.42(1)
W-N(41)	2.22(1)	C $_{\gamma}$ (5)-O(6)	1.36(1)
W-N(51)	2.22(1)	W-C(2)	1.98(1)
W-C(1)	2.00(1)		
Bond Angles (deg)			
W-C $_{\alpha}$ (3)-C $_{\beta}$ (4)	168(1)	C $_{\beta}$ (4)-C $_{\gamma}$ (5)-O(6)	119(1)
C $_{\alpha}$ (3)-C $_{\beta}$ (4)-C(11)	118(1)	C $_{\gamma}$ (5)-O(6)-C(21)	115(1)
C $_{\alpha}$ (3)-C $_{\beta}$ (4)-C $_{\gamma}$ (5)	115(1)	Cco(1)-W-Cco(2)	85.6(4)
C $_{\alpha}$ (3)-W-N(31)	173.5(3)		
Torsion Angles (deg)			
Cco(1)-W-C $_{\beta}$ (4)-C $_{\gamma}$ (5)			-37(1)

Crystals of **11b** suitable for X-ray analysis were isolated, and the structure confirmed the formulation of **11b** as a vinylcarbyne complex (Figure 9, Table 5). The structure of **11b** reveals the delocalized nature of the π -orbitals in the vinylcarbyne ligand. The tungsten-carbyne carbon (W-C $_{\alpha}$) bond length obtained for **11b** (1.85(1) Å), W-C $_{\alpha}$) is only slightly longer than the W-C $_{\alpha}$ bond length in the phenylacyl carbyne complex $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{C-C}(\text{O})\text{Ph}$ (1.83(1) Å, W-C $_{\alpha}$),¹⁴ but the C $_{\alpha}$ -C $_{\beta}$ bond length in **11b** (1.40(1) Å, C $_{\alpha}$ -C $_{\beta}$) is almost 0.1 Å shorter than the C $_{\alpha}$ -C $_{\beta}$ bond length in the phenylacyl carbyne complex (1.49(1) Å, C $_{\alpha}$ -C $_{\beta}$). The formal double bond in the pendant vinyl group of **11b** (1.42(1) Å, C $_{\beta}$ -C $_{\gamma}$) is approximately the same length as the C $_{\alpha}$ -C $_{\beta}$ bond length. The structure of vinylcarbyne complex **11b** is similar to that of the vinylcarbyne complex $(\text{dppe})(\text{CO})_2\text{CIW}\equiv\text{C-CH=C}(\text{CH}_2)_4$ (1.83(1) Å, W-C $_{\alpha}$; 1.43(1) Å, C $_{\alpha}$ -C $_{\beta}$; 1.40(1) Å, C $_{\beta}$ -C $_{\gamma}$).²²

Several examples of terminal carbyne complexes with vinyl substituents directly bound to the carbyne carbon are known.^{22,23} Protonation or alkylation of alkenyl-vinylidene (or allenylidene) complexes,^{22,23e,23g-i} deprotonation and oxidation of hydrocarbon-bridged dimers,^{23c} hydroamination of an alkynyl-carbyne ligand,^{23d} and other methods have been used to synthesize vinylcar-

(22) Zhang, L.; Gamasa, M. P.; Gimeno, J.; Carbajo, R. J.; Lopez-Ortiz, F.; Lanfranchi, M.; Tiripicchio, A. *Organometallics* **1996**, *15*, 4274.

byne complexes.^{23f,23j-1} Mechanistically, it is attractive to postulate deprotonation of $[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha\text{C}_\beta\text{C}_\gamma)\text{=CPh-CH=CH-OAr})]^+$ (**6**) at C_β and phenyl migration from C_α to C_β ; however, formation of a vinylcarbyne product was not observed after addition of $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ to **6a'**.

Conclusion

A cationic agostic carbene intermediate resulting from protonation of an aryloxycarbene complex was observed to form a cationic η^3 -vinylcarbene complex upon addition of phenylacetylene. Previously reported η^3 -vinylcarbene complexes were observed to react primarily at the carbene carbon,^{2,3a} but the aryloxy-substituted η^3 -vinylcarbene complexes reported here react with nucleophiles at the terminal carbon of the vinyl fragment. Modifications of the vinyl fragment provided a synthetic route to metallacyclopentene (η^2 -vinyl) complexes and allowed isolation of a metallacyclopentene aldehyde complex. Isomerization of the metallacyclopentene aldehyde complex to a metallafuran complex was accelerated by acid. The intermediate in the acid-catalyzed isomerization resembles the isolated cationic η^3 -vinylcarbene complexes. The metallafuran complex, the thermodynamically favored product, could be converted into the metallacyclopentene aldehyde complex by photochemical isomerization. This sequence of reactions reflects the interplay of the $\text{Tp}'\text{W}(\text{CO})_2$ fragment and the oxygen functionality originating in the $\text{W}\equiv\text{C}-\text{O}-\text{Ar}$ fragment (Scheme 16).

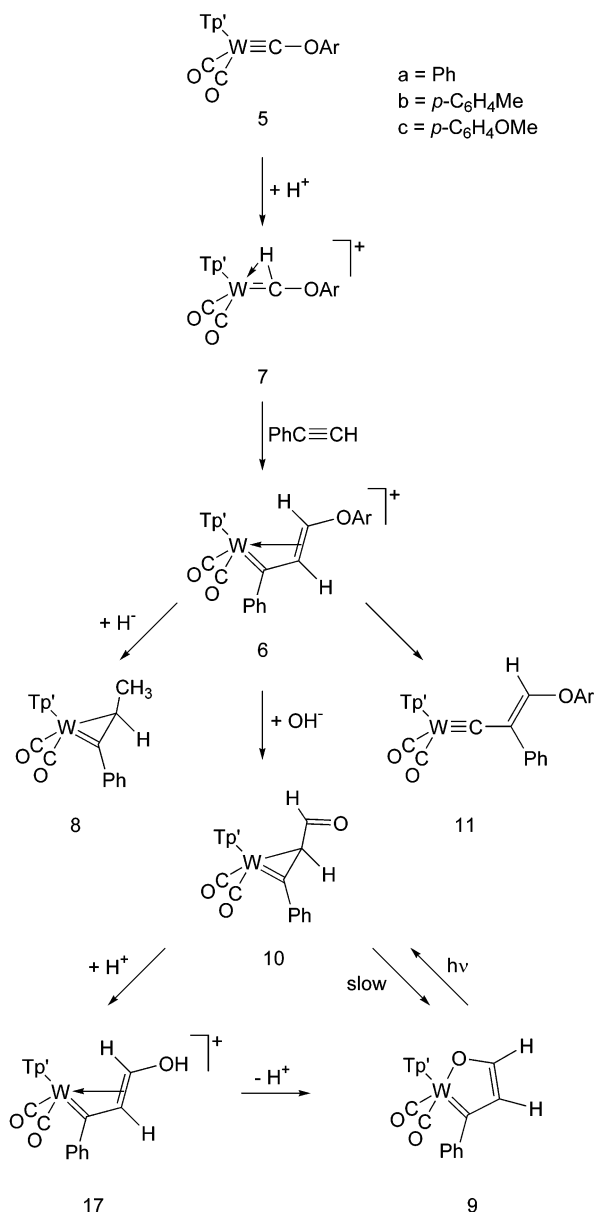
Experimental Section

All reactions were run under dry argon or nitrogen with the use of standard Schlenk techniques unless otherwise noted. Solvents were obtained from Fisher or Mallinckrodt and were used as obtained or dried under nitrogen or argon by standard methods.²⁴ Tetrafluoroboric acid, phenylacetylene, and lithium triethylborohydride (Super-Hydride) were used as obtained from Aldrich Chemicals. Potassium hydroxide was used as obtained from Mallinckrodt and methylene- d_2 chloride obtained from Cambridge Isotope Laboratories was used as obtained or dried with CaH_2 and vacuum transferred before being used. Alumina (80–200 mesh) was used as obtained from Fisher and silica (200–400 mesh) was used as obtained from Aldrich or Fisher. $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{COPh}$ (**5a**), $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CO}(p\text{-C}_6\text{H}_4\text{Me})$ (**5b**), $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CO}(p\text{-C}_6\text{H}_4\text{OMe})$ (**5c**),²⁵ and $[\text{H}(\text{OEt})_2][\text{BAr}'_4]$ ²⁶ were prepared according to literature methods.

(23) (a) Zhang, L.; Silva, M. F. C. G.; Kuznetsov, M. L.; Gamasa, M. P.; Gimeno, J.; Silva, J. J. R. F.; Pombeiro, A. J. L. *Organometallics* **2001**, *20*, 2782. (b) Zhang, L.; Gamasa, M. P.; Gimeno, J.; Carballo, R. J.; Lopez-Ortiz, F.; Silva, M. F. C. G.; Pombeiro, A. J. L. *Eur. J. Inorg. Chem.* **2000**, 341. (c) Woodworth, B. E.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 828. (d) Fischer, E. O.; Kalder, H. J.; Koehler, F. H. *J. Organomet. Chem.* **1974**, *81*, C23. (e) Casey, C. P.; Ha, Y.; Powell, D. R. *J. Organomet. Chem.* **1994**, *472*, 185. (f) Terry, M. R.; Kelley, C.; Lugan, N.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3607. (g) Kelley, C.; Lugan, N.; Terry, M. R.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 6735. (h) Kolobova, N. E.; Ivanov, L. L.; Zhvanko, O. S.; Khitrova, O. M.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *262*, 39. (i) Crochet, P.; Esteruelas, M. A.; Lopez, A. M.; Ruiz, N.; Tolosa, J. I. *Organometallics* **1998**, *17*, 3479. (j) Weber, B.; Steinert, P.; Windmueller, B.; Wolf, J.; Werner, H. *J. Chem. Soc., Chem. Commun.* **1994**, 2595. (k) Espuelas, J.; Esteruelas, M. A.; Lahoz, F. J.; Oro, L. A.; Ruiz, N. *J. Am. Chem. Soc.* **1993**, *115*, 4683. (l) Rappert, T.; Nuernberg, O.; Mahr, N.; Wolf, J.; Werner, H. *Organometallics* **1992**, *11*, 4156.

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Scheme 16. Species Derived from $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{COAr}$



Infrared spectra were obtained with a Mattson Polaris Fourier transform spectrophotometer or with an ASI (Mettler-Toledo) ReactIR 1000 FTIR spectrometer sampling with either a SiComp probe or a transmission cell. Processing of spectra and reaction profile data sets was performed with ReactIR 2.21 and ConcIRT 1.0a. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker DRX-500, Bruker Avance 400WB, Bruker DRX-400, or a Bruker AMX-300 spectrometer. Gradient COSY, HMQC, and HMBC 2D NMR were recorded on the DRX-500 or the Avance 400WB. Elemental analyses were performed by Oneida Research Services, Whitesboro, NY and Atlantic Microlab, Inc., Norcross, GA.

$[\text{Tp}'(\text{CO})_2\text{W}(\eta^3\text{-}(\text{C}_\alpha\text{C}_\beta\text{C}_\gamma)\text{=CPh-CH=CH-OPh})][\text{BAr}'_4]$ (**6a**). A flask was charged with 0.25 g (0.39 mmol) of **5a** and 0.47 g (0.47 mmol) of $[\text{H}(\text{Et}_2\text{O})_2][\text{BAr}'_4]$ and cooled to -78°C in a dry ice/2-propanol bath. Cold dichloromethane (40 mL) was added, and the clear yellow solution was stirred while phenylacetylene (170 μL , 1.56 mmol) was injected. After the

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

solution turned greenish yellow, about 60 min, the solution was allowed to warm to 0 °C. The resulting dichroic solution was observed to have IR absorptions at 2051 and 1966 cm⁻¹. The oil remaining after rotary evaporation was dissolved in 2 mL of acetonitrile and filtered through a cellulose plug before the concentrated solution was dripped into 70 mL of acetonitrile. Acetonitrile was removed by rotary evaporation after filtering the solution with a filter cannula. The resulting oil was taken up in Et₂O, filtered through a cellulose plug, and dripped into 70 mL of pentane. An orange powder was isolated during the acetonitrile and Et₂O filtrations (see **11a** below). The red-brown oil recovered after decanting the yellow Et₂O/pentane supernate was precipitated from Et₂O/pentane at -25 °C as an oily solid. After the supernate was decanted, 10 mL of pentane was added and then Et₂O was added until only a white powder remained undissolved. The supernate was decanted and rotovapped before being placed under vacuum. The resulting powder (0.35 g) was dissolved in 20 mL of Et₂O and acidified with 65 μL of 7 M H[BF₄] in Et₂O. The solution was filtered by filter cannula into a clean flask and pentane was added until a brown precipitate was observed. The flask was cooled to -25 °C and allowed to sit overnight. Recrystallization from a cloudy Et₂O/pentane solution cooled to 0 °C afforded 0.20 g of crystalline material. Yield: 32%. IR (KBr): 2050, 1953 cm⁻¹ (ν_{CO}). ¹H NMR (CD₂Cl₂, 298 K): δ 7.89, 7.72, 7.66, 7.55 (m:m:m:s, 2:10:1:4 H, *CPh*, *BAR'*), 7.13, 6.13 (m, 3:2 H, *OPh*), 6.69 (d, 1 H, ³J_{HH} = 10 Hz, *WCPHCHCHO*), 6.57 (d, 1 H, ³J_{HH} = 10 Hz, ³J_{WH} = 11 Hz, *WCPHCHCHO*), 6.12, 6.10, 5.91 (br s:s:br s, *TP'CH*), 2.70, 2.50, 2.38, 2.27, 2.21, 1.76 (s:br s:s:br s:br s:br s, *TP'CH*₃). Anal. Calcd for C₆₄H₄₆B₂F₂₄N₆O₃W: C, 47.79; H, 2.88; N, 5.22. Found: C, 48.14; H, 3.21; N, 5.04.

[Tp'(CO)₂W(η³-(C_α,C_β,C_γ)=CPh-CH=CH-OPh)][BF₄] (**6a**). After 0.95 g (1.48 mmol) of phenoxycarbyne complex **5a** was dissolved into 60 mL of CH₂Cl₂ the solution was cooled to -78 °C. Phenylacetylene (0.78 mL, 7.1 mmol) was added to the cold solution, and 5 min later 0.35 mL of a 7 M H[BF₄] solution in Et₂O (2.5 mmol) was added. The solution was allowed to warm to 0 °C, and after 30 min solvent was removed by rotary evaporation leaving a black oily residue. The residue was dissolved in 30 mL of acetonitrile, and following filtration through fine sand, the solvent was removed by rotary evaporation. The resulting viscous liquid was dissolved again in acetonitrile and eluted through a 15 cm by 1 cm column of silica with acetonitrile. The orange-red solid recovered after evaporation of acetonitrile was dissolved in a minimal amount of CH₂Cl₂, filtered through cellulose, and precipitated by slowly dripping the dichloromethane solution into 20 vol equiv of rapidly stirring Et₂O. The resulting orange solid was precipitated from a CH₂Cl₂/Et₂O solution two more times, and the orange powder (**6a**) was recovered in 30% yield (0.4 g). NMR signals from two pyrazolyl rings of the Tp' ligand were observed to be broad at room temperature for complexes of this type. IR (KBr): 2040, 1947 cm⁻¹ (ν_{CO}). ¹H NMR (CD₂Cl₂, 253 K): δ 7.89, 7.72, 7.66 (m, 2:2:1 H, *CPh*), 7.12, 6.08 (m, 3:2 H, *OPh*), 6.65 (d, 1 H, ³J_{HH} = 10 Hz, *WCPHCHCHO*), 6.57 (d, 1 H, ³J_{HH} = 10 Hz, ³J_{WH} = 11 Hz, *WCPHCHCHO*), 6.16, 6.12, 5.88 (s, *TP'CH*), 2.70, 2.53, 2.37, 2.24, 2.18, 1.73 (s, *TP'CH*₃). ¹³C{¹H} NMR (CD₂Cl₂, 253 K): δ 238.1 (s, *WCPh*), 214.1, 210.6 (s, *WCO*), 154.7, 154.0, 151.5, 148.9, 147.8, 147.4 (s, *TP'CCH*₃), 154.4, 128.7, 125.7, 115.2 (s, 1:2:1:2 C, *OPh*), 147.2 (s, *WCPHCHCHO*), 141.8, 133.2, 133.1, 130.2 (s, 1:2:1:2 C, *CPh*), 109.8, 109.3, 109.0 (s, *TP'CH*), 66.0 (s, *WCPHCHCHO*), 16.6, 14.9, 14.8, 13.3, 12.5, 12.3 (s, *TP'CH*₃).

[Tp'(CO)₂W(η³-(C_α,C_β,C_γ)=CPh-CH=CH-O(p-C₆H₄Me))][BF₄] (**6b**). Yield: 5%. IR (KBr): 2042, 1945 cm⁻¹ (ν_{CO}). ¹H NMR (CD₂Cl₂, 263 K): δ 7.90, 7.72, 7.66 (m, 2:2:1 H, *CPh*), 6.92, 5.99 (m, 2:2 H, *O(p-C₆H₄Me)*), 6.64 (d, 1 H, ³J_{HH} = 10 Hz, *WCPHCHCHO*), 6.51 (d, 1 H, ³J_{HH} = 10 Hz, ³J_{WH} = 12 Hz, *WCPHCHCHO*), 6.15, 6.13, 5.91 (s, *TP'CH*), 2.70, 2.55, 2.39, 2.30, 2.19, 1.73 (s, *TP'CH*₃), 2.27 (s, 3 H, *O(p-C₆H₄Me)*).

¹³C{¹H} NMR (CD₂Cl₂, 263 K): δ 238.0 (s, *WCPh*), 214.4 (s, ¹J_{WC} = 119 Hz, *WCO*), 210.9 (s, ¹J_{WC} = 166 Hz, *WCO*), 154.8, 154.2, 151.6, 149.0, 147.9, 147.5 (s, *TP'CCH*₃), 152.8, 135.9, 130.1, 115.2 (s, 1:1:2:2 C, *O(p-C₆H₄Me)*), 149.4 (s, *WCPHCHCHO*), 142.1, 133.3, 133.1, 130.1 (s, 1:2:1:2 C, *CPh*), 109.8, 109.4, 109.2 (s, *TP'CH*), 65.5 (s, *WCPHCHCHO*), 20.5 (s, *O(p-C₆H₄Me)*), 16.7, 14.9, 14.8, 13.4, 12.6, 12.4 (s, *TP'CH*₃). Anal. Calcd for C₃₃H₃₆N₆B₂F₄O₃W·Et₂O: C, 48.29; H, 5.04; N, 9.13. Found: C, 48.18; H, 4.49; N, 9.56.

[Tp'(CO)₂W(η³-(C_α,C_β,C_γ)=CPh-CH=CH-O(p-C₆H₄O-Me))][BF₄] (**6c**). Yield: 18%. IR (KBr): 2038, 1957 cm⁻¹ (ν_{CO}). ¹H NMR (CD₂Cl₂, 253 K): δ 7.89, 7.72, 7.66 (m, 2:2:1 H, *CPh*), 6.62, 6.05 (m, 2:2 H, *O(p-C₆H₄OMe)*), 6.58 (d, 1 H, ³J_{HH} = 10 Hz, *WCPHCHCHO*), 6.47 (d, 1 H, ³J_{HH} = 10 Hz, ³J_{WH} = 12 Hz, *WCPHCHCHO*), 6.12, 5.94 (s, 2:1 H, *TP'CH*), 3.73 (s, 3 H, *O(p-C₆H₄OMe)*), 2.70, 2.53, 2.39, 2.33, 2.19, 1.72 (s, *TP'CH*₃). ¹³C{¹H} NMR (CD₂Cl₂, 253 K): δ 237.8 (s, *WCPh*), 214.5, 210.9 (s, *WCO*), 157.2, 148.7, 116.7, 114.3 (s, 1:1:2:2 C, *O(p-C₆H₄OMe)*), 154.8, 154.2, 151.7, 149.0, 147.8, 147.4 (s, *TP'CCH*₃), 150.3 (s, *WCPHCHCHO*), 142.0, 133.3, 133.1, 130.2 (s, 1:2:1:2 C, *CPh*), 109.8, 109.4, 109.2 (s, *TP'CH*), 65.0 (s, *WCPHCHCHO*), 55.8 (s, *O(p-C₆H₄OMe)*), 16.7, 15.0, 14.8, 13.4, 12.6, 12.4 (s, *TP'CH*₃). Anal. Calcd for C₃₃H₃₆N₆B₂O₄F₄W: C, 45.97; H, 4.21; N, 9.75. Found: C, 46.43; H, 4.30; N, 9.16.

[Tp'(CO)₂W=C(H)O(p-C₆H₄OMe)][BX₄] (**BX₄** = **BF₄**, **7**; **BX₄** = **BAR'**, **7**): **Monitored by in Situ IR Spectroscopy.** The SiComp probe was rinsed with CH₂Cl₂ before being attached to an O-ring sealed ground glass joint adapter, which was connected to an oven-dried two-neck 300-mL Schlenk flask. The flask was charged with 40 mL of CH₂Cl₂ and immersed in a -50 °C dry ice-acetonitrile bath. After 10 min, Tp'(CO)₂W≡CO(p-C₆H₄OMe) (**5c**) was added (400 mg, 0.60 mmol). [H(Et₂O)₂][BAR'] (720 mg, 0.71 mmol, 1.2 equiv) dissolved in CH₂Cl₂ was transferred to the yellow solution. Absorbance peaks due to **7'** appeared immediately at 2061 and 1980 cm⁻¹ and continued to slowly increase in intensity while the absorbance peaks at 1966 and 1866 cm⁻¹ due to starting material decreased. The orange reaction solution was warmed to -10 °C and the ratio of the intensity of the absorption peaks due to the carbene and carbyne complexes became 1:1 in about 3 min. A similar reaction in which 4 equiv of H[BF₄] (180 μL, 54 wt % H[BF₄] in Et₂O, 1.31 mmol) was added to a CH₂Cl₂ solution (-45 °C, 40 mL) of Tp'(CO)₂W≡CO(p-C₆H₄OMe) (220 mg, 0.33 mmol) resulted in the complete disappearance of absorptions at 1965 and 1868 cm⁻¹ and the appearance of absorptions at 2061 and 1980 cm⁻¹ (from **7**) in less than a minute. Complexes [Tp'(CO)₂W=C(H)O(p-C₆H₄OMe)][BF₄] (**7**) and [Tp'(CO)₂W=C(H)O(p-C₆H₄OMe)][BAR'] (**7'**) possessed similar IR spectra. IR (CH₂Cl₂): 2571 (ν_{BH}), 2061, 1980 (ν_{CO}), 1544 (ν_{CN}) cm⁻¹.

Monitored by NMR Spectroscopy. CD₂Cl₂ was vacuum transferred to a J. Young NMR tube containing 20 mg of Tp'(CO)₂W≡CO(p-C₆H₄OMe) (**5c**) (0.030 mmol) and 37 mg of [H(Et₂O)₂][BAR'] (0.036 mmol, 1.2 equiv) cooled with liquid N₂. At -50 °C the cationic carbene complex **7'** was present in a 1:3 ratio with the starting material and increased in concentration such that a 2:1 ratio of carbene-to-carbyne complexes was present a room temperature. For the BF₄⁻ salt **7**, an NMR tube was sealed with a rubber septum and purged with N₂ after adding 20 mg of Tp'(CO)₂W≡CO(p-C₆H₄OMe) (**5c**) (0.030 mmol). The yellow solid was dissolved in 0.7 mL of CD₂Cl₂ and a ¹H NMR spectrum was obtained before and after addition of 17 μL of 54% H[BF₄] in Et₂O (0.123 mmol, 4 equiv) to the solution at -45 °C. [Tp'(CO)₂W=C(H)O(p-C₆H₄OMe)][BAR'] (**7**): ¹H NMR (CD₂Cl₂, 273 K) δ 7.72, 7.56 (s, 2:1 H ratio, *BAR'*), 7.33, 7.04 (m, 2:2 H, *OC₆H₄OMe*), 6.09, 6.04 (s, 2:1 H, *TP'CH*), 3.82 (s, 3 H, *OC₆H₄OMe*), 2.39, 2.38, 2.36, 2.33 (s, 6:6:3:3 H, *TP'CH*₃), -0.22 (s, 1 H, ²J_{WH} = 12 Hz, ¹J_{CH} = 89 Hz, *W=C(H)OAr*). ¹³C NMR (CD₂Cl₂, 273 K) δ 208.4 (*W-CO*), 201 (*W=C*). [Tp'(CO)₂W=C(H)O(p-C₆H₄OMe)][BF₄] (**7**): ¹H NMR (CD₂Cl₂, 228 K) δ 7.37, 7.04 (m, 2:2 H, *OC₆H₄OMe*), 6.10,

6.05 (s, 2:1 H, Tp'CH), 3.82 (s, 3 H, OMe), 2.40, 2.38, 2.35, 2.30 (s, 6:6:3:3 H, Tp'CH₃), 0.21 (s, 1 H, W=C(H)OAr).

Formation of [Tp'(CO)₂W(η³-(C_αC_βC_γ)=CPh-CH=CHO-(p-C₆H₄OMe))] [BX₄] (BX₄ = BF₄⁻, 6c; BX₄ = BAR'₄, 6c'); Monitored by in Situ IR Spectroscopy. Phenylacetylene (0.15 mL, 1.37 mmol, 4 equiv) was added to the carbene complex [Tp'(CO)₂W=C(H)O(p-C₆H₄OMe)] [BF₄] (7) generated in CH₂Cl₂ solution at -45 °C by addition of 4 equiv of H[BF₄] to Tp'(CO)₂W≡CO(p-C₆H₄OMe). Carbonyl signals from 6c grew in at 2054 and 1961 cm⁻¹ as carbonyl signals from 7 at 2061 and 1980 cm⁻¹ diminished. The intensity of the absorptions due to starting material decreased by half after 4 min, and the absorptions due to the η³-vinylcarbene complex [Tp'(CO)₂W(η³-(C_αC_βC_γ)=CPh-CH=CHO-(p-C₆H₄OMe))] [BF₄] (6c) increased at approximately the same rate.

Monitored by NMR Spectroscopy. Phenylacetylene (7 μL, 0.064 mmol, 2 equiv) was added to the carbene complex [Tp'(CO)₂W=C(H)O(p-C₆H₄OMe)] [BAR'₄] (7') generated in CD₂-Cl₂ solution by addition of 1.2 equiv of [H(Et₂O)₂] [BAR'₄] to Tp'(CO)₂W≡CO(p-C₆H₄OMe) (5c). Signals due to the η³-vinylcarbene complex [Tp'(CO)₂W(η³-(C_αC_βC_γ)=CPh-CH=CHO-(p-C₆H₄OMe))] [BAR'₄] (6c') were observed and no carbene complex 7' was detected. Addition of phenylacetylene (13 μL, 0.12 mmol, 4 equiv) to the BF₄⁻ salt of the carbene complex 7 in -45 °C CD₂Cl₂ solution also resulted in the η³-vinylcarbene complex [Tp'(CO)₂W(η³-(C_αC_βC_γ)=CPh-CH=CHO-(p-C₆H₄OMe))] [BF₄] (6c).

Tp'(CO)₂W(η²-(C_αC_β)CPhCHMe) (8). Complex 6a (0.080 g, 0.096 mmol) was reacted with Li[HB(Et)₃] (1 M THF solution, 0.11 mL) at -78 °C in THF. After the solution was warmed to room temperature, the only absorptions in the ν_{CO} region observed by IR were due to the η²-vinyl complex 8 at 1945 and 1864 cm⁻¹. The green solution was stripped by rotary evaporation and the mixture was separated on silica with a 2:1 hexanes:dichloromethane solvent system. The first green band contained 8 with IR absorptions at 1942 and 1849 cm⁻¹ in CH₂-Cl₂. The complex was identified by comparing IR and NMR data to literature values.^{5e} The methyl group in the vinyl ligand was observed at 2.67 ppm in contrast to the literature report of 2.27 ppm. The synthesis of 8 from [Tp'(CO)₂W(PhC≡CH)]⁺ and MeLi was reproduced and the chemical shift of 2.67 ppm was confirmed to be correct.

Tp'(CO)₂W(κ²-(C_αO)=CPh-CH=CHO) (9): Method A. The reaction solution from the synthesis of 6b (1.03 g of 5b, 0.86 mL of HCCPh, 0.22 mL of 54% H[BF₄] in Et₂O) was reduced on a rotary evaporation apparatus after adding 15 mL of silica. The resulting brown powder was transferred with dichloromethane to a 15 cm by 3 cm silica column, eluted with 50 mL of dichloromethane followed by neat acetone, and collected as one fraction. The solvent was removed by rotary evaporation, and the resulting solid was chromatographed on silica with 1:1 CH₂Cl₂:hexanes to obtain an orange band (9 and 11b) and a green band (10). Following solvent removal, the solid from the orange band was chromatographed on silica with 3:1 Et₂O:pentane to obtain two orange bands. The first orange band was determined to be the metallafuran complex 9 (0.13 g, 12% yield based on 5b) and the second orange band was identified as 11b (vide infra).

Method B. Recrystallized 10 (100 mg, 0.15 mmol) was dissolved in 20 mL of CH₂Cl₂ in an open flask with a stir bar. The solution was acidified with 0.5 mL of an H[BF₄] solution prepared by mixing H[BF₄] in Et₂O (43 μL, 0.3 mmol) and 10 mL of CH₂Cl₂ and the reaction solution turned from dark purple-green to orange in 10 min, and only 9 was detected by IR after 15 min. The solvent was removed by rotary evaporation, and a silica column was prepared with Et₂O as the solvent. The orange residue was added and eluted with 5:1 pentane:Et₂O and dried overnight under vacuum after solvent removal. Yield: 85%. IR (KBr): 1964, 1870 cm⁻¹ (ν_{CO}). ¹H NMR (CD₂Cl₂, 298 K): δ 8.78 (d, 1 H, ³J_{HH} = 1 Hz, ³J_{WH} = 13 Hz, WOC_H), 7.64, 7.45, 7.24 (m, 2:2:1 H, CPh), 7.13 (d, 1 H,

³J_{HH} = 1 Hz, WCP_HCH), 5.98, 5.89 (s, 1:2 H, Tp'-CH), 2.43, 2.41, 1.66 (s, 3:9:6 H, Tp'-CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 295 K): δ 241.3 (s, ¹J_{WC} = 29 Hz, WCP_H), 238.0 (s, ¹J_{WC} = 151 Hz, WCO), 172.1 (s, WOC_H), 156.6, 128.0, 127.1, 126.9 (s, 1:2:1:2 C, WCP_HCH), 154.1, 152.2, 147.0, 144.9 (s, 1:2:1:2 C, Tp'-CCH₃), 124.8 (s, WCP_HCH), 108.5, 107.1 (s, 1:2 C, Tp'-CH), 16.4, 13.5, 13.2, 12.6, (1:1:2:2 C, Tp'-CH₃). Anal. Calcd for C₂₆H₂₉N₆BO₃W: C, 47.68; H, 4.86; N, 11.92. Found: C, 47.77; H, 4.85; N, 11.82.

Tp'(CO)₂W(η²-(C_αC_β)=CPh-CHCHO) (10): Method A. Complex 6a was prepared in a manner similar to the procedure described above from 5a (0.90 g, 1.4 mmol), phenylacetylene (0.77 mL, 7.0 mmol), and tetrafluoroboric acid in diethyl ether (430 μL, 3.1 mmol). After the volume of the reaction solution was reduced by rotary evaporation, the viscous solution was diluted with 5 mL of CH₂Cl₂ before precipitating 6a from 250 mL of cooled Et₂O and subsequently 250 mL of cooled hexanes. The resulting brown powder was dried under vacuum for an hour before being dissolved in THF, cooled to -30 °C, and added to a stirring solution consisting of 10 mL of H₂O, 0.3 g of KOH, and 50 mL of THF in an open flask cooled to -30 °C. The solution was stirred for 5 min at -30 °C before the cooling bath was removed and the solution slowly warmed to room temperature. The resulting brown solution was run through a short alumina column and the THF was removed by rotary evaporation. Water was decanted from the solid residue before the residue was dried for 2 h under vacuum. A silica column was prepared with Et₂O as the solvent, and the residue was added and eluted with a 4:3:2 Et₂O:pentane:CH₂Cl₂ solution. An orange band primarily consisting of the unidentified contaminant from the synthesis of 6a was eluted from the column before a purple-green band was eluted. After solvent removal, the green residue was dissolved in a minimal amount of a 1:1 Et₂O:CH₂Cl₂ solution. The volume of the solution was doubled by layering pentane, and green-black crystals formed overnight. The supernatant was rotary evaporated, and a second crop of crystals was collected. Yield: 35.9% based on 5a.

Method B. After solvent removal following chromatography (see 9 above), the dark green residue was recrystallized from CH₂Cl₂, Et₂O, and pentane as described in Method A. Yield: 11% based on 5b. IR (KBr): 1980, 1888, 1644 cm⁻¹ (ν_{CO}). ¹H NMR (CD₂Cl₂, 298 K): δ 9.08 (d, 1 H, ³J_{HH} = 8 Hz, WCP_H-CHCHO), 7.84, 7.56, 7.45 (m, 2:2:1 H, CPh), 5.97, 5.96, 5.92 (s, Tp'CH), 3.53 (d, 1 H, ³J_{HH} = 8 Hz, ³J_{WH} = 12 Hz, WCP_HCHCHO), 2.68, 2.49, 2.45, 2.37, 2.13, 1.74 (s, Tp'CH₃). ¹³C{¹H} NMR (CD₂Cl₂, room temperature): δ 232.3 (s, ¹J_{WC} = 34 Hz, WCP_H), 221.7 (s, ¹J_{WC} = 164 Hz, WCO), 220.7 (s, ¹J_{WC} = 141 Hz, WCO), 202.5 (s, ²J_{WC} = 7 Hz, WCP_HCHCHO), 153.8, 153.7, 151.0, 146.69, 146.66, 145.4 (s, Tp'CCH₃), 144.6, 133.6, 130.0, 129.6 (s, 1:2:1:2 C, CPh), 108.2, 108.1, 107.9 (s, Tp'CH), 46.4 (s, ¹J_{WC} = 19 Hz, WCP_HCHCHO), 16.4, 16.0, 14.2, 13.14, 13.09, 12.6 (s, Tp'CH₃). Anal. Calcd for C₂₆H₂₉N₆-BO₃W-CH₂Cl₂: C, 43.06; H, 4.15; N, 11.59. Found: C, 43.18; H, 4.15; N, 11.25.

Tp'(CO)₂W=C-CPh=C(H)OPh (11a). The orange powder recovered from the synthesis of 6a' (see above) was taken up in dichloromethane over which was layered acetonitrile. Orange crystals (10 mg) were obtained. Complex 11a was also recovered in low yield from the conversion of 6a' to 9 and 10 on alumina. Two isomers are observed in a ratio of about 5:1. Yield: 4% based on 5a. IR (KBr): 1953, 1868 cm⁻¹ (ν_{CO}). ¹H NMR (CD₂Cl₂, 298 K, major isomer): δ 7.69, 7.36, 7.25, 7.14 (m, 2:4:1:3 H, CPh, OP_H), 7.27 (s, 1 H, C(H)OP_H), 5.92, 5.82 (s, 2:1 H, Tp'CH), 2.54, 2.41, 2.39, 2.35 (s:s:br s:s, 6:3:6:3 H, Tp'CH₃). ¹³C{¹H} NMR (CD₂Cl₂, 298 K, major isomer): δ 276.5 (s, W=C), 224.6 (s, W-CO), 157.3, 134.1, 130.2, 128.9, 128.4, 127.5, 124.3, 117.3 (s, 1:1:2:2:2:1:1:2 C, OP_H, CPh), 152.6, 152.5, 145.9, 145.3 (s, 1:2:1:2 C, Tp'CCH₃), 149.8 (s, W=C-CPh=CHOP_H), 135.7 (s, W=C-CPh=CHOP_H), 106.8, 106.6 (s, 1:2 C, Tp'CH), 16.3, 15.3, 12.8, 12.7 (s, 6:3:6:3 C, Tp'CH₃).

Table 6. Crystal and Data Collection Parameters for [Tp'(CO)₂W(η³-(C_αC_βC_γ)=CPh-CH=CH-CHOPh)][BAR₄] (6a') and [Tp'(CO)₂W(η³-(C_αC_βC_γ)=CPh-CH=CH-CHOTol)][BF₄] (6b)

	6a'	6b
formula	C ₆₉ H ₅₈ N ₆ B ₂ F ₂₄ O ₃ W	C ₃₃ H ₃₆ N ₆ B ₂ F ₄ O ₃ W
formula wt	1680.67	846.14
color	brown	red
cryst system	triclinic	orthorhombic
space group	<i>P</i> 1	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> , Å	15.2443(3)	17.833(7)
<i>b</i> , Å	16.5507(4)	18.174(4)
<i>c</i> , Å	16.5988(4)	10.6851(12)
α, deg	84.254(2)	
β, deg	63.651(2)	
γ, deg	85.276(2)	
<i>V</i> , Å ³	3730.60(15)	3463.0(15)
<i>d</i> , g/cm ³	1.496	1.623
<i>Z</i>	2	4
temp, K	298	298
<i>R</i> (int)	0.050	
no. of params refined	912	443
final <i>R</i> indices	<i>R</i> _f = 0.050	<i>R</i> _f = 0.069
(<i>I</i> > 2σ(<i>I</i>))	<i>R</i> _w = 0.068	<i>R</i> _w = 0.085
<i>R</i> indices (all data)	<i>R</i> _f = 0.059	<i>R</i> _f = 0.123
	<i>R</i> _w = 0.100	<i>R</i> _w = 0.087
GoF	1.9751	2.50

Table 7. Crystal and Data Collection Parameters for Tp'(CO)₂W(κ²-(C_αO)=CPh-CH=CH-O) (9)

formula	C ₂₈ H ₂₉ N ₆ BO _{3.5} W
formula wt	700.23
color	orange
cryst system	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	10.2883(3)
<i>b</i> , Å	14.2184(4)
<i>c</i> , Å	19.9191(4)
β, deg	90.443(2)
<i>V</i> , Å ³	2913.6(1)
<i>d</i> , g/cm ³	1.596
<i>Z</i>	4
temp, K	173
<i>R</i> (int)	0.037
no. of params refined	370
final <i>R</i> indices	<i>R</i> _f = 0.038
(<i>I</i> > 2σ(<i>I</i>))	<i>R</i> _w = 0.042
<i>R</i> indices (all data)	<i>R</i> _f = 0.063
	<i>R</i> _w = 0.046
GoF	1.7144

Anal. Calcd for C₃₂H₃₃N₆BO₃W: C, 51.64; H, 4.47; N, 11.29. Found: C, 51.45; H, 4.57; N, 11.30.

Tp'(CO)₂W≡C-CPh=C(H)O(*p*-C₆H₄Me) (11b). The second orange band (see **9** above) was recrystallized from CH₂-Cl₂:pentane. The product appeared to form in a 6:1 ratio of isomers according to ¹H NMR that was unchanged by recrystallization. Yield: 2% based on **5b**. IR (KBr): 1953, 1870 cm⁻¹ (ν_{CO}). ¹H NMR (CD₂Cl₂, 298 K, major isomer): δ 7.69, 7.34, 7.25 (m, 2:2:1 H, *CPh*), 7.24 (s, 1 H, *C(H)OTol*), 7.18, 7.01 (m, 2:2 H, *O(p-C₆H₄Me)*), 5.92, 5.82 (s, 2:1 H, *Tp'CH*), 2.45, 2.41, 2.39, 2.35 (s, 2:1:2:1 H, *Tp'CH₃*), 2.33 (s, 3 H, *O(p-C₆H₄Me)*). ¹³C{¹H} NMR (CD₂Cl₂, 298 K, major isomer): δ 276.9 (s, ¹*J*_{WC} = 190 Hz, W≡C), 224.6 (s, ¹*J*_{WC} = 167 Hz, WCO), 155.3, 134.1, 130.6, 117.2 (s, 1:1:2:2 C, *O(p-C₆H₄Me)*), 152.6, 152.5, 145.9, 145.3 (s, 1:2:1:2 C, *Tp'CCH₃*), 150.5 (s, WCCPhCHOTol), 135.2 (s, ²*J*_{WC} = 41 Hz, WCCPhCHOTol), 134.2, 128.8, 128.4, 127.4 (s, 1:2:2:1 C, WCCPhCHOTol), 106.8, 106.6 (s, 1:2 C, *Tp'CH*), 20.7 (s, *O(p-C₆H₄Me)*), 16.3, 15.3, 12.8, 12.7 (s, 2:1:2:1 C, *Tp'CH₃*). Anal. Calcd for C₃₃H₃₅N₆BO₃W: C, 52.27; H, 4.65; N, 11.08. Found: C, 52.07; H, 4.68; N, 10.92.

[Tp'(CO)₂W(η³-(C_αC_βC_γ)=CPh-CH=CHOH)][BF₄] (17). A 18-mg (27 μmol) sample of **10** was added to an NMR tube and subsequently dissolved in 0.7 mL of CD₂Cl₂. The NMR tube was cooled to -90 °C in a heptane slurry. The ¹H NMR

Table 8. Crystal and Data Collection Parameters for Tp'(CO)₂W(η²-(C_αC_β)=CPh-CH=CH=O) (10) and Tp'(CO)₂W≡C-CPh=CHOTol (11b)

	10	11b
formula	C ₂₇ H ₃₁ N ₆ BCl ₂ O ₃ W	C ₃₃ H _{34.85} N ₆ BO ₃ W
formula wt	753.14	758.18
color	dark green	orange
crystal system	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> , Å	10.2748(5)	11.2797(4)
<i>b</i> , Å	17.0818(8)	13.8440(5)
<i>c</i> , Å	17.1379(8)	20.9676(8)
β, deg	101.585(1)	102.265(1)
<i>V</i> , Å ³	2946.63(24)	3199.49(20)
<i>d</i> , g/cm ³	1.698	1.574
<i>Z</i>	4	4
temp, K	-173	-173
<i>R</i> (int)	0.032	0.049
no. of params refined	362	398
final <i>R</i> indices	<i>R</i> _f = 0.036	<i>R</i> _f = 0.045
(<i>I</i> > 2σ(<i>I</i>))	<i>R</i> _w = 0.041	<i>R</i> _w = 0.048
<i>R</i> indices (all data)	<i>R</i> _f = 0.052	<i>R</i> _f = 0.074
	<i>R</i> _w = 0.043	<i>R</i> _w = 0.053
GoF	1.4667	1.7025

spectrum of **10** was obtained at 183 K before addition of acid (vide supra). After addition of 3.4 μL of 7 M H[BF₄] in Et₂O (24 μmol) a trace amount of **9** was observed in addition to a new species assigned as **17**. The concentration of **9** was observed to increase once the temperature of the solution was raised above 243 K. Peaks corresponding to the proton signals from two pyrazolyl rings of the Tp' ligand were observed to broaden when compared to similar signals that remained sharp at 273 K. Further warming of the solution resulted in further broadening and the peaks became sharp again when the solution was cooled. In a separate experiment, addition of 0.1 equiv of acid at room temperature resulted in catalytic conversion of **10** to **9**. ¹H NMR (CD₂Cl₂, 243 K): δ 10.0 (br s, 1 H, WCPHCHCHOH), 7.81, 7.65, 7.58 (m, 2:2:1 H, *CPh*), 6.87 (d, 1 H, ³*J*_{HH} = 11 Hz, WCPHCHCHOH), 6.09, 6.08, 6.05 (s, *Tp'CH*), 5.93 (d, 1 H, ³*J*_{HH} = 11 Hz, ³*J*_{WC} = 11 Hz, WCPHCH-CHOH), 2.63, 2.50, 2.46, 2.37, 2.17, 1.73 (s, *Tp'CH₃*).

X-ray Crystal Structure Determinations. Crystals of **6a'**, **9**, **10**, and **11b** measuring 0.40 × 0.35 × 0.20 mm³, 0.30 × 0.25 × 0.05 mm³, 0.33 × 0.25 × 0.20 mm³, and 0.33 × 0.25 × 0.15 mm³, respectively, were placed on a Bruker SMART 1K diffractometer, and intensity data were collected by using the ω-scan mode. A crystal of **6b** measuring 0.40 × 0.30 × 0.15 mm³ was placed on a Rigaku AFC6/S diffractometer, and the intensity data were collected by using the θ/2θ scan mode. Data were collected in the ±*h*, *k*, ±*l* hemisphere for **6a'**, the *h*, *k*, *l* octant for **6b**, the ±*h*, *k*, *l* quadrant for **9**, and the ±*h*, *k*, *l* quadrant for **10** and **11b**. The structures of **6a'** and **9** contain disordered solvent. The solvent in the structure of **6a'** was modeled as rigid pentane, and the structure of **9** contains half an ether molecule disordered about a center of symmetry. ¹H NMR data and elemental analysis of recrystallized **6a'** suggest that a significant amount of diethyl ether may be incorporated into the crystal lattice. The BF₄⁻ component of **6b** possesses large thermal parameters that indicate some disorder. Crystal and data collection parameters are listed in Tables 6, 7, and 8.

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Supporting Information Available: X-ray data for **6a'**, **6b**, **9**, **10**, and **11b** are available as PDF and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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