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Articles

Formation of Derivative Carbyne Complexes from $Tp'(CO)_2M{\equiv}CCH_3$ (M = Mo, W)

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Chloride displacement from $Tp'(CO)_2M{\equiv}CCl$ (M = Mo, W (**1**); Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate) with $LiMe_2Cu$ affords the methylcarbyne complex $Tp'(CO)_2M{\equiv}CCH_3$ (M = Mo (**2**), W (**3**)). Deprotonation of this methylcarbyne forms $[Tp'(CO)_2M{=}C{=}CH_2]^-$ (M = Mo, W (**4**)), a nucleophilic vinylidene anion which reacts with a variety of substrates. Reaction of **4** with CH_3I yields $Tp'(CO)_2W{\equiv}CCH_2CH_3$ (**5**), while PhC(O)H yields $Tp'(CO)_2W{\equiv}CCH_2CH(OH)(Ph)$ (**8**) and $PhC(O)CH_3$ yields $Tp'(CO)_2W{\equiv}CCH_2C(OH)(CH_3)(Ph)$ (**10**). In the presence of base complex **8** undergoes elimination to form a conjugated vinyl carbyne complex $Tp'(CO)_2W{\equiv}CCH{=}CH(Ph)$ (**11**). Reaction of **4** with PhC(O)Cl and then base forms $Tp'(CO)_2W{\equiv}CCH_2C(O)Ph$ (**14**), which rearranges in solution to a metallafuran complex, $Tp'(CO)_2\overline{WCHCHC(O)}Ph$ (**15**). Spectroscopic data suggests that a dinuclear intermediate, $Tp'(CO)_2W{\equiv}CCH_2CPh(OH)CH_2C{\equiv}W(CO)_2Tp'$ (**13**), is first formed from **4** and PhC(O)Cl before the addition of base produces the expected monomeric product, $Tp'(CO)_2W{\equiv}CCH_2C(O)Ph$ (**14**).

Introduction

Conversion of heteroatom stabilized carbenes to carbynes remains one of few unique routes to form carbyne complexes.[1] The majority of transition metal carbyne preparations involve carbenes as reagents, and even O^{2-} abstraction from acyl complexes[2] falls under the same reaction paradigm. Some carbyne complexes have been formed through reactions of vinyl, vinylidene, allenylidene, and acetylide complexes.[3] Among the less general methods is the formation of $Tp'(CO)_2M{\equiv}CCl$ (M = Mo, W) (Tp′ = hydridotris(3,5-dimethylpyrazole)borate) from oxidation of $[Et_4N][Tp'(CO)_3M]$ with $[ArN_2][BF_4]$ in CH_2Cl_2.[4]

Transformations of carbyne complexes have been reviewed in the literature;[3a,b; 5] most relevant to the work reported here are reactions of carbyne complexes with nucleophiles and carbyne−vinylidene interconversions.

Nucleophiles have been reported to react with carbyne complexes to promote carbyne−carbonyl coupling,[6] attack the metal−carbon triple bond,[7] or displace a substituent on the carbyne carbon.[8] Lalor's $Tp'(CO)_2M{\equiv}CCl$[4] has been shown to react with nucleophiles with loss of chloride to form new carbynes (eq 1).[8a,b] Phosphines (eq 2),[8d] aryloxides (eq 3),[8d] and $[Cp(CO)_2Fe]^-$

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[1] Fischer, E. O.; Kreis, G.; Kreiter, C. G.; Müller, J.; Huttner, G.; Lorenz, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 564−565. Fischer, E. O. *Adv. Organomet. Chem.* **1976**, *14*, 1. Fischer, E. O.; Kreis, G. *Chem. Ber.* **1976**, *109*, 1673−1683.

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[5] Mayr, A.; Bastos, C. M. *Prog. Inorg. Chem.* **1992**, *40*, 1−98.

[6] For example, see: (a) Mayr, A.; Chang, R. T.; Lee, T.-Y.; Cheung, O. K.; Kjelsberg, M. A.; McDermott, G. A.; Van Engen, D. *J. Organomet. Chem.* **1994**, *479*, 47−53. (b) Gamble, A. S.; Birdwhistell, K. R.; Templeton, J. L. *J. Am. Chem. Soc.* **1990**, *112*, 1818−1824. (c) Doyle, R. A.; Angelici, R. J. *Organometallics* **1989**, *8*, 2207−2214. (d) Dossett, S. J.; Hill, A. F.; Jeffery, J. C.; Marken, F.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2453−2465. (e) Kim, H. P.; Kim, S.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1986**, *5*, 2481−2488. (f) Birdwhistell, K. R.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 4474−4483. (g) Kreissl, F. R.; Frank, A.; Schubert, U.; Lindner, T. L.; Huttner, G. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 632−633.

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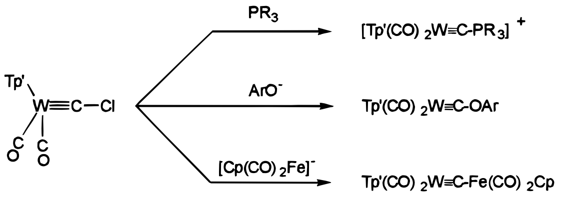
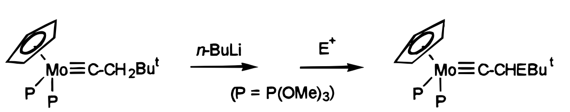
(eq 4)[8e] have all been shown to react with Tp′(CO)$_2$W≡CCl to displace chloride and form new carbyne complexes.

$$\mathrm{Tp'(CO)_2M{\equiv}C\text{-}Cl} \xrightarrow[\mathrm{Nu = SR^-,\ SeR^-}]{\mathrm{Nu^-}} \mathrm{Tp'(CO)_2M{\equiv}C\text{-}Nu} \quad (1)$$



(2)
(3)
(4)

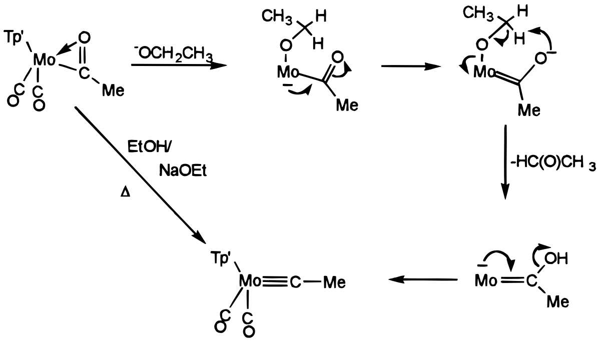
Metal vinylidene chemistry has been thoroughly reviewed.[9] Green pioneered the interconversion of vinylidenes and carbynes; deprotonation of Cp(P(OMe)$_3$)$_2$Mo≡CCH$_2$Bu^t followed by electrophile addition leads to new carbynes via a vinylidene intermediate (eq 5).[10] Other vinylidene to carbyne transformations have been reported.[6f,11]



(5)

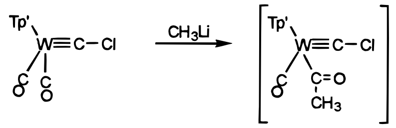
The methylcarbyne complex Tp′(CO)$_2$Mo≡CCH$_3$ can be deprotonated to form a vinylidene anion which reacts with MeI to form Tp′(CO)$_2$Mo≡CCH$_2$CH$_3$.[12] Reaction of the vinylidene anion K[Tp′(CO)$_2$M=C=CH$_2$] (M = Mo, W) with Tp′(CO)$_2$Mo≡CCl forms the bimetallic complexes Tp′(CO)$_2$M≡CCH$_2$C≡Mo(CO)$_2$Tp′ (M = Mo, W).[13] We now report reaction of the vinylidene anion Li[Tp′(CO)$_2$M=C=CH$_2$] with a variety of electrophiles to form elaborated carbyne complexes. Rearrangement of a ketone derivative, Tp′(CO)$_2$W≡CCH$_2$C(O)Ph, to a metallacyclic product via hydrogen migration is also described.

Results and Discussion



(6)

Synthesis of Tp′(CO)$_2$W≡CCH$_3$. A low-yield synthesis of Tp′(CO)$_2$Mo≡CCH$_3$ through oxygen atom removal from an η^2-acyl precursor has been reported (eq 6).[12] Previous reports have shown that nucleophiles will attack the carbyne carbon and displace chloride from Tp′(CO)$_2$M≡CCl (M = Mo, W) to form new carbynes (vide supra). Attempted synthesis of Tp′(CO)$_2$W≡CCH$_3$ by reaction of Tp′(CO)$_2$W≡CCl (**1**) with CH$_3$Li leads to attack at a carbonyl carbon as an acyl anion forms (eq 7). This product has been observed by IR and ^{13}C NMR spectroscopy. Addition of CH$_3$Li to a THF solution of **1** resulted in a change in the metal−carbonyl stretching frequency from a dicarbonyl pattern ($\nu_{\mathrm{CO(THF)}}$ = 1986, 1894 cm^{-1}) for **1** to a monocarbonyl stretch ($\nu_{\mathrm{CO(THF)}}$ = 1846 cm^{-1}) for the terminal carbon monoxide in the putative acyl complex. Evidence for this acyl complex is also observed in the ^{13}C NMR spectrum. An NMR tube was charged with **1** along with a sealed capillary tube containing acetone-d_6 in order to achieve a lock signal. At −78 °C, an excess of CH$_3$Li was added to the THF solution, and the ^{13}C NMR spectrum was obtained at −20 °C. Resonances at 313 and 249 ppm are assigned to the carbyne carbon and metal−carbonyl carbon, respectively. A resonance at 188 ppm is assigned to the acyl carbon while the methyl group on the acyl resonates at 54.5 ppm.



(7)

We previously reported a synthesis of Tp′(CO)$_2$M≡CCH$_3$ (M = Mo, (**2**), W, (**3**)) from reaction of Tp′(CO)$_2$M≡CCl with Me$_2$LiCu (Scheme 1).[14] This reaction occurs at −22 °C and presumably goes through attack at the α-carbon followed by chloride loss. Reaction of **1** with Me$_2$CuLi beginning at 0 °C and continuing at room temperature results in the formation of Tp′(CO)$_2$W(η^2-C(CH$_3$)=CH$_2$) through reaction with a second equivalent of CH$_3$- and net hydride loss. Similar behavior was seen for the molybdenum analogue. The η^2-vinyl complexes

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(7) For example, see: (a) Carriedo, G. A.; Riera, V.; Rodriguez, M. L.; Jeffery, J. C. *J. Organomet. Chem.* **1986**, *314*, 139−149. (b) Fischer, E. O.; Wanner, J. K. R.; Müller, G.; Riede, J. *Chem. Ber.* **1985**, *118*, 3311−3319. (c) Fischer, E. O.; Chen, J.; Scherzer, K. *J. Organomet. Chem.* **1983**, *253*, 231−241. (d) Fischer, E. O.; Schambeck, W. *J. Organomet. Chem.* **1980**, *201*, 311−318. (e) Kreissl, F. R.; Uedelhoven, W.; Kreis, G. *Chem. Ber.* **1978**, *111*, 3283−3293.

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(10) (a) Beevor, R. G.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1983**, 673−675. (b) Beevor, R. G.; Freeman, J. J.; Green, M.; Morton, C. E.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 68−70. (c) Beevor, R. G.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1319−1328. (d) Gill, D. S.; Green, M. *J. Chem. Soc., Chem. Commun.* **1981**, 1037−1038.

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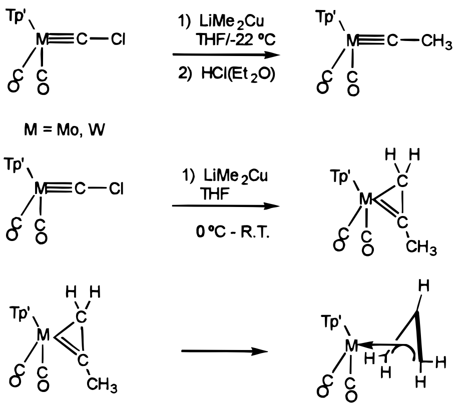
Table 1. Selected Spectroscopic Data[a] for [Tp′(CO)$_2$W] Complexes, [W]−C$_\alpha$−C$_\beta$−C$_\gamma$

	ν_{CO}	C$_\alpha$	C$_\beta$	C$_\gamma$	CO
3	1968, 1867	289	37.3, $^1J_{CH} = 130$, $^2J_{WC} = 43$		223, $^1J_{WC} = 168$
5	1960, 1862	297	44.2, $^1J_{CH} = 127$, $^2J_{WC} = 40$	11.6, $^1J_{CH} = 128$	223, $^1J_{WC} = 168$
6	1964, 1865	301	49.3, $^1J_{CH} = 126$, $^2J_{WC} =38$	20.7, $^1J_{CH} = 128$	224, $^1J_{WC} = 168$
7	1963, 1864	293	52.7, $^1J_{CH} = 127$, $^2J_{WC} = 39$	33.4, $^1J_{CH} = 128$	223, $^1J_{WC} = 168$
8	1967, 1866	289, $^1J_{WC} = 187$	60.4, $^1J_{CH} = 128$, $^2J_{WC} = 437$	72.6, $^1J_{CH} = 144$	223.5, 223.4, $1J_{WC} = 166$
9[b]	1971, 1872	292, $^1J_{WC} = 188$	59.0, $^1J_{CH} = 127$, $^2J_{WC} = 37$	71.3, $^1J_{CH} = 145$	224.2, 224.1 $1J_{WC} = 166$
10	1969, 1873	291	64.2, $^1J_{CH} = 127$, $^2J_{WC} = 38$	75.2	224.3, 224.2, $1J_{WC} = 168$
11	1969, 1967	278, $^1J_{WC} = 184$	138, $^1J_{CH} = 138$	137, $^1J_{CH} = 146$	225, $^1J_{WC} = 167$
14	1971, 1876	273	61.3, $^1J_{CH} = 127$	190	223
15	1948, 1860	218, $^1J_{CH} = 187$	117, $^1J_{CH} = 162$	177	232

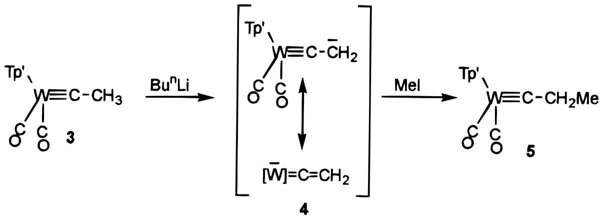
[a] IR data recorded as KBr pellets, values in cm^{-1}. NMR data recorded in CDCl$_3$ unless noted. Chemical shifts given in ppm; coupling constant values in Hz. $^1J_{WC}$ values for some carbyne carbons could not be determined due to broad C$_\alpha$ resonances. [b] NMR data recorded in CH$_2$Cl$_2$.

Scheme 1



slowly rearrange to stable η^3-allyl products in nonaromatic solvents.[15]

Reactions of Anionic Vinylidene Complexes with Alkyl Halides. In analogy to the carbyne/vinylidene interconversion reported by Green (vide supra),[10] the methyl carbyne complexes (**2**, **3**) can be deprotonated to form vinylidene anions [Tp′(CO)$_2$M=C=CH$_2$]$^-$ (M = Mo, W, **4**)).[12−14] Li[Tp′(CO)$_2$Mo=C=CH$_2$] has been shown to be nucleophilic and reacts with CH$_3$I to form an ethylcarbyne complex where the methyl group has added to the β-carbon.[12] We have reproduced this reactivity with the tungsten analogue (eq 8). The ethylcarbyne complex (**5**) can be deprotonated and methylated to yield an isopropylcarbyne (**6**). Complex **4** reacts with benzyl bromide to form Tp′(CO)$_2$W≡CCH$_2$CH$_2$Ph (**7**). These carbyne complexes are isolated as bright yellow powders with similar carbonyl stretching frequencies (see Table 1).



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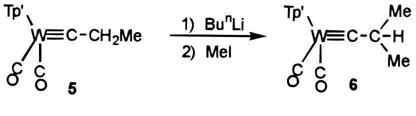
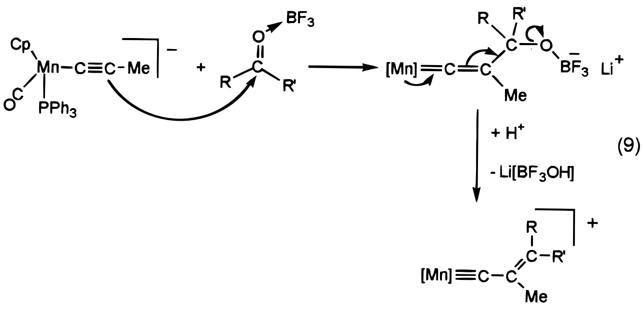
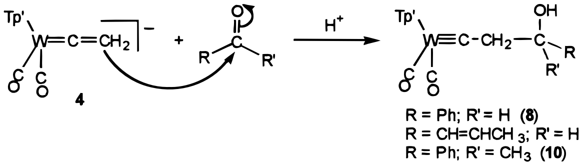


Reaction with Aldehydes and Ketones. Aldehydes and ketones are susceptible to attack by nucleophiles at the carbonyl carbon. Geoffroy reported reaction of the propynyl complex Li[Cp(CO)(PPh$_3$)MnC≡CMe] with BF$_3$-activated aldehydes and ketones to form vinylcarbyne products.[16] This reaction reportedly goes through a vinylidene intermediate (eq 9).



Complex **4** is nucleophilic and adds at the carbonyl carbon of aldehydes and ketones (eq 10). Reaction of **4** with RC(O)H at low temperature followed by protonation forms Tp′(CO)$_2$W≡CCH$_2$CH(OH)(R) (R = Ph, (**8**), CH$_2$=CHCH$_3$, (**9**)). Similarly, the low-temperature reaction of **4** with PhC(O)CH$_3$, followed by protonation, yields Tp′(CO)$_2$W≡CCH$_2$C(OH)(Ph)(CH$_3$) (**10**) (eq 10). The methylene protons are diastereotopic due to the stereogenic carbon center. The Tp′ regions of the ^{1}H and ^{13}C NMR spectra are only slightly perturbed by the presence of a distal chiral center at the γ position.



(10)

Vinylcarbyne Formation. Vinylcarbyne complexes have been reported by a number of groups.[16,17] Most relevant here is the formation of vinylcarbyne complexes reported by Geoffroy (vide supra).[16] Complexes **8**−**10** containing an alcohol functionality can be considered intermediates on the path to vinylcarbynes similar to those described by Geoffroy (see eq 9).

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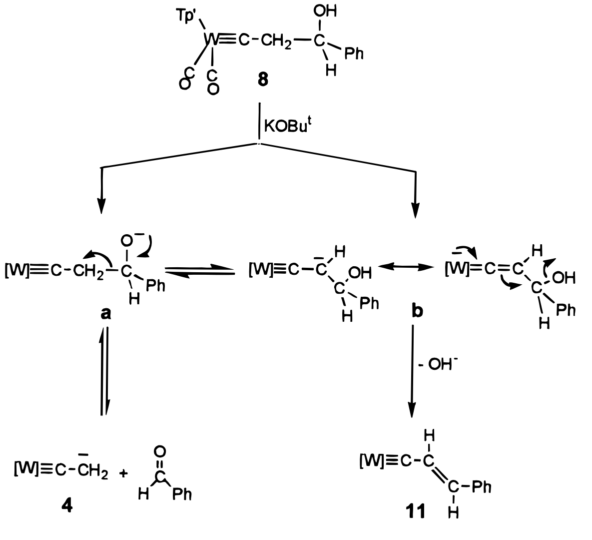
(15) Frohnapfel, D. S.; White, P. S.; Templeton, J. L.; Ruegger, H.; Pregosin, P. S. *Organometallics* **1997**, *16*, 3757−3750.

(16) Terry, M. R.; Kelley, C.; Lugan, N.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3607−3617.

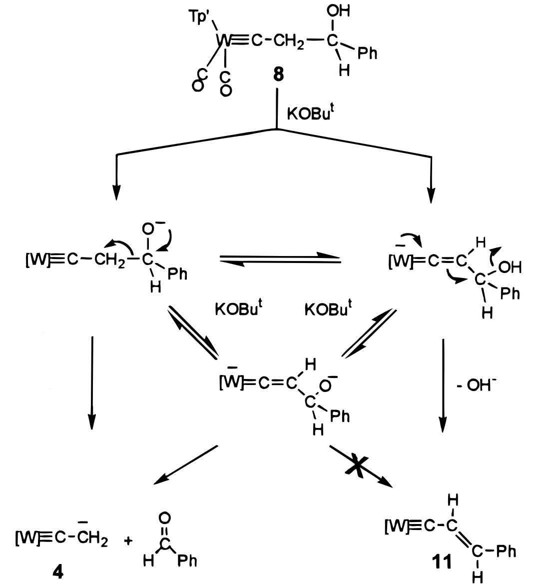
Scheme 2



In **8**−**10** the most acidic proton is the alcohol proton.[18] The protons on C_β have also been shown to be acidic, no doubt due to delocalization of charge in the vinylidene anion.[19] Reaction of **8** with 1 equivalent of $KOBu^t$ results in formation of the brown-red conjugated carbyne complex $Tp'(CO)_2W{\equiv}CCH{=}CHPh$ (**11**) as the major product, and it is isolated in 53% yield (Scheme 2). We believe that addition of 1 equiv of base removes the alcohol proton to form an anionic intermediate with the negative charge localized on the oxygen (**a**). We propose that this intermediate is reluctant to lose oxide and form the vinylcarbyne directly. Rather it can undergo proton addition to re-form starting material, undergo proton loss at C_β to form a dianion, or undergo proton migration to form a tautomer of **a**, the enol isomer. This resonance-stabilized anion (**b**) can then lose hydroxide to form the observed vinylcarbyne product.

The ^1H NMR spectrum for **11** displays an AB pattern centered at 6.91 ppm for the trans olefinic protons ($^3J_{HH}$ = 16 Hz) as well as resonances in the ^{13}C NMR spectrum at 278 ppm for the carbyne carbon and at 138 and 137 ppm for the olefinic carbons ($^1J_{CH}$ = 155 and 146 Hz, respectively) which are diagnostic for a vinylcarbyne complex. The trans isomer may be preferentially formed due to steric factors in the product-forming step. In the transition state, steric factors are minimized with the phenyl group located away from the Tp′ ligand. Elimination of hydroxide from this conformation would result in formation of the trans isomer. In solution, **11** isomerizes over a period of days to give approximately a 1:1 mixture of cis/trans products. The cis isomer (**12**) is characterized by an AB pattern centered at 6.43 ppm having $^3J_{HH}$ = 12 Hz.

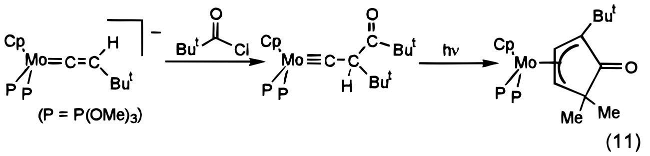
Scheme 3



Scheme 2 is predicated on results observed when 1 equiv of base is used. Treatment of **8** with 2 equiv of $KOBu^t$ (under reaction conditions identical to those described for 1 equiv) gives approximately a 1:1 mixture of **11**/**3**. Scheme 3 accounts for the observed products. Two equivalents of base may deprotonate both acidic sites and thus decrease the amount of enol available with hydroxide as a potential leaving group for vinyl carbyne formation. Aldehyde loss and vinylidene anion formation may be favored by the excess base, so acid quench allows methylcarbyne formation to occur.

For the alcohol, $Tp'(CO)_2W{\equiv}CCH_2C(OH)(Me)(Ph)$ (**10**), derived from acetophenone, no vinylcarbyne is observed after reaction with $KOBu^t$. Reaction of **10** with 1 equiv of $KOBu^t$ yields only the methylcarbyne complex, **3**. In this case, ketone loss is apparently fast enough to prohibit vinylcarbyne formation.

Reaction with Benzoyl Chloride. Green reported that reaction of the vinylidene anion $Li[Cp(P(OMe)_3)_2Mo{=}C{=}CHBu^t]$ with $Bu^tC(O)Cl$ resulted in attack at the carbonyl carbon; chloride loss formed a carbyne with a ketone substituent.[10a] Upon irradiation, C−H bond activation occurred to form an unusual η^3-product (eq 11). Reaction of the tungsten vinylidene anion (**4**) with PhC(O)Cl at low temperature followed by acid quench results in a bright yellow product (**13**). Reaction of this intermediate product (**13**) with $KOBu^t$ results in formation of the ketone-containing carbyne $Tp'(CO)_2W{\equiv}CCH_2C(O)Ph$ (**14**) and methylcarbyne (**3**) in approximately a 1:1 ratio. The ketone-containing carbyne is characterized by a singlet at 4.26 ppm in the ^1H NMR spectrum for the methylene protons and resonances at 273 and 190 ppm for the carbyne carbon and the ketone



(11)

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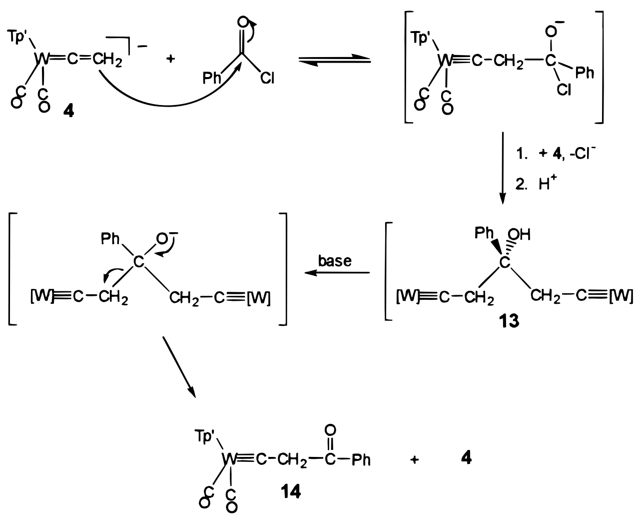
[18] The alcohol proton rapidly exchanges with deuterium upon addition of D_2O.

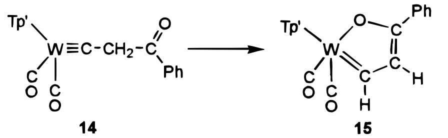
[19] Addition of 2 equiv of Bu^nLi followed by D_2O quench forms $[W]{\equiv}CCHDCH(OD)(Ph)$.

Scheme 4



carbon in the ^{13}C NMR spectrum. Although we were unable to obtain analytical data for the yellow intermediate **13**, which was isolated as a solid, NMR spectra indicate the presence of one phenyl group and one OH group per two $Tp'(CO)_2W$ moieties. Tentative assignment as dinuclear complex **13** (Scheme 4) is consistent with NMR data and the observed reactivity.

In solution, the ketone complex (**14**) slowly rearranges to a metallafuran product $Tp'(CO)_2\overline{WCHCHC(O)}Ph$ (**15**) (eq 12). This isomerization is accompanied by a shift in the metal–carbonyl ν_{CO} from 1979, 1885 cm^{-1} for **14** to 1954, 1865 cm^{-1} for **15**. Hydrogen migration from C_β to C_α along with donation from the oxygen lone pair on the carbonyl carbon forms this cyclic metallafuran complex. The ^1H NMR spectrum suggests carbene character as it displays a doublet at 12.15 ppm with $^3J_{HH} = 6$ Hz and tungsten satellites $^2J_{WH} = 19$ Hz (14% ^{183}W abundance; $I = {}^1/_2$) for the proton on C_α. A doublet at 7.99 ppm ($^3J_{HH} = 6$ Hz) is observed for the proton on C_β. Gated decoupled ^{13}C NMR spectroscopy yields a doublet at 232 ppm ($^3J_{CH} = 5$ Hz) for the metal–carbonyl carbon as well as resonances at 218 ppm for the carbene-like C_α ($^1J_{CH} = 156$ Hz) and 117 ppm ($^1J_{CH} = 162$ Hz) for C_β. A singlet is observed at 177 ppm for C_γ. These carbon-13 chemical shift values are slightly upfield of those reported for the analogous complexes, $Tp'(CO)_2\overline{MoCRCRC(O)}Et$ (R = Et, Ph) ($C_\alpha = 250$ ppm, $C_\beta = 135$ ppm, and $C_\gamma = 192$ ppm).[20a]



(12)

Metallafuran Crystal Structure. Orange-red crystals of **15** were obtained by slow diffusion of MeOH into a CH_2Cl_2 solution of **15**. An ORTEP drawing of **15** is shown in Figure 1. Crystallographic data and collection parameters, complete bond lengths and angles, and atomic parameters for **15** are deposited as Supporting Information. Complex **15** crystallizes with one molecule of CH_2Cl_2 in a monoclinic *Cc* space group. The planar metallafuran ring lies along the mirror plane of the molecule. In this 7-coordinate molecule, C_α bisects the $W(CO)_2$ fragment resulting in an obtuse OC–W–CO angle of 97.8°, and the metallacyclic oxygen is proximal to the Tp′ ligand. The overall geometry of **15** approaches that of a face-capped octahedron with the three pyrazole nitrogens, the carbonyl carbons, and the ketonic oxygen forming the octahedron and the carbenic C_α capping the face opposite the Tp′ ligand. The general features of metallafuran structures have been discussed in detail,[20a] and a variety of similar complexes have been reported in the literature.[20]

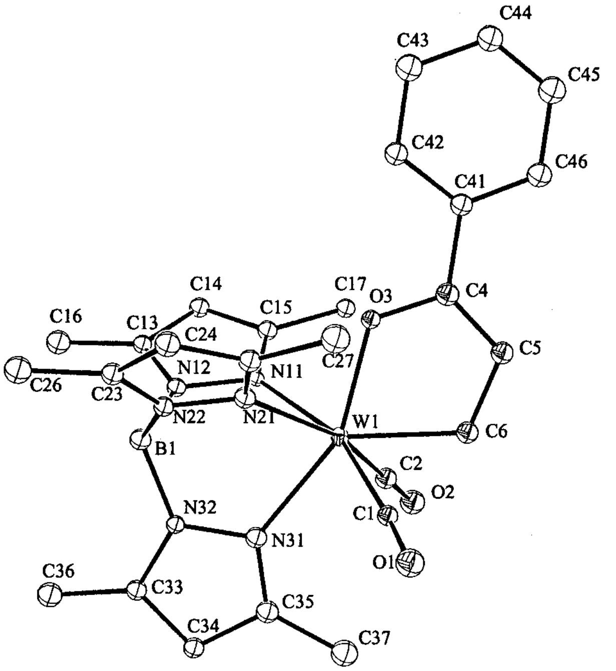


Figure 1. ORTEP diagram for $Tp'(CO)_2\overline{WCHCHC(O)}Ph$ (**15**).

Summary

A convenient synthesis of a useful methylcarbyne monomer through reaction of a chlorocarbyne monomer with $LiMe_2Cu$ has been described. Deprotonation of the methylcarbyne complex results in an anionic vinylidene

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(20) For example, see: (a) Rusik, C. A.; Collins, M. A.; Gamble, A. S.; Tonker, T. L.; Templeton, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 2550–2560. (b) Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *Organometallics* **1994**, *13*, 1235–1242. (c) Crochet, P.; Demerseman, B.; Rocaboy, C.; Schleyer, D. *Organometallics* **1996**, *15*, 3048–3061. (d) Shih, K.-Y.; Fanwick, P. E.; Walton, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 9319–9320. (e) Adams, R. D.; Chen, L.; Wu, W. *Organometallics* **1993**, *12*, 1623–1628. (f) Lowe, C.; Shklover, V.; Berke, H. *Organometallics* **1991**, *10*, 3396. (g) Adams, R. D.; Chen, G.; Chen, L.; Wu, W.; Yin, J. *J. Am. Chem. Soc.* **1991**, *113*, 9406–9408. (h) Allevi, C.; Garlaschelli, L.; Malatesta, M. C.; Ganazzoli, F. *Organometallics* **1990**, *9*, 1383–1391. (i) Stack, J. G.; Simpson, R. D.; Hollander, F. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1990**, *112*, 2716–2729. (j) Strickler, J. R.; Bruck, M. A.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1990**, *9*, 266–273. (k) DeShong, P.; Slough, G. A.; Sidler, D. R.; Rybczynski, P. J.; von Philipsborn, W.; Kunz, R. W.; Bursten, B. E.; Clayton, T. W., Jr. *Organometallics* **1989**, *8*, 1381–1388. (l) Garrett, K. E.; Sheridan, J. B.; Poureau, D. B.; Feng, W. C.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383–8391. (m) Alt, H. G.; Herrmann, G. S.; Engelhardt, H. E.; Rogers, R. D. *J. Organomet. Chem.* **1987**, *331*, 329–339. (n) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022–2039. (o) Werner, H.; Weinand, R.; Otto, H. *J. Organomet. Chem.* **1986**, *307*, 49–59. (p) Alt, H. G. *J. Organomet. Chem.* **1985**, *288*, 149–163. (q) Allen, S. R.; Green, M.; Norman, N. C.; Paddick, K. E.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1983**, 1625–1633. (r) Herrmann, W. A.; Ziegler, M. L.; Serhadli, O. *Organometallics* **1983**, *2*, 958.

complex that reacts with a variety of electrophiles to form elaborated carbyne complexes. Reaction of the vinylidene anion with aldehydes and ketones provides a stepwise synthetic route to vinylcarbyne complexes. The vinylidene anion reacts with benzoyl chloride to ultimately form $Tp'(CO)_2W{\equiv}CCH_2C(O)Ph$ after formation of an intermediate which is believed to be dinuclear. The ketone-functionalized carbyne monomer rearranges in solution to form a structurally characterized cyclic metallafuran complex.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques unless noted. Solvents were dried and distilled under nitrogen by standard methods. Alumina was deactivated before use by adding 5 mL of distilled water for every 100 mL of alumina; a typical column was 1 in. in diameter and packed from 6 to12 in. in height; compound elution was monitored visually. All other reagents were used as obtained from commercial sources. ^{1}H NMR spectra were recorded on a Bruker WM250 or AC200 or a Varian XL400 spectrometer. ^{13}C NMR spectra were obtained on a Varian XL400 spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

$Tp'(CO)_2W{\equiv}CCH_3$ (3). $Tp'(CO)_2W{\equiv}CCl$, 4.05 g (6.93 mmol), was dissolved in THF resulting in a bright yellow solution. The solution was cooled to −22 °C (CCl_4/dry ice). In a separate flask, a suspension of CuI, 0.86 g (4.5 mmol), in THF was cooled to 0 °C. Methyllithium (9.01 mmol) was added to the CuI/THF suspension to form $LiMe_2Cu$, resulting in a clear homogeneous solution. The $LiMe_2Cu$ solution was cooled to −78 °C and then transferred via cannula to the $Tp'(CO)_2W{\equiv}CCl$ solution. The progress of the reaction was followed by quenching aliquots of the reaction mixture with HCl (in Et_2O) and observing the carbonyl region of the resulting IR spectrum. After approximately 30 min, the reaction was complete and the reaction mixture was treated with 1 equiv of HCl (in Et_2O). The reaction mixture was then quickly run through an alumina column with CH_2Cl_2. The solvent was removed in the presence of about 3 g of deactivated alumina to adsorb the product. The adsorbed product was then loaded onto a dry alumina column and eluted with 9:1 hexanes/CH_2Cl_2. **3** eluted as a bright yellow band. Upon solvent removal, 2.9 g (5.0 mmol) of **3** was isolated as a bright yellow solid, yield = 72%: IR (KBr) 1968, 1867 cm^{-1} (ν_{W-CO}); ^{1}H NMR (250 MHz, $CDCl_3$): δ 5.85, 5.74 (s, 2:1, Tp′C*H*), 2.43 (s, 3H, $^3J_{WH}$ = 7 Hz, CCH_3), 2.52, 2.41, 2.33, 2.30 (s, 6:3:6:3, Tp′CC*H*$_3$); ^{13}C NMR (100.56 MHz, $CDCl_3$): δ 289.3 (s, $W{\equiv}C-$), 222.8 (s, $^1J_{WC}$ = 168 Hz, $W-C{\equiv}O$), 152.2, 151.6, 144.8, 144.2 (s, 1:2:1:2, Tp′*C*CH$_3$), 106.4, 106.3 (d, $^1J_{CH}$ = 175 Hz, 1:2, Tp′*C*H), 37.32 (q, $^1J_{CH}$ = 130 Hz, $^2J_{WC}$ = 43 Hz, $-CH_3$), 16.37, 15.17, 12.62, 12.55 (q, 2:1:2:1, $^1J_{CH}$ = 127 Hz, Tp′C*C*H$_3$).

$Tp'(CO)_2W(\eta^2\text{-}C(CH_3){=}CH_2)$. A solution containing 1.00 g (1.71 mmol) of $Tp'(CO)_2W{\equiv}CCl$ (**1**) in 20 mL of THF was prepared and cooled to 0 °C. A stoichiometric amount of freshly prepared $LiCuMe_2$ (MeLi (1.4 M Et_2O), 2.5 mL, 3.5 mmol; CuI, 0.33 g, 1.73 mmol) in 20 mL of THF at 0 °C was added to this solution. The solution was allowed to warm to room temperature and stir for 3 h. Solvent volume was reduced until ca. 5 mL of THF remained. A 40 mL volume of a 50/50 hexanes/CH_2Cl_2 mixture was added. The solution was stirred for 16 h. Solvent was removed, and the oily residue was chromatographed on alumina with hexanes/CH_2Cl_2 (5:1) as the eluent. An orange band was collected. Solvent was removed to produce 0.400 g of an orange solid comprised of 70% $Tp'(CO)_2W(\eta^2\text{-}C(CH)_3{=}CH_2)$ and 30% $Tp'(CO)_2W{\equiv}CCH_3$ (**3**). The corrected yield for the η^2-vinyl complex is 29%. Using 1.25 equiv of $LiCuMe_2$ (**1**, 3.4 g (5.82 mmol); MeLi (1.4 M Et_2O), 10.0 mL, 14 mmol; CuI, 1.35 g, 7.1 mmol) and a similar protocol produced pure η^2-vinyl complex as the only isolable product, but a low yield (7%) was obtained. IR (KBr, cm^{-1}): ν_{BH} = 2540; ν_{CO} = 1951, 1852; ν_{CN} = 1545. ^{1}H NMR ($CDCl_3$, δ): 5.86, 5.83 (1:2, Tp′C*H*), 3.23 (t, $^4J_{HH}$ = 3 Hz, η^2-C(C*H*$_3$)=CH$_2$), 2.61, 2.41, 2.36, 1.92 (3:6:3:6, Tp′C*H*$_3$), 1.37 (b, η^2-C(CH$_3$)=C*H*$_2$). ^{13}C NMR ($CDCl_3$, δ): 248.0 (br, η^2-*C*-(CH$_3$)=CH$_2$), 220.0 ($^1J_{WC}$ = 160 Hz, *C*O), 153.1, 151.1, 144.5, 143.8 (1:2:1:2, Tp′*C*CH$_3$), 107.0, 106.8 (1:2, Tp′*C*CH), 34.6 (t, $^1J_{CH}$ = 127, η^2-C(*C*H$_3$)=CH$_2$), 17.5 (t, $^1J_{CH}$ = 157, η^2-C-(CH$_3$)=*C*H$_2$), 15.7, 14.3, 12.8, 12.6 (1:2:1:2, Tp′*C*H$_3$). Anal. Calcd for $Tp'(CO)_2W(\eta^2\text{-}C(CH)_3{=}CH_2)$ ($WC_{20}H_{27}N_6BO_2$): C, 41.55; H, 4.71; N, 14.54. Found: C, 41.42; H, 4.77; N, 14.46.

$Tp'(CO)_2W{\equiv}CCH_2CH_3$ (5). In a synthesis representative of that used for complexes **5**−**7**, an oven-dried Schlenk flask was charged with 0.544 g (0.965 mmol) of **3** and put under a nitrogen atmosphere. THF (30 mL) was then added, and the bright yellow solution was cooled to −78 °C. To this solution was added Bu^{n}Li, 0.39 mL (0.97 mmol); the resulting solution was orange-red in color. An excess of MeI, 0.24 mL (3.9 mmol), was then added, and the solution was warmed to room temperature. After 15 min, the solution returned to a bright yellow color. The reaction mixture was allowed to stir for 1 h. Excess HCl (in Et_2O) was added to quench any unreacted base. The solvent was removed, and the product was loaded onto an alumina column and eluted with 9:1 hexanes/CH_2Cl_2. A bright yellow band was collected. About 3 g of alumina was added to the solution of **5**, and the solvent was removed, adsorbing **5** on the alumina. This alumina mixture was added on top of a dry alumina column. Complex **5** was eluted with 8:2 hexanes/CH_2Cl_2. Upon solvent removal and drying, 0.508 g (0.879 mmol) of **5** was isolated as a bright yellow solid, yield = 91%: IR (KBr) 1960, 1862 cm^{-1} (ν_{W-CO}); ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.86, 5.74 (s, 2:1, Tp′C*H*), 2.67 (q, $^3J_{HH}$ = 7 Hz, $^3J_{WH}$ = 7 Hz, 2 H, W≡CC*H*$_2$CH$_3$), 2.54, 2.42, 2.33, 2.30 (s, 6:3:6:3, Tp′CC*H*$_3$), 1.24 (t, $^3J_{HH}$ = 7 Hz, 3 H, CCH$_2$C*H*$_3$); ^{13}C NMR (100.56 MHz, $CDCl_3$) (J_{CH} for Tp′ ligand is omitted) δ 296.5 (s, W≡*C*−), 223.2 (s, $^1J_{WC}$ = 168 Hz, W−*C*≡O), 152.2, 151.5, 144.7, 143.3 (s, 1:2:1:2, Tp′*C*CH$_3$), 106.4, 106.3 (d, 1:2, Tp′*C*H), 44.2 (tq, $^1J_{CH}$ = 127 Hz, $^2J_{CH}$ = 4 Hz, $^2J_{WC}$ = 40 Hz, W≡C*C*H$_2$-CH$_3$), 16.6, 15.1, 12.6, 12.5 (q, 2:1:2:1, Tp′C*C*H$_3$), 11.6 (qt, $^1J_{CH}$ = 128 Hz, $^2J_{CH}$ = 5 Hz, CCH$_2$*C*H$_3$). Anal. Calcd for $BC_{20}H_{27}N_6O_2W$: C, 41.55; H, 4.71; N, 14.54. Found: C, 41.66; H, 4.71; N, 14.64.

$Tp'(CO)_2W{\equiv}CCH(CH_3)_2$ (6). A procedure identical to that described for **5** was used. A THF solution at −78 °C of **5**, 0.353 g (0.611 mmol), reacted with 0.24 mL (0.61 mmol) of Bu^{n}Li resulting in an orange-red solution. To this mixture was added 0.15 mL (2.4 mmol) of methyl iodide, and the resulting solution was warmed to room temperature and stirred for 1 h. Acid quench and workup identical to that described for **5** yielded 0.338 g (0.571 mmol) of **6** as a bright yellow solid, yield = 93%: IR (KBr) 1964, 1865 cm^{-1} (ν_{W-CO}); ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.86, 5.73 (s, 2:1, Tp′C*H*), 2.85 (septet, $^3J_{HH}$ = 7 Hz, $^3J_{WH}$ = 7 Hz, 1 H, W≡CC*H*(CH$_3$)$_2$), 2.55, 2.42, 2.33, 2.29 (s, 6:3:6:3, Tp′CC*H*$_3$), 1.24 (d, $^3J_{HH}$ = 7 Hz, 6 H, CCH(C*H*$_3$)$_2$); ^{13}C NMR (100.56 MHz, $CDCl_3$) (J_{CH} for Tp′ ligand is omitted) δ 300.8 (s, W≡*C*−), 223.7 (s, $^1J_{WC}$ = 168 Hz, W−*C*≡O), 152.2, 151.4, 144.7, 144.4 (s, 1:2:1:2, Tp′*C*CH$_3$), 106.4, 106.3 (d, 1:2, Tp′*C*H), 49.3 (d, $^1J_{CH}$ = 126 Hz, $^2J_{WC}$ = 38 Hz, W≡C*C*H(CH$_3$)$_2$), 20.7 (q, $^1J_{CH}$ = 128 Hz, CCH(*C*H$_3$)$_2$), 16.8, 15.1, 12.7, 12.5 (q, 2:1:2:1, Tp′C*C*H$_3$). Anal. Calcd for $BC_{21}H_{29}N_6O_2W$: C, 42.60; H, 4.94; N, 14.19. Found: C, 42.57; H, 4.91; N, 14.14.

$Tp'(CO)_2W{\equiv}CCH_2CH_2Ph$ (7). A procedure identical to that described for **5** was used. A THF solution at −78 °C of **3**, 0.505 g (0.896 mmol), reacted with 0.36 mL (0.90 mmol) of Bu^{n}Li resulting in an orange-red solution. To this mixture was added 0.43 mL (3.6 mmol) of benzyl bromide, and the resulting solution was warmed to room temperature and stirred for 1 h. Acid quench and workup identical to that described for **5** yielded 0.523 g (0.800 mmol) of **7** as a bright yellow solid, yield = 89%: IR (KBr) 1963, 1864 cm^{-1} ($\nu_{\mathrm{W-CO}}$); ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$) δ 7.3−7.1 (m, 5 H, $\mathrm{CH_2}\mathit{Ph}$), 5.88, 5.74 (s, 2:1, Tp′C*H*), 3.1−2.9 (AA′BB′, 4 H, $\mathrm{W{\equiv}CC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{Ph}$), 2.54, 2.44, 2.35, 2.31 (s, 6:3:6:3, $\mathrm{Tp'CC}\mathit{H}_3$); ^{13}C NMR (100.56 MHz, $\mathrm{CDCl_3}$) (J_{CH} for Tp′ ligand is omitted) δ 292.7 (s, $\mathrm{W{\equiv}}\mathit{C}-$), 223.3 (s, $^1J_{\mathrm{WC}}$ = 168 Hz, $\mathrm{W-}\mathit{C}\mathrm{{\equiv}O}$), 152.2, 151.5, 144.8, 144.3 (s, 1:2:1:2, $\mathrm{Tp'}\mathit{C}\mathrm{CH_3}$), 140.8 (s, Ph_{ipso}), 128.4, 128.2, 126.0 (d, $\mathit{Ph}_{ortho/meta/para}$), 106.4, 106.3 (d, 1:2, Tp′*C*H), 52.7 (t, $^1J_{\mathrm{CH}}$ = 127 Hz, $^2J_{\mathrm{WC}}$ = 39 Hz, $\mathrm{W{\equiv}C}\mathit{C}\mathrm{H_2CH_2Ph}$), 33.4 (t, $^1J_{\mathrm{CH}}$ = 129 Hz, $\mathrm{CH_2}\mathit{C}\mathrm{H_2Ph}$), 16.6, 15.1, 12.6, 12.5 (q, 2:1:2:1, $\mathrm{Tp'C}\mathit{C}\mathrm{H_3}$), 11.6 (t, $^1J_{\mathrm{CH}}$ = 128 Hz, $\mathrm{CCH_2}\mathit{C}\mathrm{H_2Ph}$). Anal. Calcd for $\mathrm{BC_{26}H_{31}N_6O_2W}$: C, 47.73; H, 4.78; N, 12.85. Found: C, 47.80; H, 4.77; N, 12.86.

$\mathbf{Tp'(CO)_2W{\equiv}CCH_2CH(OH)(Ph)}$ (8). To an oven-dried Schlenk flask was added **3**, 0.301 g (0.534 mmol), and this was then dissolved in THF (30 mL) and cooled to −78 °C. Next, 0.32 mL (0.54 mmol) of Bu^{t}Li was added resulting in an orange-red solution. To this solution was added 0.06 mL (0.54 mmol) of PhC(O)H via syringe. The reaction solution immediately turned bright yellow. Excess HCl (in $\mathrm{Et_2O}$) was added to quench the reaction, and then the crude reaction mixture was eluted through a plug of alumina with $\mathrm{CH_2Cl_2}$. A bright yellow band eluted, and the solvent was removed in the presence of about 3 g of alumina. The reaction product, adsorbed on alumina, was loaded onto a dry alumina column and eluted with 8:2 hexanes/$\mathrm{CH_2Cl_2}$. A faint yellow band eluted which was determined to be **3**. Eluent strength was increased to 7:3 hexanes/$\mathrm{CH_2Cl_2}$ and excess PhC(O)H eluted. **8** eluted as a bright yellow band with 9:1 $\mathrm{CH_2Cl_2}$/MeOH. After solvent removal, the product was dried under vacuum and yielded 0.254 g (0.379 mmol) of **8** as a bright yellow solid, yield = 71%. IR (KBr) 1967, 1866 cm^{-1} ($\nu_{\mathrm{W-CO}}$); ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$) δ 7.45−7.25 (m, 5 H, *Ph*), 5.97, 5.85 (s, 2:1, Tp′C*H*), 5.17 (m, 1 H, $\mathrm{CH_2C}\mathit{H}\mathrm{(OH)(Ph)}$)), 3.11 (AB, 2 H, $\mathrm{CC}\mathit{H}_2\mathrm{CH(OH)(Ph)}$)), 2.56, 2.46, 2.41, 2.37 (s, 6:3:6:3, $\mathrm{Tp'C}\mathit{H}_3$); ^{13}C NMR (100.56 MHz, $\mathrm{CDCl_3}$) (J_{CH} for Tp′ ligand is omitted) δ 289.3 (s, $^1J_{\mathrm{WC}}$ = 187 Hz, $\mathrm{W{\equiv}}\mathit{C}-$), 223.5, 223.4 (s, $^1J_{\mathrm{WC}}$ = 166 Hz, W−*C*O), 152.2, 151.7, 151.6, 144.9, 144.4 (s, 1:1:1:1:2, $\mathrm{Tp'}\mathit{C}\mathrm{CH_3}$), 143.2 (s, Ph_{ipso}), 128.5, 127.6, 125.7 (d, $\mathit{Ph}_{ortho/meta/para}$), 106.5, 106.4 (d, 1:2, Tp′*C*H), 72.62 (d, $^1J_{\mathrm{CH}}$ = 144 Hz, $\mathrm{CH_2}\mathit{C}\mathrm{H(OH)(Ph)}$)), 60.40 (t, $^1J_{\mathrm{CH}}$ = 128 Hz, $^2J_{\mathrm{WC}}$ = 37 Hz, $\mathrm{C}\mathit{C}\mathrm{H_2CH(OH)(Ph)}$)), 16.54, 16.45, 15.16, 12.65, 12.55 (q, $\mathrm{Tp'}\mathit{C}\mathrm{H_3}$). Anal. Calcd for $\mathrm{BC_{26}H_{31}N_6O_3W}$: C, 46.59; H, 4.66; N, 12.54. Found: C, 46.61; H, 4.65; N, 12.53.

Reaction of 8 with Bu^{n}Li and Then $\mathbf{D_2O}$ Quench: Formation of $\mathbf{Tp'(CO)_2W{\equiv}CCHDCH(OD)(Ph)}$ (8a). To an oven-dried Schlenk flask was added 0.021 g (0.031 mmol) of **8**. Complex **8** was dissolved in THF (10 mL), the solution was then cooled to −78 °C, and Bu^{n}Li, 0.02 mL (0.06 mmol), was then added forming a reddish solution. $\mathrm{D_2O}$, 0.1 mL, was added, and immediately a bright yellow solution formed. The reaction solution was warmed to room temperature, and the solvent was removed. By ^{13}C NMR spectroscopy, deuterium incorporation into C_β was observed: a 1:1:1 pattern centered at 60.03 ppm ($^1J_{\mathrm{CD}}$ = 20 Hz) was observed for **8a**.

$\mathbf{Tp'(CO)_2W{\equiv}CCH_2CH(OH)(CH{=}CHCH_3)}$ (9). In a reaction identical to that described for the preparation of **8**, 0.300 g (0.532 mmol) of **3** reacted with 0.23 mL (0.57 mmol) of Bu^{n}Li in THF at −78 °C. *trans*-Crotonaldehyde, 0.05 mL (0.65 mmol), was added resulting in a bright yellow solution. Acidification and workup, as for **8**, yielded 0.216 g (0.340 mmol) of **9** as a bright yellow solid, yield = 64%: IR (KBr) 1971, 1872 cm^{-1}($\nu_{\mathrm{W-CO}}$); ^{1}H NMR (250 MHz, $\mathrm{CD_2Cl_2}$) δ 5.95, 5.83 (s, 2:1, Tp′C*H*), 5.78 (m, 1 H, $\mathrm{CH_2CH(OH)(C}\mathit{H}\mathrm{{=}CHCH_3)}$)), 5.62 (m, 1 H, $\mathrm{CH_2CH(OH)(CH{=}C}\mathit{H}\mathrm{CH_3)}$)), 4.48 (m, 1 H, $\mathrm{CH_2C}\mathit{H}\mathrm{(OH)(CH{=}CHCH_3)}$)), 2.91 (m, $\mathrm{CC}\mathit{H}_2\mathrm{CH(OH)(CH{=}CHCH_3)}$ 2.57, 2.56, 2.44, 2.39, 2.35 (s, 3:3:3:6:3, $\mathrm{Tp'C}\mathit{H}_3$), 1.73 (m, 3 H, $\mathrm{CH_2CH(OH)(CH{=}CHC}\mathit{H}_3)$)); ^{13}C NMR (100.56 MHz, $\mathrm{CD_2Cl_2}$) (J_{CH} for Tp′ ligand is omitted) δ 291.6 (s, $^1J_{\mathrm{WC}}$ = 188 Hz, $\mathrm{W{\equiv}}\mathit{C}-$), 224.2, 224.1 (s, $^1J_{\mathrm{WC}}$ = 166 Hz, W−*C*O), 152.7, 152.2, 145.9, 145.3 (s, 1:2:1:2, $\mathrm{Tp'}\mathit{C}\mathrm{CH_3}$), 133.7, 127.6 (each a d, $^1J_{\mathrm{CH}}$ = 155 Hz, $\mathit{C}\mathrm{H{=}}\mathit{C}\mathrm{HCH_3}$), 106.8, 106.7 (d, 1:2, Tp′*C*H), 71.32 (d, $^1J_{\mathrm{CH}}$ = 145 Hz, $\mathrm{CH_2}\mathit{C}\mathrm{H(OH)(CH{=}CHCH_3)}$)), 58.99 (t, $^1J_{\mathrm{CH}}$ = 127 Hz, $^2J_{\mathrm{WC}}$ = 37 Hz, $\mathrm{C}\mathit{C}\mathrm{H_2CH(OH)(CH{=}CHCH_3)}$)), 17.87, 16.63, 16.60, 15.23, 12.77, 12.68 (each a q, 1:1:1:1:2:1, $\mathrm{Tp'}\mathit{C}\mathrm{H_3}$ and $\mathrm{CH(OH)(CH{=}CH}\mathit{C}\mathrm{H_3)}$)). Anal. Calcd for $\mathrm{BC_{23}H_{31}N_6O_3W}$: C, 43.63; H, 4.78; N, 13.27. Found: C, 43.60; H, 4.83; N, 13.13.

$\mathbf{Tp'(CO)_2W{\equiv}CCH_2C(OH)(CH_3)(Ph)}$ (10). In a reaction identical to that described for the preparation of **8**, 0.505 g (0.896 mmol) of **3** reacted with 0.896 mmol of Bu^{n}Li in THF at −78 °C. To this solution was added 0.11 mL (0.90 mmol) of acetophenone, resulting in a yellow solution. Acidification and workup, as for **8**, yielded 0.380 g (0.556 mmol) of **10** as a bright yellow solid, yield = 62%. Traces of excess acetophenone were removed by washing with hexanes: IR (KBr) 1969, 1873 cm^{-1} ($\nu_{\mathrm{W-CO}}$); ^{1}H NMR (200 MHz, $\mathrm{CDCl_3}$) δ 7.54−7.18 (m, 5 H, *Ph*), 5.83, 5.71 (s, 2:1, Tp′C*H*), 3.26 (AB, $^2J_{\mathrm{CH}}$ = 17 Hz, $^3J_{\mathrm{WH}}$ = 7 Hz, 2 H, $\mathrm{CC}\mathit{H}_2\mathrm{C(OH)(Me)(Ph)}$)), 2.60 (s, 1 H, CO*H*), 2.39, 2.37, 2.35, 2.31, 2.27 (s, 3:3:3:6:3, $\mathrm{Tp'C}\mathit{H}_3$), 1.66 (s, 3 H, $\mathrm{C(OH)(C}\mathit{H}_3\mathrm{)(Ph)}$; ^{13}C NMR (100.56 MHz, $\mathrm{CDCl_3}$) δ 290.6 (s, $^1J_{\mathrm{WC}}$ = 187 Hz, $\mathrm{W{\equiv}}\mathit{C}-$), 224.3, 224.0 (s, $^1J_{\mathrm{WC}}$ = 166 Hz, W−*C*O), 152.2, 152.0, 151.9, 144.8, 144.5 (s, 1:1:1:1:2, $\mathrm{Tp'}\mathit{C}\mathrm{CH_3}$), 147.7 (s, Ph_{ipso}), 128.2, 126.8, 124.8 (d, $\mathit{Ph}_{ortho/meta/para}$), 106.5, 106.4 (d, 1:2, Tp′*C*H), 75.2 (s, $\mathrm{CH_2}\mathit{C}\mathrm{(OH)(Me)(Ph)}$)), 64.24 (t, $^1J_{\mathrm{CH}}$ = 128 Hz, $^2J_{\mathrm{WC}}$ = 37 Hz, $\mathrm{C}\mathit{C}\mathrm{H_2C}$), 30.65 (q, $^1J_{\mathrm{CH}}$ = 128 Hz, $\mathrm{C(OH)(}\mathit{C}\mathrm{H_3)(Ph)}$)), 16.36, 16.29, 15.13, 12.66, 12.52 (q, 1:1:1:2:1, $\mathrm{Tp'}\mathit{C}\mathrm{H_3}$).

Reaction of 8 with 1 equiv of KOBu^t: Synthesis of *trans*-$\mathbf{Tp'(CO)_2W{\equiv}CCH{=}CHPh}$ (11). To an oven-dried Schlenk flask was added **8**, 0.124 g (0.185 mmol), and KOBu^t, 0.021 g (0.185 mmol). The flask was cooled to −78 °C, and THF (20 mL) was added. The resulting bright yellow solution darkened slightly upon stirring for 5 min. The cold bath was removed, and the solution was warmed to room-temperature resulting in a reddish-brown solution. The reaction mixture was stirred for 5 h at room temperature. An excess of HCl ($\mathrm{Et_2O}$) was added to quench any unreacted base; no color change was observed. The solvent was removed leaving a brown residue. A ^{1}H NMR spectrum showed mainly **11** with a minor amount of **3** and the cis isomer, **12**. The crude product was run through an alumina column with 8:2 hexanes/$\mathrm{CH_2Cl_2}$. A broad, faint red-purple band was collected and solvent removed. Product was dried under vacuum yielding 0.064 g (0.098 mmol) of **11** as a red-purple solid, yield = 53%. Upon sitting in an NMR tube in $\mathrm{CDCl_3}$ for 1 week, the sample isomerized to form a 1:1 ratio of cis/trans. **11** (trans): IR (KBr): 1967, 1867 cm^{-1} ($\nu_{\mathrm{W-CO}}$); ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$) δ 7.50−7.25 (m, 5 H, *Ph*), 6.94 (d, $^3J_{\mathrm{HH}}$ = 16 Hz, $\mathrm{CCH{=}C}\mathit{H}\mathrm{Ph}$), 6.88 (d, $^3J_{\mathrm{HH}}$ = 16 Hz, $^3J_{\mathrm{WH}}$ = 4 Hz, $\mathrm{CC}\mathit{H}\mathrm{{=}CHPh}$), 5.92, 5.80 (s, 2:1, Tp′*H*), 2.60, 2.46, 2.40, 2.36 (s, 6:3:6:3, $\mathrm{Tp'C}\mathit{H}_3$); ^{13}C NMR (100.56 MHz, $\mathrm{CDCl_3}$) δ 277.8 (s, $^1J_{\mathrm{WC}}$ = 184 Hz, $\mathrm{W{\equiv}}\mathit{C}-$), 224.5 (s, $^1J_{\mathrm{WC}}$ = 166 Hz, W−*C*O), 152.2, 151.9, 145.0, 144.4 (s, 1:2:1:2, $\mathrm{Tp'}\mathit{C}\mathrm{CH_3}$), 137.8 (d, $^1J_{\mathrm{CH}}$ = 155 Hz, $\mathrm{C}\mathit{C}\mathrm{H{=}CHPh}$), 137.1 (d, $^1J_{\mathrm{CH}}$ = 146 Hz, $\mathrm{CCH{=}C}\mathit{H}\mathrm{Ph}$), 136.5 (s, Ph_{ipso}), 128.8, 128.3, 126.1 (d, $\mathit{Ph}_{\mathrm{ortho/meta/para}}$), 106.5, 106.4 (d, 1:2, Tp′*C*H), 16.56, 15.20, 12.62, 12.58 (q, 2:1:2:1, $\mathrm{Tp'}\mathit{C}\mathrm{H_3}$). **12** (cis): ^{1}H NMR (250 MHz, $\mathrm{CDCl_3}$) δ 7.95−7.88, 7.15−6.84 (m, 5 H, *Ph*), 6.44 (d, $^3J_{\mathrm{HH}}$ = 12 Hz, $^3J_{\mathrm{WH}}$ = 4 Hz, $\mathrm{CC}\mathit{H}\mathrm{{=}CHPh}$), 6.34 (d, $^3J_{\mathrm{HH}}$ = 12 Hz, $\mathrm{CCH{=}C}\mathit{H}\mathrm{Ph}$), 5.81, 5.76 (s, 2:1, Tp′*H*), 2.41, 2.34 (s, 9:9, $\mathrm{Tp'C}\mathit{H}_3$). Anal. Calcd for $\mathrm{BC_{26}H_{29}N_6O_2W}$ (**11**): C, 47.76; H, 4.63; N, 12.86. Found: C, 48.06; H, 4.58; N, 12.66.

Reaction of 8 with 2 equiv of KOBu^t. In a procedure identical to that described above, 2 equiv of KOBu^t and 1 equiv of **8** were dissolved in THF. After workup, ^{1}H NMR spectroscopy revealed approximately a 1:1 ratio of **3**/**11**.

Reaction of $\mathbf{Tp'(CO)_2W{\equiv}CCH_2C(OH)(CH_3)(Ph)}$ (10) with KOBu^t. In a reaction identical to that described for the preparation of **11**, 0.185 g (0.271 mmol) of **10** was combined with 0.030 g (0.271 mmol) of KOBu^t in THF (25 mL) at −78 °C. The solution was warmed to room temperature resulting in a yellowish-brown solution. Acidification and workup, as described for **11**, yielded 0.130 g (0.231 mmol) of **3**, yield = 85%.

Reaction of 4 with PhC(O)Cl: Formation of Unknown 13. To an oven-dried Schlenk flask was added 0.203 g (0.360 mmol) of **3**. THF (30 mL) was then added resulting in a bright yellow solution. The solution of **3** was cooled to −78 °C, and 0.14 mL (0.36 mmol) Bu^{n}Li was added forming an orange-red solution. In a glovebox, a flame-dried Schlenk tube was charged with 0.05 mL (0.40 mmol) PhC(O)Cl and sealed with a septum. This reagent was removed from the glovebox and transferred to a Schlenk line. The benzoyl chloride was added via cannula to the THF solution of **3** and Bu^{n}Li. Any residual PhC(O)Cl was washed from the Schlenk tube with THF (5 mL) and added via cannula. The reaction solution was stirred for 5 min, and the color lightened. The reaction was quenched with excess HCl (in Et_2O), resulting in a light orange solution. The solvent was removed leaving a dark orange oil. Methanol was added to the oil, forming a yellow precipitate. The solvent was removed, and the ^{1}H NMR spectrum showed mostly product **13** along with a minor amount of **3**. The product was loaded on an alumina column with a minimal amount of CH_2Cl_2 and eluted with 8:2 hexanes/CH_2Cl_2. Complex **3** was eluted as a yellow band. The eluent strength was increased to neat CH_2Cl_2, and then **13** eluted from the column. Crude **13** was loaded onto an alumina column with a minimal amount of 1:1 hexanes/CH_2Cl_2. The column was eluted with 100 mL of 8:2 hexanes/CH_2Cl_2. The eluent strength was increased to 75:25 hexanes/CH_2Cl_2, and two yellow bands separated. A faint yellow band eluted first and was discarded. A major yellow band followed and was collected as a bright yellow solution. The solvent was removed, and **13** was collected as a bright yellow solid: IR(KBr) 1967, 1867 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60−7.22 (C_6H_5), 5.80, 5.69 (s, 4:2, Tp′C*H*), 3.38 (AB, $^2J_{HH}$ = 18 Hz, $^3J_{WH}$ = 7 Hz, 4 H, CCH_2−C), 2.92 (1 H, CO*H*), 2.34, 2.32, 2.30, 2.26 (s, 12:6:12:6, Tp′CH_3); ^{13}C NMR (100.56 MHz, $CDCl_3$) δ 290.0 (s, W≡*C*−), 224.2, 224.1 (s, W−*C*O), 152.1, 152.0, 144.7, 144.3 (s, 2:1:1:2, Tp′*C*CH_3), 146.0 (s, *Ph*$_{ipso}$), 128.3, 126.9, 125.7 (d, *Ph*$_{ortho/meta/para}$), 106.4, 106.3 (d, Tp′*C*H), 77.88 (s, CH_2*C*(R)(OH)(Ph)), 63.21 (t, $^1J_{CH}$ = 127 Hz, $^2J_{WC}$ = 38 Hz, C*C*H_2C), 16.36, 16.31, 15.11, 12.66, 12.52 (q, 1:1:1:2:1, Tp′*C*H_3).

Reaction of 13 with KOBu^t: Synthesis of Tp′(CO)$_2$W≡CCH$_2$C(O)Ph (14). To an oven-dried Schlenk flask was added **13**, 0.147 g, and KOBu^t, 0.070 g (0.624 mmol). The flask was cooled to −78 °C, and THF (30 mL) was added resulting in a dark brown-orange solution. The cold bath was removed, and the solution was warmed to room temperature. The reaction mixture was stirred for 12 h. Excess HCl (in Et_2O) was added to quench any unreacted base. The color of the solution changed to a light brownish-orange. The solvent was removed, and the crude product was chromatographed on alumina and eluted with 8:2 hexanes/CH_2Cl_2. A yellow fraction was collected and the solvent was removed yielding 0.043 g (0.076 mmol) of **3**. The eluent strength was increased to 2:8 hexanes/CH_2Cl_2, eluting **14** as a golden-yellow solution. After solvent removal and drying, 0.037 g (0.055 mmol) of **14** was isolated as a dull-yellow solid: IR (KBr) 1971, 1876 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 8.2−7.2 (m, 5 H, *Ph*), 5.85, 5.71 (s, 2:1, Tp′C*H*), 4.26 (s, 2 H, $^1J_{WH}$ = 7 Hz, C*C*H_2C(=O)), 2.43, 2.32, 2.28 (s, 6:9:3, Tp′C*H*$_3$); ^{13}C NMR (100.56 MHz, $CDCl_3$) δ 273.3 (s, W≡*C*−), 223.1 (s, W−*C*O), 190.3 (s, −*C*(O)−), 152.3, 151.8, 144.9, 144.4 (s, 1:2:1:2, Tp′*C*CH_3), 136.8 (s, *Ph*$_{ipso}$), 133.3, 129.3, 128.7 (d, *Ph*$_{ortho/meta/para}$), 106.5, 106.4 (d, Tp′*C*H), 61.3 (t, $^1J_{CH}$ = 126 Hz, C*C*H_2C(=O)), 16.46, 15.11, 12.62, 12.54 (q, Tp′*C*H_3). Anal. Calcd for $BC_{26}H_{29}N_6O_3W$: C, 46.69; H, 4.37; N, 12.57. Found: C, 46.56; H, 4.46; N, 12.46.

Tp′(CO)$_2\overline{\text{WCHCHC(O}}$)Ph (15). A CH_2Cl_2 solution of **14** was allowed to stir under N_2 for 2 days. The solvent was removed, and the dark orange residue was dissolved in a minimal amount of CH_2Cl_2 and loaded on an alumina column. The column was eluted with 7:3 hexanes/CH_2Cl_2. An intense orange band eluted first Tp′(CO)$_2\overline{\text{WCHCHC(O}}$)Ph (**15**), and this orange solution of **15** was collected and the solvent was removed. A yellow band containing **14** remained on the column. Upon recrystallization from CH_2Cl_2/MeOH or CH_2Cl_2/hexanes, an analytically pure orange solid of **15** was collected: IR (KBr) 1948, 1860 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 12.15 (d, 1 H, $^3J_{CH}$ = 7 Hz, $^1J_{WH}$ = 19 Hz, WC*H*CH), 7.99 (d, 1 H, $^3J_{CH}$ = 7 Hz, WCHC*H*C), 7.72−7.19 (m, 5 H, Ph), 5.98, 5.78 (s, 1:2, Tp′C*H*), 2.66, 2.43, 1.53 (s, 3:9:6, Tp′C*H*$_3$); ^{13}C NMR (100.56 MHz, $CDCl_3$) δ 231.5 (s, W−*C*O), 217.6 (d, $^1J_{CH}$ = 156 Hz, W*C*HCH), 176.7 (s, CH*C*(O)Ph) 153.7, 151.6, 145.5, 143.6 (s, 1:2:1:2, Tp′*C*CH_3), 135.4 (s, *Ph*$_{ipso}$), 128.3, 128.2, 127.0 (d, *Ph*$_{ortho/meta/para}$), 117.1 (d, $^1J_{CH}$ = 161 Hz, WCH*C*HC), 108.1, 106.4 (d, Tp′*C*H), 14.12, 13.49, 13.25, 12.52 (q, Tp′*C*H_3). Anal. Calcd for $BC_{26}H_{29}N_6O_3W$: C, 46.69; H, 4.37; N, 12.57. Found: C, 46.73; H, 4.37; N, 12.58.

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Supporting Information Available: Text and tables providing complete crystallographic data for **15** (9 pages). Ordering information is given on any current masthead page.

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