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Reactions of an Amphoteric Terminal Tungsten Methylidyne Complex

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Abstract: Treatment of $[Tp'(CO)_2W{\equiv}C{-}PPh_3][PF_6]$ ($Tp' =$ hydridotris(3,5-dimethylpyrazolylborate)) with $Na[HBEt_3]$ in THF forms the methylidyne complex $Tp'(CO)_2W{\equiv}C{-}H$ via formyl and carbene intermediates $Tp'(CO)(C(O)H)W{\equiv}C{-}PPh_3$ and $Tp'(CO)_2W{=}C(PPh_3)(H)$, respectively. Spectroscopic features reported for $Tp'(CO)_2W{\equiv}C{-}H$ include the $W{\equiv}C$ stretch (observed by both IR and Raman spectroscopy) and the ^{183}W NMR signal (detected by a ^{1}H, ^{183}W 2D HMQC experiment). Protonation of the $Tp'(CO)_2W{\equiv}C{-}H$ methylidyne complex with $HBF_4{\cdot}Et_2O$ yields the cationic α-agostic methylidene complex $[Tp'(CO)_2W{=}CH_2][BF_4]$. The methylidyne complex $Tp'(CO)_2W{\equiv}C{-}H$ can be deprotonated with alkyllithium reagents to provide the anionic terminal carbide $Tp'(CO)_2W{\equiv}C{-}Li$; a downfield resonance at 556 ppm in the ^{13}C NMR spectrum has been assigned to the carbide carbon. The terminal carbide $Tp'(CO)_2W{\equiv}C{-}Li$ adds electrophiles at the carbide carbon to generate $Tp'(CO)_2W{\equiv}C{-}R$ ($R = CH_3$, $SiMe_3$, I, $C(OH)Ph_2$, $CH(OH)Ph$, and $C(O)Ph$) Fischer carbynes. A pK_a of 28.7 was determined for $Tp'(CO)_2W{\equiv}C{-}H$ in THF by titrating the terminal carbide $Tp'(CO)_2W{\equiv}C{-}Li$ with 2-benzylpyridine and monitoring its conversion to $Tp'(CO)_2W{\equiv}C{-}H$ with in situ IR spectroscopy. Addition of excess $Na[HBEt_3]$ to neutral $Tp'(CO)_2W{\equiv}C{-}H$ generates the anionic methylidene complex $[Na][Tp'(CO)_2W{=}CH_2]$. The synthetic methodology for generating an anionic methylidene complex by hydride addition to neutral $Tp'(CO)_2W{\equiv}C{-}H$ contrasts with routes that utilize α-hydrogen abstraction or hydride removal from neutral methyl precursors to generate methylidene complexes. Addition of PhSSPh to the anionic methylidene complex in solution generates the saturated tungsten product $Tp'(CO)_2W(\eta^2\text{-}CH_2\text{-}SPh)$ by net addition of the SPh^+ moiety.

Introduction

Monomeric $L_nM{\equiv}C{-}H$ methylidynes remain scarce[1−10] among transition metal carbyne complexes.[11−14] Preparation of monomeric methylidyne complexes $Tp'(CO)_2M{\equiv}C{-}H$ ($M =$ W, Mo; $Tp' =$ hydridotris(3,5-dimethylpyrazolyl)borate) has been accomplished in two ways: (1) through fluoride-induced desilylation of silylcarbynes and (2) via dimethylphenyl phosphine abstraction by iodomethane from the zwitterionic carbene complex $Tp'(CO)_2W{=}C(H)(PMe_2Ph)$ (Scheme 1). The chemistry of the parent $M{\equiv}C{-}H$ carbyne unit in these Tp′ complexes has been difficult to access because of limitations associated with these synthetic routes: low yields of the silyl carbyne $Tp'(CO)_2W{\equiv}C{-}SiMe_2Ph$ required for path 1 and only milligram quantities of the methylidyne complex obtained from path 2. Dimerization of the carbyne monomers to form the vinylidene-bridged dinuclear products, $Tp'(CO)_2M(\mu\text{-}CCH_2)M(CO)_2Tp'$ ($M =$ Mo, W), also complicates using the monomers as reagents.[4,5]

The cationic phosphonium carbyne complexes $[Tp'(CO)_2W{\equiv}CPMe_2R][PF_6]$ ($R =$ Me, Ph) are derived from Lalor's $Tp'(CO)_2W{\equiv}C{-}Cl$[15,16] by nucleophilic displacement of chloride with the corresponding phosphine. These phosphonium carbynes are susceptible to nucleophilic attack by anionic reagents at C_α to generate neutral $Tp'(CO)_2W{=}C(PMe_2R)(Nu)$ zwitterionic carbenes.[5,17] In light of this reactivity, we hypothesized that the cationic triphenylphosphonium carbyne analogue $[Tp'(CO)_2W{\equiv}C{-}PPh_3][PF_6]$ would provide a better leaving group (PPh_3) for

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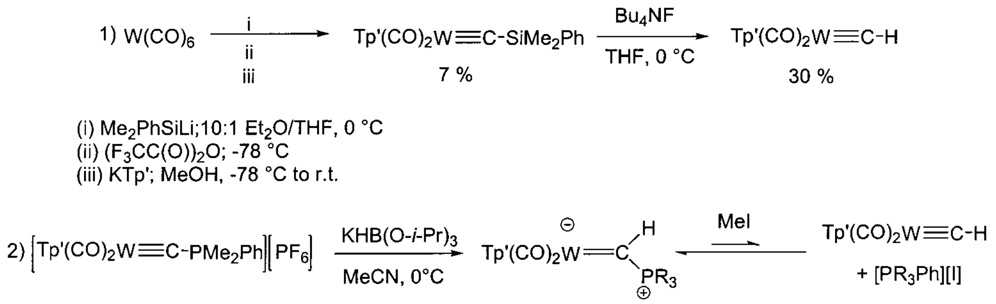
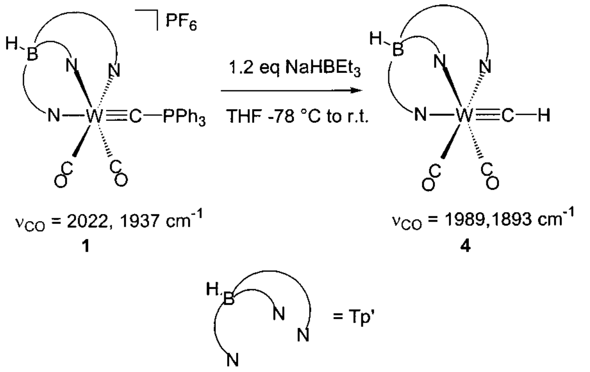
Scheme 1. Synthetic Routes to Tp′(CO)$_2$W≡C-H



Scheme 2. Synthesis of Tp′(CO)$_2$W≡CH



nucleophilic substitution reactions than does Tp′(CO)$_2$W≡C−Cl or [Tp′(CO)$_2$W≡C−PMe$_2$R]$^+$.

We now report an efficient synthesis of Tp′(CO)$_2$W≡C−H. The availability of hundreds of milligrams of Tp′(CO)$_2$W≡C−H provides a conduit to three important products via protonation, deprotonation, and hydride addition: a new cationic α-agostic methylidene complex [Tp′(CO)$_2$W=CH$_2$]$^+$, an anionic terminal tungsten carbide complex Tp′(CO)$_2$W≡C−Li, and an anionic methylidene complex [Na][Tp′(CO)$_2$W=CH$_2$]. Studies probing (1) the spectroscopic features of the methylidyne complex, (2) the mechanism of formation of the methylidyne complex, (3) equilibrium isotope effects in the α-agostic methylidene cation, (4) addition of electrophiles to the anionic carbide, and (5) addition of electron rich electrophile, PhSSPh, to trap the anionic carbene are included in this report.

Results and Discussion

Synthesis and Spectroscopic Properties of Tp′(CO)$_2$W≡C−H. Addition of Na[HBEt$_3$] to a red THF solution of [Tp′(CO)$_2$W≡C−PPh$_3$][PF$_6$] **(1)** at −78 °C resulted in a rapid color change to blue. Gradual warming afforded a brownish-yellow solution at room temperature, and infrared spectroscopy indicated that Tp′(CO)$_2$W≡C−H **(4)** was the only product detectable in the $\nu_{(CO)}$ region. Alumina chromatography produced a single yellow fraction, and evaporation of the solvent left a dull yellow powder consisting of the desired terminal methylidyne complex contaminated with PPh$_3$. Removal of PPh$_3$ was achieved by exhaustive rinsing with ether to afford bright yellow methylidyne **4** in 60% yield (Scheme 2). The deuterated terminal methylidyne **4-*d*** was generated in a similar fashion with Li[DBEt$_3$].

The reflectance IR spectrum of methylidyne **4** shows an absorption of medium intensity at 903 cm^{-1} which we have assigned as the W≡C stretch. This band shifts to 864 cm^{-1} in the reflectance IR spectrum of **4-*d***. An absorbance at 905 cm^{-1} in the Raman spectrum of **4** shifts to 868 cm^{-1} in the Raman spectrum of **4-*d***, thus mirroring the reflectance IR data. The shift of the W≡C triple bond stretching mode is close to the 31 cm^{-1} shift predicted if the CH fragment is allowed to vibrate as a single mass against tungsten in a pseudodiatomic fashion. These IR and Raman studies of **4** and **4-*d*** are consistent with the definitive vibrational assignments for (PMe$_3$)$_4$(Cl)W≡C−H reported by Hopkins and co-workers.[18]

IR spectra of **4** and **4-*d*** obtained as Fluorolube mulls were nearly superimposable. An absorption at 2927 cm^{-1} assigned primarily to Tp′ C−H stretches appears to be slightly more intense in **4** than in **4-*d***. We tentatively attribute this slight intensity increase to a weak absorption for the methylidyne C−H moiety.[19] For **4-*d*** this assignment would predict an absorption for the C−D stretch near 2050 cm^{-1}, but no absorption was observed. This area is obfuscated both by a shoulder on a strong metal carbonyl absorption at 1980 cm^{-1} and also by an unknown absorption of weak intensity at 2063 cm^{-1} in the Tp′(CO)$_2$W≡C−H spectrum. No absorbances for the C−H or C−D stretch of the carbyne were observed in the solution Raman spectra of either **4** or **4-*d***.

The ^{183}W NMR spectrum of methylidyne **4** was obtained by exploiting the $^2J_{WH}$ = 83 Hz coupling for the terminal methylidyne proton observed in the ^{1}H NMR spectrum. This two-bond tungsten−hydrogen coupling in complex **4** is ideally suited for two-dimensional indirect ^{1}H, ^{183}W recording techniques. Indirect detection of ^{183}W with a ^{1}H, ^{183}W HMQC pulse sequence establishes a ^{183}W chemical shift for **4** of $\delta = -1407$ ppm. This resonance falls within the −1365 to −2116 ppm chemical shift range reported for isoelectronic neutral monomeric tungsten alkyl carbynes of the type (L$_2$)(CO)$_2$(Cl)W≡C−R [L$_2$ =1,2-bis(diphenylphosphino)ethane (dppe); R = Me, Ph, thienyl, furyl][20] and (L$_2$)(CO)$_2$(X)W≡C−(CH=C(C$_5$H$_8$)) [X = CN and L$_2$ = dppe;[21] X = Cl, Br, I and L$_2$ = 1,1′-bis(diphenylphosphino)ferrocene (dppf)].[22]

Mechanism of Tp′(CO)$_2$W≡C−H Formation. Mechanistic insight into the formation of **4** from **1** was obtained by monitoring the reaction with NMR and in situ IR techniques. When the reaction is monitored by in situ IR, the initial products observed at −78 °C are (1) a metal monocarbonyl product with a single CO absorption at 1926 cm^{-1} which we have assigned as the neutral formyl complex Tp′(CO)(C(O)H)W≡C−PPh$_3$ (**2**) (the formyl C=O stretch was not observed[23]) and (2) the zwitterionic metal dicarbonyl carbene complex Tp′(CO)$_2$W=

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[19] Fluorolube mull IR spectra of Tp′W(CO)$_3$H, Tp′(CO)$_2$WCCl, and Tp′(CO)$_2$WCD display the same absorption pattern in the C−H stretching region between 3200 and 2800 cm^{-1}. The only C−H bonds in these compounds occur in the Tp′ ligand.

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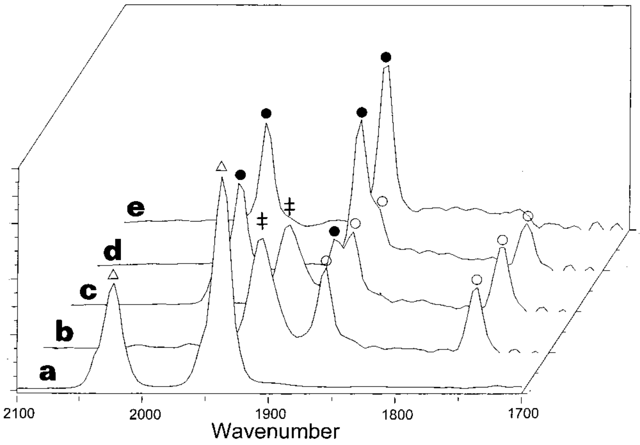


Figure 1. In situ IR spectra for the addition of Na[HBEt$_3$] to a THF solution of [Tp′(CO)$_2$W≡C−PPh$_3$][PF$_6$]: (a) THF solution of **1** at −78 °C before addition of Na[HBEt$_3$], (b) −78 °C after addition of Na[HBEt$_3$], (c) the reaction mixture warmed to −41 °C, (d) the reaction mixture warmed to 0 °C, and (e) the reaction mixture warmed to room temperature. △ = phosphonium carbyne reagent **1**, ‡ = monocarbonyl formyl **2**, ○ = zwitterionic carbene **3**, and ● = W≡C−H methylidyne product **4**.

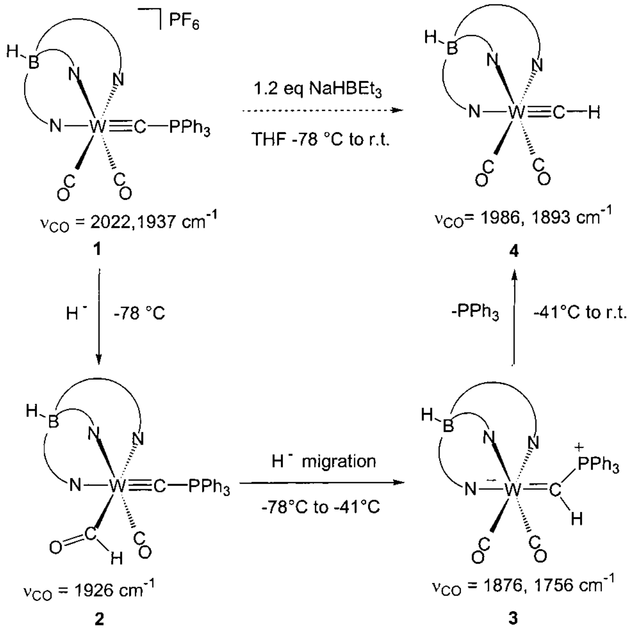
C(H)(PPh$_3$) (**3**) with ν_{CO} absorbances at 1876 and 1756 cm^{-1}. Once the solution is warmed to −41 °C, the relative intensities of the ν_{CO} absorptions for both **2** and **3** diminish, and the dicarbonyl absorbances for methylidyne product **4** appear at 1984 and 1894 cm^{-1}. Upon reaching 0 °C the monocarbonyl stretch for formyl **2** had disappeared, and the absorbances for carbene **3** were significantly diminished in intensity, while absorbances for methylidyne **4** dominated. Once the sample was warmed to room temperature, only carbonyl absorbances due to the parent carbyne **4** were visible (Figure 1).

Variable-temperature NMR data obtained after addition of 1 equiv of Na[HBEt$_3$] to a THF-d_8 sample of reagent **1** parallel the in situ IR data. At −80 °C immediately after adding Na[HBEt$_3$] to the sample, three key ^{1}H NMR resonances are observed. Singlet resonances at 13.6 (major ~92%) and 14.9 ppm (minor ~8%), typical chemical shifts for transition metal metal formyls,[24,25] are assigned to two isomers of the formyl complex **2**. A doublet at 14.0 ppm, $^2J_{PH}$ = 14 Hz, is diagnostic for carbene complex **3**.[17] The ^{31}P{^{1}H} spectrum at −80 °C shows resonances for **1**, **2**, and **3** at 12.8 ($^2J_{WP}$ = 159 Hz), 1.4 ($^2J_{WP}$ = 207 Hz), and 35.6 ppm ($^2J_{WP}$ = 61 Hz), respectively.

At −40 °C, both formyl proton signals decrease in intensity and undergo mutual site exchange to produce a broad averaged formyl isomer resonance at 13.8 ppm in the ^{1}H NMR spectrum. Also, the 14.0 ppm doublet of carbene **3** begins to reveal tungsten coupling ($^2J_{WH}$ = 19 Hz).

The ^{31}P{^{1}H} NMR spectrum at −40 °C shows signals for formyl **2** and carbene **3** while the signal for the cationic phosphonium carbyne **1** has disappeared. Upon warming to 0 °C the signal for **2** disappears, and the signal for **3** decreases drastically in intensity in both ^{1}H and ^{31}P{^{1}H} NMR spectra. At room temperature a signal at 8.2 ppm for the W≡C−H methylidyne hydrogen of **4** dominates the ^{1}H NMR, and only free PPh$_3$ is observed in the ^{31}P{^{1}H} spectrum.

Scheme 3. Proposed Mechanism of Tp′(CO)$_2$≡WCH Formation from Addition of Na[HBEt$_3$] to [Tp′(CO)$_2$W≡C−PPh$_3$][PF$_6$]



These spectroscopic data support the mechanism outlined in Scheme 3 for the formation of terminal methylidyne complex **4**. At −78 °C complex **1** undergoes initial attack by hydride at one of the metal-bound carbonyl groups to form neutral monocarbonyl formyl compound **2**. Between −78 and −40 °C the hydride migrates to the electrophilic carbyne carbon to form the well-characterized dicarbonyl zwitterionic carbene **3**,[17] which loses PPh$_3$ between −41 °C and room temperature to form the neutral terminal carbyne **4**. Precedence for hydride attack at a carbonyl ligand followed by migration to an adjacent W≡X$_\alpha$−R X$_\alpha$ site has been established in the reaction of [Tp′(CO)$_2$W≡NPh]$^+$ with a hydride source.[26]

Protonation of Tp′(CO)$_2$W≡C−H. Tp′(CO)$_2$W≡C−H reacted with [H(OEt$_2$)][BAr′$_4$F][27] (BAr′$_4$F = tetrakis[3,5-trifluoromethylphenyl] borate) at low temperature in CH$_2$Cl$_2$ to give [Tp′(CO)$_2$W=CH$_2$][BAr′$_4$F] **(5)**; recrystallization provided brown crystals. Although [Tp′(CO)$_2$W=CH$_2$][BF$_4$] **(6)** could be generated in situ by treating Tp′(CO)$_2$W≡C−H with HBF$_4$·Et$_2$O, the tetrafluoroborate salt decomposed at room temperature. Complexes **5** and **6**, differing only in counterions, have similar spectroscopic features, but low-temperature NMR studies were difficult with [BAr′$_4$F] salt **5** since it precipitated from solution in the NMR tube. The [BF$_4^-$] salt **6** was soluble in dichloromethane at low temperatures, so it was used for variable-temperature NMR experiments.

The IR spectrum of [Tp′(CO)$_2$W=CH$_2$][BF$_4$] in dichloromethane shows metal carbonyl absorptions at 2074 and 2001 cm^{-1}, consistent with a cationic tungsten complex. At room temperature in CD$_2$Cl$_2$ only signals from Tp′ and ether are observed in the ^{1}H NMR spectrum of the cationic methylidene complex **6**. The σ symmetry of the cationic methylidene on the NMR time scale is reflected by the 2:1 pattern of the Tp′ methine proton resonances at room temperature. Upon cooling to −30

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(23) Neutral formyl complexes often exhibit medium intensity CO infrared absorptions between 1530 and 1630 cm^{-1}. These frequencies suggest contributions by a Fischer carbene resonance form with a formal negative charge on the oxygen bound to the "carbene-like carbon".[24,25] The formyl stretch for **3** is either obfuscated by the CN absorbance of Tp′ at 1544 cm^{-1} or the contribution of the Tp′(CO)W(=C(H)(O))(≡C−PPh$_3$) resonance form is so significant that the formyl CO stretch is unusually low in energy and unobservable in the IR spectrum.

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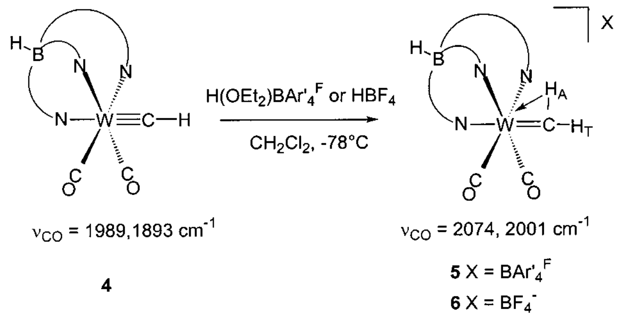
Scheme 4. Synthesis of an α-Agostic Methylidene Complex

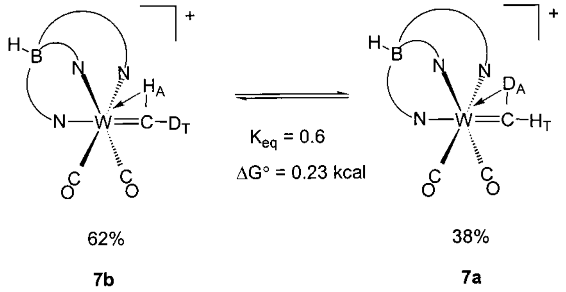


°C the spectrum becomes more informative as the rate of a fluxional process decreases and two additional signals are evident. A resonance integrating for one proton appears as a doublet at 1.92 ppm with $^2J_{HH} = 3.6$ Hz; the signal is flanked by both tungsten (^{183}W, 14.4% with $I = {}^1/_2$, $^2J_{WH} = 23$ Hz) and ^{13}C (^{13}C, 1.1%, $^1J_{CH} = 93$ Hz) satellites. A second resonance integrating for one proton simultaneously appears as a doublet at 9.18 ppm with a matching $^2J_{HH}$ of 3.6 Hz and tungsten satellites with $^2J_{WH} = 63$ Hz and natural abundance ^{13}C satellites with $^1J_{CH} = 191$ Hz. The ^{13}C NMR spectrum at −30 °C has a resonance for the α-methylene carbon at 228 ppm which appears as a doublet of doublets arising from two distinct one-bond carbon−hydrogen couplings ($^1J_{CH} = 191$ and 93 Hz). These data are consistent with a complex containing a T-shaped methylene ligand where the proton resonating at 1.92 ppm is the α-agostic proton (H_A) and the proton resonating at 9.18 ppm is the terminal "alkylidyne like" proton (H_T) (Scheme 4).[7,28,29] Cationic complex **6** is easily deprotonated as demonstrated by reformation of neutral W≡C−H methylidyne complex **2** upon treatment of **6** in CH_2Cl_2 with nucleophiles such as PMe_2Ph or NaSPh. Even dissolution of the cationic methylidene complex **6** in THF leads to deprotonation and formation of the neutral methylidyne complex **2**.

The outcome of protonation reactions of alkylidyne metal complexes depends strongly on the steric and electronic properties of the ancillary ligands. For example, protonation of $(PMe_3)_4(Cl)W{\equiv}C{-}H$ with HOTf (OTf = trifluoromethanesulfonate) gave the α-agostic methylidene complex $[(W{=}CH_2)(PMe_3)_4(Cl)][OTf]$, whereas treatment of $(dmpe)_2(Cl)W{\equiv}C{-}H$ with HOTf gave the hydrido carbyne complex $[(dmpe)_2(Cl)(H)W{\equiv}C{-}H][OTf]$.[7,28] The site of protonation was rationalized based on steric factors, arguing that a methylidene hydride complex is inaccessible in a molecule where four PMe_3 ligands and a hydride ligand are required to reside in the pentagonal plane of a pentagonal bipyramidal molecule. However, the hydrido carbyne product results from protonation of $(dmpe)_2(Cl)W{\equiv}C{-}H$ with HOTf because the two dmpe ligands are small enough to accommodate a hydride ligand in a pentagonal plane.[7,28]

Protonation of the Fisher carbynes $CpL_2Mo{\equiv}C{-}{}^nBu$ (Cp = cyclopentadienide) and $TpL_2Mo{\equiv}C{-}{}^nBu$ (Tp = hydridotrispyrazolylborate; L = CO, $P(OR)_3$; R = Me, Ph) provided insight into how the site of protonation can change as the electronic properties, particularly the π-acidities, of the ancillary ligands are systematically altered.[30] In the absence of π-acid ligands, the molybdenum center is sufficiently electron rich to form an alkylidyne hydride $[Cp(P(OMe)_3)_2(H)Mo{\equiv}C{-}Bu][BF_4]$ upon protonation with HBF_4. Replacement of one phosphite with a carbonyl group results in a decrease in the electron density at the molybdenum center, and treatment with HBF_4 generates the α-agostic alkylidenes $[Cp(P(OPh)_3)(CO)Mo{=}C(H)(Bu)][BF_4]$ and $[Tp(P(OMe)_3)(CO)Mo{=}C(H)(Bu)][BF_4]$. Protonation of $Tp(CO)_2Mo{\equiv}C{-}Bu$ with HBF_4 generated a cationic carbene, $[Tp(CO)_2Mo{=}C(H)(Bu)][BF_4]$.[30]

Scheme 5. H/D Site Preference for the α-Agostic Methylidene **7** at 243 K



Protonation of W≡C−H methylidyne **4** with HBF_4 yields the α-agostic product **6**. Two features of complex **4** can account for this site of protonation: (1) tungsten, a third row transition metal, has a greater electron density than molybdenum, its second row congener, and (2) the more electron rich Tp′ ligand provides greater electron density to the metal center than Tp.

If complex **4** is more electron rich by virtue of having a metal with more electron density and a more electron rich ligand, why does protonation of **4** not generate a hydrido carbyne? The reason is 2-fold. First, the steric bulk of the Tp′ ligand makes seven-coordinate Tp′ metal complexes less attractive than for smaller ligands. Second, even though complex **4** is more electron rich than $Tp(CO)_2Mo{\equiv}C{-}Bu$, there is not enough electron density at the metal center to support simple protonation at tungsten. The α-agostic methylidene complex **6** is formed instead.

Protonation of Tp′(CO)$_2$W≡C−D. Protonation of **4-*d*** in CD_2Cl_2 at −30 °C with $HBF_4{\cdot}Et_2O$ revealed three distinct isotopomers in the ^{1}H NMR spectrum. At −30 °C the products included $[Tp'(CO)_2W{=}C(H_T)(H_A)][BF_4]$ **(6)**, $[Tp'(CO)_2W{=}C(H_T)(D_A)][BF_4]$ **(7a)**, and $[Tp'(CO)_2W{=}C(H_A)(D_T)][BF_4]$ **(7b)** ($[Tp'(CO)_2W{=}C(D_A)(D_T)][BF_4]$ is presumably formed but was not observed in the ^{1}H NMR spectrum). The key signal for **7a** appears as a singlet at 9.16 ppm while for **7b** a singlet appears at 1.89 ppm; each of these proton signals is flanked by tungsten satellites. As expected, integration of these signals showed a preference for D to reside in the terminal position of the methylidene sites.[31−33] Integration of the two methylidene hydrogen resonances provided the ratio of **7a**:**7b** as 38:62, corresponding to $K_{eq} = 0.6$ and $\Delta G° = 0.23$ kcal/mol at 243 K (Scheme 5).

Note that a characteristic upfield 0.02 ppm shift results for the geminal hydrogen on the methylidene carbon.[34,35] This observation is consistent with slow exchange between the

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[29] A is designated as the proton undergoing the agostic interaction with the tungsten metal center and T is the proton located in the terminal "methylidyne-like" position of the carbene.

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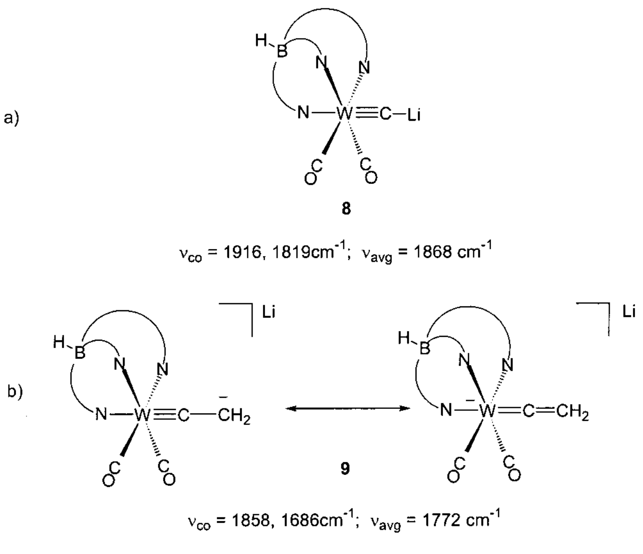
Scheme 6. (a) Localization of Negative Charge on Carbide Carbon on Complex **8** and (b) Resonance Stabilization of Negative Charge by Complex **9**



terminal position and the agostic bridging position on the NMR time scale at −30 °C. The small isotopic shift of the proton resonances for **7a** and **7b** contrasts with those reported for a similarly distorted methylidene complex displaying an averaged methylene ^{1}H shift where a large chemical shift difference of 1.2 ppm between the isotopomers $[(W{=}CH_2)(PMe_3)_4(Cl)]^+$ and $[(W{=}C(H)(D))(PMe_3)_4(Cl)]^+$ results from a weighted average of the chemical shifts as a consequence of H and D rapidly exchanging between $[(W{=}C(H_A)(D_T))(PMe_3)_4(Cl)]^+$ and $[(W{=}C(D_A)(H_T))(PMe_3)_4(Cl)]^+$.[7,28]

Deprotonation of Tp′(CO)$_2$W≡C−H. Treatment of the six-coordinate Fisher carbyne complex Tp′(CO)$_2$W≡C−H with *n*-BuLi, *t*-BuLi, or LDA at −78 °C in THF generated the terminal lithium carbide complex Tp′(CO)$_2$W≡C−Li **(8)**. This product was spectroscopically characterized by IR and by both ^{1}H and ^{13}C NMR. The IR spectrum of **8** obtained in THF at −78 °C showed that the metal carbonyl absorptions of **4** (1986 and 1893 cm^{-1}, ν_{av} = 1940 cm^{-1}) were replaced by absorptions at 1916 and 1819 cm^{-1} (ν_{av} = 1868 cm^{-1}). In comparison, the IR spectrum of [Li][Tp′(CO)$_2$W=C=CH$_2$] **(9)** obtained by deprotonating Tp′(CO)$_2$W≡C−CH$_3$ **(10)** with *n*-BuLi in THF at −78 °C showed that the metal carbonyl absorptions of methyl carbyne **10** at 1968 and 1876 (ν_{av} = 1922 cm^{-1}) were replaced by the carbonyl bands at 1858 and 1686 cm^{-1} (ν_{av} = 1772 cm^{-1}) in the vinylidene anion **9**. The 150 cm^{-1} difference in the average stretching frequencies between neutral methyl carbyne **10** and anionic vinylidene **9** reflects the impact of an important resonance form in which tungsten houses the formal negative charge in complex **9**. This contrasts with the much smaller 72 cm^{-1} decrease in the average stretching frequency of the carbonyl bands when neutral methylidyne **4** is converted to anionic carbide complex **8**. Presumably the negative charge on **8** is localized primarily in a C$_\alpha$ carbon s orbital rather than being localized on the metal. These data support assignment of **8** as the terminal tungsten carbide (Scheme 6).

The ^{1}H and ^{13}C NMR spectra of the lithium salt of carbide complex **8** were obtained by dissolving W≡C−H compound **4** and solid LDA in THF-*d*$_8$ in an NMR tube at −80 °C. The ^{1}H NMR spectrum of anion **8** shows only Tp′ signals and reflects the σ symmetry of the molecule with 2:1 signal intensity patterns for the Tp′ methine protons and the 6:3:6:3 intensity pattern for the protons of the methyl groups in the 3 and 5 positions on the pyrazole rings. The ^{13}C spectrum also shows signals for a symmetric Tp′ species with a resonance for the tungsten-bound carbonyl groups at 232 ppm with $^1J_{WC}$ = 197 Hz. The unique and definitive feature of the ^{13}C spectrum is a broad (∼300 Hz) resonance at 556 ppm assigned to the carbide carbon (Figure 2). This chemical shift is further downfield than those reported for other transition metal carbides[2,6,36−43] and also lies below the chemical shifts of the cationic diiron bridging methylidyne complexes reported by Casey.[44,45] The chemical shift of the terminal carbon of anionic complex **8**, a six-coordinate transition metal carbide, can be compared to that of the four-coordinate molybdenum carbide ({N(R)Ar}$_3$Mo≡C:)$_2$K$_2$ [R = C(CD$_3$)$_2$-CH$_3$, Ar = C$_6$H$_3$Me$_2$-3,5] with a 494 ppm resonance.[2,6,37]

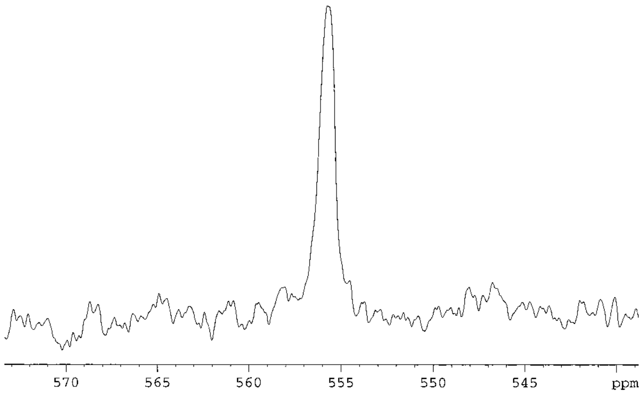


Figure 2. ^{13}C NMR resonance of the terminal carbon atom of carbide **8**.

Reactivity of Tp′(CO)$_2$W≡C−Li. Anionic carbide complex **8** reacts with a variety of electrophiles including iodomethane, trimethylsilyl triflate, benzophenone, benzaldehyde, iodine, and benzoyl bromide. Treatment of **8** with these electrophiles generates carbyne complexes **10**−**15** in moderate yields (Scheme 7). All of these carbyne complexes have a mirror plane except for chiral complex **14**, which has a stereocenter in the carbyne substituent. The ^{1}H NMR and IR spectra of methyl carbyne complex **10** match literature values.[46] The salient spectroscopic feature of the new trimethysilyl derivative **11** is a low-field resonance for C$_\alpha$ of the silylcarbyne moiety at 345 ppm with $^1J_{WC}$ = 188 Hz. This feature compares favorably with the C$_\alpha$ resonance at 339 ppm ($^1J_{WC}$ = 160 Hz) reported for the closely related Tp′(CO)$_2$W≡C−SiMe$_2$Ph complex.[4,5]

Lalor and co-workers have prepared halo carbynes of the form Tp′(CO)$_2$M≡C−X for M = Mo, W and X = Cl, Br.[15,16] They reported formation of Tp′(CO)$_2$Mo≡C−I from oxidation of [Et$_4$N][Tp′(CO)$_3$Mo] with [IPh$_2$][BF$_4$] in CHI$_3$.[15] Addition of

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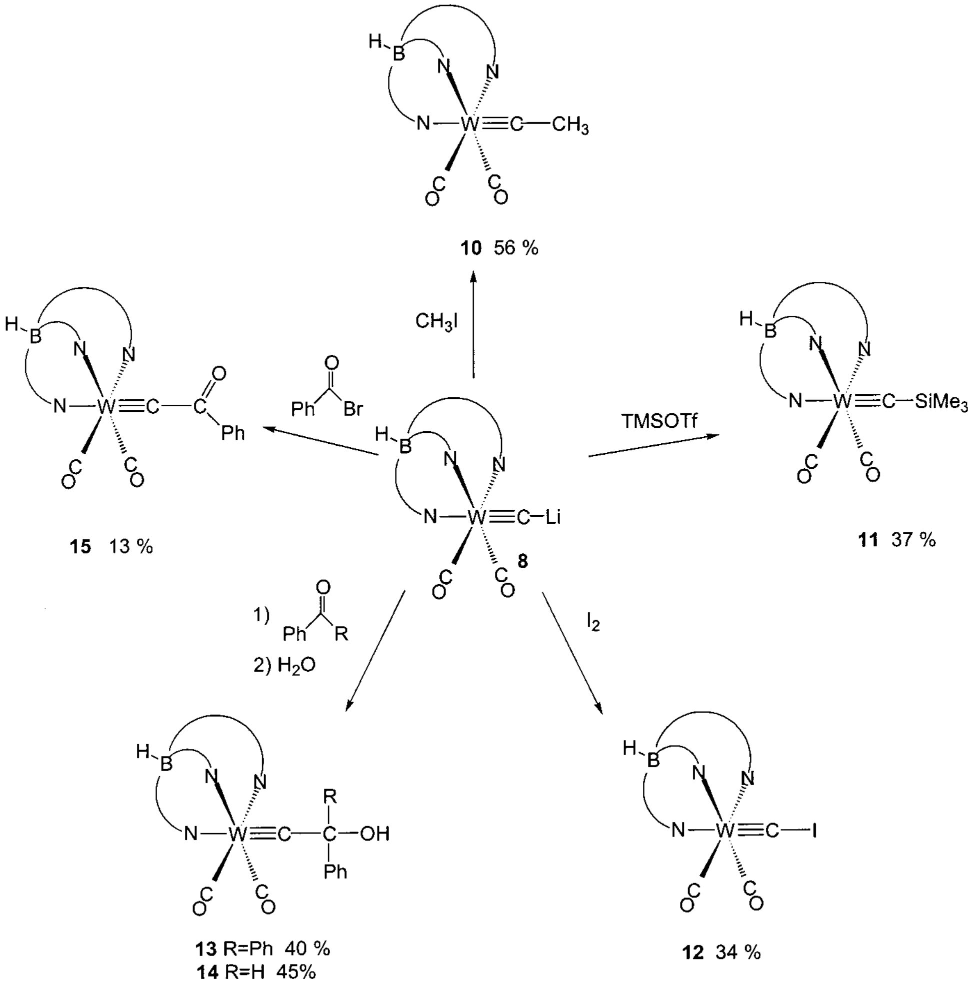
Scheme 7. Carbyne Complexes Obtained from Addition of Electrophiles to Complex **8**



iodine to anionic carbide **8** generates Tp′(CO)$_2$W≡C−I (**12**). Complex **12** shows a characteristic upfield ^{13}C resonance for the iodocarbyne C$_\alpha$ carbon at 183 ppm. Metal carbonyl stretches are observed in the IR spectrum of **12** in cyclohexane at 1992 and 1907 cm^{-1}.

Hydroxo derivatives **13** and **14** both show ^{13}C NMR resonances at 284 ppm for C$_\alpha$ with tungsten coupling of 190 Hz. The C$_\beta$ resonance for the benzophenone derived product **13** appears at 90 ppm as a singlet with $^2J_{WC} = 34$ Hz whereas the resonance for benzaldehyde product **14** appears at 86 ppm with $^2J_{WC} = 40$ Hz. These ^{13}C NMR signals track reported values for C$_\alpha$ and C$_\beta$ of alkyl carbynes derived from deprotonation at C$_\beta$ of methyl carbyne complex **10** and subsequent alkylation.[46]

For the phenylacyl carbyne **15**, C$_\alpha$ resonates at 277 ppm with $^1J_{WC} = 188$ Hz. The $^2J_{WC}$ value of 45 Hz for C$_\beta$ is normal; this C$_\beta$ of the carbonyl group resonates downfield at 198 ppm. Dark green crystals of phenylacyl carbyne **15** were obtained by slow diffusion of pentane into a CH$_2$Cl$_2$ solution of **15**. An ORTEP drawing of **15** with selected bond lengths and bond angles is shown in Figure 3. Crystallographic data and collection parameters, complete bond lengths and angles, and atomic parameters are deposited as Supporting Information.

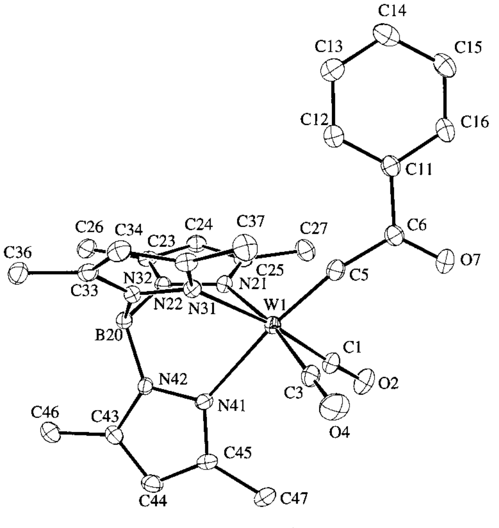


Figure 3. ORTEP diagram for Tp′(CO)$_2$W≡C−C(O)(Ph) (**12**). Selected bond lengths (Å) and bond angles (deg): W(1)−C(5) 1.831(5), C(5)−C(6) 1.492(7), C(6)−O(7) 1.234(6), C(6)−C(11) 1.500(7); W(1)−C(5)−C(6) 168.7(4), C(5)−C(6)−O(7) 121.7(5), C(5)−C(6)−C(11) 117.6(4), O(7)−C(6)−C(11) 120.7(4).

Relative pK_a of Tp′(CO)$_2$W≡C−H. Extensive studies of lithium ion-pair acidities in THF have been reported by several groups. Streitwieser and co-workers have pioneered a scale of proton transfer indicators in THF based on the solvent-separated lithium ion-pair salts of hydrocarbons with convenient UV−vis spectral characteristics.[47−49] The resulting scale has been used to study the ion pair acidities of various substrates in THF.

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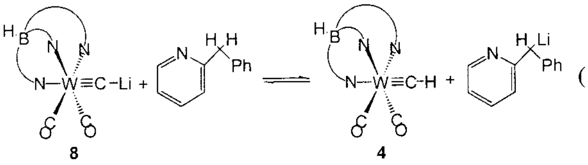
Fraser et al. have developed a technique that uses ^{13}C NMR to measure the relative equilibrium concentrations of all four relevant species in THF.[50−52] The relative concentrations defined the effective pK_a values of several different hydrocarbon compounds with tetramethylpiperidine as a reference acid ($pK_a = 37.8$).

We determined the relative pK_a of **4** in THF using in situ IR. Anionic carbide **8** was generated in situ by adding a known amount of excess *n*-BuLi to a −78 °C THF solution of the parent carbyne **4**. The terminal carbide **8** was partially converted to **4** by titrating with varying amounts of 2-HBP (2-HBP = 2-benzylpyridine; pK_a 28.4 relative to tetramethylpiperidine). The lithium/hydrogen exchange between the 2-HBP and the carbide **8** can be monitored by in situ IR. After a known amount of 2-benzylpyridine was added to the reaction mixture, the relative concentrations of **8** and **4** were determined by measuring the peak heights of their respective metal carbonyl absorbances. Once the relative concentrations of **8** and **4** were known, the concentrations of 2-HBP and $2\text{-}BP^-$ were calculated. The pK_a of **4** in THF was calculated to be 28.7 ± 0.3 by using the equilibrium expression for eq 1. Note that the terminal tungsten carbyne is less acidic than terminal alkyne analogues $Ph{-}C{\equiv}C{-}H$ (pK_a(cyclohexylamine) = 23.2) and $t\text{-}Bu{-}C{\equiv}C{-}H$, ($pK_a$(cyclohexylamine) = 25.5).[53] Presumably this reflects polarization of the $W{\equiv}C$ bond because of the electropositive metal. The increased carbon s-character in the metal carbon triple bond decreases the s-character in the C−H bond. The terminal proton is then less acidic than terminal alkynes, and this decrease in the C−H bond s-character is reflected by a $^1J_{CH}$ value of only 142 Hz for the parent carbyne.



(1)

Hydride Addition to $Tp'(CO)_2W{\equiv}C{-}H$. The first isolable transition metal methylidene complex was prepared from the cationic tantalum complex $[Cp_2Ta(CH_3)_2][BF_4]$ by deprotonation of a metal-bound methyl group to generate the neutral methylidene complex $Cp_2Ta(CH_3)({=}CH_2)$.[54−57] The related neutral methylidenes $[P_2N_2](Me)Ta{=}CH_2$[58] ($[P_2N_2] = PhP(CH_2SiMe_2NSiMe_2(CH_2)_2PPh)$) and $Cp_2Zr({=}CH_2)(PPh_2Me)$[59] are generated by the elimination of methane upon irradiation of the $[P_2N_2]TaMe_3$ precursor and addition of $Ph_3P{=}CH_2$ to $Cp_2Zr(PPh_2Me)_2$, respectively. Olefin metathesis with ethylene by nonheteroatom-substituted carbenes[60,61] and the oxidative addition of methylene chloride to $Ru(H)_2(H_2)_2(PR_3)_2$[62] provide neutral methylidenes of the type $Ru({=}CH_2)Cl_2(PR_3)_2$, while adding diazomethane to neutral transition metal−halo compounds of Ir,[63] Ru,[64,65] and Os[65−67] containing PPh_3 and a strong π-acid in the coordination sphere also generates neutral methylidenes.

Numerous cationic transition metal methylidene complexes have been reported. These cationic methylidenes are commonly made by α-abstraction of either a hydride or a halide from neutral transition metal alkyl precursors[68−74] or by acid treatment of an ether precursor.[75,76] Less common synthetic routes involve treatment of an iron thioether methylidene precursor[77] or an osmium hydride[78,79] with cationic methylating reagents. To our knowledge, anionic transition metal methylidene complexes have yet to be reported.

Cationic carbynes with good π-accepting ligands can add nucleophiles at C_α to give neutral heteroatom[17,80−85] or nonheteroatom[14,86−88] carbene complexes. The parent carbyne complex **4** is neutral but contains two π-acidic carbonyls and the sterically bulky Tp′ ligand in the coordination sphere. Given the reactivity of the cationic carbynes in this system and the

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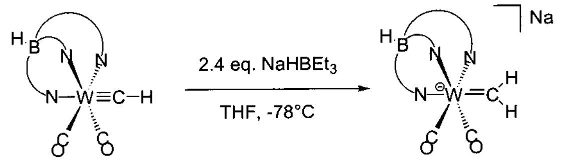
Scheme 8. Synthesis of an Anionic Methylidene Complex from a Parent Fischer Carbyne



4 ν_{CO} = 1989,1893 cm^{-1}

16 ν_{CO} = 1822, 1679 cm^{-1}

ability of Tp′ to deflect incoming nucleophiles away from the metal to the ligands, we decided to probe the reactivity of the neutral parent carbyne toward hydride transfer reagents with the goal of generating the first anionic methylidene complex. The stability of Tp′(CO)$_2$W=C(H)PMe$_3$, electronically similar to the target molecule [Tp′(CO)$_2$W=CH$_2$]$^-$, was particularly relevant.[17,80−85]

The parent carbyne **4** reacts with 2.4 equiv of sodium triethylborohydride in THF solution to form the anionic methylidene compound [Na][Tp′(CO)$_2$W=CH$_2$] (**16**). Complex **16** was not isolated, but it is stable in THF solution for days at room temperature. The IR spectrum of anionic methylidene complex **16** shows carbonyl bands at 1822 and 1679 cm^{-1} (υ_{avg} = 1750 cm^{-1}). Note that carbonyl absorbances of **16** are substantially below those of anionic carbide complex **8** indicating that the negative charge is primarily housed at the metal in **16**. At 193 K the ^{1}H NMR for **16** has a mirror plane of symmetry as shown by the 6:3:6:3 intensity pattern for the protons of the Tp′ methyl groups. Resonances at 13.9 and 12.7 ppm each integrate for a single proton; neither geminal H−H nor tungsten coupling was observed in either signal. These data are diagnostic of a methylidene moiety and indicate that the orientation of the methylidene at 193 K places the CH$_2$ moiety in the symmetry plane that bisects the carbonyl ligands as depicted in Scheme 8.

As the NMR sample is warmed from 193 K, the proton resonances of the methylidene ligand broaden into the baseline. These two signals coalesce at 260 K in a 400 MHz spectrometer. The rate of exchange at 260 K is compatible with a barrier to rotation of the methylidene fragment of 11.6 kcal/mol. A broad singlet at 13.3 ppm is observed for both methylidene protons at room temperature (Figure 4). The methylidene carbon resonates at 265 ppm with $^1J_{WC}$ = 132 Hz and $^1J_{CH}$ = 122 Hz in the room temperature ^{13}C NMR spectrum.

Treatment of the anionic methylidene complex **16** with Ph−S−S−Ph in THF initially forms an unknown metal monocarbonyl product with a CO absorbance at 1733 cm^{-1}.[89] This monocarbonyl complex gradually converts to a dicarbonyl complex that has CO absorptions at 1938 and 1803 cm^{-1}. Alumina chromatography and solvent evaporation yields the sulfide-trapped methylidene product Tp′(CO)$_2$W(η^2-CH$_2$SPh) (**17**) as an orange solid (Scheme 9). Thus the net result is addition of SPh$^+$ to the anionic methylidene complex.

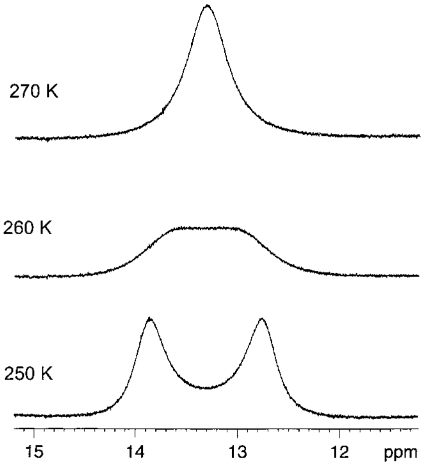
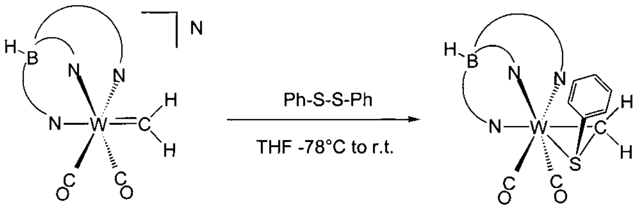


Figure 4. Variable-temperature ^{1}H NMR spectra of anionic methylidene **16** showing coalescence of the two methylidene proton resonances at 260 K.

Scheme 9. Synthesis of Tp′(CO)$_2$WCH$_2$(η^2-S-Ph) from the Anionic Fischer Methylidene **16**



ν_{CO} = 1822, 1679 cm^{-1} **16**

ν_{CO} = 1938, 1803 cm^{-1} **17**

The ^{1}H NMR spectrum of **17** in C$_6$D$_6$ shows that the complex is chiral. The diastereotopic protons of the W−CH$_2$−SPh ring resonate as doublets at 4.5 and 4.2 ppm, each with $^2J_{HH}$ = 6.4 Hz. The key feature of the ^{13}C NMR spectrum is the signal for the carbon of the ring which resonates at 46.8 ppm as a triplet with $^1J_{CH}$ = 159 Hz. X-ray quality orange prismatic crystals of **17** were obtained by dissolving the orange solid in a minimal amount of refluxing benzene followed by cannula filtration and cooling to room temperature. The ORTEP diagram of **17** is shown in Figure 5. Disorder in the ring limits the reliability of the distances and angles. Crystallographic data and collection parameters, complete bond lengths and angles, and atomic parameters are deposited as Supporting Information.

Conclusion

A convenient synthesis of the terminal methylidyne monomer Tp′(CO)$_2$W≡C−H from a phosphonium carbyne precursor has been described. Assignment of the W≡C stretching vibration was achieved with IR and Raman spectroscopy, and the ^{183}W NMR spectrum was obtained. A pK_a value of 28.7 in THF for Tp′(CO)$_2$W≡C−H was determined. Protonation of Tp′(CO)$_2$W≡C−H forms an α-agostic methylidene complex while deprotonation forms the lithium carbide monomer Tp′(CO)$_2$W≡C−Li. Reaction of the lithium carbide complex with a variety of electrophiles provides access to additional Fischer tungsten carbyne complexes. Treatment of Tp′(CO)$_2$W≡C−H with excess Na[HBEt$_3$] generates an anionic Fischer methylidene complex, [Na][Tp′(CO)$_2$W=CH$_2$], which reacts with diphenyl disulfide to form Tp′(CO)$_2$W(η^2-CH$_2$SPh).

Experimental Section

General Procedures. All reactions were carried out under a dry atmosphere of nitrogen or argon with standard Schlenk or drybox techniques. All solvents except tetrahydrofuran were dried by passage

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(89) One helpful referee correctly noted that observing a single carbonyl band is insufficient evidence for a monocarbonyl complex since a trans configuration of the CO ligands would also give a single IR absorption. Such a trans geometry could arise only if addition of Ph$_2$S$_2$ to [Na][Tp′(CO)$_2$W=CH$_2$] is releasing one of the "arms" of the Tp′ ligand from tungsten. Given the overwhelming propensity for the Tp′ ligand to remain facially coordinated in tungsten complexes we favor a monocarbonyl formulation.

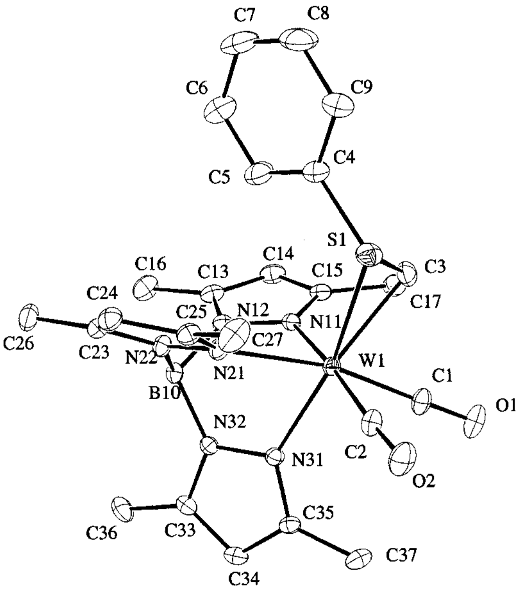

Figure 5. ORTEP diagram of **17**. Selected bond lengths (Å) and bond angles (deg): W(1)−C(3) 2.210(5), W(1)−S(1) 2.4715(13), S(1)−C(3) 1.736(6), S(1)−C(4) 1.838(4); W(1)−S(1)−C(3) 60.41(16), W(1)−C(3)−S(1) 76.49(18), S(1)−W(1)−C(3) 43.09(15), W(1)−S(1)−C(4) 113.94(15), C(3)−S(1)−C(4) 98.06(24).

through activated alumina columns. Tetrahydrofuran was distilled under nitrogen from sodium and benzophenone. $Tp'(CO)_2W{\equiv}C{-}Cl$[16] and $[H(OEt_2)][BAr'_4F]$[27] were synthesized by literature methods. All other reagents were used as obtained from commercial sources. Complexes $[Tp'(CO)_2W{\equiv}C{-}PPh_3][PF_6]$,[85] $Tp'(CO)_2W{\equiv}C{-}H$,[4,5] and $Tp'(CO)_2W{\equiv}C{-}CH_3$[46] have all been reported previously; improved synthetic procedures for $[Tp'(CO)_2W{\equiv}C{-}PPh_3][PF_6]$ and $Tp'(CO)_2W{\equiv}C{-}H$ are reported below. $[Tp'(CO)_2W{=}CH_2][BF_4]$, $Tp'(CO)_2W{\equiv}C{-}Li$, and $[Na][Tp'(CO)_2W{=}CH_2]$ were generated in situ and characterized spectroscopically in solution.

Raman spectra were obtained on a JYU 100 Double Monochromator Raman System equipped with Princeton Instruments liquid cooled CCD. The argon laser power was set at 0.3 W and attenuated with a neutral density filter (absorbance = 2). The entrance and intermediate slit were set to 20 μm and the system was calibrated to Ar^+ plasma lines.[90] In situ infrared spectra were obtained on an ASI React IR 1000 spectrometer equipped with a SiComp probe. All ^1H and ^{13}C NMR spectra were obtained on a Bruker Avance 400 or Bruker Avance 500 spectrometer. The ^{183}W spectrum was obtained on a Bruker AMX-300 with the standard indirect detection experiment ^1H, ^{183}W 2D HMQC. A solution of Na_2WO_4 in D_2O (pD ~11) was used as the external reference. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA.

$[Tp'(CO)_2W{\equiv}CPPh_3][PF_6]$ (1). $Tp'(CO)_2W{\equiv}C{-}Cl$ (5.66 g, 9.68 mmol), PPh_3 (10.22 g, 39.0 mmol), and KPF_6 (2.00 g, 10.9 mmol) were dissolved in 500 mL of THF, resulting in a yellow solution with carbonyl absorptions at $\nu_{CO} = 1986$ and 1895 cm^{-1}. Upon heating to reflux for one week, a gradual color change from yellow to purple was observed and new IR absorbances appeared at $\nu_{CO} = 2022$ and 1937 cm^{-1}. The resulting purple solution was evaporated under reduced pressure to leave a purple-brown solid that was dissolved in a minimal amount of CH_2Cl_2 and transferred to a hexanes packed alumina column. A single dark red band was collected upon elution with dichloromethane. The solvent was evaporated under reduced pressure and the solid residue was recrystallized from 50 mL of CH_2Cl_2 layered with 500 mL of hexanes to give 8.75 g (95% yield) of red crystalline $[Tp'(CO)_2W{\equiv}CPPh_3][PF_6]$.[85]

$Tp'(CO)_2W{\equiv}C{-}H$ (4). A Schlenk flask was charged with $[Tp'(CO)_2W{\equiv}CPPh_3][PF_6]$ (1.05 g, 1.10 mmol), 40 mL of THF, and a stirbar. It was then submerged into a dry ice−2-propanol bath. Once the solution had cooled to −78 °C, an aliquot of 1 M $NaHBEt_3$ in THF (1.3 mL, 1.3 mmol) was added to the red solution which immediately turned blue. Gradual warming to room temperature was accompanied by color changes from blue to green and ultimately to brown. The solvent was removed under reduced pressure to leave a brown residue. This residue was suspended in 20 mL of diethyl ether, and the ether suspension was added via cannula to a hexanes packed alumina column. A single yellow band was collected upon elution with diethyl ether. Removal of the ether solvent under reduced pressure gave a brown yellow solid that was rinsed with 3 × 5 mL aliquots of ether. After each rinse, the resulting brown ether supernatant was removed by using a filter cannula covered with Whatman No. 5 filter paper. A bright yellow powder, $Tp'(CO)_2W{\equiv}C{-}H$, remained (0.370 g, 61% yield).[4,5]

$Tp'(CO)_2W{\equiv}C{-}D$ (4-*d*). The synthesis of $Tp'(CO)_2W{\equiv}C{-}D$ was identical to that used to prepare $Tp'(CO)_2W{\equiv}C{-}H$ except 1 M $LiDBEt_3$ in THF was used instead of $NaHBEt_3$.

$[Tp'(CO)_2W{=}CH_2][BAr'_4F]$ (5). A Schlenk flask was charged with $Tp'(CO)_2W{\equiv}C{-}H$ (0.101 g, 0.184 mmol), $[H(OEt)_2[BAr'_4F]$ (0.187 g, 0.184 mmol), and a stirbar. The flask was immersed into a dry ice 2-propanol bath and cooled to −78 °C. A 40 mL aliquot of dichloromethane was slowly added to the flask resulting in the formation of an orange-red solution. Upon warming the solution to 0 °C the IR spectrum showed absorbances at $\nu_{CO} = 2076$, 2003 cm^{-1}. The solution was reduced to one-fourth of its original volume under reduced pressure, and then it was layered with 100 mL of pentane. After 8 h, the supernatant layer was removed via filter cannula. Residual solvent was removed under vacuum to give brown needles of crystalline $[Tp'(CO)_2W{=}CH_2][BAr'_4F]$ (0.143 g, 55% yield). IR (KBr): 2568 cm^{-1} (ν_{BH}), 2078, 2009 cm^{-1} (ν_{CO}), 1542 cm^{-1} (ν_{CN}). ^1H NMR (CD_2Cl_2, 243 K): δ 9.05 (d, $^2J_{HH} = 3.6$ Hz, $^2J_{WH} = 65$ Hz, nonagostic $W{=}C(H)(\mathit{H})$), 7.72 (s, 8 H from BAr'_4F), 7.55 (s, 4 H from BAr'_4F), 6.13, 6.05 (s, 2:1 H, $Tp'C\mathit{H}$), 2.40, 2.37, 2.32 (s, 3:12:3 H, $Tp'CC\mathit{H}_3$), 1.38 (d, $^2J_{HH} = 3.6$ Hz, $^2J_{WH} = 22$ Hz, agostic $W{=}C(\mathit{H})(H)$). ^{13}C NMR (CD_2Cl_2, 243 K): δ 224.8 (s, $^1J_{CH(nonagostic)} = 194$ Hz, $^1J_{CH(agostic)} = 92$ Hz, $W{=}\mathit{C}H_2$), 207.4 (s, $^1J_{WC} = 141$ Hz, 2 $W(\mathit{C}O)$), 161.1 (m, 4 ipso $\mathit{C}{-}B$), 155.5, 152.1, 149.7, 148.7 (1:2:1:2, $Tp'\mathit{C}CH_3$), 135.1 (s, 8 ortho $\mathit{C}{-}H$) 129.0 (q, $^2J_{CF} = 31$ Hz, 8 meta $\mathit{C}{-}CF_3$) 124.9 (q, $^1J_{CF} = 271$ Hz, 8 $C{-}\mathit{C}F_3$'s), 118.0 (s, 4 para $\mathit{C}{-}H$), 110.1, 108.7 (1:2, $Tp'\mathit{C}H$), 16.4, 16.3, 13.9, 12.8 (2:1:1:2, $Tp'C\mathit{C}H_3$). Anal. Calcd for $C_{50}H_{36}N_6B_2O_2F_{24}W$: C, 42.43; H, 2.57; N, 5.94. Found: C, 41.98; H, 2.82; N, 5.89.

$[Tp'(CO)_2W{=}CH_2][BF_4]$ (6). A 5 mm NMR tube was charged with $Tp'(CO)_2W{\equiv}C{-}H$ (0.051 g, 0.093 mmol) and 0.7 mL of CD_2Cl_2, sealed with a rubber septum, then immersed in a −78 °C dry ice−acetone bath. An aliquot of 85% $HBF_4{\cdot}Et_2O$ (18 μL, 0.12 mmol) was added via syringe to the NMR tube to give a dark red/orange solution. The sample was inserted into the cooled spectrometer probe at 243 K. IR (CD_2Cl_2): 2572 cm^{-1} (ν_{BH}), 2074, 2001 cm^{-1} (ν_{CO}), 1544 cm^{-1} (ν_{CN}). ^1H NMR (CD_2Cl_2, 243 K): δ 9.19 (d, $^2J_{HH} = 3.6$ Hz, $^2J_{WH} = 65$ Hz, nonagostic $W{=}C(H)(\mathit{H})$), 6.16, 6.12 (s, 2:1 H, $Tp'C\mathit{H}$), 2.44, 2.42, 2.40, 2.37 (s, 3:6:6:3 H, $Tp'CC\mathit{H}_3$), 1.92 (d, $^2J_{HH} = 3.6$ Hz, $^2J_{WH} = 23$ Hz agostic $W{=}C(\mathit{H})(H)$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 243 K): δ 228 (s,$^1J_{CW} = 56$ Hz, $^1J_{CH(nonagostic)} = 191$ Hz, $^1J_{CH(agostic)} = 93$ Hz, $W{=}\mathit{C}H_2$), 208.2 (s, $^1J_{WC} = 143$ Hz, $2W(\mathit{C}O)$, 155.4, 152.4, 149.5, 148.4 (1:2:1:2, $Tp'\mathit{C}CH_3$), 109.9, 108.6 (1:2, $Tp'\mathit{C}H$), 16.4, 16.2, 14.0, 12.9 (2:1:1:2, $Tp'C\mathit{C}H_3$).

$Tp'(CO)_2W{\equiv}C{-}Li$ (8): Method a. A 5 mm NMR tube was charged with $Tp'(CO)_2W{\equiv}C{-}H$ (0.040 g, 0.073 mmol) and solid lithium diisopropyl amide (LDA) (0.038 g, 0.35 mmol), and then sealed with a rubber septum. It was then immersed in a −78 °C dry ice−acetone bath before a 0.7 mL aliquot of THF-d_8 was added via syringe to the NMR tube to give a dark red/orange solution. The sample was inserted into the cooled spectrometer probe at 243 K. ^1H NMR (THF-d_8): δ 5.86, 5.59 (s, 2:1 H, $Tp'C\mathit{H}$) 2.87, 2.31, 2.28, 2.25 (s, 6:3:6:3 H, $Tp'CC\mathit{H}_3$). $^{13}C\{^1H\}$ NMR: δ 556 (s, br $W{\equiv}\mathit{C}{-}Li$), 232.0 (s, $^1J_{WC} = 197$ Hz, $W(\mathit{C}O)$), 150.5, 143.7, 143.6 (3:2:1, $Tp'\mathit{C}CH_3$), 105.7, 105.4 (2:1, $Tp'\mathit{C}H$), 17.51, 14.92, 13.18, 12.55 (2:1:2:1, $Tp'C\mathit{C}H_3$)

Method b. In a representative in situ synthesis of $Tp'(CO)_2W{\equiv}C{-}Li$, a Schlenk flask was charged with $Tp'(CO)_2W{\equiv}C{-}H$ (0.154 g, 0.279 mmol), 30 mL of THF, and a stirbar and immersed in a dry ice−2-

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(90) Carter, D. A.; Thompson, W. R.; Taylor, C. E.; Pemberton, J. E. *Appl. Spectrosc.* **1995**, *49*, 1561−1576.

propanol bath. Once the solution had cooled to −78 °C, a 0.50 mL aliquot of 1.7 M *t*-BuLi in pentane (0.85 mmol, 3 equiv) was added to the yellow solution (3 equiv of *n*-BuLi can also be used instead of *t*-BuLi). After 30 min of stirring at −78 °C, the solution was orange in color. A solution IR spectrum obtained in an oven-dried, nitrogen-purged CaF_2 infrared cell displayed absorbances at $\nu_{CO} = 1916$ and 1819 cm^{-1}.

$Tp'(CO)_2W\equiv C-CH_3$ (10). A Schlenk flask was charged with $Tp'(CO)_2W\equiv C-H$ (0.125 g, 0.227 mmol) and 30 mL of THF. $Tp'(CO)_2W\equiv C-Li$ was generated in situ with method b. After 30 min of stirring at −78 °C, an aliquot of iodomethane (100 μL, 1.60 mmol) was added to the freshly generated orange $Tp'(CO)_2W\equiv C-Li$ solution. After a rapid color change from orange to brown-yellow, the IR spectrum revealed absorbances at $\nu_{CO} = 1969, 1875\ cm^{-1}$. The reaction was gradually warmed to room temperature before the solvent was evaporated under reduced pressure to give a brown residue. The brown residue was dissolved in a minimal amount of dichloromethane and transferred to a hexanes packed alumina column. A single bright yellow fraction was collected with 4:1 hexanes:dichloromethane as eluent. Removal of solvent under reduced pressure gave 0.0746 g (56% yield) of bright yellow $Tp'(CO)_2W\equiv C-CH_3$.[46]

$Tp'(CO)_2W\equiv C-SiMe_3$ (11). A Schlenk flask was charged with $Tp'(CO)_2W\equiv C-H$ (0.119 g 0.217 mmol) and $Tp'(CO)_2W\equiv C-Li$ was generated in situ with method b. After the mixture was stired for 30 min, an aliquot of trimethylsilyl trifluoromethanesulfonate (TMS-OTf) (60 μL, 0.33 mmol) was added to the orange $Tp'(CO)_2W\equiv C-Li$ solution. An immediate color change from bright orange to reddish brown was observed. The IR spectrum revealed absorbances at $\nu_{CO} = 1980, 1891\ cm^{-1}$. The reaction was allowed to stir for 15 min at −78 °C, and then it was gradually allowed to warm to room temperature. The solvent was evaporated under reduced pressure to leave a brown residue that was dissolved in a minimal amount of hexanes and transferred to a hexanes-packed alumina column. A single bright yellow fraction eluted with 9:1 hexanes:CH_2Cl_2. Removal of solvent under reduced pressure and recrystallization from CH_2Cl_2 layered with MeOH at −30 °C gave yellow starbursts. The supernatant layer was removed by a filter cannula covered with Whatman No. 5 filter paper. Residual solvent was removed under reduced pressure to give $Tp'(CO)_2W\equiv C-SiMe_3$ (0.050 g 37% yield). IR (neat solid): 2548 cm^{-1} (ν_{BH}), 1976, 1884 cm^{-1} (ν_{CO}), 1540 cm^{-1} (ν_{CN}). ^{1}H NMR (CD_2Cl_2): δ 5.98, 5.79 (s, 2:1 H, $Tp'CH$), 2.61, 2.39, 2.37, 2.32 (s, 6:3:3:6 H, $Tp'CCH_3$), 0.14 (s, 9 H $Si(CH_3)_3$. $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 344.6 ($^{1}J_{WC} = 160$ Hz, $W\equiv C-SiMe_3$), 225.9 ($^{1}J_{WC} = 154$ Hz, 2W(*C*O)), 152.8, 151.7, 145.1, 145.6 (1:2:1:2, $Tp'CCH_3$), 106.9, 106.7 (1:2, $Tp'CH$), 17.1, 15.0 12.8, 12.7 (2:1:2:1, $Tp'CCH_3$). Anal. Calcd for $C_{21}H_{31}N_6O_2BSiW$: C, 40.53; H, 5.02; N, 13.50. Found: C, 40.87; H, 5.00; N, 13.00.

$Tp'(CO)_2W\equiv C-I$ (12). A Schlenk flask was charged with $Tp'(CO)_2W\equiv C-H$ (0.123 g, 0.224 mmol). $Tp'(CO)_2W\equiv C-Li$ was generated in situ with method b. After being stirred at −78 °C for 30 min, a separately prepared 10 mL THF solution of iodine (0.143 g, 1.13 mmol, 5 equiv) cooled to −78 °C was transferred via cannula to the orange $Tp'(CO)_2W\equiv C-Li$ solution. A color change from orange to reddish-brown was observed. After addition of the iodine solution, metal carbonyl absorbances at $\nu_{CO} = 1988, 1895\ cm^{-1}$ are observed in the IR spectrum. Gradual warming to room temperature followed by solvent removal under reduced pressure gave a brown residue that was dissolved in a minimal amount of dichloromethane and transferred to a hexanes packed alumina column. A single yellow fraction eluted with 1:1 hexanes:dichloromethane. This yellow fraction was adsorbed onto and chromatographed on silica gel. Five 20 mL yellow fractions were collected with hexanes as eluent. Assay of the first three fractions by IR showed absorbances for $Tp'(CO)_2W\equiv C-I$. Removal of solvent from these three fractions under reduced pressure gave $Tp'(CO)_2W\equiv C-I$ (0.051 g, 34% yield). IR (cyclohexane): 2532 cm^{-1} (ν_{BH}), 1992, 1907 cm^{-1} (ν_{CO}), 1544 cm^{-1} (ν_{CN}). ^{1}H NMR (CD_2Cl_2): δ 5.94, 5.81 (s, 2:1 H, $Tp'CH$), 2.51, 2.39, 2.36, 2.33 (s, 6:3:3:6 H, $Tp'CCH_3$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 223.3 ($^{1}J_{CH} = 164$ Hz, 2W(*C*O)), 183.2 (s, $W\equiv C-I$), 153.2, 152.8, 146.4, 145.5 (1:2:1:2, $Tp'CCH_3$), 107.2, 106.9 (1:2, $Tp'CH$), 16.3, 15.5, 12.8, 12.7 (2:1:1:2, $Tp'CCH_3$). Anal. Calcd for $C_{18}H_{22}N_6BO_2WI$: C, 31.98; H, 3.28; N, 12.43. Found: C, 33.87; H, 3.61; N, 12.01.

$Tp'(CO)_2W\equiv C-C(Ph)_2(OH)$ (13). A Schlenk flask was charged with $Tp'(CO)_2W\equiv C-H$ (0.154 g, 0.279 mmol). $Tp'(CO)_2W\equiv C-Li$ was generated in situ with method b. After being stirred for 30 min at −78 °C, a separately prepared 10 mL THF solution of benzophenone (0.256 g, 1.400 mmol, 5 equiv) cooled to −78 °C was transferred via cannula to the orange $Tp'(CO)_2W\equiv C-Li$ solution. An immediate color change from orange to green was observed. An additional 30 min of stirring at −78 °C resulted in a gradual color change from green to yellow, and the reaction was then quenched with 0.1 mL of water. The THF solvent was removed under reduced pressure to give a brown residue that was dissolved in a minimal amount of dichloromethane and transferred to a hexanes packed alumina column. Gradual increase of eluent strength from 1:1 dichoromethane:hexanes to dicloromethane elutes a small yellow fraction of the starting material $Tp'(CO)_2W\equiv C-H$, as assayed by IR. A further increase in eluent strength to 4:1 CH_2Cl_2:MeOH elutes a large bright yellow fraction. The solvent from the bright yellow fraction was removed under reduced pressure to give a green-yellow oil that was dissolved in 10 mL of *n*-pentane. Sonication of this yellow pentane solution results in the precipitation of a bright yellow powder. The supernatant pentane was filtered away from the bright yellow solid with a cannula covered with Whatman No. 5 filter paper. Rinsing of the solid with 3 × 10 mL aliquots of pentanes followed by removal of residual solvent under reduced pressure gave $Tp'(CO)_2W\equiv CCPh_2OH$ (0.080 g, 40% yield). IR (neat solid): 3552 cm^{-1} (ν_{OH}), 2549 cm^{-1} (ν_{BH}), 1974, 1876 cm^{-1} (ν_{CO}), 1544 cm^{-1} (ν_{CN}). ^{1}H NMR (CD_2Cl_2): δ 7.63 (m, 4 *H*Ph), 7.33 (m, 6 *H*Ph), 5.94, 5.84 (s, 2:1 H, $Tp'CH$), 3.22 (s, O*H*), 2.44, 2.43, 2.37, 2.28 (s, 6:3:3:6 H, $Tp'CCH_3$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 284.4 ($^{1}J_{WC} = 193$ Hz, $W\equiv C-C(Ph)_2OH$), 224.3 ($^{1}J_{CH} = 165$ Hz, W(*C*O)), 152.8, 152.3, 145.9, 145.51 (1:2:1:2, $Tp'CCH_3$), 144.9 (2 C ipso), 128.2 ($^{1}J_{CH} = 169$ Hz, 2 C ortho), 127.6 ($^{1}J_{CH} = 158$ Hz, 2 C meta), 127.5 ($^{1}J_{CH} = 159$ Hz, 1 C para), 107.0, 106.7 (1:2, $Tp'CH$), 90.1 ($^{2}J_{CW} = 34$ Hz, $W\equiv C-C(Ph)_2OH$), 16.7, 15.2, 12.8, 12.5 (2:1:2:1, $Tp'CCH_3$). Anal. Calcd for $C_{31}H_{33}N_6BO_3W$: C, 50.80; H, 4.54; N, 11.45. Found: C, 51.41; H, 4.95; N, 11.25.

$Tp'(CO)_2W\equiv C-C(Ph)(H)(OH)$ (14). A Schlenk flask was charged with $Tp'(CO)_2W\equiv C-H$ (0.122 g, 0.222 mmol). $Tp'(CO)_2W\equiv C-Li$ was generated in situ with method b. After the mixture was stirred for 30 min at −78 °C, an aliquot of benzaldehyde (31 μL, 0.32 mmol) was added to the orange $Tp'(CO)_2W\equiv C-Li$ solution. An immediate color change from bright orange to yellow was observed. The IR spectrum reveals absorbances at $\nu_{CO} = 1980, 1888\ cm^{-1}$ and 1964, 1872. The solution was stirred for 15 min then 55 μL of distilled water was added and the solution was allowed warmed to room temperature. The IR spectrum of the resulting yellow solution showed a single carbonyl containing species with $\nu_{CO} = 1980, 1888\ cm^{-1}$. The THF solvent was removed under reduced pressure to give a brown residue that was dissolved in a minimal amount of dichloromethane and transferred to a hexanes-packed alumina column. A single yellow fraction elutes with 9:1 dichloromethane:THF. The solvent from the bright yellow fraction was removed under reduced pressure to give a brown residue that was washed with 3 × 5 mL of pentane. The pentane was filtered away from the bright yellow solid by using a cannula equipped with Whatman No. 5 filter paper. Removal of residual solvent under reduced pressure gave $Tp'(CO)_2W\equiv C-C(Ph)(H)(OH)$ as a yellow powder (0.145 g, 45% yield). IR (KBr): 3447 cm^{-1} (ν_{OH}), 2548 cm^{-1} (ν_{BH}), 1976, 1880 cm^{-1} (ν_{CO}), 1544 cm^{-1} (ν_{CN}). ^{1}H NMR (C_6D_6): δ 7.53 (m, 2 *H* ortho), 7.19 (m, 2 *H* meta), 7.08 (m, 1 *H* para) 5.53, 5.51, 5.32 (s, 1:1:1 H, $Tp'CH$), 5.28 (s, $^{3}J_{WH} = 5$ Hz, $[W]\equiv C-C(H)(Ph)(OH)$) 2.50, 2.48, 2.38, 2.04, 2.03, 1.97 (s, 3 H each, $Tp'CCH_3$). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): δ 284.3 ($^{1}J_{WC} = 191$ Hz, $W\equiv C-C(Ph)(H)(OH)$), 224.2, 224.1 ($^{1}J_{CW} = 164$, 164 Hz, 2 diastereotopic W(*C*O)), 152.7, 152.2, 152.1, 144.9, 144.4, 144.3 (1 C each, 1:1:1:1:1:1, $Tp'CCH_3$), 141.5 (*C* ipso), 128.8, 128.3, 128.1, 127.9, 127.3 (1 C each 5 aryl carbons), 107.2, 106.91, 106.88 (1:1:1, $Tp'CH$), 86.3 ($^{2}J_{CW} = 40.0$ Hz, $W\equiv C$-*C*(Ph)(H)(OH), 16.9, 15.4, 12.6, 12.5 (2:1:2:1, $Tp'CCH_3$). Anal. Calcd for $C_{25}H_{29}N_6BO_3W$: C, 45.76; H, 4.45; N, 12.81. Found: C, 45.11; H, 4.74; N, 12.26.

$Tp'(CO)_2W\equiv C-C(O)Ph$ (15). A Schlenk flask was charged with $Tp'(CO)_2W\equiv C-H$ (0.151 g, 0.275 mmol). $Tp'(CO)_2W\equiv C-Li$ was generated in situ with method b. After the mixture was stirried for 30 min at −78 °C, an aliquot of benzoyl bromide (76 μL, 0.66 mmol) was syringed into the orange $Tp'(CO)_2W{\equiv}C{-}Li$ solution. The solution immediately changed to a brown-green color. After removing the cold bath and gradually warming to room temperature, the solvent was removed under reduced pressure to yield a brown-green residue. The solid was dissolved in 5 mL of dichloromethane and transferred to a hexanes packed alumina column. Gradual increase of eluent strength from hexanes to 1:1 hexanes:dichloromethane elutes a bright yellow band that was $Tp'(CO)_2W{\equiv}C{-}H$ as assayed by IR. Increasing eluent strength to CH_2Cl_2 elutes a bright green band containing the desired product. Removal of solvent via rotary evaporation, trituration with 3 × 5 mL of pentanes, and removal of residual solvent under vacuum gave emerald green microcrystalline solid $Tp'(CO)_2W{\equiv}C{-}C(O)Ph$ (0.026 g, 13% yield). Recrystallization from 1 mL of dichloromethane layered with 20 mL of pentane at −30 °C gives crystals suitable for X-ray crystallography. IR (KBr): 2548 cm^{-1} (ν_{BH}), 1999, 1918 cm^{-1} (ν_{CO}), 1542 cm^{-1} (ν_{CN}). ^{1}H NMR (CD_2Cl_2): δ 8.15 (d) 7.55 (t), 7.44 (t) (2:1:2 phenyl H) 5.88, 5.85 (s, 2:1 H, Tp′C*H*), 2.45, 2.38, 2.37, (s, 9:6:3 H Tp′CC*H*$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 277.3 ($^1J_{WC}$ = 188 Hz, W≡*C*−C(O)Ph), 225.5 ($^1J_{WC}$ = 161 Hz, 2 C W(*C*O)), 189.8 ($^2J_{WC}$ = 45 Hz, W≡C−(*C*O)(Ph)), 153.2, 152.2, 146.6, 145.8 (1:2:1:2, Tp′*C*CH$_3$), 136.5 (s, C ipso), 133.0 (d, $^1J_{CH}$ = 169 Hz, 2 C para) 130.2 (d, $^1J_{CH}$ = 160.2 Hz, 2 C meta), 129.0 (d, $^1J_{CH}$ = 161 Hz, 1 C ortho) 107.3, 107.0 (2:1, Tp′*C*H), 16.6, 15.4, 12.8 (2:1:3, Tp′CC*H*$_3$). Anal. Calcd for $C_{25}H_{27}N_6O_2BW$: C, 45.86; H, 4.16; N, 12.84. Found: C, 45.49; H, 4.36; N, 12.14.

[Na][Tp′(CO)$_2$W=CH$_2$] (16): Method a. A 5 mm NMR tube was charged with $Tp'(CO)_2W{\equiv}C{-}H$ (0.046 g, 0.084 mmol) and 0.6 mL of THF-*d*$_8$ then sealed with a rubber septum. The tube was then immersed in a −78 °C dry ice−acetone bath. Once cooled, an aliquot of 1 M $NaHBEt_3$ in ether solution (200 μL, 0.20 mmol, 2.4 equiv) was added via syringe to the NMR tube which was then shaken. The sample was inserted into the cooled spectrometer probe at 193 K. NMR spectra were obtained at ∼10 K increments between 193 and 298 K. ^{1}H NMR (THF-*d*$_8$ at 193 K): δ 13.90, 12.73 (both s, 1 H each, W=C*H*$_2$), 5.66, (s, 3 H, Tp′C*H*), 2.45, 2.40, 2.34, 2.02 (s, 6:3:6:3 H, Tp′CC*H*$_3$). ^{13}C{^{1}H} NMR (THF-*d*$_8$ at 298 K): δ 265.0 (t, $^1J_{CH}$ = 122 Hz, $^1J_{WC}$ = 132 Hz, W=*C*H$_2$), 258.5 (s, $^1J_{WC}$ = 178 Hz, W(*C*O)), 154.8, 150.9, 143.5, 142.6 (1:2:1:2, Tp′*C*CH$_3$). 105.9, 105.5 (1:2, Tp′*C*H). The Tp′C*C*H$_3$ signals could not be assigned due to the carbon resonances from excess $NaHBEt_3$ in that region. Complex **16** was stable in THF-*d*$_8$ solution for several days before decomposition could be observed by NMR.

Method b. A Schlenk flask was charged with $Tp'(CO)_2W{\equiv}C{-}H$ (0.199 g, 0.362 mmol), 20 mL of THF, and a stirbar. The flask was immersed in a −78 °C dry ice−acetone bath and an aliquot of 1 M $NaHBEt_3$ in ether solution (0.90 mL, 0.90 mmol, 2.5 equiv) was added to the yellow solution. Upon hydride addition, the solution turns brownish orange. After the mixture was stirred at −78 °C for 5 min the methylidene could be observed by IR. IR (THF): 2521 cm^{-1} (ν_{BH}), 1822, 1679 cm^{-1} (ν_{CO}), 1544 cm^{-1} (ν_{CN}).

Tp′(CO)$_2$W(η^2-CH$_2$SPh) (17). Complex **16** was generated with method b above. The brown THF solution of **16** was warmed to room temperature and solid PhSSPh (0.198 g, 0.90 mmol) was added to the vessel under positive nitrogen pressure. A rapid color change to bright yellow was observed. The IR spectrum displays three carbonyl absorbances at 1733, 1799, and 1934 cm^{-1}. After the mixture was stirred at room temperature for 15 min the intensity of the carbonyl absorption at 1733 cm^{-1} shrank while the 1934 and 1799 cm^{-1} absorptions grew. After 15 more minutes of stirring, the solvent was removed in vacuo to give a yellow green residue that was dissolved in CH_2Cl_2 and transferred to a hexanes packed alumina column. An orange fraction that elutes with CH_2Cl_2 was collected. The solvent was evaporated to give 0.045 g (20% yield) of orange solid Tp′(CO)$_2$W(η^2CH$_2$SPh). Complex **17** was recrystalized into X-ray quality orange prismatic crystals containing half a molecule of benzene per unit cell by dissolving the orange solid into refluxing benzene followed by filtration and cooling to room temperature. IR (KBr): 2544 cm^{-1} (ν_{BH}), 1926, 1799 cm^{-1} (ν_{CO}), 1544 cm^{-1} (ν_{CN}). ^{1}H NMR (C_6D_6): δ 6.7 (m, 5 *H*, S−C$_6$*H*$_5$), 5.53, 5.34, 5.33 (s, 1:1:1 H, Tp′C*H*), 4.50, 4.23 (1 H each, each a d, $^2J_{HH}$ = 6 Hz, W−C*H*$_2$−S), 2.82, 2.68, 2.14, 1.99, 1.97 (s, 3:3:6:3:3 H, Tp′CC*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 229.1, 222.8, (2 diastereotopic W(*C*O)), 155.4, 154.4, 153.4, 144.4, 144.3, 144.1(1 C each, 1:1:1:1:1:1, Tp′*C*CH$_3$), 136.1 (*C* ipso), (1 C each 5 aryl carbons), 107.9, 107.7, 107.3 (1:1:1, Tp′C*H*), 46.8 (1 C, t, $^1J_{CH}$ = 159 Hz, W−*C*H$_2$−S), 16.6, 16.5, 14.2, 12.7, 12.5 (1:1:1:1:2, Tp′C*C*H$_3$). Anal. Calcd for $C_{27}H_{32}N_6BO_2SW$: C, 46.37; H, 4.61; N, 12.01. Found: C, 46.70; H, 4.66; N, 12.00.

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Supporting Information Available: Tables of crystallographic data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anistotropic thermal parameters for **15**, [**15**][$Tp'(CO)_2W{\equiv}C{-}C(O)Ph$], **17**, and [**17**]-[Tp′(CO)$_2$W(η^2-CH$_2$SPh)], reflectance IR spectra of **4,** [**4**][$Tp'(CO)_2W{\equiv}C{-}H$], **4-*d*** and [**4-*d***][$Tp'(CO)_2W{\equiv}C{-}D$], and a stacked plot of the Fluorolube mull IR spectra of **4** and **4-*d*** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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