Articles

Synthesis and β'-Site Deprotonation/Alkylation Reactions of $Tp'(CO)_2W(\eta^2$-vinyl) Complexes

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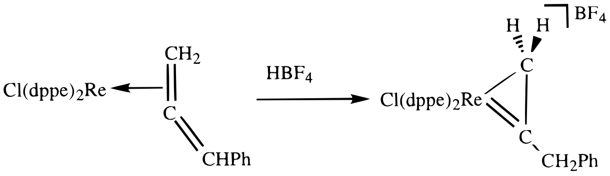
Addition of hydride to the terminal alkyne carbon of $[Tp'(CO)_2W(\eta^2\text{-}RCH_2C{\equiv}CH)][OTf]$ (Tp' = hydridotris(3,5-dimethylpyrazolyl)borate; R = H, Pr^n, Ph; OTf = O_3SCF_3) complexes with $LiHBEt_3$ as the nucleophile yields the η^2-vinyl complexes $Tp'(CO)_2W(\eta^2\text{-}C(CH_2R){=}CH_2)$, which have β'-hydrogens[1] located on the vinyl substituent. Deprotonation of the η^2-vinyl (or 1-metallacyclopropene) complexes with *n*-BuLi or *t*-BuLi removes a β'-hydrogen and produces reactive, anionic η^2-allene species, $[Li][Tp'(CO)_2W(\eta^2\text{-}CH_2{=}C{=}CHR)]$. Quenching of the allene intermediates for R = H, Pr^n with MeI results in methylation to form derivative η^2-vinyl complexes, $Tp'(CO)_2W(\eta^2\text{-}C(CHRMe){=}CH_2)$. Addition of benzaldehyde to the anionic η^2-propylallene intermediate followed by acidification yields diastereomers of the alcohol product $Tp'(CO)_2W(\eta^2\text{-}C(CH(CHOH)Ph)Pr){=}CH_2)$.

Introduction

The isolobal analogy between η^2-vinyl and four-electron-donor alkyne ligands[2,3] has been a driving force in the synthetic methodology leading to η^2-vinyl ligands. Addition of nucleophiles to d^4 transition metals with four-electron-donor alkyne ligands is the most common route to d^4 $L_nM(\eta^2$-vinyl) (M = Mo(II), W(II), Re(III)) transition-metal η^2-vinyl complexes (Scheme 1).[3−8] In contrast, nucleophilic addition to two-electron-donor alkyne ligands in Fe(II) d^6 complexes produces η^1-vinyl complexes.[9−11] Comparable reactions between a variety of nucleophiles and bis(alkyne) complexes yield either η^1-vinyl ($2e^-$ donor) complexes[12] or η^2-vinyl ($4e^-$ donor) complexes, depending on the donor properties of the ancillary ligands.[13−17]

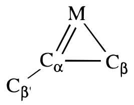
Relevant to the work reported here, the protonation of allene complexes has also produced η^2-vinyl complexes. Pombeiro and co-workers have reported the first η^2-vinyl complex of rhenium, $[(dppe)_2(Cl)Re(\eta^2\text{-}C(CH_2Ph){=}CH_2)][BF_4]$, via protonation of $(dppe)_2(Cl)Re(\eta^2\text{-}CH_2{=}C{=}CHPh)$ with HBF_4 (eq 1).[18−20] Green et al. have reported that the deprotonation of $[Cp(dppe)Re(\eta^2\text{-}C(CH_3){=}CHPh)][BF_4]$ yields an allene complex, $Cp(dppe)Re(\eta^2\text{-}CH_2{=}C{=}CHPh)$, which can be reprotonated



(1)

[†] Presently at Mercyhurst College, Erie, PA.

(1) To differentiate between the two β-positions of the η^2-vinyl ligands, the carbon bound to the metal is termed β and the first carbon of the η^2-vinyl substituent is termed β':



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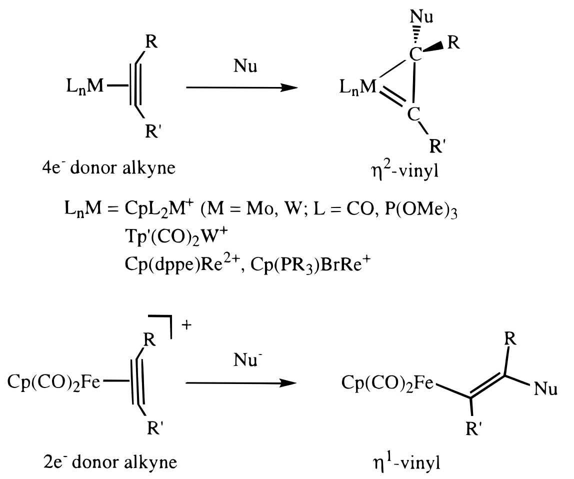
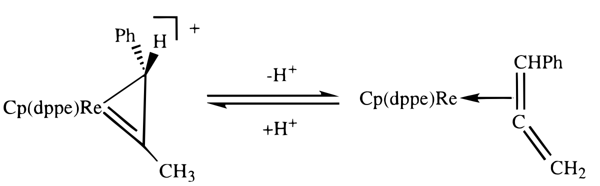
Scheme 1. Nucleophile Addition to 4e− and 2e− Donor Alkyne Ligands



to form the original η^2-vinyl complex (eq 2).[8] In both cases, the allene complex is ultimately derived from an alkyne ligand.[8,21] Casey and co-workers have recently exposed relationships between alkyne, η^2-vinyl, η^3-allyl, and allene ligands in a rhenium system by observing acid-catalyzed rearrangements of alkyne ligands in Cp*-(CO)$_2$Re(RC≡CR) complexes to allene and η^3-allyl ligands through observable η^2-vinyl intermediates.[22,23]



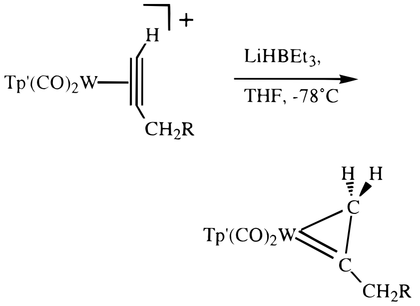
(2)

The propargyl site of 4e$^-$ donor alkynes in neutral Tp′-(CO)(I)W(RC≡CR′) complexes can be regioselectively deprotonated and alkylated to form new alkyne derivatives.[24,25] The isolobal link between 4e$^-$ donor alkyne ligands and η^2-vinyl ligands suggests that similar reactivity could be available to η^2-vinyl ligands. This reasoning is further supported by noting that η^2-vinyl complexes are also isolobal with η^2-acyl complexes, which can also undergo β-deprotonation followed by alkylation to form new η^2-acyl complexes.[26−28] Would deprotonation/alkylation of the β'-site of an η^2-vinyl ligand, the analogue of the alkyne propargyl site and the η^2-acyl β-site, lead to derivative η^2-vinyl complexes? Extension of the results seen for the rhenium systems forecasts β'-deprotonation/alkylation for Tp′(CO)$_2$W(η^2-C(CH$_2$R)═CR$_2$) complexes, but access to such complexes has been hindered by facile isomerization into η^3-allyl complexes.[6,29,30]

Surveys of stable η^2-vinyl ligand substituents reveal an abundance of phenyl groups; *tert*-butyl, trimethylsilyl, and trifluoromethyl groups are common, but there are relatively few simple alkyl substituents.[4,33] In general, the most prevalent mode of reaction for L$_n$M-(η^2-C(CH$_2$R′)═CR$_2$) complexes is isomerization to allyl isomers, L$_n$M(η^3-CR$_2$CHCHR′).[4−6,22,23,29−32] The availability of Tp′(CO)$_2$W(η^2-C(CH$_2$R)═CH$_2$) (R = H, Pr^n, Ph) complexes with β'-hydrogens has allowed us to test the orbital analogies for reactivity at the β'-site in this system. We report here the elaboration of Tp′(CO)$_2$W-(η^2-C(CH$_2$R)═CH$_2$) complexes by deprotonation to form anionic η^2-allene species, [Li][Tp′(CO)$_2$W(η^2-H$_2$C═C═CHR)], and subsequent alkylation to form Tp′(CO)$_2$W-(η^2-C(CHRR′)═CH$_2$) complexes.

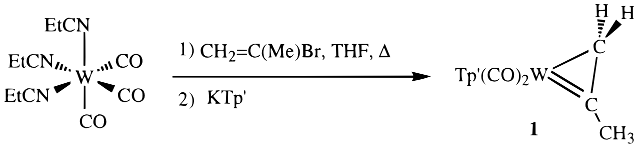
Results

Synthesis of Tp′(CO)$_2$W(η^2-C(CH$_2$R)═CH$_2$) Complexes. Low-temperature addition of LiHBEt$_3$ to THF solutions of cationic, four-electron-donor alkyne complexes, Tp′(CO)$_2$W(η^2-RC≡CH), produced the corresponding α-substituted η^2-vinyl complexes (eq 3); yields for the reactions decreased roughly as the size of the alkyne substituent increased. Formation of the η^2-vinyl complexes appears to be immediate at −78 °C and is accompanied by a sharp color change from dark green to bright orange. No intermediates such as σ-vinyl or metal hydride complexes have been detected.



1: R = H; 81%
2: R = *n*-Pr; 65%;
3: R = Ph; 45%

(3)



(4)

Reaction of (CH$_3$CH$_2$CN)$_3$W(CO)$_3$ with 2-bromopropene in refluxing THF followed by the addition of KTp′ produced the methyl η^2-vinyl complex **1**, in very low yield (6%) (eq 4). Multiple carbonyl containing species were noted in the IR spectrum of the reaction mixture

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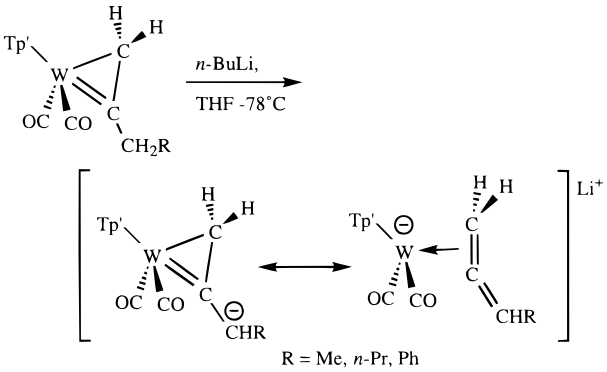
Table 1. Selected Spectroscopic Data for Tp′(CO)$_2$W(η^2-C(R)=CH$_2$) Complexes[a]

	^{1}H NMR		^{13}C NMR			
R, R′	H$_b$	H$_{b'}$	C$_a$	C$_b$	C$_{b'}$	CO
1: R = R′ = H	1.37	3.23, $^4J_{HH} = 3$	248.0	17.5; (157)	34.6 (127)	220.0 [160]
2: R = H, R′ = Pr^n	1.28	3.36 (7.2), $^4J_{HH} = 3$	260.4	15.6 (158)	48.7 (127)	220.0 [158]
4: R = H, R′ = Me	1.30	3.43 (7.5), $^4J_{HH} = 2.5$	252.7[b]	15.0	42.0	220.0
5: R = Me, R′ = Pr^n	1.18, $^4J_{HH} = 3$	3.82, m	254.3 [29]	obscured	52.3 (130)	220.0 [158]
						219.8 [157]
6: R = CH(CH(OH)Ph, R′ = Pr^n	1.30	4.05, m	246.0 [29]	15.7 (158)	65.2 (132)	220.3 [157]
						220.1 [151]

[a] Atoms are labeled as follows: Tp′(CO)$_2$W(η^2-C$_\alpha$(C$_{\beta'}$)=C$_\beta$). NMR data were taken in CDCl$_3$, except as noted. Chemical shift values are in ppm. Coupling constant values are in Hz: $^3J_{HH}$ and $^1J_{CH}$ coupling constant values are given in parentheses; $^1J_{WX}$ values are given in brackets. [b] Value obtained in CD$_2$Cl$_2$.

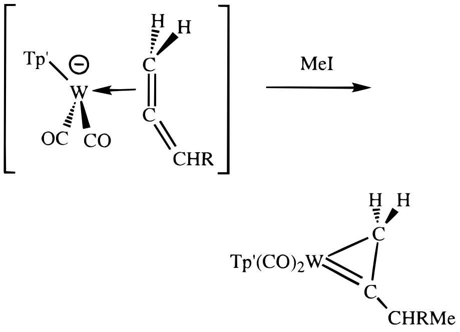
during each stage of the reaction. However, **1** was the only complex isolated after alumina chromatography.

Deprotonation at the β' Site and Elaboration with Electrophiles. Low-temperature addition of *n*-BuLi or *t*-BuLi to orange THF solutions of Tp′(CO)$_2$W(η^2-C(CH$_2$R)=CH$_2$) (R = H, Pr^n, Ph) produced color changes to brilliant yellow. Monitoring of the reaction solutions by IR showed the appearance of intense low-energy absorbance bands near 1880 and 1670 cm^{-1} due to the carbonyl ligands of anionic allene intermediates, [Li][Tp′(CO)$_2$W(η^2-CH$_2$=C=CHR)] (eq 5).



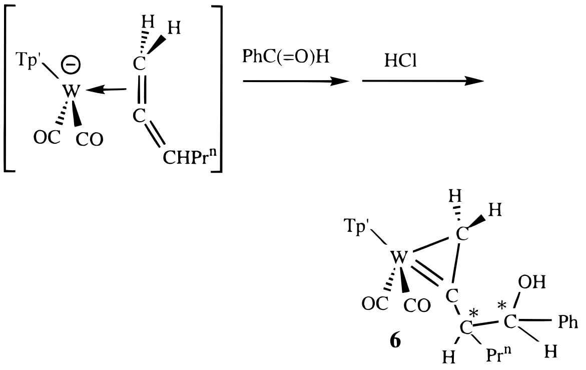
(5)

Quenching of the allene intermediates for R = H and R = Pr^n with MeI produced the derivative η^2-vinyl products Tp′(CO)$_2$W(η^2-C(CH(Me)(R)=CH$_2$ (**4**, R = H; **5**, R = Pr^n) (eq 6). In contrast, the anionic phenylallene species [Li][Tp′(CO)$_2$W(η^2-CH$_2$=C=CHPh)], produced by deprotonation of the benzyl substituent in complex **3**, did not react with MeI at room temperature. Reaction of the propylallene species [Li][Tp′(CO)$_2$W(η^2-CH$_2$=C=CHPr^n)] with benzaldehyde followed by treatment with HCl produced a 1:1 mixture of diastereomers (**6**) in which an alcohol functionality had been incorporated into the η^2-vinyl ligand (eq 7). Low-temperature recrystallization with CH$_2$Cl$_2$/hexanes allowed the isolation of one diastereomer of **6** for complete characterization.



4: R = H
5: R = Pr^n

(6)



(7)

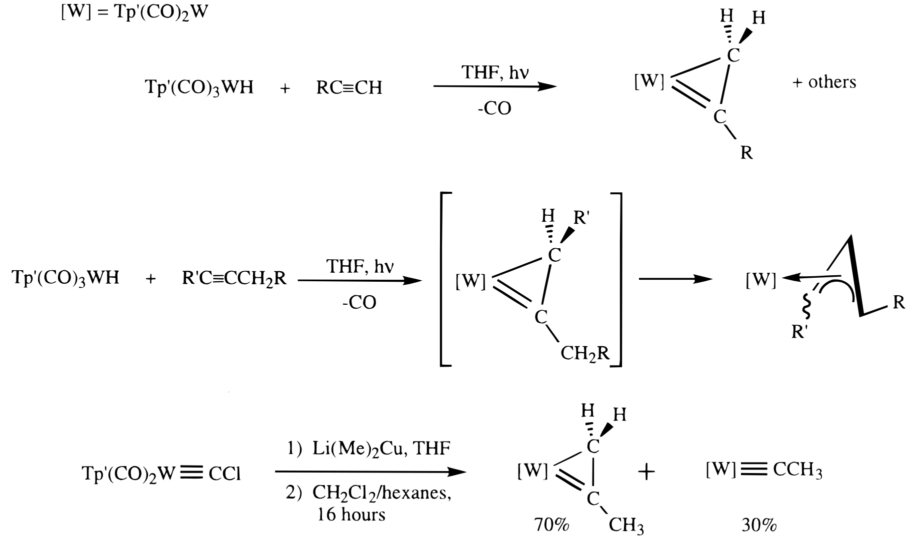
Spectroscopic Characterization of Tp′(CO)$_2$W(η^2-vinyl) Complexes. NMR spectra for complexes **1**−**6** (Table 1) are consistent with the 1-metallacyclopropene resonance form. The ^{1}H NMR spectra of the complexes lacking chiral substituents (**1**−**4**) revealed effective mirror planes in solution. Signals for the β-methylene groups of **1**−**6** were found at moderately high fields (1.2−1.6 ppm) as broadened signals, presumably because of a 90° back-and-forth oscillation (a “windscreen wiper” motion) common to related η^2-vinyl complexes.[4,5] Signals for the methylene groups in the β'-site were located at lower fields (3.2−4.6 ppm) compatible with proximity to an effective metal−carbon double bond.

In the ^{13}C NMR spectra, signals for the α-carbons of **1**−**6** were found in the range of 230−260 ppm, whereas signals for the β-carbons resonated considerably upfield (14−18 ppm). The β-carbons also exhibited $^1J_{CH}$ values near 160 Hz. Coupling values to tungsten of about 30 Hz were observed in complexes **5** and **6** for the C$_\alpha$ carbons. Signals for the terminal carbonyl ligands of **1**−**6** were found near 220 ppm with moderate $^1J_{WC}$ values of 150−160 Hz. The chirality of the substituents in derivatives **5** and **6** was reflected in unique resonances for the pyrazole ring carbons and both of the carbonyl carbons in the ^{13}C NMR spectra.

Discussion

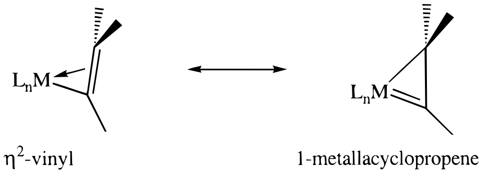
Access to Tp′(CO)$_2$W(η^2-C(CH$_2$R)=CR′$_2$) complexes is necessary in order to probe acid/base reactivity at the β'-site, but such complexes have a propensity to isomerize into the η^3-allyl isomer, Tp′(CO)$_2$W(η^3-CHRCH-CR′$_2$).[6,29,30] Here, three η^2-vinyl complexes with β'-hydrogens (R = H (**1**), Pr^n (**2**), and Ph (**3**)), have been

Scheme 2. Alternative Synthetic Routes to Tp′(CO)$_2$W(η^2-vinyl) Complexes



prepared and characterized in order to explore deprotonation at the β'-site prior to competing rearrangement to the η^3-allyl isomers. Complexes **1**−**3** will isomerize into η^3-allyl isomers at room temperature in nonaromatic solvents or under reflux conditions in toluene. However, these rearrangements are slow compared to those of Tp′(CO)$_2$W(η^2-C(CH$_2$R)=CHR′) complexes that have β'-hydrogens and a substituent at the vinyl β-site. For example, Tp′(CO)$_2$W(η^2-C(Me)=CHR) (R = Me, Ph) complexes rearrange into Tp′(CO)$_2$W(η^3-CH$_2$CHCHR) isomers within a few hours,[6] whereas the complete conversion of Tp′(CO)$_2$W(η^2-C(Bu^n)=CH$_2$) into Tp′(CO)$_2$W(η^3-CH$_2$CHCHPr^n) takes more than 1 week at room temperature. In related CpL$_2$Mo systems, reaction of [Cp(P(OMe)$_3$)$_2$Mo(η^2-MeC≡CR)]$^+$ complexes with KHB(*sec*-Bu)$_3$ produces η^3-allyl complexes without detectable η^2-vinyl intermediates.[32] We believe that the sluggish kinetics for the η^2-vinyl → η^3-allyl isomerization for Tp′(CO)$_2$W(η^2-C(CH$_2$R)=CH$_2$) complexes is due to a combination of (1) minimal steric repulsion between the vinyl β-substituents and the metal coordination sphere, (2) the general kinetic inertness of tungsten relative to molybdenum, and (3) the reluctance for Tp′-containing complexes to adopt 7-coordination relative to Cp-containing complexes.[34] Although several different routes have produced η^2-vinyl complexes in the Tp′(CO)$_2$W system (Scheme 2), simple hydride addition to cationic alkyne complexes remains the preferred synthetic route. Photolysis of Tp′(CO)$_3$WH with terminal alkynes has been used to produce Tp′(CO)$_2$W(η^2-vinyl) complexes, although competing carbyne, η^2-acyl, and metallafuran formation has limited the utility of this method.[30] The use of internal alkynes having propargyl hydrogens in the photochemistry available from Tp′(CO)$_3$WH generally leads to η^3-allyl complexes, although η^2-vinyl intermediates have been detected spectroscopically.[29,30] An unusual thermal route to **1** from Tp′(CO)$_2$W≡CCl and lithium dimethylcuprate has also been reported.[35] Efforts here to synthesize η^2-vinyl complexes directly from a tungsten(0) reagent and avoid the use of silver salts necessary to produce cationic alkyne complexes were only marginally successful. The reaction of (CH$_3$CH$_2$CN)$_3$W(CO)$_3$ with 2-bromopropene and KTp′ produced the methyl η^2-vinyl complex **1**, in yields too low to be useful. The oxidative addition of 2-bromopropene is complete within 5 min, and the reaction with KTp′ occurs on a similar time scale, but multiple products form (as monitored via IR) and isolation via chromatography produces only a small amount of the η^2-vinyl product.

Scheme 3. Alternative Bonding Representations for L$_n$M(η^2-CR=CR$_2$) Complexes



Of the two common representations for η^2-vinyl ligands (Scheme 3), the 1-metallacyclopropene form more accurately reflects the physical properties of the metal−ligand unit. In the ^{13}C NMR spectra, the crucial parameters are a high-frequency (low-field) shift (>200 ppm) for the carbon with only one substituent (C$_\alpha$) and a low-frequency shift (10−50 ppm) for the carbon with two substituents (C$_\beta$).[4,5] These chemical shift values reflect M−C$_\alpha$ double-bond character and sp^3 hybridization around C$_\beta$, respectively. Accordingly, $^1J_{\text{CH}}$ coupling constant values for C$_\beta$ (150−160 Hz) are in the appropriate range for strained-ring systems. The C$_\alpha$ and C$_\beta$ chemical shifts (246−260 and 35−65 ppm, respectively) and C$_\beta$ $^1J_{\text{CH}}$ coupling constant values (155−158 Hz) for complexes **1**−**6** are typical for L$_n$M(η^2-vinyl) complexes. Single-crystal X-ray studies of η^2-vinyl complexes also support the 1-metallacyclopropene formalism with a short M−C$_\alpha$ bond and a longer M−C$_\beta$ bond.[4,5]

Casey has recently argued accurately and persuasively for the 1-metallacyclopropene nomenclature as the preferred description for these ligands. Why has the η^2-vinyl, or η^2-alkenyl, nomenclature been retained in

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[34] It is generally assumed that a 7-coordinate allene hydride intermediate forms in the η^2-vinyl to η^3-allyl rearrangement. See refs 3, 5, 6, and 29 for additional information.

[35] Woodworth, B. E.; Frohnapfel, D. S.; White, P. S.; Templeton, J. L. *Organometallics* **1998**, *17*, 1655.

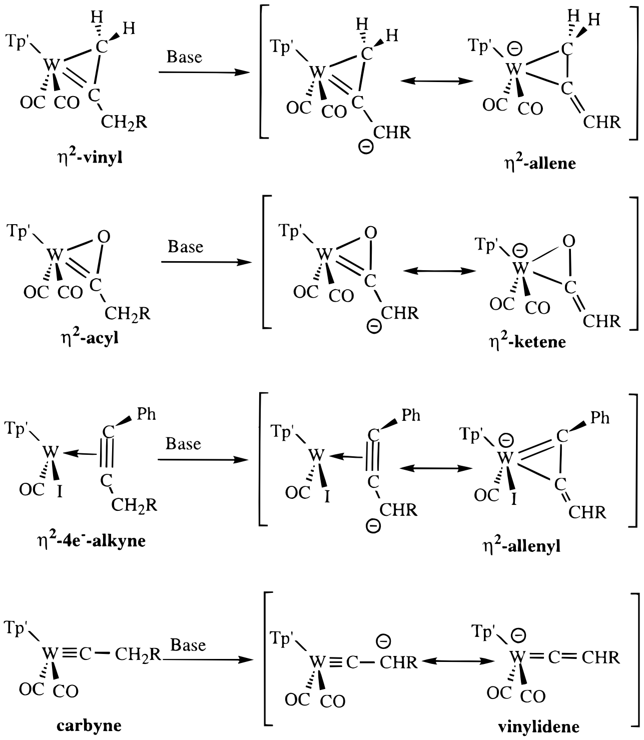
the literature? In the same way that the metallacyclopropene name is accurate for physical properties, many 4e$^-$ donor alkyne ligands, the most common precursor to the η^2-vinyl ligand, are best described as metallacyclopropenes, as judged by structural and spectroscopic parameters.[4] Yet, the alkyne terminology is still used to describe this nonlinear RC≡CR ligand. Perhaps more importantly, chemists can readily visualize hydride addition to an alkyne ligand (RC≡CR) as a route to the vinyl fragment ([CR=CRH]$^-$), while hydride addition to a 3-metallacyclopropene to form a 1-metallacyclopropene is not as intuitively attractive.

A second possible reason for utilizing the η^2-vinyl nomenclature is to highlight the possibility of changes in binding mode, either $\eta^2 \rightarrow \eta^1$ or $\eta^1 \rightarrow \eta^2$, for vinyl ligands. Rationales for studying transition-metal η^2-vinyl complexes have been predicated on the observation that σ-vinyl intermediates in alkyne polymerization pathways could be stabilized through an η^1(2e$^-$) → η^2(4e$^-$) change in coordination mode.[13,36] A similar thought is that η^2-vinyl species may provide a low-energy route for *E*/*Z* isomerization of η^1-vinyl ligands.[14,37] Exchange of the β-carbon substituents for η^2-vinyl ligands[16,38] and the isomerization into η^3-allyl isomers[5,6] are both assumed to proceed by an initial $\eta^2 \rightarrow \eta^1$ change in coordination mode for the η^2-vinyl ligand.

Deprotonation of the β'-site of the η^2-C(CH$_2$R)=CH$_2$ ligands leads to reactive anionic complexes that are postulated to be allene complexes on the basis of their reactivity and by analogy to the rhenium chemistry mentioned earlier.[8,18] Delocalization of negative charge onto the metal center is reflected in a large decrease in the terminal carbonyl stretching frequencies. The large separation of nearly 200 cm^{-1} between the two CO bands suggests strong, site-specific ion pairing between the lithium counterion and one of the carbonyl oxygens, as opposed to lithiation at the β'-carbon.[39,40] The allene intermediates are immediately quenched by any traces of water in the IR cells to re-form the parent compounds. Addition of methyl iodide leads to derivative η^2-vinyl products for both the methyl (**1**) and *n*-butyl (**2**) η^2-vinyl starting materials. Likewise, benzaldehyde adds to the uncoordinated allene carbon of the anionic intermediate formed via deprotonation of **2**. The absence of nucleophilicity for the phenylallene species here is probably due to steric congestion at the reactive site as well as dispersal of charge around the aromatic ring.

Successful derivatization of Tp′(CO)$_2$W(η^2-C(CH$_2$R)=CH$_2$) complexes by simple deprotonation/alkylation sequences highlights the value of isolobal arguments in predicting the chemistry available to η^2-vinyl ligands. As shown in Scheme 4, deprotonation of η^2-vinyl ligands to form complexed allene ligands directly parallels the deprotonation of η^2-acyl ligands and 4e$^-$ donor alkyne ligands to produce η^2-bound ketene and allenyl ligands, respectively. A similar correspondence also exists in the deprotonation of carbyne ligands to form vinylidene ligands. In each case, the β-protons of alkyl substituents are activated toward removal by bases due to the ability of the metal to house two additional electrons in the resonance form favored by the anionic intermediate. Each of the reactive anionic intermediates is stabilized by a formal reduction at the metal via resonance delocalization of the negative charge away from the carbanion. For the η^2-vinyl to η^2-allene transformation reported here, this feature is clearly reflected in the low-energy IR absorbances for the CO groups in the allene intermediates. A similar drop in ν_{CO} absorbances relative to the parent compounds has been noted for anionic η^2-ketenyl, [Tp′(CO)(L)Mo(η^2-C(=O)=CHR)]$^-$,[27,28] and anionic vinylidene, [Tp′(CO)$_2$W=C=CHR]$^-$,[41] complexes.

Scheme 4. Resonance Delocalization in Anionic Tp′(CO)$_2$W(η^2-allene) and Related Ligands



Experimental Section

General Methods. Manipulations involving air-sensitive reagents were performed under a dry nitrogen atmosphere with standard Schlenk techniques. Solvents were purified either by distillation via standard procedures or passage through activated alumina. Alkyne complexes ([Tp′(CO)$_2$W(HC≡CR)][OTf]) were prepared by a literature route, except that AgOTf was used in place of AgBF$_4$;[42] KTp′ was prepared by Trofimenko's route,[43] and (EtCN)$_3$W(CO)$_3$ was prepared by Kubas' method.[44] NMR spectra were recorded at 400 MHz. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Tp′(CO)$_2$W(η^2-C(CH$_3$)=CH$_2$) (1). Method a. A solution containing 4.15 g (5.71 mmol) of [Tp′(CO)$_2$W(η^2-HC≡CCH$_3$)][OTf] in 225 mL of THF was prepared and cooled to −78 °C. A slight excess of LiHBEt$_3$ (1.0 M in hexanes, 7.2 mL, 7.2 mmol) was added to the green solution. A color change to dark

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red-orange accompanied the addition. The solvent was evaporated, and the residue was chromatographed on alumina with hexanes/CH$_2$Cl$_2$ (5/1) as the eluent. An orange band was collected. Evaporation of solvent and dynamic vacuum for 1 h at 60 °C produced 3.30 g (81%) of **1** as a bright, red-orange solid.

Method b. A solution of 0.990 g (2.42 mmol) of (EtCN)$_3$W(CO)$_3$ in 50 mL of THF was prepared and heated to reflux. The addition of 0.25 mL (2.69 mmol) of 2-bromopropene produced no visible changes. The IR spectrum of the solution after 5 min showed the presence of multiple species. After 35 min, a slurry of KTp′ in THF (2.67 mmol of KTp′, 50 mL of THF) was added. The solution was refluxed for 2.5 h. Multiple species were noted in the IR spectrum during this time. The solvent was evaporated, and the brown residue was chromatographed on alumina with hexanes−CH$_2$Cl$_2$ (7:1) as the eluent. An orange band was collected. Evaporation of solvent and dynamic vacuum overnight yielded 0.080 g (6%) of **1**. 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 (br, 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*H), 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 WC$_{20}$H$_{27}$N$_6$BO$_2$: C, 41.55; H, 4.71; N, 14.54. Found: C, 41.42; H, 4.77; N, 14.46.

Tp′(CO)$_2$W(η^2-C(CH$_2$CH$_2$CH$_2$CH$_3$)=CH$_2$) (2). Method a, using [Tp′(CO)$_2$W(η^2-HC≡CBu^n)][O$_3$SCF$_3$] and LiHBEt$_3$, gave a 65% yield of orange **3**. IR (KBr, cm^{-1}): ν_{BH} 2542; ν_{CO} 1956, 1863; ν_{CN} 1545. ^{1}H NMR (CDCl$_3$, δ): 5.84, 5.80 (1:2, Tp′C*H*), 3.36 (tt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 3 Hz, η^2-C(C*H*$_2$CH$_2$CH$_2$CH$_3$)=CH$_2$), 2.59, 2.39, 2.34, 1.91 (3:6:3:6, Tp′C*H*$_3$), 1.84 (m, η^2-C(CH$_2$C*H*$_2$CH$_2$CH$_3$)=CH$_2$), 1.52 (m, η^2-C(CH$_2$CH$_2$C*H*$_2$CH$_3$)=CH$_2$), 1.28 (br, η^2-C(Bu^n)=C*H*$_2$), 0.995 (t, $^3J_{HH}$ = 7.3 Hz, η^2-C(CH$_2$CH$_2$CH$_2$C*H*$_3$)=CH$_2$). ^{13}C NMR (CDCl$_3$, δ): 251.6 (br, η^2-*C*(Bu^n)=CH$_2$), 220.0 ($^1J_{WC}$ = 158 Hz, *C*O), 153.1, 151.1, 144.5, 143.9 (1:2:1:2, Tp′*C*CH$_3$), 107.0, 106.9 (1:2, Tp′*C*H), 48.7 (t, $^1J_{CH}$ = 127, η^2-C(*C*H$_2$CH$_2$CH$_2$CH$_3$)=CH$_2$), 30.9 (t, $^1J_{CH}$ = 127, η^2-(CH$_2$*C*H$_2$CH$_2$CH$_3$)=CH$_2$), 23.1 (t, $^1J_{CH}$ = 125, η^2-C(CH$_2$CH$_2$*C*H$_2$CH$_3$)=CH$_2$), 15.6 (t, $^1J_{CH}$ = 158, η^2-C(Bu^n)=*C*H$_2$), 15.7, 14.4, 14.2, 12.8, 12.6 (1:2:1:1:2, Tp′*C*H$_3$, η^2-C(CH$_2$CH$_2$CH$_2$*C*H$_3$)=CH$_2$). Anal. Calcd for WC$_{23}$H$_{33}$N$_6$BO$_2$: C, 44.54; H, 5.36; N, 13.55. Found: C, 44.64; H, 5.42; N, 13.46.

Tp′(CO)$_2$W(η^2-C(CH$_2$Ph)=CH$_2$) (3). Method a, using [Tp′(CO)$_2$W(η^2-HC≡CCH$_2$Ph)][O$_3$SCF$_3$] and LiHBEt$_3$, gave a 45% yield of rust-colored **3**. IR (KBr, cm^{-1}): ν_{BH} 2548; ν_{CO} 1952, 1860; ν_{CN} 1545. ^{1}H NMR (CDCl$_3$, δ): 7.46 (br, *Ph*$_{ortho}$), 7.32 (d, $^3J_{HH}$ = 7.4 Hz, *Ph*$_{meta}$), 7.21 (tt, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = unres, *Ph*$_{para}$), 5.87, 5.78 (1:2, Tp′C*H*), 4.63 (br, η^2-C(C*H*$_2$Ph)=CH$_2$), 2.64, 2.39, 2.35, 1.77 (3:6:3:6, Tp′C*H*$_3$), 1.23 (vbr, η^2-C(CH$_2$Ph)=C*H*$_2$). ^{13}C NMR (CDCl$_3$, δ): 247.5 (br, η^2-*C*(CH$_2$Ph)=CH$_2$), 220.4 (br, *C*O), 153.1, 151.2, 144.6, 143.8 (1:2:1:2, Tp′*C*CH$_3$), 139.0 (br, *Ph*$_{ipso}$), 129.2, 128.2, 126.0 (2:2:1, *Ph*), 107.0, 106.8 (1:2, Tp′*C*H), 55.1 (t, $^1J_{CH}$ = 129, η^2-C(*C*H$_2$Ph)=CH$_2$), 16.7 (t, $^1J_{CH}$ = 155, η^2-C(CH$_3$)=*C*H$_2$), 15.7, 14.2, 12.8, 12.6 (1:2:1:2, Tp′*C*H$_3$). Anal. Calcd for WC$_{26}$H$_{31}$N$_6$BO$_2$: C, 47.73; H, 4.78; N, 12.85. Found: C, 48.08; H, 5.13; N, 12.26.

Tp′(CO)$_2$W(η^2-C(CH$_2$CH$_3$)=CH$_2$) (4). A solution containing 0.588 g (1.02 mmol) of Tp′(CO)$_2$W(η^2-C(Me)=CH$_2$) in 50 mL of THF was prepared and cooled to −78 °C. Addition of *t*-BuLi (1.7 M in pentane, 0.78 mL, 1.31 mmol) caused a color change from orange to yellow. An IR spectrum of the anionic allene intermediate exhibited ν_{CO} bands at 1873, 1673, and 1655 cm^{-1} (ν_{CC}(H$_2$C=C=CH$_2$) 1610 cm^{-1}). Quenching of the reaction with a large excess of MeI (3.0 mL, 48 mmol, 47 equiv) resulted in a color change to orange (ν_{CO} 1954, 1861 cm^{-1}). Removal of solvent and chromatography on alumina resulted in 0.368 g (61%) of orange **4.** A separate experiment in which only 2.3 equiv of MeI was used to quench the allene complex produced a mixture composed of 60% Tp′(CO)$_2$W(η^2-C(Et)=CH$_2$) and 40% Tp′(CO)$_2$W(η^2-C(Me)=CH$_2$). IR (KBr, cm^{-1}): ν_{BH} 2540; ν_{CO} 1951, 1852; ν_{CN} 1545. ^{1}H NMR (CDCl$_3$, δ): 5.85, 5.82 (1:2, Tp′C*H*), 3.43 (tt, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 2.5 Hz, η^2-C(C*H*$_2$CH$_3$)=CH$_2$), 2.60, 2.41, 2.35, 1.93 (3:6:3:6, Tp′C*H*$_3$), 1.40 (t, $^3J_{HH}$ = 7.4 Hz, η^2-C(CH$_2$C*H*$_3$)=CH$_2$), 1.30 (b, η^2-C(CH$_2$CH$_3$)=C*H*$_2$). ^{13}C{^{1}H} NMR (CDCl$_3$, δ): 252.7 (br, η^2-C(Et)=CH$_2$), 220.0 (*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*H), 41.98 (η^2-C(*C*H$_2$CH$_3$), 15.7, 14.4, 12.8, 12.6 (1:2:1:2, Tp′*C*H$_3$), 15.0 (η^2-C(CH$_2$CH$_3$)=*C*H$_2$), 12.4 (η^2-C(CH$_2$*C*H$_3$)=CH$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, δ): 252.7 (η^2-*C*(Et)=CH$_2$). Anal. Calcd for WC$_{21}$H$_{28}$N$_6$BO$_2$: C, 42.55; H, 4.94; N, 14.19. Found: C, 42.33; H, 4.99; N, 14.28.

Tp′(CO)$_2$W(η^2-C(CH(CH$_3$)Pr^n)=CH$_2$) (5). A solution containing 0.100 g (0.161 mmol) of Tp′(CO)$_2$W(η^2-C(Bu^n)=CH$_2$) in THF was prepared and cooled to −78 °C. The slow addition of 0.10 mL of BuLi (2.0 M in hexane, 0.20 mmol) caused a color change from orange to bright yellow. The IR spectrum of the solution showed peaks at 1869 and 1659 cm^{-1} corresponding to the anionic allene species [Li][Tp′(CO)$_2$W(η^2-CH$_2$=C=CHPr^n)]. An excess of MeI (0.400 mL, 6.4 mmol) was used to quench the reaction. No immediate change was evident. When it was warmed, the solution darkened and returned to the original color. The solvent was removed in vacuo, and the residue was chromatographed on alumina with hexanes−CH$_2$Cl$_2$ (1:1) as the eluent. An orange band was collected. Solvent removal yielded 0.065 g (64%) of bright orange **5**. IR (KBr, cm^{-1}): ν_{BH} 2542; ν_{CO} 1954, 1859; ν_{CN} 1545. ^{1}H NMR (CDCl$_3$, δ): 5.83, 5.81, 5.80 (Tp′C*H*), 3.82 (m (6 lines), $^3J_{HH}$ ≅ 6.3 Hz, η^2-C(C*H*(CH$_3$)Pr^n=CH$_2$), 2.60, 2.39, 2.33, 1.95, 1.91 (1:2:1:1:1, Tp′C*H*$_3$), 1.71−1.13 (m, η^2-C(CH(CH$_3$)C*H*$_2$C*H*$_2$CH$_3$)=CH$_2$), 1.23 (d, $^3J_{HH}$ = 6.3 Hz, η^2-C(CH(C*H*$_3$)Pr^n)=CH$_2$), 1.18 (d, $^4J_{HH}$ = 2.3 Hz, η^2-C(CH(CH$_3$)Pr^n=C*H*$_2$), 0.96 (t, $^3J_{HH}$ = 7 Hz, η^2-C(CH(CH$_3$)CH$_2$CH$_2$C*H*$_3$)=CH$_2$). ^{13}C NMR (CDCl$_3$, δ): 254.3 ($^1J_{WC}$ = 29 Hz, η^2-*C*(CH(CH$_3$)Pr^n=CH$_2$), 220.0, 219.8 ($^1J_{WC}$ = 158, 157 Hz, *C*O), 153.1, 151.1, 151.0, 144.4, 143.8 (1:1:1:1:2, Tp′*C*CH$_3$), 107.0, 106.8 (1:2, Tp′*C*H), 52.3 (d, $^1J_{CH}$ = 130.4 Hz, η^2-C(*C*H(CH$_3$)Pr^n)=CH$_2$), 36.6 (t, $^1J_{CH}$ = 124 Hz, η^2-C(CH(CH$_3$)*C*H$_2$CH$_2$CH$_3$)=CH$_2$), 31.6 (t, $^1J_{CH}$ = 128 Hz, η^2-C(CH(CH$_3$)CH$_2$*C*H$_2$CH$_3$)=CH$_2$), 20.2, 16.0, 15.6, 14.5, 14.4, 14.4, 12.8, 12.6 (Tp′C*C*H$_3$, η^2-C(CH(*C*H$_3$)CH$_2$CH$_2$*C*H$_3$)=CH$_2$). Anal. Calcd for WC$_{24}$H$_{35}$N$_6$BO$_2$: C, 45.50; H, 5.57; N, 13.27. Found; C, 45.24, H, 5.70, N, 13.10.

Tp′(CO)$_2$W(η^2-C(CH(CH(OH)Ph)Pr^n)=CH$_2$) (6). A solution containing 0.340 g (0.548 mmol) of Tp′(CO)$_2$W(η^2-C(CH$_2$CH$_2$CH$_2$CH$_3$)=CH$_2$) in THF was prepared and cooled to −78 °C. The slow addition of 0.22 mL of BuLi (2.5 M in hexanes, 0.55 mmol) caused a color change from orange to bright yellow. The IR spectrum of the solution showed peaks at 1869 and 1659 cm^{-1} corresponding to the anionic allene species [Tp′(CO)$_2$W(η^2-CH$_2$=C=CHPr^n)]. An excess of benzaldehyde (0.10 mL, 0.98 mmol) was used to quench the reaction. The reaction mixture was warmed to room temperature, and dilute acid was added (0.6 mL as 2 drops of concentrated HCl in 1 mL of H$_2$O). The solvent was removed, and the residue was triturated with 25 mL of hexanes for 1 h in order to remove unreacted starting material. After storage at −40 °C for 1 h, a yellow-orange precipitate was isolated via filtration. The solid was chromatographed on alumina with THF as the eluent. An orange band was collected. Removal of solvent yielded 0.170 mg (42%) of a yellow-orange solid consisting of a 1:1 diastereomer mixture, as assayed by ^{1}H NMR. Recrystallization from CH$_2$Cl$_2$−hexanes at low temperature (−40 °C) yielded a small portion of one diastereomer for characterization. IR (KBr, cm^{-1}): ν_{BH} 2546; ν_{CO} 1950, 1857; ν_{CN} 1545. ^{1}H NMR (CDCl$_3$, δ): 1 diastereomer, 7.6−7.2 (m, *Ph*), 5.87, 5.83 (1:2, Tp′C*H*), 5.16 (br, O*H*), 4.05 (m, η^2-C(C*H*(CH(OH)Ph)Pr^n)=CH$_2$), 2.90 (br, η^2-C(CH(C*H*(OH)Ph)Pr^n)=CH$_2$), 2.65, 2.41, 2.35, 1.96, 1.95 (1:2:1:1:1, Tp′C*H*$_3$), 1.9−1.7 (m, η^2-C(CH(CH(OH)Ph)C*H*$_2$CH$_2$CH$_3$)=CH$_2$), 1.30 (br, η^2-C(CH(CH(OH)Ph)Pr^n)=C*H*$_2$), 1.4−0.9 (br, m, η^2-C(CH(CH(OH)Ph)CH$_2$C*H*$_2$CH$_3$)=CH$_2$), 0.71 (t, $^3J_{HH}$ = 7 Hz,

η^2-C(CH(CH(OH)Ph)CH$_2$CH$_2$C*H*$_3$)=CH$_2$). ^{13}C NMR (CDCl$_3$, δ): 1 diastereomer, 246.0 ($^1J_{WC}$ = 29 Hz, η^2-C(CH(CH(OH)Ph)Pr^n)=CH$_2$), 220.3 ($^1J_{WC}$ = 157 Hz, *C*O), 220.1 ($^1J_{WC}$ = 151 Hz, *C*O), 153.2, 151.1, 150.9, 144.6, 144.0 (1:1:1:1:2, Tp′*C*CH$_3$) 128.2, 127.9, 126.6, 125.7 (*Ph*), 107.1, 107.0 (1:2, Tp′*C*H), 73.8 ($^1J_{CH}$ = 146 Hz, η^2-C(CH(*CH(OH)*Ph)Pr^n)=CH$_2$), 65.2 ($^1J_{CH}$ = 132 Hz, η^2-*C*(*C*H(CH(OH)Ph)Pr^n)=CH$_2$), 28.8 ($^1J_{CH}$ = 127 Hz, η^2-C(CH(CH(OH)Ph)*C*H$_2$CH$_2$CH$_3$)=CH$_2$), 21.4 ($^1J_{CH}$ = 125 Hz, η^2-C(CH(CH(OH)Ph)CH$_2$*C*H$_2$CH$_3$=CH$_2$), 15.7 (br, $^1J_{CH}$ = 158 Hz, η^2-C(CH(CH(OH)Ph)Pr^n)=*C*H$_2$), 15.5, 14.4, 14.1, 12.7, 12.5 (2:1:1:1:2, Tp′C*C*H$_3$, η^2-C(CH(CH(OH)Ph)CH$_2$CH$_2$*C*H$_3$=CH$_2$). Anal. Calcd for $WC_{30}H_{39}N_6BO_3$: C, 49.61; H, 5.41; N, 11.57. Found: C, 49.67; H, 5.30; N, 11.48.

Attempted Elaboration of 4. A solution containing 0.100 g (0.15 mmol) of Tp′(CO)$_2$W(η^2-C(CH$_2$Ph)=CH$_2$) in 15 mL of THF was prepared and cooled to −78 °C. Addition of *n*-BuLi caused a color change from orange to yellow-orange. An IR of the solution showed only the anionic allenyl complex [Li][Tp′(CO)$_2$W(η^2-CH$_2$=C=CHPh)] in solution (ν_{CO} 1880, 1678 cm^{-1}, ν_{CC}(H$_2$C=C=CHPh) 1624 (1610) cm^{-1}, ν_{CC}(Ph) 1585 cm^{-1}, ν_{CN} 1545 cm^{-1}). The addition of MeI (0.040 mL, 0.64 mmol, 4 equiv) produced no change in either the color or the IR spectrum. Warming of the reaction mixture to room temperature had no effect. Monitoring of the reaction via IR showed the slow growth of starting material over a 4 h period. Removal of solvent and chromatography on alumina produced only starting material (0.085 g, 85% recovery), as assayed by ^{1}H NMR.

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