Chiral Tungsten(II) η^1-Ketone and η^1-Aldehyde Complexes

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*Received March 17, 1993**

Abstract: The neutral complex Tp'(CO)(PhC≡CMe)WI (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate) reacts with lithium dimethylcuprate to effect net replacement of the iodide ligand by a methyl group. The resulting methyl complex Tp'(CO)(PhC≡CMe)WMe (**1**) can be protonated in the presence of ketones (acetone, 2-butanone, acetophenone, and 3,3-dimethyl-2-butanone) or aldehydes (benzaldehyde and trimethylacetaldehyde) to afford cationic η^1-ketone or η^1-aldehyde complexes $[Tp'(CO)(PhC{\equiv}CMe)W(\eta^1\text{-}O{=}CRR')]^+$ (**2a-d** and **3a,b**). These complexes exist as a mixture of *E* and *Z* isomers about the C=O bond, as judged by variable temperature NMR studies. Barriers for isomer interconversion range from 11 to 15 kcal/mol. Addition of hydride to complexes **2a-c** and **3a,b** with K[HB(*sec*-Bu_3)] as the hydride-transfer reagent yields neutral alkoxide complexes of the type Tp'(CO)(PhC≡CMe)WOCHRR'. Hydride transfer from K[HB(*sec*-Bu_3)] to the 2-butanone complex **2b** gives a 3:2 mixture of metal alkoxide diastereomers Tp'(CO)(PhC≡CMe)WOCHMeEt (**5b**), while the acetophenone complex **2c** gives an 11:2 mixture of metal alkoxides Tp'(CO)(PhC≡CMe)WOCHMePh (**5c**). Regeneration of cationic ketone or aldehyde complexes can be achieved by addition of 2 equiv of acid to the alkoxide complexes in the presence of the appropriate ketone or aldehyde. An X-ray structure of one tungsten alkoxide species, Tp'(CO)(PhC≡CMe)WOCH$_2$^{t}Bu (**6b**) (space group $P2_1/c$, a = 16.261(5) Å, b = 17.044(5) Å, c = 12.673(4) Å, Z = 4, R = 0.037, R_w = 0.044), is reported.

Introduction

Ketones and aldehydes are known to bind to transition metals.[1] Rosenblum synthesized several complexes of the type $CpFe(CO)_2L^+$ (L = aldehyde, ketone) by abstracting bromide from $CpFe(CO)_2Br$ with silver in the presence of aldehydes or ketones.[2] Taube has succeeded in preparing complexes such as $[Os(NH_3)_5(\eta^2\text{-}O{=}CMe_2)]^{2+}$ via reduction of an Os(III) complex in acetone.[3] Beck, in turn, has made benzaldehyde complexes by hydride abstraction from $Cp(CO)_3WH$ with [PhCO][SbF_6] to form $[Cp(CO)_3W(\eta^1\text{-}O{=}CHPh)]^+$.[4] Gladysz has made several rhenium aldehyde and ketone complexes via displacement of dichloromethane from the coordination sphere of rhenium.[5] Mayer has prepared a number of tungsten bis(η^2-ketone) and bis(η^2-aldehyde) complexes via ketone or aldehyde displacement of phosphine from $WCl_2(PMePh_2)_4$.[6] Schrock and co-workers synthesized η^2-acetone and η^2-propionaldehyde complexes by substitution of a phosphine ligand in $W(NAr)_2(PMe_2Ph)_2$ by acetone or propionaldehyde.[7]

Stereoselective reduction of organic carbonyl groups is an important reaction. Prochiral ketones and aldehydes have been stereoselectively reduced to alcohols with varying degrees of success using a number of reagents, such as chiral aluminum hydrides,[8] organolithium[9] and organomagnesium reagents,[9b] zirconium and titanium complexes,[10] and dialkylzincs.[11] Rhenium complexes bind one aldehyde enantioface stereoselectively;[5d-f] cyanide additions to the carbonyl carbon of the coordinated aldehyde form cyanohydrin alkoxide complexes with high diastereoselectivity.[12]

The chiral fragment $[Tp'Mo(CO)(P(OMe)_3)]^+$ has been shown to effect diastereoselective η^2-acyl ligand elaboration reactions.[13] In Tp'W(CO)(PhC≡CMe)I, the alkyne propargylic protons are acidic and can be deprotonated to form coordinated propargyl anions. Electrophilic additions at the propargyl site have proven to be highly diastereoselective.[14] Coordinated acetonitrile in $Tp'W(CO)(PhC{\equiv}CMe)(N{\equiv}CMe)^+$ can be reduced to ethylamine by a series of H^-/H^+ additions across the nitrogen-carbon triple bond.[15] Addition of cyanide to C_α of the imine ligand, in the third step of the reduction sequence, is diastereoselective.[16] Resolution of the chiral complex $Tp'W(CO)(PhC{\equiv}CMe)L^{n+}$ (L = I, n = 0; L = N≡CMe, n = 1) has been accomplished, so these complexes are available as single enantiomers.[17] The objectives of this project were to bind aldehydes and ketones to the chiral tungsten alkyne fragment $Tp'W(CO)(PhC{\equiv}CMe)^+$ and to study the stereoselectivity of ligand reductions.

In this paper we report (1) a high yield synthesis of Tp'(CO)(PhC≡CMe)WMe, which upon protonation gives a metal fragment capable of binding and activating organic substrates,

* Abstract published in *Advance ACS Abstracts*, February 15, 1994.

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Table 1. Selected Spectroscopic Data for Ketone and Aldehyde Complexes (**2a–d, 3a,b**) [Tp'W(CO)(PhC≡CMe)(η^1-O=CRR')][X] (X = BF_4^- or BAr'_4^-)

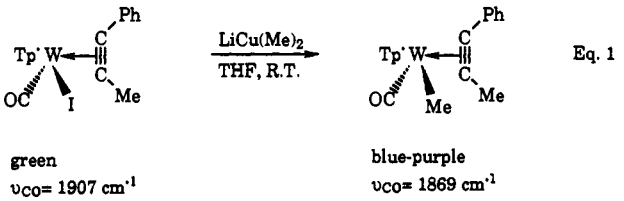
complex (R, R')	IR $\nu_{C=O}$ (cm^{-1}, KBr)	IR ν_{C-O} (cm^{-1}, KBr)[a]	^1H NMR[b] η^1-O=CRR' R = Me or H (ppm)	^{13}C NMR[b] η^1-O=CRR' (ppm)
2a (Me, Me)	1925	1635	2.29 (CH_3)	226.7
2b (Me, Et)	1921	1635	0.80 (CH_3)	229.4
2c (Me, Ph)	1915		*c*	203.4 (202.7)[f]
2d (Me, ^{t}Bu)	1932		1.62 (2.04)[d] (CH_3)	233.1 (232.3)[g]
3a (H, Ph)	1923		7.93[e] (H)	196.2
3b (H, ^{t}Bu)	1938		7.64[e] (H)	219.0

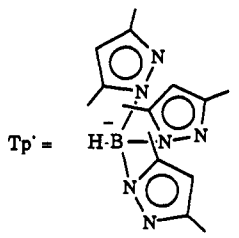
[a] For the aromatic aldehyde and ketone complexes, the C=O stretch was not observed in the 1700–1600 cm^{-1} region. [b] ^1H and ^{13}C NMR spectra recorded in CD_2Cl_2. [c] Degenerate with Tp' methyl groups. [d] There are two isomers at room temperature. [e] These resonances correspond to the aldehydic protons. [f] The ^{13}C NMR spectrum (–29 °C) displays two isomers. [g] The ^{13}C NMR spectrum (–39 °C) displays two isomers.

(2) syntheses of chiral tungsten aldehyde and ketone complexes, (3) reduction of aldehyde and ketone complexes to yield alkoxide complexes, (4) independent syntheses of alkoxide complexes, and (5) the X-ray structure of a tungsten alkoxide complex, Tp'(CO)(PhC≡CMe)$WOCH_2{}^t$Bu.

Results and Discussion

Synthesis and Characterization of Tp'(PhC≡CMe)(CO)WMe (1). Methyl replacement of iodide in the neutral Tp'(PhC≡CMe)(CO)WI complex has been accomplished by adding a freshly prepared $LiCu(Me)_2$/THF solution to the tungsten iodide complex (eq 1). As the reaction proceeds, the carbonyl stretching absorption of the starting material (ν_{CO} = 1907 cm^{-1}) decreases in intensity as that of complex **1** (ν_{CO} = 1869 cm^{-1}) grows in the infrared spectrum. The lower C≡O stretching frequency of the product reflects the electron-donating ability of the methyl ligand relative to iodide. The tungsten methyl complex is obtained in high yield (91%).





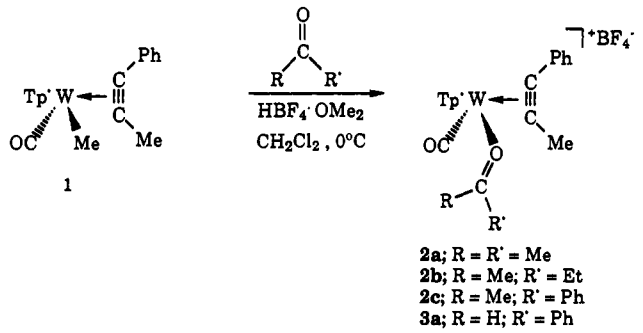
Hydridotris(3,5-dimethylpyrazolyl)borate

Tungsten(II) methyl complexes have previously been synthesized by methyl displacement of chloride in $WCl_2(CO)_2(PMe_3)_3$ with MeLi,[18a] and a tungsten(IV) methyl complex has been prepared by methyl displacement of chloride in Cp_2WCl_2 with MeMgBr.[19b] Combining Tp'(PhC≡CMe)(CO)WI with reagents such as MeLi led to deprotonation at the propargyl site of the alkyne to form η^2-allenyl complexes.[14]

The ^1H NMR spectrum of the methyl complex **1** reveals a chiral-at-metal complex, with three separate signals for the three pyrazole protons and six signals for the inequivalent pyrazole methyl groups. The ^1H NMR spectrum displays a singlet at 3.32 ppm that is assigned to the alkyne methyl group, while the signal at 0.29 ppm with a two-bond tungsten–hydrogen coupling constant of 6.8 Hz (^{183}W 14%, I = 1/2) is assigned to the methyl bound to the tungsten center. This high-field methyl chemical shift is typical of other metal-bound methyl groups,[18] and the two-bond tungsten–hydrogen coupling constant is within the range of values reported for other tungsten methyl complexes.[19] The ^{13}C NMR spectrum has a characteristic carbonyl signal at 245.1 ppm with a tungsten coupling constant of 145 Hz.

[Tp'(PhC≡CMe)(CO)W(η^1-O=CRR')][BF_4] (R = R' = Me; R = Me, R' = Et; R = Me, R' = Ph) (2a-c). The methyl complex **1** and the respective ketone (acetone, 2-butanone, or acetophenone) in CH_2Cl_2 were cooled to 0 °C. Upon dropwise addition of $HBF_4{\cdot}OMe_2$, the solution turned from dark blue-purple to blue-green when aliphatic ketones were used and from dark blue-purple to brown when acetophenone was used. The resulting σ-ketone complexes were obtained in yields of 70%–80% (Scheme 1). The ketone complexes **2a–c** were characterized by IR, ^1H NMR, and ^{13}C NMR spectroscopy. Ketones and aldehydes failed to react with Tp'(PhC≡CMe)(CO)W(OTf) to form comparable products.

Scheme 1



A similar method for synthesizing rhenium ketone complexes has been reported.[20] Gladysz synthesized a dichloromethane adduct via protonation of a rhenium methyl compound.[21] The dichloromethane ligand is then easily displaced by ketones.[5a-c] In the tungsten system here, the ketone must be present during protonation of the methyl complex, **1**, and it then coordinates directly to form the cationic products.

The acetone complex **2a** displays a terminal metal carbonyl stretching frequency of 1925 cm^{-1} in the infrared spectrum, characteristic of cationic tungsten(II) complexes of the type [Tp'(CO)(PhC≡CMe)WL][BF_4] (Table 1). The IR spectrum also shows a carbonyl stretching absorption at 1635 cm^{-1}, which is assigned to the acetone ligand. The ^1H NMR spectrum reveals chirality at the metal center. The alkyne methyl group is assigned to a singlet at 3.92 ppm. A singlet at 2.29 ppm that integrates for six protons is then assigned to the two methyl groups of the

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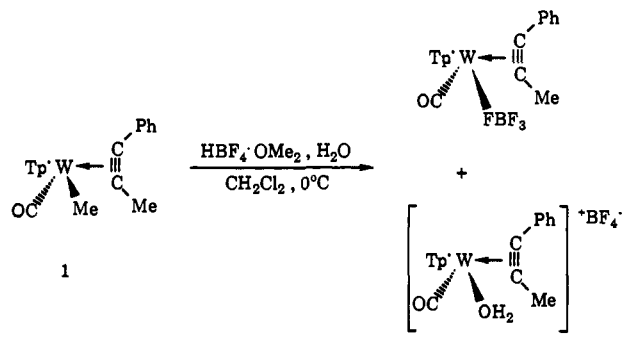
Scheme 2



acetone ligand. The two methyl groups exhibit only one resonance, but two separate signals should be seen for the two distinct methyl groups for any static geometry. The ^{13}C NMR spectrum displays a terminal carbonyl carbon resonance at 225.1 ppm and an acetone carbonyl carbon resonance at 226.7 ppm (Table 1). The two carbonyls are distinguishable in the off-resonance decoupled spectrum. The terminal carbonyl remains a singlet, while the acetone carbonyl carbon is a septet with a two-bond carbon–hydrogen coupling constant of 6 Hz. The two methyl substituents of the acetone ligand also appear as a single resonance in the ^{13}C NMR spectrum (30.2 ppm). Table 1 contains selected infrared, ^1H NMR, and ^{13}C NMR data for complexes **2a–d** and **3a,b**.

The ^1H NMR spectrum of the 2-butanone tungsten complex **2b** shows a single isomer with the alkyne methyl resonance at 3.92 ppm. The methylene protons on the 2-butanone ligand are diastereotopic and appear as a multiplet centered at 2.86 ppm. Among ^{13}C NMR data is the 2-butanone carbonyl resonance at 229.4 ppm (Table 1).

The acetophenone complex **2c** displays a terminal metal carbonyl stretching frequency at 1932 cm^{-1} (Table 1). At room temperature, signals in the ^1H NMR spectrum of **2c** are broad, presumably denoting fluxionality in the molecule. A spectrum recorded at −11 °C shows two isomers in a 3:2 ratio. The alkyne methyl singlet in the ^1H NMR spectrum is a convenient resonance for assessment of isomer ratios because of its unique chemical shift. The major and minor isomers have alkyne methyl signals at 4.00 and 4.02 ppm, respectively. The ^{13}C NMR spectrum was also recorded at low temperature, −29 °C, and two isomers were clearly visible as evident in the terminal carbonyl carbon signals at 224.6 and 224.3 ppm.

The ketones appear to bind to the metal center in a σ coordination mode in complexes **2a–c**. This conclusion was based on the ketone C=O stretch evident in the infrared spectrum and the chemical shift of the ketonic carbon observed in the ^{13}C NMR spectrum. The ketone carbon–oxygen bond order of 2 does not decrease much upon η^1-coordination, so the infrared stretching frequency of the ketone carbonyl unit is not lowered more than 100 cm^{-1}.[1] In ^{13}C NMR spectra the ketonic carbons of the σ-bound ketones resonate near the frequency of organic C=O carbons, around 210–240 ppm.[1] If the ketones were π-bound to the metal center in an η^2-binding mode, the ketone carbon–oxygen bond order would decrease significantly and dramatically lower the C=O stretching frequency in the infrared spectrum, while the ketonic carbon would resonate far upfield, around 100 ppm.[1]

The synthesis of η^1-ketone complexes in this system is complicated by traces of water. In the presence of water, the reaction yields some of the desired tungsten ketone complex, but two other products are also formed: Tp′(CO)(PhC≡CMe)-$WFBF_3$[17] and a cationic complex with a water ligand in the coordination sphere of tungsten (Scheme 2). In complexes such as $Cp(CO)_3WFBF_3$, the BF_4^- ligand is labile and is easily displaced by ketones and aldehydes.[4]

The aqua complex has not been fully characterized; it is unstable. The infrared spectrum of [Tp′(CO)(PhC≡CMe)W-(H_2O)]$^+$ displays a terminal carbonyl stretching frequency at 1915 cm^{-1} (KBr), consistent with the carbonyl stretching frequency of a typical cationic tungsten(II) alkyne complex. The ^1H NMR spectrum has a peak that integrates for two protons thar varies between 7 and 8 ppm in different NMR samples. This peak disappears upon addition of D_2O to an NMR sample of the complex in CD_2Cl_2. These data suggest an aqua complex has been formed as a result of moisture present during the reaction. Similar behavior has been observed in other systems,[22] although water complexes do not usually persist in the presence of other potential ligands such as ketones, alcohols, or acetonitrile.[23]

[Tp′(PhC≡CMe)(CO)W(η^1-O=CMe^{t}Bu)][BAr′$_4$] (BAr′$_4^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) (2d). The synthesis of complex **2d** followed a procedure similar to those used for other ketone complexes, but the acid used for protonation of the methyl ligand in Tp′(PhC≡CMe)(CO)WMe was $HBAr'_4 \cdot 2OEt_2$ (BAr′$_4$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, Scheme 6), an acid containing a noncoordinating counterion. Counterions vary in their ability to coordinate to metals, and it was necessary to substitute $HBAr'_4 \cdot 2OEt_2$ for $HBF_4 \cdot OMe_2$ because the BF_4^- counterion competes with the sterically bulky ligand, 3,3-dimethyl-2-butanone, for the empty tungsten coordination site. Upon addition of the acid, $HBAr'_4 \cdot 2OEt_2$, to a CH_2Cl_2 solution of complex **1** and 3,3-dimethyl-2-butanone, the [Tp′(PhC≡CMe)(CO)W(η^1-O=CMe^{t}Bu)[BAr′$_4$] complex formed cleanly. It was isolated in 67% yield. The large tetraarylborate counterion seems to stabilize complex **2d**, and a satisfactory elemental analysis was obtained for this compound. In contrast the BF_4^- salts of the other ketone complexes, **2a–c**, decomposed readily and were not analyzed.

The terminal C≡O ligand stretching frequency appears at 1932 cm^{-1} (Table 1). At room temperature, the ^1H NMR spectrum of **2d** shows broad signals and in this regard is reminiscent of complex **2c**. Two isomers (3:2 isomer ratio) of the cationic tungsten 3,3-dimethyl-2-butanone complex are evident at room temperature. The ketone methyl substituent appears at 1.62 and 2.04 ppm for the major and minor isomers, respectively, while the ketone *tert*-butyl group appears at 1.02 and 0.93 ppm for the major and minor isomers, respectively. The ^{13}C NMR spectrum was recorded at −39 °C in order to detect both isomers in the slow exchange limit. The ketonic carbons for the two isomers were observed at 233.1 and 232.3 ppm, both in the range of σ-bound ketone ligands (Table 1). The *tert*-butyl methyl carbons were found at 26.2 and 25.8 ppm.

Variable Temperature NMR Experiments. The ^1H NMR spectra of complexes **2c** and **2d** displayed broad signals at room temperature, hinting that these two complexes are fluxional. Variable temperature ^1H NMR experiments were therefore undertaken for complexes **2a–d** to explore dynamic processes involving isomer interconversion. A CD_2Cl_2 NMR sample of the tungsten acetone complex **2a** was prepared. The ^1H NMR spectrum was recorded at room temperature, where the acetone methyl groups appeared as a single resonance at 2.29 ppm. As the temperature was lowered, the singlet broadened, being broadest at −74 °C, but this methyl resonance did not resolve cleanly into two separate signals even at −90 °C.

The 2-butanone complex **2b** appeared to be either a single isomer or else in the fast exchange limit according to the ^1H NMR spectrum at room temperature. Indeed low temperature NMR measurements revealed that two isomers were interconverting rapidly on the NMR time scale. There are several possible sources of isomerization, two of which seem most plausible: the ketone orientation or the alkyne orientation.

One possibility for geometric isomers in our system stems from the optimal alkyne orientation parallel to the metal–carbonyl

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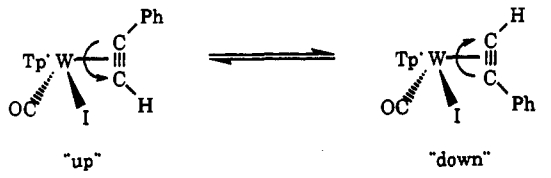
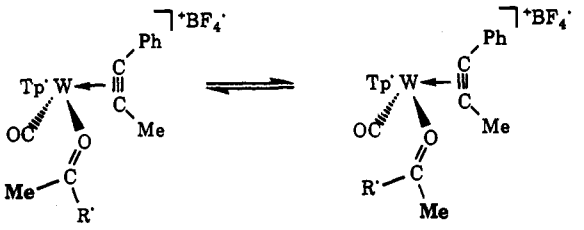
Scheme 3



Scheme 4



R' = Et, Ph

vector. Terminal alkyne ligands can place either alkyne substituent near the Tp′ ligand, and indeed two different alkyne orientations, "up" or "down", are observed for PhC≡CH in related systems (Scheme 3); variable temperature studies indicate that a high rotational barrier characterizes alkyne rotation.[24] The 1-phenyl-1-propyne ligand, however, routinely populates predominantly one isomer in complexes such as $[Tp'(CO)_2(PhC{\equiv}CMe)W]^+$, Tp′(CO)(PhC≡CMe)WI, and $[Tp'(CO)(PhC{\equiv}CMe)W(N{\equiv}CMe)]^+$,[24] so it seems unlikely that the alkyne would adopt two orientations in the ketone complexes reported here.

Tungsten σ-ketone ligands are believed to adopt a bent W–O–C ground-state geometry. Several theoretical studies of boron and aluminum σ-ketone complexes have shown that bent complexes are lower in energy than linear σ-complexes.[25] η^1-Ketone complexes can exist as either *E* or *Z* isomers about the keto unit, and these can interconvert via a formal 180° rotation about the O–C vector (Scheme 4). The actual pathway for *E*/*Z* conversion is probably more complex, such as flexing to a linear η^1-W–OC unit followed by rotation around the W–O bond. In rhenium,[5c] tungsten,[26a] and platinum[26b,c] acetone complexes, the acetone methyl groups exchange sites with a low barrier. Low-temperature NMR studies have successfully frozen separate signals for the *E*/*Z* methyl substituents of acetone complexes. For asymmetric ketone ligands, such as 2-butanone, only one NMR signal has been observed, even at low temperature. Boron ketone complexes exhibit similar behavior.[27] In the symmetric 3-pentanone boron complex, ethyl group exchange occurs with a barrier of 8.3 kcal/mol. Isomers of the 2-butanone boron complex, however, could not be detected. Whether this reflects population of only a single isomer or whether the rotation barrier is inexplicably low is not known.

Variable temperature ^{1}H NMR spectroscopic studies were also undertaken on the 2-butanone complex, **2b** (Figure 1). In this case, the alkyne methyl signal was the most informative signal as the temperature was lowered. At room temperature, only one signal was evident for the alkyne methyl group, but at −78 °C two isomers were apparent. Upon warming the sample, the two alkyne methyl signals coalesced at −54.5 °C. This coalescence

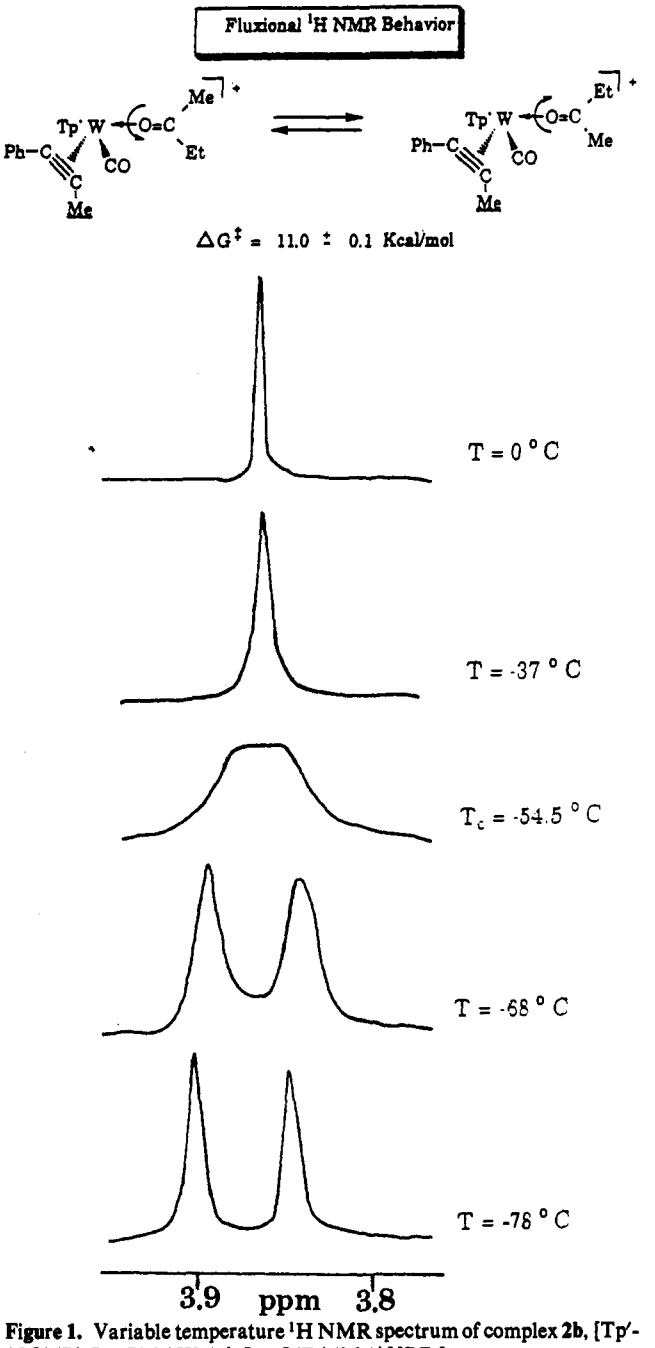


Figure 1. Variable temperature ^{1}H NMR spectrum of complex **2b**, [Tp′(CO)(PhC≡CMe)W-(η^1-O=C(Et)(Me))][BF_4].

temperature and the difference in chemical shifts for the two isomers allowed us to calculate a rate constant which yielded a $\Delta G^{\ddagger}$ of 11.0 kcal/mol.

The ^{1}H NMR spectrum of the acetophenone complex **2c**, was also broad at room temperature. At −30 °C two isomers were clearly identified in the ^{1}H NMR spectrum. At 28 °C the two signals coalesced, indicating a $\Delta G^{\ddagger}$ of 15.1 kcal/mol. Similar behavior was observed for the tungsten pinacolone complex **2d**. The barrier for isomer interconversion for **2d** was found to be 14.9 kcal/mol (T_c = 25 °C).

The barriers for interconversion of isomers we observe are large relative to other η^1-ketone or aldehyde systems. If indeed the process we monitor corresponds to lone pair hop and W–O bond rotation, it seems likely that the barrier height here reflects the d^4 configuration at the metal center. Note that the distinction between dπ orbitals directed toward the η^1-ketone ligand here is one of filled and vacant rather than filled and of differing energy. In contrast the rhenium monomer presents filled dπ orbitals differentiated by back-bonding to nitrosyl and phosphine ligands.

(24) Feng, S. G.; Gamble, A. S.; Philipp, C. C.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 3504.
(25) (a) Branchadell, V.; Oliva, A. *J. Am. Chem. Soc.* **1991**, *113*, 4132. (b) LePage, T. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 6642.
(26) (a) Faller, J. W.; Ma, Y. *J. Am. Chem. Soc.* **1991**, *113*, 1579. (b) Auffret, J.; Courtot, P.; Pichon, R.; Salaün, J. Y. *J. Chem. Soc., Dalton Trans.* **1987**, 1687. (c) Courtot, P.; Pichon, R.; Salaün, J. Y. *J. Organomet. Chem.* **1985**, *286*, C17.
(27) Hartman, J. S.; Stilbs, P.; Forsén, S. *Tetrahedron Lett.* **1975**, *40*, 3497.

As a result, higher rotational barriers are expected in the d^4 case relative to d^6 monomers, and this may account for the higher barriers observed here.

A particularly helpful reviewer has also mentioned the possibility of rotamers resulting from restricted rotation around the W–O bond with no need to invoke *E*/*Z* isomers to account for the two species observed by NMR. While barriers of 11–15 kcal/mol are surprisingly high for rotamer interconversion, the steric bulk around the metal leaves this option as one deserving of consideration in designing future experiments.

[Tp′(PhC≡CMe)(CO)W(η¹-O=CHR)][X] (R = Ph, X = BF_4^-; R = ^{t}Bu, X = BAr'_4^- = tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate (3a,b). The methyl complex **1** and benzaldehyde in CH_2Cl_2 were cooled to 0 °C. Upon dropwise addition of HBF_4·OMe_2, the solution turned from dark blue-purple to intense red-purple. The resulting σ-aldehyde complex was obtained in 80% yield. The benzaldehyde complex displays a terminal metal carbonyl stretching frequency of 1923 cm^{-1} in the infrared spectrum. The ^{1}H NMR spectrum reveals only one isomer: the aldehydic proton resonates at 7.93 ppm, and the alkyne methyl group appears at 3.99 ppm (Table 1). The ^{13}C NMR spectrum displays a terminal carbonyl carbon signal at 224.6 ppm and an aldehyde carbonyl carbon at 196.2 ppm.

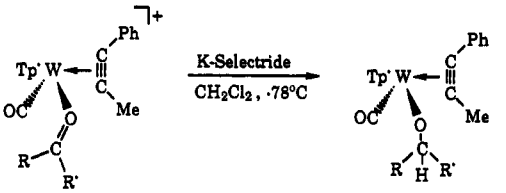
The synthesis of the trimethylacetaldehyde [(^{t}Bu)(H)C=O] adduct, **3b**, required the use of $HBAr'_4$·$2OEt_2$ (BAr'_4 = tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate) instead of HBF_4·OMe_2 in order to avoid incorporation of BF_4^- into the tungsten coordination sphere. As in the synthesis of the tungsten 3,3-dimethyl-2-butanone complex **2d**, the BF_4^- anion competes with the sterically bulky trimethylacetaldehyde ligand and complicates the reaction. The $\nu_{C=O}$ in the IR spectrum was at 1938 cm^{-1} (Table 1). The aldehyde proton resonates at 7.64 ppm in the proton NMR spectrum (Table 1). The alkyne methyl and the aldehyde *tert*-butyl groups appear at 3.95 and 0.98 ppm, respectively. The carbon-13 spectrum displays a characteristic σ-aldehyde ligand carbonyl signal at 219.0 ppm. The BAr'_4 counterion stabilized the complex, **3b**, sufficiently that elemental analysis was possible.

These aldehydes also bind to the tungsten center in an η¹-coordination mode, as was determined by ^{1}H and ^{13}C NMR spectroscopy (Table 1). ^{13}C NMR data show an aldehyde carbonyl carbon at 196.2 ppm for **3a** and at 219.0 ppm for **3b**, with both resonances well within the range of organic carbonyl carbon resonances. The ^{1}H NMR spectrum was also informative. The aldehydic proton appeared downfield at 7.93 and 7.64 ppm for complexes **3a** and **3b**, respectively. If the aldehydes were π-bonded to the metal, these signals would be shifted significantly upfield.[1] Although many aldehydes are found to bind η¹ to a metal,[1,28] in rhenium systems some aldehydes are known to coordinate in a η² fashion.[5d-g] Aromatic aldehydes coordinate to rhenium in both π- and σ-binding modes, and several studies of π/σ equilibria of rhenium aldehyde complexes have been performed.[29]

The σ-mode of coordination directs the carbonyl carbon away from the metal center, whereas π-binding holds the carbonyl substituents close to the metal. In sterically bulky systems, such as in these Tp′W(CO)(PhC≡CMe)L⁺ compounds, the σ-bonding option minimizes unfavorable steric interactions.

Reduction of the η¹-Ketone (2a-c) and η¹-Aldehyde (3a,b) Complexes. The ketone and aldehyde ligands are susceptible to nucleophilic attack. Aldehyde and ketone complexes have been reduced to the corresponding alkoxides in other systems.[5c-f] The nucleophile utilized here to transfer hydride was K-Selectride [KB(*sec*-butyl)$_3$H]. Reactions with other hydride sources, such as superhydride [LiB(Et)$_3$H] and sodium borohydride [NaBH_4], were also investigated. When superhydride was used to reduce ketone or aldehyde complexes, the reduction appeared to occur as expected, but the boron Lewis acids generated in the reaction reacted with the products, perhaps through metal–oxygen bond cleavage, as was observed in a rhenium system.[5c] Sodium borohydride was also used to attempt ketone reduction; in this case the ketone ligand was replaced by a hydride ligand to form a tungsten hydride complex.[30] Sodium borohydride is known to displace acetonitrile from cationic tungsten complexes to form the neutral tungsten hydride complex.

Scheme 5



2a: R = R′= Me
2b: R = Me, R′ = Et (2 isomers, 1:1)
2c: R = Me, R′ = Ph (2 isomers, 3:2)
3a: R = H, R′ = Ph
3b: R = H, R′ = t-Bu

5a
5b (2 diastereomers, 3:2)
5c (2 diastereomers, 11:2)
6a
6b

The reduction reactions here were performed in dichloromethane at −78 °C. K-Selectride was added to the ketone or aldehyde complexes (**2a–c** and **3a,b**) and the blue or purple products were obtained in 60–75% yield (Scheme 5). The products were characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy and elemental analysis.

The acetone complex **2a** was reduced with hydride to the corresponding tungsten isopropoxide complex, **5a**. The low stretching frequency of the metal carbonyl ligand (1859 cm^{-1}) reflects increased electron density at the metal center relative to the cationic reagent. The ^{1}H NMR spectrum displayed a septet with a three-bond coupling constant of 6.0 Hz at 5.14 ppm that is assigned to the isopropoxide C–*H*. The two methyl groups on the isopropoxide ligand are diastereotopic and appear as doublets at 1.03 and 0.56 ppm.

Reduction of unsymmetrical ketone complexes gives rise to two diastereomers. The ketones used in the synthesis of **2b,c** have two potential faces for hydride attack, and indeed two diastereomers are formed in the reduction of complexes **2b,c**. The 2-butanone complex affords a 3:2 mixture of isomers upon reduction (Scheme 5). The alkyne methyl signal is a convenient resonance for determining diastereomeric ratios with resonances at 3.38 and 3.36 ppm for the major and minor isomers, respectively.

The reduction of the acetophenone complex, **2c**, proceeded with better selectivity as the resulting alkoxide product, **5c**, analyzed as an 11:2 diastereomeric mixture. The ^{1}H NMR signal for the alkyne methyl group of the major isomer appears at 2.90 ppm, while that of the minor isomer appears at 3.48 ppm.

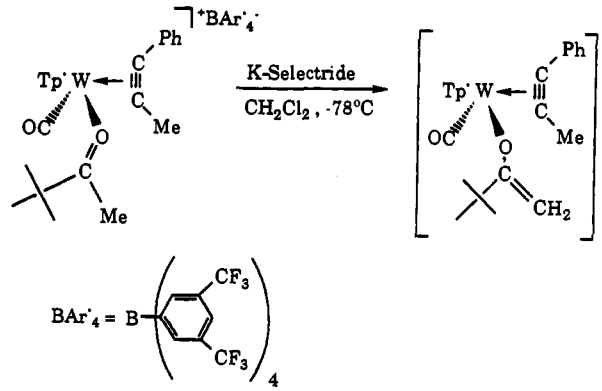
The stereoselectivity of asymmetric ketone reduction is not high. Given that two isomers of the 2-butanone complex, **2b**, and the acetophenone complex, **2c**, are present in the reagent, it is not surprising that two diastereomers are formed. The acetophenone reagent exists in a 3:2 isomer ratio, while the reduction product (before workup) exhibits an 11:2 isomer ratio. Thus the diastereomeric ratio of product **5c** does not simply reflect the isomer ratio in the acetophenone complex **2c**.

(28) (a) Bullock, R. M.; Ricci, J. S.; Szalda, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 2741. (b) Bullock, R. M.; Rappoli, B. J.; Samsel, E. G.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1989**, 261. (c) Denmark, S. E.; Almstead, N. G. *J. Am. Chem. Soc.* **1993**, *115*, 3133.

(29) (a) Klein, D. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 8710. (b) Klein, D. P.; Dalton, D. M.; Quirós Méndez, N.; Arif, A. M.; Gladysz, J. A. *J. Organomet. Chem.* **1991**, *412*, C7. (c) Quirós Méndez, N.; Mayne, C. L.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1475. (d) Quirós Méndez, N.; Arif, A. M.; Gladysz, J. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1473.

(30) Caffyn, A. J. M.; Feng, S. G.; Dierdorf, A.; Gamble, A. S.; Eldredge, P. A.; Vossen, M. R.; White, P. S.; Templeton, J. L. *Organometallics* **1991**, *10*, 2842.

Scheme 6



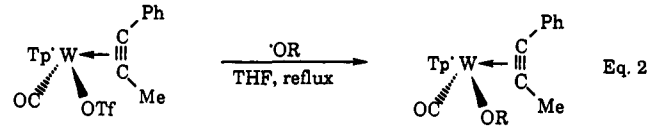
An attempt to reduce the pinacolone complex **2d** was made by using K-Selectride as the hydride source. Complexes of the type Tp′W(CO)(PhC≡CMe)L$^+$ are sterically hindered, and formation of an alkoxide derivative with a chiral carbon bearing three substituents (methyl, *tert*-butyl, and hydrogen) is probably not favorable. Indeed, deprotonation of the pinacolone methyl group was observed instead of reduction (Scheme 6). The deprotonation product, an enolate complex, contains a less bulky ligand.

The neutral enolate complex has also been formed from the reaction of [Tp′(PhC≡CMe)(CO)W(η^1-O=CMe^{t}Bu)][BAr′$_4$] with KH in THF. The reaction solution was filtered away from unreacted KH and the solvent removed. Dissolution in cold CH_2Cl_2 allowed separation from insoluble salt byproducts and produced samples suitable for spectroscopic characterization. Key spectroscopic data include a terminal metal carbonyl infrared adsorption at 1876 cm^{-1}, proton NMR signals at 3.66 and 3.60 ppm assigned to the geminal hydrogens of the enolate, and ^{13}C NMR signals at 180.8 and 81.9 ppm (t, $^1J_{CH}$ = 152 Hz) assigned to the vinyl carbons.

The aldehyde complexes can be reduced to primary alkoxide compounds using the K-Selectride reagent (Scheme 5). The benzaldehyde complex, **3a**, was reduced to the benzylalkoxide complex, **6a**. This complex exhibits a terminal C≡O band in the IR spectrum at 1857 cm^{-1}. The proton NMR displays typical signals for the diastereotopic protons at 6.07 and 5.47 ppm with a geminal coupling constant of 12.4 Hz.

The reduction product of the trimethylacetaldehyde complex, **6b**, displays diastereotopic proton signals as doublets ($^2J_{HH}$ = 10 Hz) at 4.87 and 4.60 ppm. The ^{13}C NMR spectrum shows alkyne carbons at 183.8 and 181.2 ppm, at higher field than the alkyne carbons in Tp′(CO)(PhC≡CMe)WI, for example (^{13}C NMR W–C_{alkyne} δ 208.9 and 206.5 ppm).[24] These chemical shifts denote decreased electron donation from the alkyne $\pi_\perp$ to the metal; the alkoxide ligand contains an oxygen lone pair that competes with the alkyne for the single vacant metal dπ orbital (vide infra).

Independent Syntheses of Methoxide and Phenoxide Tungsten(II) Complexes. To verify that the reductions of ketone and aldehyde complexes yielded alkoxides, an alternate route to the synthesis of alkoxide complexes was sought. The Tp′(CO)(PhC≡CMe)WOTf complex contains a weakly coordinating triflate anion which can be displaced by a number of nucleophiles.[17] A methanol solution of lithium methoxide was added to a refluxing THF solution of the tungsten triflate complex; substitution of the triflate ligand by methoxide was complete in 4 h (eq 2). The methanol solvent is necessary to solubilize LiOMe. An infrared spectrum of the blue product displayed a characteristic metal carbonyl adsorption at 1850 cm^{-1}, lower than that of the methyl complex **1**, reflecting the more electron-donating character of the alkoxide ligands. The ^{1}H NMR spectrum showed a signal for the methoxide methyl at 4.55 ppm with a three-bond tungsten–hydrogen coupling constant at 2.6 Hz. The phenoxide complex was synthesized in the same fashion as the methoxide compound. The metal carbonyl stretching frequency, reflecting the weaker basicity of phenoxide relative to aliphatic alkoxides, is at 1880 cm^{-1}, 20 wavenumbers higher than for aliphatic alkoxide complexes.

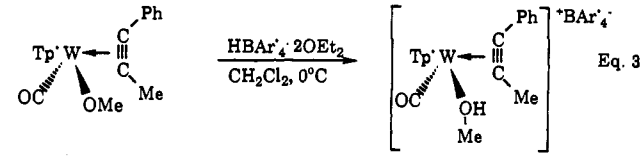


υ_{CO} = 1922 cm^{-1}

4a: R = Me, υ_{CO} = 1850 cm^{-1}
4b: R = Ph, υ_{CO} = 1880 cm^{-1}

Protonation of Tungsten Alkoxide Compounds. An important aspect of the chemistry observed for these alkoxide complexes is that an alcohol ligand can be formed by protonation and then removed from the coordination sphere in the presence of organic carbonyls to regenerate the starting cationic ketone or aldehyde complexes. The alkoxide product **5b** was protonated in CH_2Cl_2 with HBF_4·OMe_2 in the presence of 2-butanone. After 1 equiv of acid was added an alcohol adduct was formed. The 2-butanone did not displace the alcohol from the tungsten coordination sphere until a second equivalent of acid had been added (Scheme 7).

A methanol adduct (**7**) was synthesized (eq 3) by adding HBAr′$_4$·2OEt$_2$ to the methoxide complex **4a**. The infrared spectra is compatible with the formation of a cationic compound; the metal carbonyl absorption appears at 1917 cm^{-1}. The methyl peak of the coordinated methanol appears as a doublet at 3.88 ppm in the proton NMR ($^3J_{HH}$ = 5.0 Hz). The properties of this complex resemble those of other alcohol complexes.[4b,31] The methanol proton signal, a quartet, appears at low field, between 6.5 and 7.0 ppm, as is observed in a similar rhenium complex synthesized by Grundy.[31b]



υ_{CO} = 1850 cm^{-1}
4a

υ_{CO} = 1917 cm^{-1}
7

Electron-Donating Abilities of Several Neutral and Anionic Ligands in [Tp′W(CO)(PhC≡CMe)L]$^{n+}$ (Table 2). The electron-donating abilities of ligands in these complexes are reflected in the frequency of the terminal C≡O stretching absorptions in the infrared spectra (Table 2). Electron-rich metal centers exhibit more back-bonding to the carbonyl ligand, thus lowering the stretching frequency. Table 2 compiles infrared data from a number of complexes differing only in the identity of the ancillary ligand L. The general trend in $\nu_{C\equiv O}$ is intuitively appealing from amides to phosphites. It is worth noting that both σ-effects based on electronegativity and the π-donor properties of ligands with lone pair electrons influence the carbonyl vibration. Note that $\nu_{C\equiv O}$ of the tungsten fluoride complex is 29 cm^{-1} below that of the tungsten iodide compound, and $\nu_{C\equiv O}$ of the methoxide complex is 19 cm^{-1} below that of the tungsten methyl compound.

X-Ray Structure of Tp′(CO)(PhC≡CMe)WOCH$_2$^{t}Bu (6b). X-ray crystallographic data were collected under the conditions described in Table 3. The crystal structure of complex **6b** (Figure 2) shows an octahedral coordination sphere, with the alkyne occupying a single coordination site. The Tp′ ligand occupies

(31) (a) Song, J. S.; Szalda, D. J.; Bullock, R. M.; Lawrie, C. J. C.; Rodkin, M. A.; Norton, J. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1233. (b) Grundy, K. R.; Robertson, K. N. *Inorg. Chem.* **1985**, *24*, 3898. (c) Ciani, G.; Giusto, D.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1975**, 2156. (d) Agbossou, S. K.; Smith, W. W.; Gladysz, J. A. *Chem. Ber.* **1990**, *123*, 1293.

Scheme 7

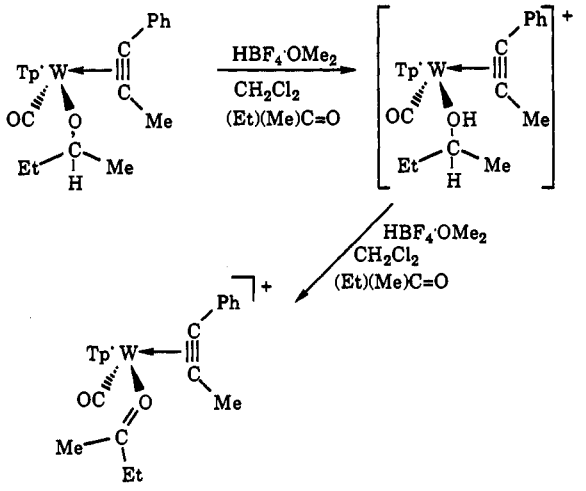


Table 2. IR ν_{CO} (cm^{-1}) Data for Complexes $[Tp'W(CO)(PhC{\equiv}CMe)L]^+$

ligand	IR $\nu_{C\equiv O}$ (cm^{-1}, KBr)	ligand	IR $\nu_{C\equiv O}$ (cm^{-1}, KBr)
$NHR^{1\,a}$	1849	BF_4	1917
OMe	1850	OTf	1917
H	1865	H_2O	1917
Me	1869	MeOH	1919
F	1876	$(Me)_2C{=}O$	1925
OPh	1880	$(Me)(^tBu)C{=}O$	1932
I	1905	MeCN	1940
$O_3SR^{2\,b}$	1910	$P(OMe)_3$	1947
NH_2R^1	1909		

^{a} R^1 = CH(Ph)(Me). ^{b} R^2 = camphor.

Table 3. Crystallographic Data Collection Parameters for $Tp'(CO)(PhC{\equiv}CMe)WOCH_2{}^tBu$ (**6b**)·CH_2Cl_2

molecular formula	$WC_{31}H_{43}BO_2N_6Cl_2$
formula weight, g/mol	797.28
crystal dimensions, mm	0.35 × 0.20 × 0.20
space group	$P2_1/c$
cell parameters	
a, Å	16.261(5)
b, Å	17.044(5)
c, Å	12.673(4)
V, Å^3	3394(2)
Z	4
density calcd, g/cm^3	1.560
Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo Kα (0.709 30 Å)
monochromator	graphite
linear abs coeff, cm^{-1}	36.7
scan type	$\theta/2\theta$
2θ limit	45.0°
h, k, l ranges	−17, 16; 0, 18; 0, 13
total no. of reflections	4441
data with $I > 2.5\sigma(I)$	3085
R	3.7%
R_w	4.4%
GOF	1.38
no. of parameters	388
maximum shift/σ	0.036

three coordination sites *trans* to the other three ligands: PhC≡CMe, CO, and $OCH_2{}^tBu$. Selected bond distances and bond angles are listed in Table 4. Atomic positional parameters are listed in Table 5.

The geometrical features of the metal alkyne fragment are typical of group VI d^4 alkyne complexes;[32] the alkyne backbone lies parallel to the metal–carbonyl axis. This orientation maximizes interactions between metal dπ and ligand π orbitals;

(32) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

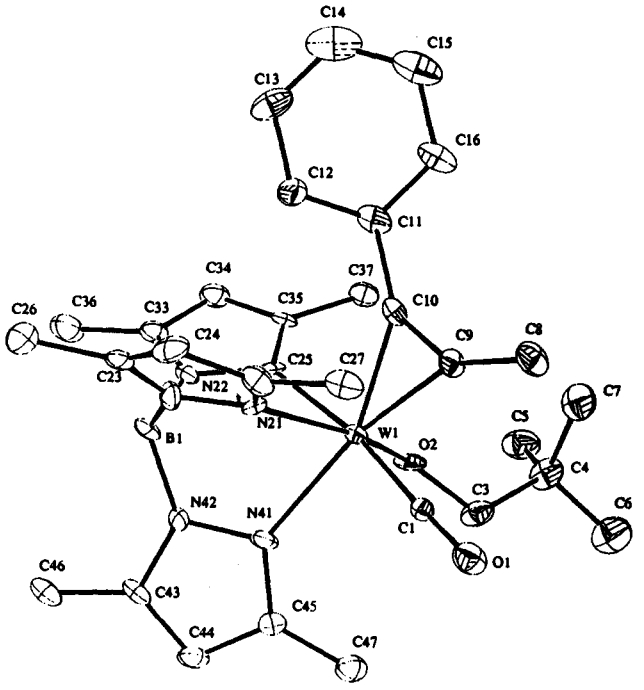


Figure 2. ORTEP diagram showing complete atomic number scheme for complex **6b** $Tp'(CO)(PhC{\equiv}CMe)W\text{-}OCH_2{}^tBu$.

Table 4. Selected Bond Distances (Å) and Bond Angles (deg) for $Tp'(CO)(PhC{\equiv}CMe)WOCH_2{}^tBu$ (**6b**)

W(1)–C(1)	1.902(8)	C(1)–O(1)	1.21(1)
W(1)–O(2)	1.971(6)	O(2)–C(3)	1.42(1)
W(1)–C(9)	2.113(9)	C(3)–C(4)	1.52(1)
W(1)–C(10)	2.039(9)	C(8)–C(9)	1.45(1)
W(1)–N(21)	2.242(7)	C(9)–C(10)	1.33(1)
W(1)–N(31)	2.253(8)	C(10)–C(11)	1.47(1)
W(1)–N(41)	2.252(7)		
C(1)–W(1)–O(2)	96.6(3)	C(10)–W(1)–N(21)	83.3(3)
C(1)–W(1)–C(9)	68.9(3)	C(10)–W(1)–N(31)	83.3(3)
C(1)–W(1)–C(10)	105.5(3)	C(10)–W(1)–N(41)	156.2(3)
C(1)–W(1)–N(21)	94.3(3)	N(21)–W(1)–N(31)	85.7(3)
C(1)–W(1)–N(31)	171.1(3)	N(21)–W(1)–N(41)	77.0(3)
C(1)–W(1)–N(41)	89.2(3)	N(31)–W(1)–N(41)	82.2(3)
O(2)–W(1)–C(9)	102.5(3)	W(1)–C(1)–O(1)	177.2(7)
O(2)–W(1)–C(10)	105.6(3)	W(1)–O(2)–C(3)	128.2(5)
O(2)–W(1)–N(21)	163.4(3)	O(2)–C(3)–C(4)	116.1(7)
O(2)–W(1)–N(31)	81.6(3)	W(1)–C(9)–C(8)	151.0(7)
O(2)–W(1)–N(41)	90.7(2)	W(1)–C(9)–C(10)	68.3(5)
C(9)–W(1)–C(10)	37.3(3)	C(8)–C(9)–C(10)	140.7(9)
C(9)–W(1)–N(21)	93.0(3)	W(1)–C(10)–C(9)	74.4(5)
C(9)–W(1)–N(31)	119.9(3)	W(1)–C(10)–C(11)	146.7(7)
C(9)–W(1)–N(41)	155.4(3)	C(9)–C(10)–C(11)	138.2(8)

the π-donor orbital of the alkyne donates electron density to the empty dπ orbital of tungsten, while the CO ligand can interact with both filled metal dπ orbitals.

The CO π^* orbitals mix with the filled d_{xz} and d_{yz} metal-based orbitals. The d_{xy} orbital is left vacant. The alkyne aligns itself parallel to the M–CO axis to optimize the interaction between the empty metal d_{xy} orbital and the filled $\pi_\perp$ orbital of the alkyne. The alkoxide is oriented in such a way that the lone pair on oxygen which is predominantly p in character can also overlap with d_{xy} to construct a three-center four-electron bond involving d_{xy} (metal), $\pi_\perp$ (alkyne), and p_x (oxygen) orbitals (Figure 3). The C_3–O_2–W_1–C_1 dihedral angle is 4.8°, denoting a nearly planar geometry for the alkoxide–tungsten–carbonyl fragment, in accord with this bonding description.

The $W\text{-}C_{alkyne}$ bond distances of complex **6b** (2.113(9) and 2.039(9) Å) are slightly longer than those typical of four-electron donor alkyne tungsten complexes[24] (the $W\text{-}C_{alkyne}$ bond distances in $Tp'(PhC{\equiv}CMe)(CO)WI$ are 2.01 and 1.98 Å). This metal–

Table 5. Atomic Parameters *x*, *y*, *z*, and Biso[a] for Tp′(CO)(PhC≡CMe)WOCH₂ᵗBu (**6b**)·CH₂Cl₂

	x	*y*	*z*	Biso
W1	0.22310(2)	0.93597(2)	0.26679(3)	1.11(1)
C1	0.1863(5)	0.8386(5)	0.1974(7)	1.1(4)
O1	0.1661(4)	0.7754(4)	0.1560(5)	2.2(3)
O2	0.3316(4)	0.9416(4)	0.2250(4)	1.7(3)
C3	0.3681(6)	0.8844(6)	0.1692(8)	2.1(4)
C4	0.4554(6)	0.8540(6)	0.2293(8)	2.3(5)
C5	0.5200(6)	0.9195(7)	0.2512(8)	3.1(5)
C6	0.4834(7)	0.7924(7)	0.1603(9)	3.4(5)
C7	0.4497(6)	0.8165(7)	0.3387(8)	2.9(5)
C8	0.2486(6)	0.7602(6)	0.4067(8)	2.1(4)
C9	0.2449(6)	0.8431(5)	0.3811(7)	1.5(4)
C10	0.2552(5)	0.9127(5)	0.4301(7)	1.3(4)
C11	0.2684(5)	0.9445(6)	0.5413(7)	1.8(4)
C12	0.2361(6)	1.0166(6)	0.5598(8)	2.1(4)
C13	0.2442(6)	1.0441(6)	0.6650(8)	2.6(5)
C14	0.2844(7)	0.9996(7)	0.7519(8)	3.5(6)
C15	0.3172(7)	0.9265(7)	0.7364(8)	3.6(6)
C16	0.1096(6)	1.1014(7)	0.2306(8)	1.6(4)
N21	0.0962(5)	0.9651(4)	0.2957(5)	1.3(3)
N22	0.0687(4)	1.0410(4)	0.2894(6)	1.5(3)
C23	−0.0008(5)	1.0450(5)	0.3320(7)	1.6(4)
C24	−0.0179(6)	0.9728(6)	0.3619*7)	1.9(4)
C25	0.0415(6)	0.9222(5)	0.3377(7)	1.8(4)
C26	−0.0461(6)	1.1216(6)	0.3385(8)	2.3(5)
C27	0.0485(5)	0.8354(6)	0.3549(7)	1.7(4)
N31	0.2602(4)	1.0594*5)	0.3230(5)	1.4(3)
N32	0.2004(4)	1.1201(4)	0.2992(6)	1.3(3)
C33	0.2353(6)	1.1873(5)	0.3409(7)	1.6(4)
C34	0.3191(6)	1.1713(5)	0.3977(7)	1.8(4)
C35	0.3306(6)	1.0921(5)	0.3833(7)	1.5(4)
C36	0.1891(7)	1.2649(6)	0.3260(8)	2.7(5)
C37	0.4088(6)	1.0461(6)	0.4310(7)	2.1(4)
N41	0.1131(4)	1.0689(4)	0.1206(5)	1.4(3)
C43	0.0776(6)	1.0957(6)	0.0174(7)	1.6(4)
C44	0.0981(6)	1.0446(5)	−0.0558(7)	1.8(4)
C45	0.1467(5)	0.9843(5)	0.0055(7)	1.2(4)
C46	0.0288(6)	1.1710(6)	−0.0031(7)	2.5(5)
C47	0.1835(6)	0.9170(5)	−0.0364(7)	1.9(4)
C51	0.383(1)	0.3938(8)	0.644(1)	5.3(8)
CL1	0.3049(2)	0.3164(3)	0.6049(3)	7.4(2)
CL2	0.4246(4)	0.4162(3)	0.5349(3)	8.7(3)

[a] Biso is the mean of the principal axes of the thermal ellipsoid.

alkyne bond elongation reflects competition between the alkyne $\pi_\perp$ electron pair and the lone pair on the alkoxide oxygen for the single vacant metal dπ orbital in the $W^{2+}d^4$ complex.

The alkyne carbons resonate at 183.8 and 181.2 ppm, somewhere between "four-electron" donor alkynes (near 200 ppm) and "three-electron" donor alkynes (near 160 ppm). In the complex Tp′(PhC≡CMe)(CO)WI, for example, the four-electron donor alkyne ligand is tightly bound to tungsten, and the alkyne carbons resonate at 208.9 and 206.5 ppm.[24]

Similar behavior is observed in tungsten–amido complexes;[15] the alkyne ligand adopts a "three-electron" donor role, due to the ability of the amide ligand to donate electron density to the metal center. The alkyne carbons in these tungsten amido complexes resonate even farther upfield (160 and 159 ppm) than those of analogous alkoxide complexes.

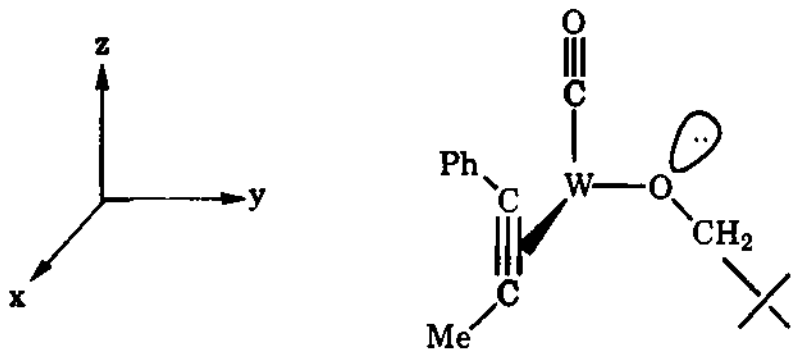
The tungsten–oxygen (1.971(6) Å) and tungsten–carbon (1.902(8) Å) bond distances are consistent with values reported in other systems.[33] The carbonyl–tungsten–oxygen bond angle is 96.6(3)° (Table 4).

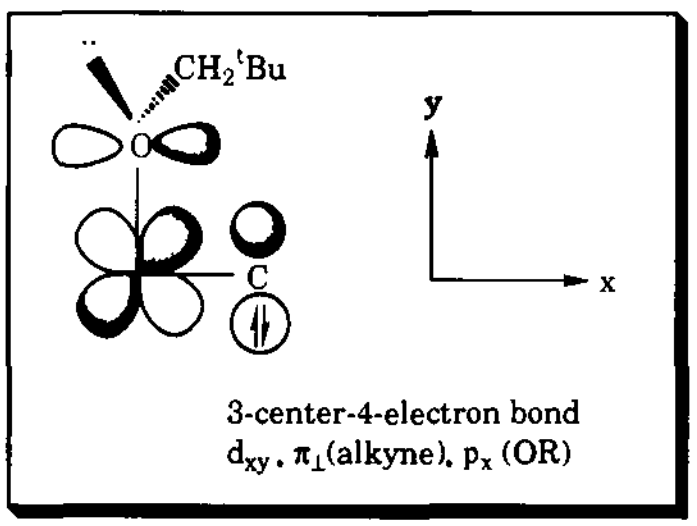
Summary

The synthesis of a chiral tungsten(II) methyl complex has been achieved via methyl substitution of iodide. This complex provides a vehicle to a number of chiral tungsten complexes. The tungsten methyl reagent can be protonated to effect loss of methane and create a vacant coordination site. In the presence of aldehydes and ketones, protonation of the methyl ligand yields cationic tungsten η^1-aldehyde and η^1-ketone complexes. These complexes exist as a mixture of isomers, believed to be *E* and *Z* C=O rotamers. The barriers for isomer interconversion are between 11 and 15 kcal/mol.

These complexes are susceptible to nucleophilic attack at the carbonyl carbon of the coordinated ketone or aldehyde. Hydride addition to these complexes affords alkoxide complexes. Upon protonation (2 equiv of acid) of alkoxides **5a–c** or **6a,b** in the presence of the corresponding aldehyde or ketone, the starting cationic complex **2a–c** or **3a,b** is formed. These reactions provide a route for the synthesis of primary and secondary alcohols via alkoxide displacement from the coordination sphere of tungsten.

Complex **2d** with the bulky pinacolone ligand cannot be reduced with K-Selectride; instead, deprotonation at the ligand's C_α methyl site yields an enolate ligand. Additional elaboration reactions of ligands in this environment are attractive future possibilities.





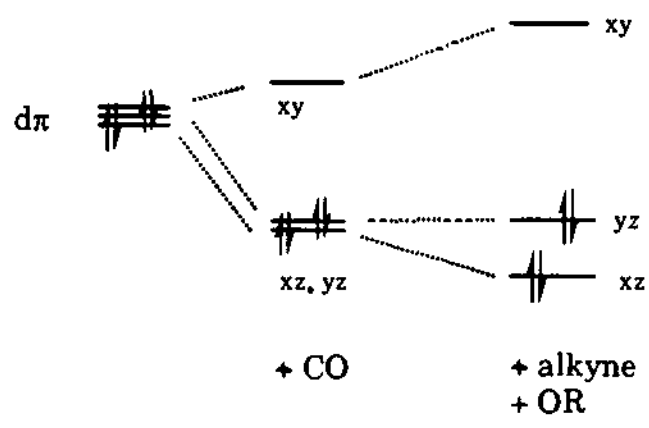


Figure 3. Three-center four-electron bond involving d_{xy}, $\pi_\perp$, and p_x.

Experimental Section

Materials and Methods. Reactions were performed under a dry nitrogen atmosphere with standard Schlenk techniques. Tetrahydrofuran (THF), hexanes, and diethyl ether (Et_2O) were distilled from potassium benzophenone ketyl. Dichloromethane was distilled from phosphorus pentoxide. All other solvents were purged with nitrogen and used without

(33) (a) Buhro, W. E.; Chisholm, M. H.; Martin, J. D.; Huffman, J. C.; Folting, K.; Streib, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8149. (b) Chisholm, M. H.; Folting, K.; Hampden-Smith, M. J.; Hammond, C. E. *J. Am. Chem. Soc.* **1989**, *111*, 7283. (c) Chisholm, M. H.; Huffman, J. C.; Hampden-Smith, M. J. *J. Am. Chem. Soc.* **1989**, *111*, 5284.

further purification. $LiCu(Me)_2$[34] and $HBAr'_4{\cdot}2OEt_2$[35] (BAr'_4 = tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate) were prepared according to literature procedures. Ketones and aldehydes were purchased from Aldrich and were dried over molecular sieves for 12 h prior to use. Metal complexes which were used as reagents, Tp'W(CO)PhC≡CMe)I,[24] Tp'W(CO)(PhC≡CMe)OTf,[17] and [Tp'W(CO)$_2$(PhC≡CMe)][OTf][17,24] were synthesized according to literature procedures. All other reagents were obtained from Aldrich and used without purification.

Infrared spectra were collected on a Mattson Polaris FTIR spectrometer. ^1H and ^{13}C NMR were recorded on a Bruker AC 200 (200 MHz), a Bruker WM 250 (250 MHz), or a Varian XL 400 (400 MHz) spectrometer. Analyses were conducted by Atlantic Microlab of Norcross, GA.

Synthesis of Tp'W(CO)(PhC≡CMe)Me (1). To a THF solution (250 mL) of Tp'W(CO)(PhC≡CMe)I (5.60 g, 7.45 mmol) was added a freshly made THF solution (50 mL) of $LiCu(Me)_2$ (1.5 equiv). The reaction mixture was allowed to stir for 4 h. The color of the solution changed from emerald green to dark purple. The solvent was evaporated, and the residue was dissolved in a minimum amount of CH_2Cl_2 and chromatographed on alumina. The blue-purple band was eluted with CH_2Cl_2. The solvent of the collected fraction was removed, and the residue was recrystallized from CH_2Cl_2/hexanes. Blue-purple crystalline product was isolated (4.62 g, 91% yield). IR (CH_2Cl_2): ν_{CO} = 1869 cm^{-1}. ^1H NMR (CD_2Cl_2) δ (ppm): 7.23–6.67 (m, 5H, C≡C*Ph*), 5.91, 5.84, 5.66 (each a s, 3H, Tp'C*H*), 3.32 (s, 3H, C≡C*Me*), 2.84, 2.57, 2.44, 2.34, 1.58, 1.43 (each a s, 18H, Tp'C*Me*), 0.29 (s, 3H, $^2J_{WH}$ = 6.8 Hz, W*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm): 245.1 ($^1J_{WC}$ = 145 Hz, CO), 207.5 ($^1J_{WC}$ = 54 Hz, C≡*C*Ph), 204.1 ($^1J_{WC}$ = 11 Hz, C≡*C*Me), 153.1, 153.0, 149.7, 144.7, 144.6, 144.1, 138.4 (Tp' *C*Me, *ipso* of Ph), 128.7, 128.6, 127.9 (*o*, *m*, *p* of Ph), 108.3, 107.8, 106.8, (Tp' *C*H), 21.2 (C≡C*Me*), 19.1 ($^1J_{WC}$ = 81 Hz, W*Me*), 16.1, 16.0, 14.9, 13.1, 13.0, 12.8 (Tp' C*Me*). Anal. Calcd: C, 46.67; H, 5.04; N, 12.32. Found: C, 46.58; H, 4.97; N, 12.49. Percentages are based on $WC_{26}H_{33}N_6OB{\cdot}0.5CH_2Cl_2$ (as determined by ^1H NMR).

Synthesis of [Tp'W(CO)(PhC≡CMe)(η^1-O=C(Me)$_2$)][BF$_4$] (2a). A CH_2Cl_2 solution (50 mL) of Tp'W(CO)(PhC≡CMe)Me (0.50 g, 0.78 mmol) and acetone (0.11 mL, 1.50 mmol) was cooled to 0 °C. To this solution was added dropwise with stirring $HBF_4{\cdot}OMe_2$ (0.08 mL, 0.78 mmol). The color of the solution changed from dark blue-purple to blue-green. The solvent was evaporated, and the residue was rinsed with Et_2O to leave 0.48 g (80% yield) of a clean light blue solid. IR (KBr): $\nu_{C\equiv O}$ = 1925 cm^{-1}, $\nu_{C=O}$ = 1635 cm^{-1}. ^1H NMR (CD_2Cl_2) δ (ppm): 7.33–6.73 (m, 5H, Ph), 6.08, 5.89, 5.80 (3s, 3H, Tp'C*H*), 3.92 (s, 3H, C≡C*Me*), 2.58, 2.55, 2.49, 2.47, 1.36, 1.17 (each a s, 18H, Tp' C*Me*), 2.29 (s, 6H, (*Me*)$_2$C=O). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm): 226.7 (C=O), 225.1 (C≡O), 209.1 ($^1J_{WC}$ = 50 Hz, PhC≡C), 208.3 ($^1J_{WC}$ = 13 Hz, C≡CMe), 153.9, 152.3, 151.6, 148.2, 147.6, 146.2, 135.7 (Tp' *C*Me, *ipso* of Ph), 130.8, 129.6, 129.2 (*o*, *m*, *p* of Ph), 108.8, 108.7, 108.3 (Tp' *C*H), 30.2 (O=C(*Me*)$_2$), 23.4 (C≡C*Me*), 16.2, 15.8, 13.6, 13.1, 12.9, 12.8 (Tp' C*Me*).

Synthesis of [Tp'W(CO)(PhC≡CMe)(η^1-O=C(Me)(Et))][BF$_4$] (2b). The procedure for the protonation of complex **1** (0.50 g, 0.78 mmol) with $HBF_4{\cdot}OMe_2$ (0.08 mL, 0.78 mmol) in the presence of 2-butanone (0.17 mL, 1.82 mmol) was the same as described above. Workup yielded 0.44 g (81% yield) of the desired blue-green product, **2b**. IR (KBr): ν_{CO} = 1921 cm^{-1}, $\nu_{C=O}$ = 1635 cm^{-1}. ^1H NMR (CD_2Cl_2) δ (ppm): 7.33–6.74 (m, 5H, Ph), 6.08, 5.88, 5.80 (each a s, 3H, Tp' C*H*), 3.92 (s, 3H, C≡C*Me*), 2.86 (m, 2H, O=C(Me)(C*H*$_2$Me)), 2.58, 2.54, 2.47, 2.01, 1.35, 1.13 (each a s, 3:3:6:3:3:3 H, Tp' C*Me*, O=C(*Me*)(Et)), 0.80 (t, 3H, $^3J_{HH}$ = 7.2 Hz, O=C(Me)(CH$_2$*Me*)). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm): 229.4 (C=O), 225.4 (C≡O), 208.6 (PhC≡C), 208.1 (C≡CMe), 153.8, 152.2, 151.4, 148.3, 147.6, 146.2, 135.7 (Tp' *C*Me, *ipso* of Ph), 130.8, 129.6, 129.3 (*o*, *m*, *p* of Ph), 108.8, 108.7, 108.3 (Tp' *C*H), 38.1 (O=C(*C*H$_2$Me)(Me)), 27.2 (O=C(Et)(*Me*)), 23.3 (C=C*Me*), 16.2, 15.9, 13.5, 13.1, 12.9, 12.8, 7.9 (Tp' C*Me*, O=C(CH$_2$*Me*)(Me)).

Synthesis of [Tp'W(CO)(PhC≡CMe)(η^1-O=C(Me)(Ph))][BF$_4$] (2c). The procedure for the protonation of complex **1** (0.40 g, 0.62 mmol) with $HBF_4{\cdot}OMe_2$ (0.06 mL, 0.60 mmol) in the presence of acetophenone (0.14 mL, 1.20 mmol) was the same as described above. Workup yielded 0.38 g (73% yield) of the desired brown product, **2c**. A fluxional process broadens some signals in the room temperature ^1H NMR spectrum of complex **2c**. The ratio of the two isomers of **2c** was determined by ^1H NMR at low temperature to be 3:2. IR (KBr): ν_{CO} = 1915 cm^{-1}. Distinctive ^1H NMR data for the minor isomer are reported in parenthesis. ^1H NMR (CD_2Cl_2, −11 °C) δ (ppm): 7.65–6.78 (m, 10H, 2Ph), 6.06, 5.81, 5.80 (6.12, 5.82, 5.81) (each a s, 3H, Tp' C*H*), 4.00 (4.02) (s, 3H, C≡C*Me*), 2.60, 2.55, 2.53, 2.50, 2.24, 1.39, 1.06 (2.58, 2.53, 2.50, 2.49, 2.15, 1.38, 0.90) (each a s, 21H, Tp' C*Me*, O=C(Ph)*Me*). The ^{13}C NMR at −39 °C exhibits resonances for two isomers, both of which are reported together. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −29 °C, two isomers): 224.6, 224.3 (C≡O), 209.9, 209.5, 208.7, 208.2 (PhC≡CMe), 203.4, 202.7 (*C*=O), 153.6, 153.1, 151.8, 151.7, 151.2, 150.7, 147.8, 147.6, 147.5, 147.1, 146.1, 145.8 (Tp' *C*Me), 135.0, 134.9, 133.0, 132.6 (*ipso* of 2Ph), 137.1, 136.7, 130.7, 130.4, 129.8, 129.6, 129.5, 129.5, 129.4, 129.3, 129.0, 128.9 (*o*, *m*, *p* of 2Ph), 108.4, 108.2, 108.1, 107.9 (1:2:1:2 C, Tp' *C*H), 23.5, 23.3, 22.8, 20.1 (O=C(Ph)(*Me*), C≡C*Me*), 16.2, 16.1, 15.9, 15.6, 13.7, 13.2, 13.0, 12.9, 12.8, 12.7 (1:1:1:1:1:1:2:1:2:1 C, Tp' C*Me*).

Synthesis of [Tp'W(CO)(PhC≡CMe)(η^1-O=C(Me)(^{t}Bu))][BAr'$_4$] (2d). A CH_2Cl_2 solution (50 mL) of Tp'W(CO)(PhC≡CMe)Me (0.20 g, 0.31 mmol) and pinacolone (*tert*-butyl methyl ketone) (0.09 mL, 0.72 mmol) was cooled to 0 °C. To this solution, $HBAr'_4{\cdot}2OEt_2$ (0.31 g, 0.31 mmol) was added slowly with stirring. The color of the solution changed from dark blue-purple to blue-green. The solvent was evaporated, and the residue was rinsed with hexanes to leave 0.35 g (67% yield) of a clean light blue solid. The ^1H NMR spectrum of complex **2d** reflects fluxionality at room temperature. The ratio of isomers was determined by low temperature ^1H NMR to be 3:2. IR (CH_2Cl_2): $\nu_{C=O}$ = 1932 cm^{-1}. ^1H NMR data for the minor isomer are reported in parenthesis. ^1H NMR (CD_2Cl_2) δ (ppm): 7.72, 7.56 (each a s, 8:4 H, Ar'), 7.32–6.75 (m, 5H, Ph), 6.06, 5.86, 5.79 (each a s, 3H, Tp' C*H*), 3.91 (s, 3H, C≡C*Me*), 2.56, 2.53, 2.46, 2.42, 1.33, 1.13 (each a s, 18H, Tp' C*Me*), 1.62 (2.04) (each a s, 3H, O=C(^{t}Bu)(*Me*)), 1.02 (0.93) (each a s, 9H, O=C(Me)(*^{t}Bu*)). The ^{13}C NMR at −39 °C exhibits resonances for two isomers, both of which are reported together. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −39 °C, two isomers): 233.1, 232.3 (C=O), 225.7, 224.8 ($^1J_{WC}$ = 150 Hz, C≡O), 211.2, 205.6 ($^1J_{WC}$ = 52 Hz, PhC≡*C*Me), 209.9, 206.9 (PhC≡*C*Me), 162.0 (q, J_{BC} = 50 Hz, *ipso* of BAr'$_4$), 153.4, 152.7, 152.0, 151.3, 151.1, 150.5, 148.0, 147.8, 147.7, 147.1, 146.2, 145.7 (Tp' *C*Me), 135.3, 135.1 (*ipso* of alkyne Ph), 134.8 (*o*-C of BAr'$_4$), 128.8 (q, J_{CF} = 30 Hz, *m*-C of BAr'$_4$), 125.0 (q, J_{CF} = 270 Hz, *C*F$_3$), 117.6 (*p*-C of BAr'$_4$), 130.9, 130.6, 129.4, 129.3, 129.0, 128.9 (*o*, *m*, *p* of alkyne Ph), 108.3, 108.2, 108.1, 108.0, 107.9, 107.8 (Tp' *C*H), 46.9, 46.5 (O=C(Me)(*C*(Me)$_3$), 26.2, 25.8 (O=C(Me)(C(*Me*)$_3$), 24.5, 23.5, 22.6, 20.3 (O=C(*Me*)(^{t}-Bu), C≡C*Me*), 16.2, 16.1, 15.5, 13.6, 13.5, 12.9, 12.7, 12.6, 12.5 (1:2:1:1:1:2:1:2:1, Tp' C*Me*). Anal. Calcd: C, 45.95; H, 3.38; N, 5.02. Found: C, 46.41; H, 3.40; N, 5.12. Percentages are based on $WC_{63}H_{54}N_6O_2B_2F_{24}{\cdot}CH_2Cl_2$ (as determined by ^1H NMR).

Synthesis of [Tp'W(CO)(PhC≡CMe)(η^1-O=C(Ph)(H))][BF$_4$] (3a). A CH_2Cl_2 solution (50 mL) of Tp'W(CO)(PhC≡CMe)Me (0.40 g, 0.62 mmol) and benzaldehyde (0.11 mL, 1.55 mmol) was cooled to 0 °C. To this solution, $HBF_4{\cdot}OMe_2$ (0.06 mL, 0.62 mmol) was added dropwise with stirring. The color of the solution changed from dark blue-purple to intense red-purple. The solvent was evaporated, and the residue was rinsed with Et_2O to leave 0.41 g (80% yield) of a clean purple solid. IR (KBr): ν_{CO} = 1923 cm^{-1}. ^1H NMR (CD_2Cl_2) δ (ppm): 7.93 (s, 1H, O=C(Ph)(*H*)), 7.66–6.79 (m, 10H, 2Ph), 6.19, 5.84, 5.81 (each a s, 3H, Tp' C*H*), 3.99 (s, 3H, C≡C*Me*), 2.57, 2.55, 2.51, 2.47, 1.37, 0.99 (each a s, 18H, Tp' C*Me*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm): 224.6 ($^1J_{WC}$ = 148 Hz, C≡O), 207.1, 206.7 (PhC≡*C*Me), 196.2 (C=O), 153.3, 151.9, 151.4, 148.6, 148.2, 146.5 (Tp' *C*Me), 135.6, 133.2 (2 *ipso* of 2 Ph), 138.7, 132.1, 131.0, 130.1, 130.0, 129.3 (*o*, *m*, *p* of 2 Ph), 109.4, 109.2, 108.4 (Tp' *C*H), 23.2 (C≡C*Me*), 16.2, 15.3, 13.7, 13.1, 13.0, 12.8 (Tp' C*Me*).

Synthesis of [Tp'W(CO)(PhC≡CMe)(η^1-O=C(^{t}Bu)(H))][BAr'$_4$] (3b). A CH_2Cl_2 solution (50 mL) of Tp'W(CO)(PhC≡CMe)Me (0.20 g, 0.31 mmol) and trimethylacetaldehyde (0.04 mL, 0.37 mmol) was cooled to 0 °C. To this solution was added slowly with stirring $HBAr'_4{\cdot}2OEt_2$ (0.31 g, 0.31 mmol). The color of the solution changed from dark blue-purple to blue-green. The solvent was evaporated, and the residue was rinsed with hexanes to leave 0.35 g (71% yield) of a clean light blue solid. IR (KBr): $\nu_{C\equiv O}$ = 1938 cm^{-1}. ^1H NMR (CD_2Cl_2) δ (ppm): 7.78, 7.60 (each a s, 8:4 H, Ar'), 7.64 (s, 1H, O=C(^{t}Bu)(*H*)), 7.34–6.79 (m, 5H, Ph), 6.12, 5.89, 5.81 (each a s, 3H, Tp' C*H*), 3.95 (s, 3H, C≡C*Me*), 2.55, 2.54, 2.46, 2.44, 1.33, 1.16 (each a s, 18H, Tp' C*Me*), 0.98 (s, 9H, O=C-(H)(*^{t}Bu*). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (ppm): 224.8 ($^1J_{WC}$ = 150 Hz, C≡O), 219.0 (C=O), 209.2, 208.5 (PhC≡*C*Me), 162.0 (q, J_{BC} = 50

(34) $LiCu(Me)_2$ was synthesized in situ, using 1 equiv of CuI and 2 equiv of MeLi in THF at 0 °C. The solution was allowed to stir for 10 min before being transferred to the reaction vessel.

(35) (a) Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600. (b) Brookhart, M.; Grant, B.; Volpe, A. F. *Organometallics* **1992**, *11*, 3920.

Hz, *ipso* of BAr'$_4$), 153.0, 151.8, 151.4, 148.9, 148.5, 146.8 (Tp' *C*Me), 135.8 (*ipso* of Ph), 135.3 (*o*-C of BAr'$_4$), 129.4 (q, J_{CF} = 30 Hz, *m*-C of BAr'$_4$), 125.0 (q, J_{CF} = 270 Hz, *C*F$_3$), 117.9 (*p*-C of BAr'$_4$), 131.2, 130.1, 129.4 (*o, m, p* of alkyne Ph), 109.5, 109.3, 108.4 (Tp' *C*H), 45.4 (O=C(H)(*C*(Me)$_3$), 24.1 (O=C(H)(C(*Me*)$_3$), 23.2 (C≡C*Me*), 16.1, 15.7, 14.0, 13.0, 12.9, 12.7 (Tp' C*Me*). Anal. Calcd: C, 47.30; H, 3.34; N, 5.34. Found: C, 47.04; H, 3.35; N, 5.27.

Synthesis of Tp'(CO)(PhC≡CMe)WOMe (4a). A THF solution (50 mL) of [Tp'W(CO)$_2$(PhC≡CMe)][OTf] (0.40 g, 0.50 mmol) was allowed to reflux until Tp'(CO)PhC≡CMe)WOTf was formed (about 4 h). The reaction was monitored by IR spectroscopy. The reagent dicarbonyl pattern (ν_{CO} = 2044, 1965 cm^{-1}) in the IR spectrum changed to a monocarbonyl pattern (ν_{CO} = 1922 cm^{-1}) as the color changed from green to blue. A methanol solution (5 mL) of LiOMe (0.04 g, 1.00 mmol) was added to the refluxing THF solution, and the mixture was heated for an additional 4 h. The solvent was evaporated, and the blue residue was chromatographed on alumina. The blue band was eluted with CH_2Cl_2. Removal of the solvent yielded 0.22 g (67% yield) of a blue powder. IR (KBr): ν_{CO} = 1850 cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ (ppm): 7.18–6.48 (m, 5H, Ph), 5.90, 5.72, 5.62 (each a s, 3H, Tp' C*H*), 4.55 (s, 3H, $^3J_{WH}$ = 2.6 Hz, WO*Me*), 3.41 (s, 3H, C≡C*Me*), 2.81, 2.49, 2.43, 2.36, 1.51, 1.49 (each a s, 18H, Tp' C*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ (ppm): 245.7 (C≡O), 188.4, 185.4 (PhC≡*C*Me), 157.4, 156.6, 154.7, 149.4, 149.1, 147.6, 141.0 (Tp' *C*Me, *ipso* of Ph), 132.9, 132.3, 131.3 (*o, m, p* of Ph), 112.0, 111.5, 110.7 (Tp' *C*H), 77.7 (O*C*H$_3$), 23.6 (C≡C*Me*), 19.8, 19.5, 17.3, 16.9, 16.8, 16.6 (Tp' C*Me*). Anal. Calcd: C, 47.60; H, 5.08; N, 12.81. Found: C, 47.52; H, 5.13; N, 12.73.

Synthesis of Tp'(CO)(PhC≡CMe)WOPh (4b). A THF solution (50 mL) of [Tp'W(CO)$_2$(PhC≡CMe)][OTf] (0.50 g, 0.62 mmol) was allowed to reflux until Tp'(CO)(PhC≡CMe)WOTf was formed (about 4 h). The reaction was monitored by IR spectroscopy as described above. A THF solution (15 mL) of KOPh, which was obtained by deprotonating phenol (0.07 g, 0.75 mmol) with an excess of KH, was added to the refluxing THF solution, and the mixture was heated for an additional 4 h. The solvent was evaporated, and the blue residue was chromatographed on alumina. The blue band was eluted with CH_2Cl_2. Removal of the solvent yielded 0.32 g (71% yield) of a blue powder. IR (THF): ν_{CO} = 1880 cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ (ppm): 7.24–6.46 (m, 10H, 2Ph), 5.88, 5.84, 5.70 (each a s, 3H, Tp' C*H*), 3.69 (s, 3H, C≡C*Me*), 2.59, 2.50, 2.42, 2.36, 1.59, 1.48 (each a s, 18H, Tp' C*Me*), ^{13}C{^{1}H} NMR (CD_2Cl_2) δ (ppm): 238.9 ($^1J_{WC}$ = 160 Hz, C≡O), 193.3 ($^1J_{WC}$ = 51 Hz, PhC≡C), 189.8 ($^1J_{WC}$ = 11 Hz, C≡*C*Me), 169.8 (*ipso* of OPh), 153.7, 152.9, 151.2, 145.7, 145.3, 144.0, 136.9 (Tp' *C*Me, *ipso* of alkyne Ph), 128.9, 128.8, 128.4, 128.0, 119.4, 118.9 (*o, m, p* of 2 Ph), 108.2, 107.6, 107.2 (Tp' *C*H), 20.7 (C≡C*Me*), 16.1, 15.5, 13.5, 13.0, 12.9, 12.8 (Tp' C*Me*). Anal. Calcd: C, 51.85; H, 4.92; N, 11.71. Found: C, 51.72; H, 4.94; N, 11.62.

Synthesis of Tp'(CO)(PhC≡CMe)W(OCH(Me)$_2$) (5a). A CH_2Cl_2 solution (50 mL) of the cationic acetone complex **2a** (0.40 g, 0.52 mmol) was cooled to −78 °C. K-Selectride (1.0 M solution in THF, 0.55 mL, 0.55 mmol) was added slowly to the cold CH_2Cl_2 solution. The solution turned from blue-green to purple, and the solvent was evaporated. The residue was chromatographed on alumina using a mixture of CH_2Cl_2 and hexanes as the eluent (removal of the boron residues sometimes requires chromatographing the product twice). The purple product was recrystallized from CH_2Cl_2/hexanes to yield 0.22 g (63% yield) of the desired product. IR (KBr): ν_{CO} = 1859 cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ (ppm): 7.16–6.40 (m, 5H, Ph), 5.89, 5.73, 5.59 (each a s, 3H, Tp' C*H*), 5.14 (septet, 1H, $^3J_{HH}$ = 6.0 Hz, OC*H*(Me)$_2$), 3.39 (s, 3H, C≡C*Me*), 2.77, 2.51, 2.41, 2.35, 1.55, 1.53 (each a s, 18H, Tp' C*Me*), 1.03 (d, 3H, $^3J_{HH}$ = 6.0 Hz, CH(Me)(*Me*)), 0.56 (d, 3H, $^3J_{HH}$ = 6.0 Hz, CH(*Me*)(Me)). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ (ppm): 241.3 ($^1J_{WC}$ = 166 Hz, C≡O), 184.1 ($^1J_{WC}$ = 52 Hz, PhC≡C), 180.3 ($^1J_{WC}$ = 10 Hz, C≡*C*Me), 153.3, 152.6, 150.8, 145.2, 145.0, 143.7, 137.3 (Tp' *C*Me, *ipso* of Ph), 128.5, 128.3, 127.2 (*o, m, p* of Ph), 108.2, 107.6, 106.7, (Tp' *C*H), 85.7 (O*C*H(Me)$_2$), 27.8, 24.6 (OCH(*Me*)$_2$), 20.0 (C≡C*Me*), 15.8, 15.4, 14.5, 13.0, 12.9, 12.8 (Tp' C*Me*). Anal. Calcd: C, 49.16; H, 5.46; N, 12.29. Found: C, 49.00; H, 5.48; N, 12.23.

Synthesis of Tp'(CO)(PhC≡CMe)W(OCH(Me)(Et)) (5b). The procedure for the reduction of the cationic 2-butanone complex **2b** (0.40 g, 0.51 mmol) was the same as that described above for the reduction of the acetone complex **2a**. Upon addition of K-Selectride (1.0 M THF solution, 0.52 mL, 0.52 mmol), the solution turned from blue-green to purple, and the solvent was evaporated. The residue was chromatographed on alumina using a mixture of CH_2Cl_2 and hexanes as the eluent. Recrystallization from CH_2Cl_2/hexanes gave 0.26 g (72% yield) of a 3:2 mixture of tungsten alkoxide diastereomers (this ratio was the same in the crude product). IR (KBr): ν_{CO} = 1859 cm^{-1}. Distinctive NMR data for the minor isomer are reported in parenthesis. ^{1}H NMR (CD_2Cl_2) δ (ppm): 7.15–6.40 (m, 5H, Ph), 5.89, 5.73, 5.59 (each a s, 3H, Tp' C*H*), 4.89 (m, 1H, OC*H*(Me)(Et)), 3.38 (3.36) (s, 3H, C≡C*Me*), 2.77 (2.79), 2.51, 2.41, 2.35, 1.53 (1.54), 1.52 (1.51) (each a s, 18H, Tp' C*Me*), 1.17 (1.50) (m, 2H, OCH(C*H*$_2$Me)(Me)), 0.53 (0.98) (d, $^3J_{HH}$ = 6.0 Hz, 3H, OCH(Et)(*Me*)), 0.75 (m, 3H, OC(CH$_2$*Me*)(Me)). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ (ppm): 241.3 (241.1) ($^1J_{WC}$ = 166 Hz, C≡O), 185.7 (183.5), 179.9 (180.1) (PhC≡CMe), 153.2, 152.5 (152.6), 150.7, 145.1 (145.2), 144.9, 143.5, 137.3 (Tp' *C*Me, *ipso* of Ph), 128.5, 128.2, 127.2 (*o, m, p* of Ph), 108.1 (108.2), 107.5 (107.6), 106.6 (Tp' *C*H), 90.8 (91.5) (O*C*H-(Me)(Et)), 34.4 (31.9) (OC(*C*H$_2$Me)(Me)), 21.1 (24.4) (OC(*Me*)(Et)), 19.9 (19.8) (C≡C*Me*), 15.8, 15.5 (15.6), 14.4, 13.0, 12.9, 12.8, 10.1 (10.5) (Tp' C*Me*, OC(Me)(CH$_2$*Me*)). Anal. Calcd: C, 49.89; H, 5.64; N, 12.04. Found: C, 49.65; H, 5.71; N, 11.93.

Synthesis of Tp'(CO)(PhC≡CMe)W(OCHMePh) (5c). The procedure for the reduction of the cationic acetophenone complex **2c** (0.35 g, 0.42 mmol) was the same as that described above for the reduction of the acetone complex **2a**. Upon addition of K-Selectride (1.0 M THF solution, 0.42 mL, 0.42 mmol), the solution turned from brown to purple, and the solvent was evaporated. The residue was chromatographed on alumina using a mixture of CH_2Cl_2 and hexanes as the eluent. Recrystallization from CH_2Cl_2/hexanes gave 0.19 g (61% yield) of an 11:2 mixture of tungsten alkoxide diastereomers (this ratio was also present in the crude product). IR (KBr): ν_{CO} = 1852 cm^{-1}. NMR data for the minor isomer are reported in parenthesis. ^{1}H NMR (CD_2Cl_2) δ (ppm): 7.31–6.25 (m, 10H, 2Ph), 6.11 (q, 1H, $^3J_{HH}$ = 6.4 Hz, OC*H*MePh), 5.94, 5.78 (5.69), 5.55 (5.62) (each a s, 3H, Tp' C*H*), 2.90 (3.48), (s, 3H C≡C*Me*), 2.53 (2.54), 2.40 (2.43), 2.37 (2.34), 2.31 (2.32), 1.81 (1.68), 1.39 (1.56) (each a s, 18H, Tp' C*Me*), 1.25 (0.82) (d, 3H, $^3J_{HH}$ = 6.4 Hz, OCH*Me*Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ (ppm): 240.2 (241.1) ($^1J_{WC}$ = 166 Hz, C≡O), 185.2 (184.7) ($^1J_{WC}$ = 53 Hz, PhC≡C), 183.6 (180.8) (C≡*C*Me), 153.6 (156.3), 152.8 (152.5), 151.0, 148.4, 145.2 (145.1), 144.9, 143.9 (143.6), 137.7 (137.3) (Tp' *C*Me, 2 *ipso* of 2 Ph), 128.4, 128.3, 128.2, 127.2, 127.0, 126.7, (128.6, 128.3, 128.1, 127.4, 126.0, 125.3) (*o, m, p* of 2 Ph), 108.4 (108.2), 108.0 (107.3), 106.8 (Tp' *C*H), 91.5 (92.9) (O*C*HPhMe), 29.1 (25.9) (OCH*Me*Ph), 18.3 (20.2) (C≡C*Me*), 15.9, 15.5 (15.2), 15.0 (14.6), 13.1, 12.9 (1:1:1:1:2, Tp' *C*Me). Anal. Calcd: C, 53.12; H, 5.28; N, 11.27. Found: C, 52.64; H, 5.37; N, 10.94.

Synthesis of Tp'(CO)(PhC≡CMe)W(OCH$_2$Ph) (6a). The procedure for the reduction of the cationic benzaldehyde complex **3a** (0.52 g, 0.63 mmol) was the same as that described above for the reduction of the acetone complex **2a**. Upon addition of K-Selectride (1.0 M THF solution, 0.63 mL, 0.63 mmol), the solution turned from red-purple to blue-purple. Workup gave 0.30 g (65% yield) of the tungsten alkoxide product. IR (KBr): ν_{CO} = 1857 cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ (ppm): 7.39–6.41 (m, 10H, 2Ph), 6.07 (d, 1H, $^2J_{HH}$ = 12.4 Hz, OC*H*HPh), 5.91, 5.69, 5.62 (each a s, 3H, Tp' C*H*), 5.47 (d, 1H, $^2J_{HH}$ = 12.4 Hz, OCH*H*Ph), 3.28 (s, 3H, C≡C*Me*), 2.81, 2.50, 2.43, 2.36, 1.51, 1.34 (each a s, 18H, Tp' C*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ (ppm): 241.0 ($^1J_{WC}$ = 165 Hz, C≡O), 185.7 ($^1J_{WC}$ = 52 Hz, PhC≡C), 182.5 (C≡*C*Me), 153.4, 152.6, 150.8, 145.3, 145.1, 144.8, 143.7, 137.3 (Tp' *C*Me, 2 *ipso* of Ph), 128.6, 128.3, 128.1, 127.6, 127.4, 126.6 (*o, m, p* of 2 Ph), 108.1, 107.6, 106.8 (Tp' *C*H), 88.5 (OCH$_2$Ph), 19.7 (C≡C*Me*), 15.8, 15.7, 14.1, 12.9, 12.8 (1:1:1:2:1, Tp' C*Me*). Anal. Calcd: C, 52.50; H, 5.10; N, 11.48. Found: C, 52.96; H, 5.31; N, 11.22.

Synthesis of Tp'(CO)(PhC≡CMe)W(OCH$_2$^{t}Bu) (6b). The procedure for the reduction of the cationic trimethylacetaldehyde complex **3b** (0.79 g, 0.50 mmol) was the same as that described above for the reduction of the acetone complex **2a**. Upon addition of K-Selectride (1.0 M THF solution, 0.50 mL, 0.50 mmol), the solution turned from blue-green to blue-purple. Workup gave 0.26 g (69% yield) of the tungsten alkoxide product. IR (CH_2Cl_2): ν_{CO} = 1857 cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ (ppm): 7.22–6.48 (m, 5H, Ph), 5.98, 5.81, 5.65 (each a s, 3H, Tp' C*H*), 4.87 (d, 1H, $^2J_{HH}$ = 10 Hz, OC*H*H^{t}Bu), 4.60 (d, 1H, $^2J_{HH}$ = 10 Hz, OCH*H*^{t}Bu), 3.41 (s, 3H, C≡C*Me*), 2.94, 2.57, 2.47, 2.43, 1.69, 1.55 (each a s, 18H, Tp' C*Me*), 0.71 (s, 9H, ^{t}Bu*Me*). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ (ppm): 241.3 ($^1J_{WC}$ = 167 Hz, C≡O), 183.8 ($^1J_{WC}$ = 52 Hz, PhC≡C), 181.2 ($^1J_{WC}$ = 11 Hz, C≡*C*Me), 153.7, 152.7, 150.7, 145.3, 145.0, 143.8, 137.7 (Tp' *C*Me, *ipso* of Ph), 128.6, 128.3, 127.3 (*o, m, p* of Ph), 107.9, 106.8 (2:1, Tp' *C*H), 100.7 (O*C*H$_2$^{t}Bu), 35.9 (OCH$_2$*C*(Me)$_3$), 26.9 (OCH$_2$C(*Me*)$_3$), 19.8 (C≡C*Me*), 16.1, 15.8, 15.1, 13.1, 13.0, 12.9 (Tp' C*Me*). Anal.

Calcd: C, 48.57; H, 5.62; N, 11.15. Found: C, 48.67; H, 5.77; N, 11.13. Percentages are based on $WC_{30}H_{41}N_6O_2B \cdot 0.5CH_2Cl_2$ (as determined by ^1H NMR).

Synthesis of [Tp'(CO)(PhC≡CMe)W(MeOH)][BAr'$_4$] (7). To a CH_2Cl_2 solution (30 mL) of Tp'(CO)(PhC≡CMe)WOMe, **4a** (0.20 g, 0.30 mmol), which had been cooled in an ice bath, was added HBAr'$_4$·2OEt$_2$ (0.30 g, 0.30 mmol). The solution turned from dark blue to aqua-blue, and the C≡O stretching frequency increased from 1857 to 1919 cm^{-1} in the infrared spectrum. The solvent was evaporated, and the residue was rinsed with hexanes to give 0.38 g (83% yield) of the desired product **7**. IR (KBr): ν_{CO} = 1917 cm^{-1}. ^1H NMR (CD_2Cl_2) δ (ppm): 7.73, 7.56 (each a s, 8:4 H, Ar') 7.32–6.61 (m, 5H, Ph), 6.55 (q, 1H, $^3J_{HH}$ = 5.0 Hz, *H*OMe), 6.06, 5.89, 5.79 (each a s, 3H, Tp' C*H*), 3.88 (d, 3H, $^3J_{HH}$ = 5.0 Hz, HO*Me*), 3.85 (s, 3H, C≡C*Me*), 2.67, 2.57, 2.54, 2.44, 1.35 (each a s, 3:3:3:3:6 H, Tp' C*Me*).

X-Ray Structure of Tp'(CO)(PhC≡CMe)(OCH$_2$^{t}Bu) (6b). Crystals were grown from CH_2Cl_2/hexanes. The crystal studied contained a CH_2Cl_2 molecule and was monoclinic with space group $P2_1/c$. Details of data collection are presented in Table 3. An ORTEP diagram is shown in Figure 2.

Acknowledgment. We gratefully acknowledge the National Science Foundation (CHE9208207) for support of this research.

Supplementary Material Available: Listings of thermal parameters, complete bond distances and angles, and labeled figure (6 pages); tables of observed and calculated structure factors (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.