Insertion Products from Photolysis of Tp′(CO)$_3$WH and Alkynes

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Irradiation of Tp′(CO)$_3$WH in the presence of alkynes produces a diverse array of products, including η^2-vinyl, η^2-acyl, metallafuran, and carbyne complexes. A common mechanistic feature consistent with the observed distribution of products is *cis* insertion of alkynes into a photogenerated "Tp′(CO)$_2$WH" species. Initial *cis* 2,1-insertion of the alkynes leads to η^2-vinyl and η^3-allyl products, while *cis* 1,2-insertion ultimately produces η^2-acyl, metallafuran, and carbyne products. An X-ray structure of a metallafuran product, Tp′(CO)$_2$W(η^2(*C*,*O*)-C(Bu^n)CHC(=O)CH=CHBu^n), shows *trans* stereochemistry for the double bond of the pendant 1-hexenyl group, which indicates that *cis* 1,2-insertion of the first equivalent of alkyne forms an intermediate η^1-vinyl complex. Additional support for η^1-vinyl intermediates is present in the η^2-acyl product Tp′(CO)$_2$W(η^2(*C*,*O*)-C(=O)CH=CHC(CH$_3$)$_3$), which evinces a trans double bond as assayed via ^{1}H NMR. Irradiation of Tp′(CO)$_3$WH in the presence of Me$_3$SiC≡CCH$_3$ produces two isomers of Tp′(CO)$_2$W(η^3-*syn*-CH$_2$CHCHSiMe$_3$) which differ in the orientation of the allyl fragment relative to the metal center. Heating of the allyl complex results in an unusual η^3-allyl to carbyne rearrangement.

Introduction

In contrast to numerous examples of alkyne insertion into metal−ligand bonds to produce σ-vinyl complexes in both early-[1−11] and late-transition-metal[12−19] systems, there is a paucity of discrete examples of alkyne insertion into metal−ligand bonds to yield η^2-vinyl complexes, L$_n$M(η^2-CR=CR$_2$) (alternatively termed 1-metallacyclopropene complexes). Recently, Richmond et al. have produced unusual η^2-vinyl complexes via a migratory insertion process involving alkynes and activated metal−perhaloaryl bonds.[20−23] Niobium η^2-vinyl species formed by intramolecular migratory insertion routes have been postulated as intermediates in the exchange of alkyne alkyl substituents with metal-bound alkyl groups in Tp′Cl(R)Nb(η^2-R′C≡CPh) complexes.[24] Transition-metal η^2-vinyl complexes have been advanced as potential intermediates in catalytic alkyne polymerization pathways and in the *E*/*Z* isomerization of σ-vinyl ligands formed from insertion of alkynes into metal−ligand bonds.[25−28]

Although thermal activation of Cp(CO)$_3$MH (M = Mo, W) complexes is facile,[29−31] similar activation of Tp^x(CO)$_3$MH (Tp^x = Tp, Tp′; M = Mo, W) complexes has not been realized. Curtis and co-workers found that reflux of Tp(CO)$_3$MoH (Tp = hydridotris(1-pyrazolyl)borate) in polar, high-boiling solvents (DMF, diglyme) results only in transient deprotonation of the hydride

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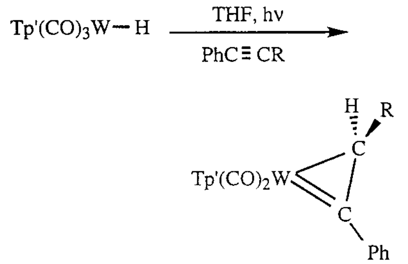
complex.[32] Likewise, our efforts to employ Tp′(CO)$_3$WH (Tp′ = hydrido(3,5-dimethyl-1-pyrazolyl)borate) as a tungsten(II) source in thermal reactions have not been productive. Extended reflux of Tp′(CO)$_3$WH in either THF or toluene in the presence of P(OMe)$_3$, alkynes, or nitriles produces no substitution or insertion products. Would photochemical reactions offer an alternative route to tungsten(II) products of interest without using halogens for oxidation of tungsten(0) reagents and then silver salts for halide removal?

Numerous examples of photochemical activation of Cp^x(CO)$_3$MR (Cp^x = Cp, Cp*; M = Mo, W) complexes exist.[30,33−40] An earlier study by Alt and co-workers on the photoreactivity of Cp*(CO)$_3$WH (Cp* = C$_5$Me$_5$) in the presence of alkynes (CH$_3$C≡CR; R = H, CH$_3$) implicated vinyl intermediates on the pathway to η^3-allyl complexes.[41] Irradiation of Tp′(CO)$_3$WH in the presence of nitriles (RC≡N) produces azavinylidene complexes, Tp′(CO)$_2$W=N=CHR, via the net insertion of nitrile into the W−H bond of a putative “Tp′(CO)$_2$W−H” intermediate.[42] Previously, we reported that photolysis of Tp′(CO)$_3$WH with alkynes possessing propargyl hydrogens, RCH$_2$C≡CR′, produces mixtures of η^2-vinyl and η^3-allyl isomers, as assayed by IR spectroscopy.[43] Heating of these mixtures induces conversion to η^3-allyl isomers, Tp′(CO)$_2$W(η^3-RHCCHCHR′), which were isolated and characterized.

We now report photolysis of Tp′(CO)$_3$WH with terminal alkynes as a route to a variety of tungsten(II) alkyne insertion products, including not only η^2-vinyl but also η^2-acyl, metallafuran, and carbyne complexes. In conjunction with the previous study,[43] our goal was to map the broad range of photoproducts available from Tp′(CO)$_3$WH and RC≡CR′. A mechanistic model involving both η^1- and η^2-vinyl species has been developed to account for the diversity of products. Photolysis of Tp′(CO)$_3$WH with Me$_3$SiC≡CCH$_3$ to produce an isolable η^3-allyl product which thermally isomerizes into a carbyne complex, Tp′(CO)$_2$W≡CCHCH$_3$SiMe$_3$, is also described.

Results and Discussion

Photochemistry of Tp′(CO)$_3$WH and PhC≡CR (R = H, Ph): η^2-Vinyl Products. Irradiation of Tp′(CO)$_3$WH in the presence of arylalkynes (PhC≡CR; R = H, Ph) produced η^2-vinyl complexes, Tp′(CO)$_2$W(η^2-CPh=CHR) (**1**, R = H; **2**, R = Ph), free of complicating side products (eq 1). These aryl η^2-vinyl complexes



1; R = H
2; R = Ph (1)

have been examined previously.[44−46] Isolation of high-quality crystals of one isomer of **2** presented an opportunity to examine the molecular structure of an η^2-vinyl group in the Tp′(CO)$_2$W system.

If the η^2-vinyl ligand is considered as a unit, the geometry about the metal in **2** can be described as psuedo-octahedral (Figure 1). Selected bond distances

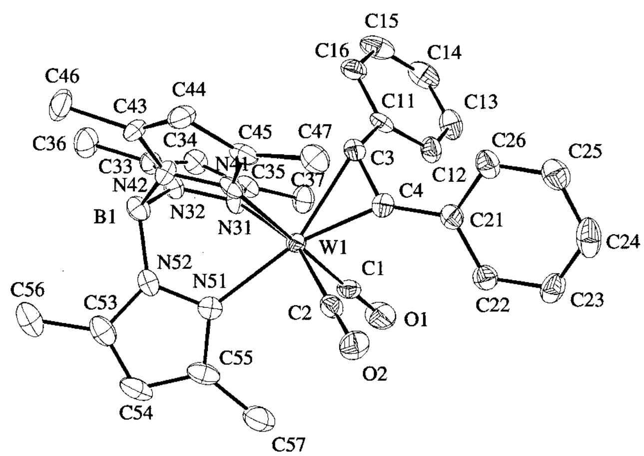


Figure 1. ORTEP representation of Tp′(CO)$_2$W(η^2-C(Ph)=CHPh) (**2**).

and bond angles are given in Table 1. The feature of note is the orientation of the vinyl ligand relative to the other ligands in the coordination sphere. The vinyl unit roughly bisects the OC−M−CO angle, and the carbenoid carbon, C$_\alpha$, is adjacent to the carbonyl ligands. The orientation of the η^2-vinyl ligand in **2** is opposite that predicted by steric arguments: rotation of the η^2-vinyl ligand by 180° would relieve steric strain between the β-Ph ring and the *cis*-pyrazole rings while still providing constructive CH-π interactions[47] between the *cis*-pyrazole rings and the α-Ph ring. The η^2-vinyliminium ligand in the related complex [Tp′(CO)$_2$Mo(η^2-C(Ph)=C(H)-C(H)=N(Bu^t)(Me)][BF$_4$] possesses a similar geometry in the solid state.[48] A slight deflection of the η^2-vinyl ligand is present, which brings the β-phenyl ring closer to the *cis*-pyrazole ring rather than farther away, as would be expected on the basis of steric arguments (Figure 2).

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Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for Tp′(CO)$_2$W(η^2-C(Ph)═CHPh) (2)

W1−C1	1.983(10)	W1−N51	2.219(7)
W1−C2	1.993(8)	C1−O1	1.149(12)
W1−C3	2.263(8)	C2−O2	1.138(10)
W1−C4	1.990(8)	C3−C4	1.405(11)
W1−N31	2.236(7)	C3−C11	1.482(11)
W1−N41	2.241(7)	C4−C21	1.465(12)
C1−W1−C2	86.4(3)	C4−W1−N31	123.5(3)
C1−W1−C3	96.8(3)	C4−W1−N41	96.7(3)
C1−WI−C4	83.2(3)	C4−W1−N51	158.6(3)
C1−W1−N31	94.0(3)	N31−W1−N41	87.11(25)
C1−W1−N41	178.7(3)	N31−W1−N51	77.77(23)
C1−W1−N51	98.4(3)	N41−W1−N51	81.30(25)
C2−W1−C3	110.8(3)	W1−C1−O1	175.8(8)
C2−W1−C4	74.8(3)	W1−C2−O2	178.8(7)
C2−W1−N31	161.6(3)	W1−C3−C4	60.5(4)
C2−W1−N41	92.4(3)	W1−C3−C11	127.5(6)
C2−W1−N51	84.0(3)	C4−C3−C11	122.4(8)
C3−W1−C4	37.9(3)	W1−C4−C3	81.6(5)
C3−W1−N31	87.4(3)	W1−C4−C21	147.4(6)
C3−W1−N41	83.9(3)	C3−C4−C21	130.6(7)
C3−W1−N51	159.5(3)		

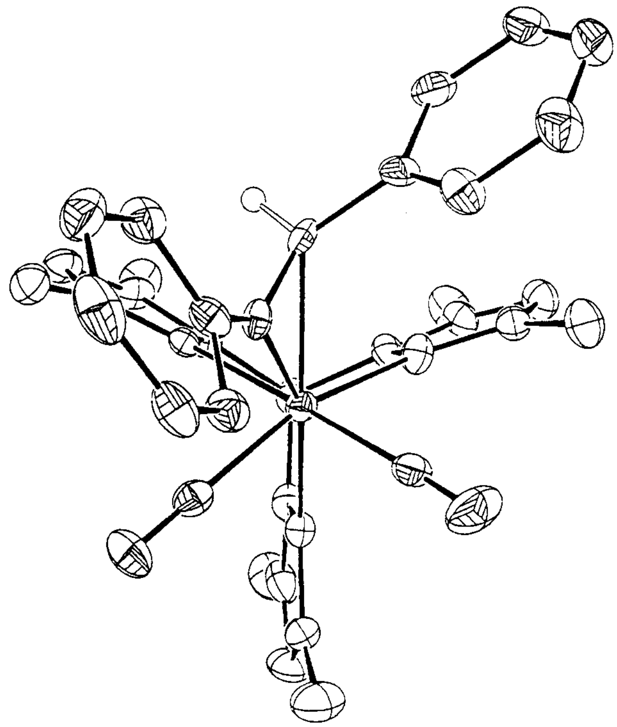
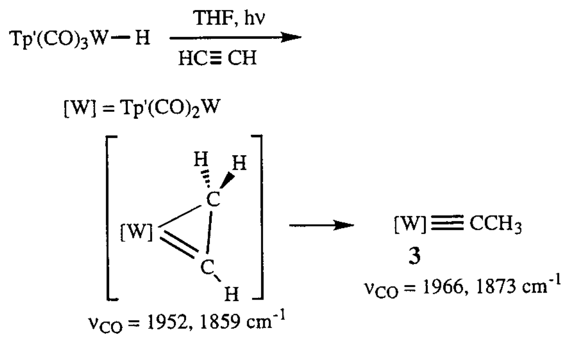


Figure 2. ORTEP representation of **2** viewed down the W−Tp′ 3-fold axis. The vinyl hydrogen is shown in a calculated position.

The orientation of the vinyl ligand in **2** is roughly orthogonal to that adopted by η^2-diphenylvinyl ligands in related Cp-based complexes.[26,49−51]

Other characteristics of the vinyl moiety include one short W−C bond (W1−C4 = 1.990 Å) and one long W−C bond (W1−C3 = 2.263 Å), indicative of metal−carbon double and single bonds, respectively. The bond distance between the carbons of the vinyl unit (C4−C3 = 1.405 Å) is intermediate between that expected for carbon−carbon single and double bonds. Inspection of the remaining ligand sphere shows a slight contraction of the W−N bond trans to the vinyl ligand (W1−N51 = 2.219 Å) relative to the W−N bonds trans to carbonyl ligands (W1−N31 = 2.236 Å, W1−N41 = 2.241 Å). This results from the weaker *trans* influence of the vinyl ligand relative to the carbonyl ligands. The OC−W−CO angle is acute at 86.4°, which is compatible with theoretical calculations on related Tp′(CO)$_2$WX complexes containing single-faced π-acceptor ligands.[52]

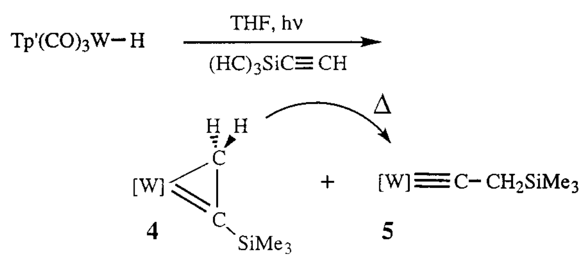
Photochemistry of Tp′(CO)$_3$WH and HC≡CH: Carbyne Formation. Irradiation of Tp′(CO)$_3$WH in the presence of acetylene resulted in the isolation of the methyl−carbyne (ethylidyne) complex Tp′(CO)$_2$W≡CCH$_3$[53] (**3**). A dicarbonyl intermediate with ν_{CO} 1952, 1859 cm^{-1} (vs 1966 and 1873 cm^{-1} for carbyne product **3**) was noted during the reaction. These results are compatible with initial formation of [Tp′(CO)$_2$W(η^2-CH═CH$_2$)] followed by a 1,2-H migration to yield the carbyne product (eq 2). An identical reaction course resulted



(2)

from stoichiometric addition of LiHBEt$_3$ to a THF solution of [Tp′(CO)$_2$W(HC≡CH)][O$_3$SCF$_3$]. An attempt to observe the putative parent η^2-vinyl via low-temperature addition of LiHBEt$_3$ to an NMR sample of [Tp′(CO)$_2$W(HC≡CH)][O$_3$SCF$_3$] in THF-d_8 was unsuccessful. Multiple Tp′-containing species were noted in the ^{1}H NMR spectrum of the solution even at −90 °C.

Photochemistry of Tp′(CO)$_3$WH and HC≡CSiMe$_3$: η^2-Vinyl and Carbyne Products. Photolysis of (trimethylsilyl)acetylene with Tp′(CO)$_3$WH and extraction of the residue with hexanes produced a mixture of Tp′(CO)$_2$W(η^2-C(SiMe$_3$)═CH$_2$) (**4**) and Tp′(CO)$_2$W≡CCH$_2$SiMe$_3$ (**5**) (**4**:**5** = 43:57) (eq 3). Chromatography on



(3)

alumina resulted in substantial decomposition along with hydrolysis to produce Tp′(CO)$_2$W≡CCH$_3$. In one attempt, chromatographic separation yielded a small portion of **4** for independent characterization. Upon standing at room temperature, a CDCl$_3$ sample of the

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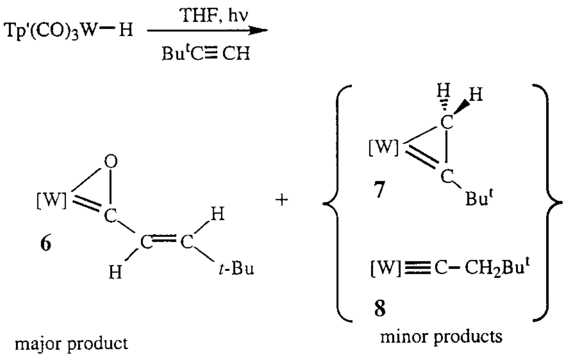
η^2-vinyl species **4** slowly rearranged into the carbyne complex **5**. The 1,2-silyl migration is slow at room temperature (>5 days); hydrolysis and decomposition accompanied the rearrangement. Given the slow rate of the isomerization at room temperature, the initial ratio of products is attributed to competing 1,2- and 2,1-insertion pathways (see below).

Photochemistry of Tp′(CO)$_3$WH and HC≡CCMe$_3$: η^2-Acyl, η^2-Vinyl, and Carbyne Products. Irradiation of Tp′(CO)$_3$WH for ca. 3 h in the presence of an excess of 3,3-dimethyl-1-butyne (*tert*-butylacetylene) generated an η^2-acyl complex, Tp′(CO)$_2$W(*trans*-η^2-C(O)CH=CH-(CH$_3$)$_3$) (**6**), as the major product (eq 4). Small amounts

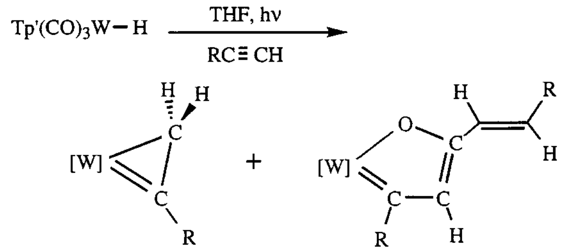


(4)

of Tp′(CO)$_2$W(η^2-C(C(CH$_3$)$_3$)=CH$_2$) (**7**) and Tp′(CO)$_2$-W≡CCH$_2$C(CH$_3$)$_3$ (**8**) also formed during the reaction. The identity of **7** was confirmed by independent synthesis via treatment of [Tp′(CO)$_2$W(η^2HC≡C(CH$_3$)$_3$)][O$_3$-SCF$_3$] with LiHBEt$_3$. Identification of **8** was by comparison to spectral data with that of known Tp′(CO)$_2$-W≡CR complexes.[53]

The IR spectrum of **6** shows CO absorption bands at 1936 and 1833 cm^{-1}. The energies of these vibrations point to η^2-acyl formulation; they are distinctively lower than those of related Tp′(CO)$_2$WX derivatives such as η^2-vinyl (1950, 1860 cm^{-1}), metallafuran (1950, 1850 cm^{-1}), or carbyne (1980, 1880 cm^{-1}) complexes. In the ^{1}H NMR spectrum of **6**, the signal for the olefinic proton nearest the acyl linkage was located downfield (7.05 ppm) of the distal proton (6.85 ppm). A trans geometry was indicated by the $^3J_{HH}$ value of 15.6 Hz. An effective mirror plane for **6** was confirmed in the ^{13}C NMR spectrum with equivalent carbonyl ligands at 229.7 ppm and 2:1 patterns for the pyrazole carbons. The carbenoid α-carbon of the acyl resonated at 235 ppm with a $^1J_{WC}$ value of 20 Hz. The β-carbon resonated at 119 ppm with a $^1J_{CH}$ value of 140 Hz. The γ-carbon was deshielded (162 ppm) relative to C$_\beta$ and showed a $^1J_{CH}$ value of 160 Hz. Similar spectroscopic properties have been reported for closely related Tp′(CO)$_2$Mo(η^2(*C,O*)-C(=O)CH=CHR)) complexes.[54]

Photochemistry of Tp′(CO)$_3$WH and RCH$_2$C≡CH (R = H, *n*-Pr): η^2-Vinyl and Metallafuran Products. Photolysis of Tp′(CO)$_3$WH with propyne or 1-hexyne in THF produces the corresponding η^2-vinyl complexes Tp′-(CO)$_2$W(η^2-C(R)=CH$_2$) (**9**, R = CH$_3$; **11**, R = *n*-Bu), in fair yield. Metallafuran coproducts, Tp′(CO)$_2$W(η^2(*C,O*)-C(R)C(H)C(=O)CH=CHR) (**10**, R = CH$_3$; **12**, R = *n*-Bu), were also formed during these reactions (eq 5). For the



(5)

major product minor product

9; R = CH$_3$ **10**; R = CH$_3$

11; R = *n*-Bu **12**; R = *n*-Bu

1-hexyne reaction, extension of the photolysis time and modification of the isolation procedure allowed the isolation of **12** free of the η^2-vinyl coproduct (see Experimental Section). In the propyne reaction, the metallafuran complex **10** could not be separated from the η^2-vinyl coproduct but was characterized spectroscopically in a mixture by comparison with the spectral properties of **12**, which has been structurally characterized by an X-ray study. The synthesis and spectroscopic characterization of complexes **9** and **11** via hydride addition to cationic alkyne complexes has been reported.[55]

The ^{1}H NMR spectra of the metallafuran complexes (**10** and **12**) show equivalent pyrazole rings trans to the carbonyl ligands. Signals for the ring β-hydrogens were located as singlets slightly downfield of 7 ppm, reflecting the delocalized nature of the metallafuran ring. For complex **12**, the β-methylene group of the butyl substituent on the ring appeared at 3.90 ppm due to proximity to an effective metal−carbon double bond. The olefinic protons of the alkenyl substituents exhibited signals between 6.1 and 6.4 ppm with the protons nearest the ketone linkage slightly deshielded relative to the distal hydrogens. A trans geometry for the olefin fragments attached at C$_\gamma$ of **10** and **12** was indicated by $^3J_{HH}$ values of 15.6 Hz. In the ^{13}C NMR spectra, the carbons in the backbone of the metallafuran linkages followed the pattern expected from comparison to related complexes:[53,54] the α-carbon signals were found at low fields (238−239 ppm), the β-carbons resonated in the olefinic region (120−123 ppm), and the ketonic carbons appeared near 180 ppm. Signals for the proximal carbons of the external double bond nearest the ketone group (125−126 ppm) were found upfield of the distal carbons (132−138 ppm).

An X-ray structure of the metallafuran complex **12** revealed a geometry about the metal center which approaches a face-capped octahedron (Figure 3). The three metal-bound nitrogens of the Tp′ ligand (N21, N31, N41), the carbons of the terminal carbonyl ligands (C1, C2), and the metallafuran oxygen (O3) provide the octahedral framework with the carbenoid carbon (C6) as the capping atom. Selected bond distances and bond angles are given in Table 2. The core structure of **12** is nearly congruent with that of Tp′(CO)$_2$Mo(η^2(*C,O*)-C(Et)C(Et)C(=O)Et).[54] A detailed structural discussion of metallafuran ligands can be found in that article. The

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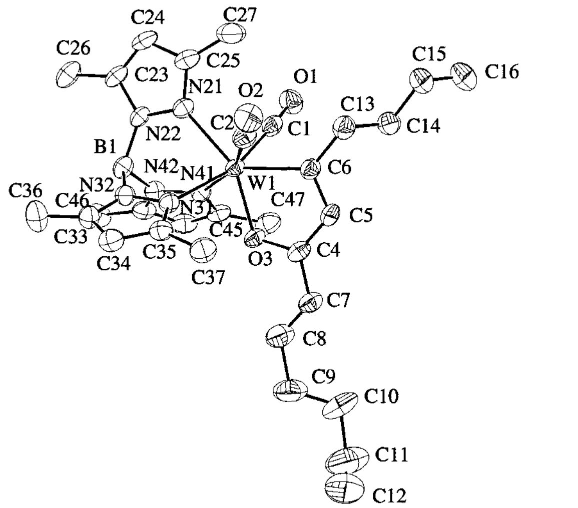


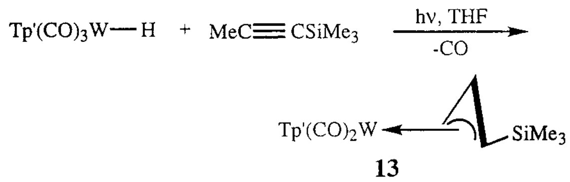
Figure 3. ORTEP representation of Tp′(CO)$_2$W(η^2(*C*,*O*)-C(Bu^n)CHC(=O)CH=CHBu^n) (**12**).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for Tp′(CO)$_2$W(η^2(*C*,*O*)-C(Bu^n)CHC(=O)CH=CHBu^n) (12)

W1−C1	1.971(8)	O3−C4	1.324(9)
W1−C2	1.952(9)	C4−C5	1.372(12)
W1−O3	2.044(4)	C4−C7	1.454(11)
W1−C6	2.157(7)	C5−C6	1.384(10)
W1−N21	2.235(6)	C6−C13	1.512(11)
W1−N31	2.231(5)	C7−C8	1.269(14)
W1−N41	2.232(6)	C8−C9	1.549(13)
C1−O1	1.138(10)	C9−C1O	1.426(20)
C2−O2	1.172(11)	C13−C14	1.520(11)
		C14−C15	1.518(12)
C1−W1−C2	100.6(3)	N21−W1−N31	81.35(21)
C1−W1−O3	116.56(24)	N21−W1−N41	82.34(21)
C1−W1−C6	69.5(3)	N31−W1−N41	80.58(20)
C1−W1−N21	79.5(3)	W1−C1−O1	176.7(6)
C1−W1−N31	158.4(3)	W1−C2−02	177.1(7)
C1−W1−N41	87.2(3)	W1−O3−C4	121.1(4)
C2−W1−O3	112.4(3)	O3−C4−C5	114.7(6)
C2−W1−C6	68.8(3)	O3−C4−C7	119.3(7)
C2−W1−N21	82.2(3)	C5−C4−C7	126.0(7)
C2−W1−N31	86.4(3)	C4−C5−C6	116.2(7)
C2−W1−N41	161.1(3)	W1−C6−C5	113.7(5)
O3−W1−C6	74.22(22)	W1−C6−C13	129.2(5)
O3−W1−N21	154.07(21)	C5−C6−C13	117.0(7)
O3−W1−N31	78.41(18)	C4−C7−C8	124.8(8)
O3−W1−N41	78.51(20)	C7−C8−C9	126.2(9)
C6−W1−N21	131.71(24)	C8−C9−C10	117.2(10)
C6−W1−N31	131.62(24)	C6−C13−C14	115.3(6)
C6−W1−N41	130.05(23)	C13−C14−C15	113.3(7)

salient feature here is the double bond between C7 and C8, as indicated by the short bond length of 1.269 Å and the sp^2 bond angles (C4−C7−C8 = 124.8° and C7−C8−C9 = 126.2°). The structure also confirms the trans arrangement of the 1-hexenyl C=C double bond indicated by ^{1}H NMR spectroscopy.

Photochemistry of Tp′(CO)$_3$WH and MeC≡CSiMe$_3$: An Unusual η^3-Allyl to Carbyne Rearrangement. Irradiation of Tp′(CO)$_3$WH in the presence of Me$_3$SiC≡CCH$_3$ produced a SiMe$_3$-substituted allyl complex, Tp′(CO)$_2$W(η^3-CH$_2$CHCHSiMe$_3$) (**13**) (eq 6). An η^2-vinyl intermediate, either Tp′(CO)$_2$W(η^2-C(Me)=CHSiMe$_3$) or Tp′(CO)$_2$W(η^2-C(SiMe$_3$)=CHMe), was suggested by the IR spectrum of the reaction mixture with ν_{CO} values of 1843 and 1945 cm^{-1} (cf. allyl product **13** at 1830 and 1924 cm^{-1}). A significant amount of



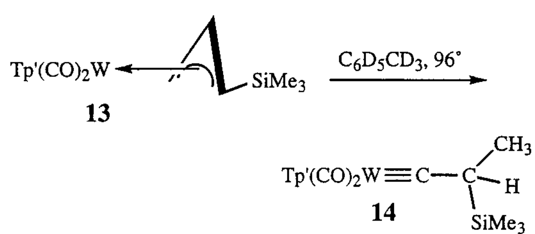
(6)

Tp′(CO)$_2$W≡CEt[53] is also formed during the preparation of **13**. Hydrolysis of an η^2-vinyl intermediate such as Tp′(CO)$_2$W(η^2-C(SiMe$_3$)=CHMe) can easily account for the production of Tp′(CO)$_2$W≡CEt (see above).

Spectroscopic data for allyl compound **13** indicated the presence of two isomers with chemical shift and coupling patterns which differ slightly from those of comparable alkyl−allyl complexes. Table 3 lists relevant data for **13** along with averaged ^{1}H NMR data for syn- and anti-substituted Tp′(CO)$_2$W(η^3-CH$_2$CHCHR) (R = H, Me, Et, Pr^n, CH$_2$Ph) complexes.[43] While the determination of allyl stereochemistry solely by J_{HH} values is sometimes ambiguous, coupling patterns for **13** indicate a *syn*-SiMe$_3$ geometry for both isomers. The chemical shift patterns follow the trends observed for Tp′(CO)$_2$W(η^3-CH$_2$CHCHR) exo and meso isomers,[56] which is in keeping with the observation that the primary determinant of chemical shift for allyl protons in Tp′(CO)$_2$W-(η^3-allyl) complexes is position relative to the *cis*-pyrazole rings.[43]

The isomer having the diagnostic H$_c$ at 5.15 ppm has been designated Tp′(CO)$_2$W(η^3-*meso*-*syn*-1-(trimethylsilyl)allyl) (**13s**), in accordance with its similarity to the meso-syn isomers of Tp′(CO)$_2$W(η^3-CH$_2$CHCHR) complexes. The opposite isomer has been tentatively assigned as Tp′(CO)$_2$W(η^3-*exo*-*syn*-1-(trimethylsilyl)allyl) (**13x**): exo due to the chemical shift patterns seen in the ^{1}H and ^{13}C NMR data and syn due to the $^3J_{HH}$ coupling values among the allyl protons.

Rinsing a mixture consisting of both isomers of **13** and Tp′(CO)$_2$W≡CEt with a minimal amount of CH$_2$Cl$_2$ left a fine yellow powder highly enriched in allyl isomer **13x**. Heating a toluene-d_8 solution of **13x** at 96 °C for 9 h effected conversion to carbyne **14** with only trace amounts of the ethyl-carbyne complex (eq 7).



(7)

A chiral substituent for carbyne **14** was indicated by the unique pyrazole groups in the ^{1}H and ^{13}C NMR spectra of **14**. In the ^{13}C NMR spectrum, the carbyne carbon resonated at 301 ppm. The diastereotopic terminal carbonyl ligands were located at 225.7 and 224.8 ppm with $^1J_{WC}$ values of 140 Hz each. The chiral β-carbon was found as a doublet at 49.7 ppm ($^1J_{CH}$ = 119 Hz) with a $^1J_{WC}$ value of 35 Hz.

A plausible mechanism for the η^3-allyl to carbyne transformation (**13** → **14**) can be designed on the basis

(56) In Tp′(CO)$_2$W(η^3-allyl) complexes, *exo* rotamers have the allyl ligand rotated ca. 30° from eclipsing the M(CO)$_2$ unit, whereas *meso* rotamers are rotated ca. 120°. See ref 43 for additional details.

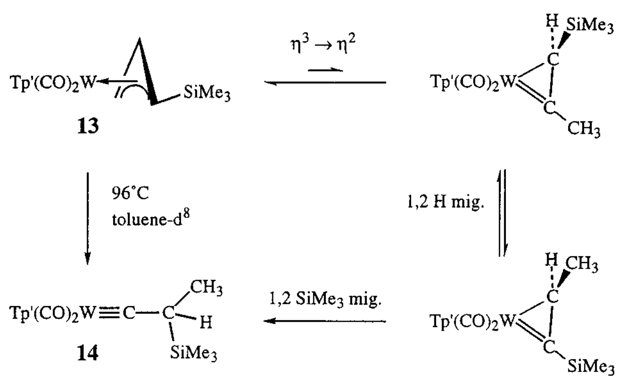
Table 3. Selected NMR Data for Tp′(CO)$_2$W(η^3-C^{1}H$_s$H$_a$C^{2}H$_c$C^{3}H$_{a'}$Si(CH$_3$)$_3$) (13) As Compared to Average Values for Alkyl Analogues[43]

	H$_a$	H$_{a'}$	H$_c$	H$_s$	H$_{s'}$	Si(CH_3)$_3$
13x	2.11 $^3J_{ac} = 9.6$ $^4J_{a's} = 0.6$	2.83 $^3J_{ac} = 9.2$ $^4J_{a's} = 3.2$	3.22 $^3J_{ac} = 9.4$ $^2J_{a'c} = 9.4$ $^3J_{sc} = 6.8$	3.13 $^3J_{sc} = 6.2$ $^2J_{as} = 3.2$		0.09 $^2J_{SiH'} = 6.1$
13s	1.59 $^3J_{ac} = 8$	1.92 $^3J_{ac} = 8$	5.15 $^3J_{ac} = 8.2$ $^2J_{a'c} = 8.2$ $^3J_{sc} = 5.2$	2.13 $^3J_{sc} = 4.8$		0.34 $^2J_{SiH'} = 6.1$
R$_{av}$ anti	2.66 $^3J_{ac} = 10$		3.21	3.31 $^3J_{sc} = 7$ $^2J_{as} = 2$ $^4J_{as} = 2$	4.19 $^3J_{s'c} = 7$	
R$_{av}$ syn	1.99 $^3J_{ac} = 8$	2.80 $^3J_{ac} = 6$	5.08	1.97 $^3J_{sc} = 6$		

	C^1	C^2	C^3	CO	CO
13x	58.5 (t) $^1J_{CH} = 159$	73.5 (d) $^1J_{CH} = 168$	55.6 (d) $^1J_{CH} = 130$	223.7 $^1J_{WC} = 150$	220.4 $^1J_{WC} = 160$
13s	60.1 (t) $^1J_{CH} = 160$	85.1 (d) $^1J_{CH} = 173$	48.6 (d) $^1J_{CH} = 129$	231.4	228.9
R$_{av}$ anti	54.8 (t) $^1J_{CH} = 158$	69.6 (t) $^1J_{CH} = 167$	69.7 (d) $^1J_{CH} = 156$	223.6	220.3
R$_{av}$ syn	54.6 (t) $^1J_{CH} = 158$	81.2 (td) $^1J_{CH} = 173$	62.9 (d) $^1J_{CH} = 159$	230.1	228.6

Data for **13** in CDCl$_3$, Chemical shift values in ppm, coupling values in Hz

Scheme 1. Rearrangement of Tp′(CO)$_2$W(η^3-CH$_2$CHCHSiMe$_3$) into Tp′(CO)$_2$W≡CHMeSiMe$_3$



of reversible steps for conversion of η^2-vinyl ligands to either carbyne or allyl ligands (Scheme 1). Isomerization of **13** into an η^2-vinyl species ($\eta^3 \rightarrow \eta^2$) followed by a 1,2-silyl shift produces carbyne **14**. The initial step is unusual, as η^3-allyl complexes are usually thermodynamically downhill from related η^2-vinyl isomers. Here, the likely driving force is relief of steric strain between the η^3-allyl group and the metal center engendered by the large SiMe$_3$ group. Hydride migration from C$_\beta$ to C$_\alpha$ to interconvert η^2-vinyl isomers has been noted in this system[45] and for related complexes.[49,51,57,58] Carbyne formation from η^2-vinyl ligands was reported for Cp(P(OMe)$_3$)$_2$Mo(η^2-C(SiMe$_3$)═CHR) (R = H, Ph) complexes, which undergo 1,2-silyl shifts upon heating to produce Cp(P(OMe)$_3$)$_2$Mo≡CHRSiMe$_3$ complexes.[59,60] The η^3-allyl to carbyne process is probably best considered as two steps: an η^3-allyl to η^2-vinyl isomerization followed by an η^2-vinyl to carbyne isomerization. The net result is an unprecedented η^3-allyl to carbyne rearrangement.

Mechanism of Alkyne Insertion. The photochemistry of Tp′(CO)$_3$WH is consistent with initial labilization of a terminal carbonyl ligand to generate a 16-electron dicarbonyl intermediate, "Tp′(CO)$_2$WH", which may well be stabilized by THF coordination.[38,61] We have been unable to observe such a species in solution at room temperature, although the analogous permethylcyclopentadienyl complex Cp*(CO)$_2$(THF)W−H has been partially characterized.[41] An alternative pathway involving homolytic cleavage of the W−H bond to form Tp′(CO)$_3$W$^\bullet$ is unlikely, since this 17-electron radical is long-lived and would easily be observable in the IR spectrum.[62]

Insertion of terminal alkynes into the putative "Tp′(CO)$_2$WH" intermediate can follow either of two pathways: cis 1,2-insertion, which places the original alkyne substituent trans to the metal in a β-position, or cis 2,1-insertion in which the substituent is positioned α to the metal (Scheme 2). Given the steric requirements of the system, only cis insertions are discussed here, even though the product of a trans 2,1-insertion for a terminal alkyne and an unlabeled metal hydride is indistinguishable from that produced by a cis 2,1-insertion. For terminal alkynes having linear alkyl substituents (HC≡CR; R = CH$_3$, n-Bu, CH$_2$Ph), the 2,1-insertion route is favored, and for phenylacetylene, only 2,1-insertion is observed. For η^1-vinyl intermediates formed by a cis 2,1-insertion, "Tp′(CO)$_2$W(η^1-C(R)═CH$_2$)", closure to the η^2-isomer is facile. The η^2-vinyl complexes are photostable, although thermal rearrangement to η^3-allyl isomers may occur.[43]

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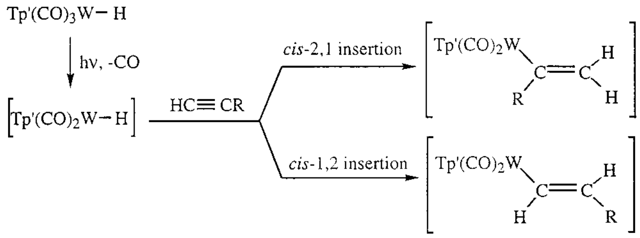
Scheme 2. Alkyne *cis*-Insertion Pathways for "Tp′(CO)$_2$WH"



The alternate pathway, cis 1,2-insertion, is ultimately responsible for the carbyne, η^2-acyl and metallafuran products. The relative amounts of 1,2-insertion products for the alkyne series suggest the following substituent dependence toward 1,2-insertion: Bu^t > SiMe$_3$ > CH$_3$, Bu^n > Ph. The initially formed 16-electron η^1-vinyl complex has the original alkyne substituent trans to the metal and a hydrogen on the α-carbon. Assuming that the preferred η^2-vinyl ligand orientation is with C$_\alpha$ directed toward the CO ligands, as shown in X-ray structures of Tp′(CO)$_2$M(η^2-vinyl) complexes (see above), coordination of the η^1-vinyl β-carbon is disfavored due to steric interactions between the vinyl β-substituents and the pendant methyl groups of the Tp′ ligand. We conclude that the η^2-coordination mode for the β-substituted vinyl ligand is not thermodynamically favored for *cis*-1,2-alkyne insertion products. Both steric hindrance at the β-site and the inability of a hydrogen attached at the carbenoid α-site to stabilize the carbene resonance form favor isomerization or further reaction of the initial *cis*-1,2-alkyne insertion product.

For a *trans*-η^1-vinyl intermediate formed from 1,2-insertion alternate pathways to electronic saturation exist: free CO can be captured from solution to yield the acyl product of vinyl migration to CO, or the α-hydrogen can undergo a 1,2-H migration to form a carbyne complex (Scheme 3). Either pathway leads to formation of an 18-electron complex. Recall that in the reaction between Tp′(CO)$_3$WH and acetylene only the carbyne complex is isolated. This suggests that in the absence of trans substituents, 1,2-hydride migration is faster than the trapping of free CO from solution. Presumably, trans substituents slow the rate of hydride migration such that CO trapping is competitive, or alternatively, they increase the rate of vinyl migration so that acyl products result.

Isolation of metallafuran complexes from intermediate Tp′(CO)$_2$W(η^2-acyl) complexes is consistent with known η^2-acyl reactivity patterns. The related acyl complex Tp′(CO)$_2$Mo(η^2-C(O)CH$_2$CH$_3$) readily loses a carbonyl ligand upon irradiation in acetonitrile.[54] The solvated intermediate [Tp′(CO)(CH$_3$CN)Mo(η^2-C(O)CH$_2$-CH$_3$)] forms dicarbonylmetallafuran complexes when exposed first to alkyne and then to carbon monoxide. Analogous chemical pathways from Cp(CO)$_2$M(η^2-acyl) complexes to metallafuran products exist.[10,63−65] Steric hindrance may inhibit additional photoreactions for η^2-acyl complex **6**.

Conclusions

All of the products here can be ratonalized on the basis of CO labilization from Tp′(CO)$_3$WH as the primary photoevent followed by cis insertion of alkyne into the tungsten−hydride bond. Coordination of alkyne in the vacant site followed by migratory insertion is a plausible mechanism for formation of tungsten vinyl species. The distribution of products, which includes not only η^2-vinyl but also η^3-allyl,[43] η^2-acyl, metallafuran, and carbyne products, provides evidence for both cis 1,2- and cis 2,1-insertion.

The proposed mechanistic pathway accounting for this diverse array of products begins with the insertion of unactivated alkynes into the W−H bond of a transient, photogenerated "Tp′(CO)$_2$WH" species. Terminal alkynes generally favor cis 2,1-insertion leading to photostable η^2-vinyl products except in the case of large substituents. Internal alkynes having propargyl hydrogens produce η^3-allyl products, although η^2-vinyl intermediates have been identified in IR spectra of reaction mixtures.[43] Evidence for σ-vinyl intermediates formed by *cis*-alkyne insertion is derived from the isolation of metallafuran products having a *trans*-alkene fragment attached to the metallafuran ring resulting from the insertion of the first equivalent of alkyne into the W−H bond followed by migration of the resultant vinyl ligand to CO and then addition of a second equivalent of alkyne and cyclization. Additional support for σ-vinyl intermediates is found in the isolation of Tp′(CO)$_2$W(*trans*-η^2-C(O)CH=CH(CH$_3$)$_3$) and Tp′(CO)$_2$W≡CCH$_2$C(CH$_3$)$_3$ from the reaction mixture produced by the photolysis of Tp′(CO)$_3$WH with HC≡CC(CH$_3$)$_3$.

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$_4$;[66] KTp′ was prepared by Trofimenko's route.[67] All photolyses were performed with a Hanovia 450 W medium-pressure Hg arc lamp at ambient temperatures. Photolysis vessels were sealed with septa, and the solutions were stirred during irradiation. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100 MHz. Microanalyses were performed by Atlantic Microlab, Inc., Norcross, GA.

Tp′(CO)$_2$W(η^2-C(Ph)=CH$_2$) (1). This compound previously has been synthesized by LiHBEt$_3$ addition to [Tp′(CO)$_2$W(η^2-PhC≡CH)][BF$_4$].[45] The present synthesis via method a using Tp′(CO)$_3$WH and phenylacetylene as the substrate produced 32% of brown **1**.

Tp′(CO)$_2$W(η^2-C(Ph)=C(H)Ph) (2). This compound previously has been synthesized by LiHBEt$_3$ addition to [Tp′(CO)$_2$W(η^2-PhC≡CPh)][BF$_4$].[45] The present synthesis via method a using Tp′(CO)$_3$WH and diphenylacetylene as the substrate produced 38% of olive green **2**.

Tp′(CO)$_2$W≡CCH$_3$ (3). Method a. A solution containing 1.00 g (1.77 mmol) of Tp′(CO)$_3$WH in 150 mL of THF was prepared. Acetylene was bubbled through the solution (ca. 1 s^{-1}) during a 3 h photolysis period. Solvent was removed, and the residue was chromatographed on alumina with hexanes−

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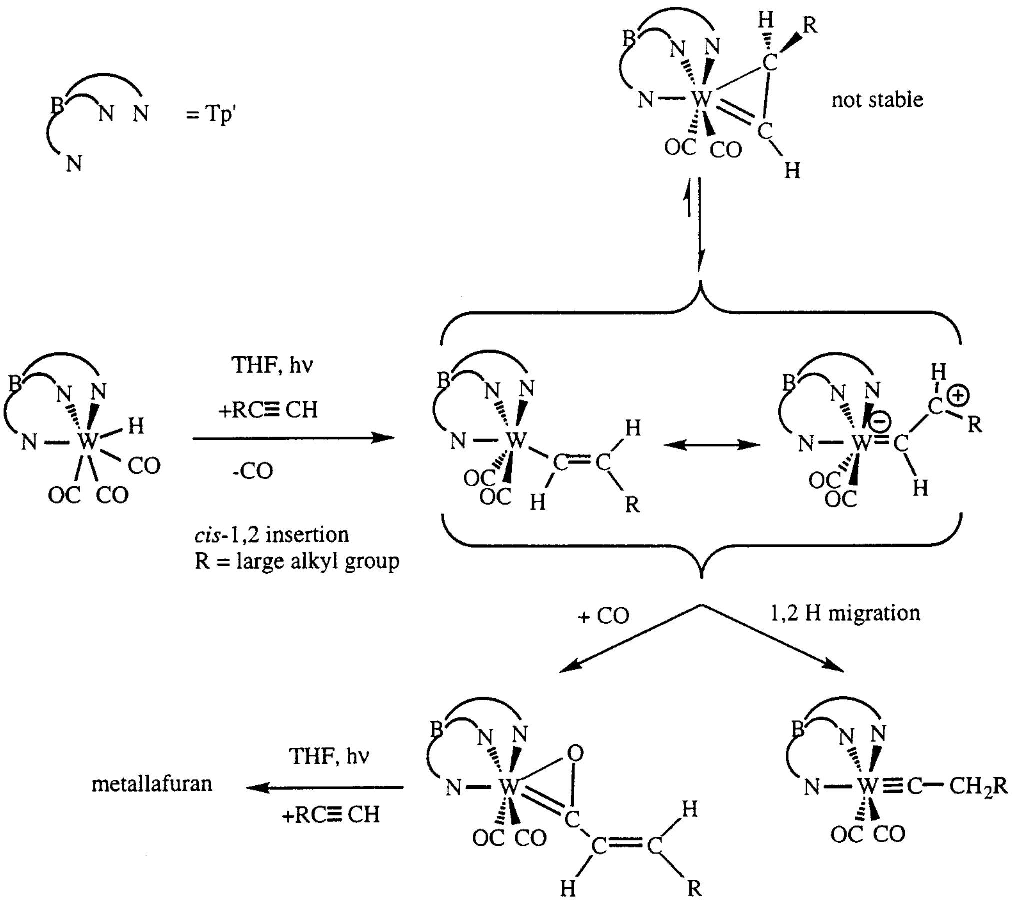
Scheme 3. Reaction Pathways for *trans*-σ-Vinyl Intermediates



CH_2Cl_2 (5:1) as the eluent. Removal of solvent produced 0.215 g (21%) of a bright yellow solid.

Method b. A solution containing 0.50 g (0.70 mmol) of [Tp′(CO)$_2$W(η^2-HC≡CH)][O_3SCF_3] in 60 mL of THF was prepared and cooled to −78 °C. Upon addition of 1 equiv of $LiHBEt_3$ (1.0 M in THF, 0.70 mL, 0.70 mmol), the green solution turned brown. An IR spectrum of the reaction after complete addition of the hydride reagent revealed the presence of Tp′(CO)$_2$W(η^2-CH═CH$_2$) (ν_{CO} = 1952, 1859 cm^{-1}) and Tp′(CO)$_2$W≡CCH$_3$ (ν_{CO} = 1966, 1873 cm^{-1}). Removal of solvent after warming to room temperature followed by chromatography on alumina produced 0.160 g (40%) of Tp′(CO)$_2$W≡CCH$_3$. Complex **3** was identified as Tp′(CO)$_2$W≡CCH$_3$ by comparison to literature data.[53] IR (THF, cm^{-1}): ν_{CO} 1966, 1873. ^{1}H NMR (CDCl$_3$, δ): 5.85, 5.74 (2:1, Tp′ *H*), 2.43 ($^3J_{WH}$ = 7.5 Hz, ≡CC*H*$_3$), 2.52, 2.41, 2.33, 2.30 (6:3:6:3, Tp′ C*H*$_3$).

Tp′(CO)$_2$W(η^2-C(SiMe$_3$)═CH$_2$) (4) and Tp′(CO)$_2$W(≡C−CH$_2$SiMe$_3$) (5). A solution containing 0.500 g (0.883 mmol) of Tp′(CO)$_3$WH and 0.20 mL (1.42 mmol) of (trimethylsilyl)acetylene in 100 mL of THF was prepared. The yellow solution was irradiated for 1.5 h, and then solvent was removed. The resultant brown oil was triturated with 20 mL of hexanes for 0.5 h to produce an orange solution over a brown precipitate. The supernatant liquid was filtered from the residue, and the residue was extracted with 2 × 10 mL portions of hexanes. Solvent was removed from the combined hexane extracts to produce 0.370 g (66%) of a brown-orange solid. Chromatographic separation was complicated by decomposition and hydrolysis to produce Tp′(CO)$_2$W≡CCH$_3$, but a portion of clean Tp′(CO)$_2$W(η^2-C(SiMe$_3$)═CH$_2$) (**4**) was obtained for spectroscopic characterization and isomerization studies.

Tp′(CO)$_2$W(η^2-C(SiMe$_3$)═CH$_2$) (4). IR (hexanes, cm^{-1}): ν_{CO} 1962, 1876; ν_{CN} 1545. ^{1}H NMR (CDCl$_3$, δ): Tp′(CO)$_2$W(η^2-C(SiMe$_3$)═CH$_2$) 5.87, 5.80 (1:2, Tp′ C*H*), 2.69(br), 2.40, 2.34, 1.81 (br) (3:6:3:6, Tp′ C*H*$_3$), 1.38 (br, η^2-C(SiMe$_3$)═C*H*$_2$), 0.35 (br, Si(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$, δ): Tp′(CO)$_2$W(η^2-C(SiMe$_3$)═CH$_2$) 252.6 (br, $^1J_{WC}$ = 32 Hz, η^2-*C*(Si(CH$_3$)$_3$)═CH$_2$), 221.7 ($^1J_{WC}$ = 156 Hz, *C*O), 153.7, 150.7, 144.6, 143.8 (1:2:1:2, Tp′ *C*CH$_3$), 107.3, 106.8 (1:2, Tp′ *C*CH), 30.6 (t, $^1J_{CH}$ = 159 Hz, η^2-C(SiMe$_3$)═*C*H$_2$), 15.7, 14.3, 12.8, 12.6 (1:2:1:2, Tp′ *C*H$_3$), −1.67 ($^1J_{SiC}$ = 53 Hz, Si(*C*H$_3$)$_3$).

Tp′(CO)$_2$W(≡C−CH$_2$SiMe$_3$) (5). IR (hexanes, cm^{-1}): ν_{CO} 1968, 1876; ν_{CN} 1545. ^{1}H NMR (CDCl$_3$, δ): 5.86, 5.73 (1:2, Tp′ C*H*), 2.55, 2.42, 2.34, 2.30 (6:3:6:3, Tp′ C*H*$_3$), 2.48 ($^3J_{WH}$ = 8 Hz, ≡CC*H*$_2$SiMe$_3$), 0.23 (Si(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$, δ): 295.1 (t, $^2J_{CH}$ = 8 Hz, ≡*C*CH$_2$SiMe$_3$), 225.1 ($^1J_{WC}$ = 170 Hz, *C*O), 152.1, 151.9, 144.6, 144.2 (1:2:1:2, Tp′ *C*CH$_3$), 106.8, 106.3 (1:2, Tp′ *C*CH), 47.2 (t, $^1J_{CH}$ = 120 Hz, (≡C*C*H$_2$SiMe$_3$), 16.5, 15.1, 12.6, 12.5 (2:1:2:1, Tp′ *C*H$_3$), −0.46 ($^1J_{SiC}$ = 51.3 Hz, Si(*C*H$_3$)$_3$).

Tp′(CO)$_2$W(*trans*-η^2-C(═O)CH═CHC(CH$_3$)$_3$) (6). A solution containing 1.00 g (1.77 mmol) of Tp′(CO)$_3$WH and 0.23 mL (1.87 mmol) of 3,3-dimethyl-1-butyne in 130 mL of THF was prepared. The mixture was irradiated for 2.5 h and then stirred for 1 h. The solvent was evaporated, and the black residue was chromatographed on alumina with hexanes as the eluent. A yellow-green band was collected. The eluent was changed to CH$_2$Cl$_2$, and a dark colored band was eluted. Solvent was evaporated from the dark band to give a black oil, which was rechromatographed on alumina with hexanes−CH$_2$Cl$_2$ (6:1) as the eluent. A yellow-green band was collected and added to the previous yellow-green fraction. A dark band was collected with CH$_2$Cl$_2$. Solvent was evaporated from the dark band to yield 0.260 g of a black solid, which was identified as Tp′(CO)$_2$W(*trans*-η^2-C(═O)CH═CHC(CH$_3$)$_3$) (23%; **6**). The green oil was identified as an inseparable mixture of Tp′(CO)$_2$W(η^2-C(C(CH$_3$)$_3$)═CH$_2$) (**7**) and Tp′(CO)$_2$W≡CCH$_2$C(CH$_3$)$_3$ (**8**).

Tp′(CO)$_2$W(*trans*-η^2-C(═O)CH═CHC(CH$_3$)$_3$) (6). IR (KBr, cm^{-1}): ν_{BH} 2554; ν_{CO} 1936, 1833; ν_{CN} 1545. ^{1}H NMR (CDCl$_3$, δ): 7.05 (d, $^1J_{HH}$ = 15.6 Hz, η^2-C(═O)C*H*═CHC(CH$_3$)$_3$), 6.85

(d, $^1J_{HH}$ = 15.6 Hz, η^2-C(=O)CH=C*H*C(CH$_3$)$_3$), 5.87, 5.81 (1:2, Tp′ C*H*), 2.41, 2.36, 2.33, 2.10 (3:6:3:6, Tp′ C*H*$_3$), 1.21 (η^2-C(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$, δ): 235.2 (dd, $^2J_{CH} \approx {}^3J_{CH} \approx 6.5$ Hz, $^1J_{WC}$ = 20 Hz, η^2-*C*(=O)CH=CHC(CH$_3$)$_3$), 229.7 ($^1J_{WC}$ = 170 Hz, *C*O), 161.5 (d of unodecaplets (11 lines each), $^1J_{CH}$ = 140 Hz, $^2J_{CH} = {}^3J_{CH}$ = 4.6 Hz, η^2-C(=O)CH=*C*HC(CH$_3$)$_3$), 152.7, 151.9, 145.5, 143.8 (1:2:1:2 Tp′ *C*CH$_3$), 119.1 (d, $^1J_{CH}$ = 160 Hz, η^2-C(=O)*C*H=CHC(CH$_3$)$_3$), 107.2, 106.8 (1:2, Tp′ *C*H), 34.4 (η^2-C(=O)CH=CH*C*(CH$_3$)$_3$), 28.7 (η^2-C(=O)CH=CHC-(*C*H$_3$)$_3$), 16.1, 13.5, 13.1, 12.4 (1:2:1:2, Tp′ C*C*H$_3$). Anal. Calcd for $WC_{24}H_{33}N_6BO_3$: C, 44.47; H, 5.13; N, 12.96. Found: C, 44.72; H, 5.16; N, 12.77.

Tp′(CO)$_2$W(C(C(CH$_3$)$_3$)=CH$_2$) (7). A solution containing 0.75 g (1.0 mmol) of [Tp′(CO)$_2$W(η^2-HC≡CBu^t)][O$_3$SCF$_3$] in 100 mL of THF was prepared and cooled to −78 °C. The addition of 1.0 mL of LiHBEt$_3$ (1.0 M in THF, 1.0 mmol) caused a color change from dark green to orange. The solvent was removed, and the residue was chromatographed on alumina with 3:1 hexanes−CH$_2$Cl$_2$ as the eluent. An orange fraction was collected. Removal of the solvent produced 0.180 g (29%) of orange **7**. IR (KBr, cm^{-1}): ν_{BH} 2538; ν_{CO} 1958, 1859; ν_{CN} 1545. ^{1}H NMR (CDCl$_3$, δ); 5.83, 5.80 (1:2, Tp′ C*H*), 2.63, 2.39, 2.36, 1.93 (3:6:3:6, Tp′ C*H*$_3$), 1.49 (C(C*H*$_3$)$_3$), 1.10 (=C*H*$_2$, $^2J_{WH}$ = 13.5 Hz). ^{13}C NMR (CDCl$_3$, δ); 260.4 (*C*(C(CH$_3$)$_3$)=CH$_2$, $^1J_{WC}$ = 30 Hz), 223.2 (*C*O, $^1J_{WC}$ = 150 Hz), 153.1, 151.1, 144.5, 143.8 (1:2:1:2, Tp′ *C*CH$_3$), 107.1, 106.9 (1:2. Tp′ *C*H), 51.6 (*C*(CH$_3$)$_3$), 27.8 (C(*C*H$_3$)$_3$, $^1J_{CH}$ = 126 Hz), 15,7, 14.3, 12.8, 12.6 (1:2:1:2, Tp′ C*C*H$_3$), 15.2 (=*C*H$_2$, $^1J_{WC}$ = 30 Hz, $^1J_{CH}$ = 157 Hz). Anal. Calcd for $WC_{23}H_{33}N_6BO_2$: C, 44.54; H, 5.36; N, 13.55. Found: C, 44.65; H, 5.35; N, 13.51.

Spectroscopic Characterization of a Mixture of 7 and 8 in Green Oil. IR (hexanes, cm^{-1}): **7**, ν_{CO} = 1956, 1864; **8**, ν_{CO} = 1969, 1875. ^{1}H NMR (250 MHz, CDCl$_3$, δ): **7**, 5.84, 5.81 (1:2, Tp′ C*H*), 2.65, 2.33, 2.29, 1.94 (3:6:3:6, Tp′ C*H*$_3$), 1.49 (C(C*H*$_3$)$_3$), 1.10 (=C*H*$_2$); **8**, 5.85, 5.72 (1:2, Tp′ C*H*), 2.64 (≡CC*H*$_2$C(CH$_3$)$_3$), 2.54, 2.41, 2.39, 2.34 (6:3:6:3, Tp′ C*H*$_3$), 1.10 (≡CCH$_2$C(C*H*$_3$)$_3$).

Tp′(CO)$_2$W(η^2-C(CH$_3$)=CH$_2$) (9). The synthesis and characterization of **9** via LiHBEt$_3$ addition to [Tp′(CO)$_2$W(η^2-MeC≡CH)][O$_3$SCF$_3$] has been reported.[55] Method a*:* a solution containing 2.00 g (3.53 mmol) of Tp′(CO)$_3$WH and 180 mL of THF was prepared. Propyne was bubbled through the solution until an appreciable concentration as monitored by IR ($\nu_{C≡C}$ 2126 cm^{-1}) was evident. The mixture was irradiated for 5 h, during which time the yellow solution turned a dark orange-brown. Solvent was removed, and the brown oil was chromatographed on alumina. Elution with hexanes−CH$_2$Cl$_2$ (6:1) allowed the collection of an orange band. Removal of solvent yielded 0.62 g of a brown-orange solid comprised of 90% of the η^2-vinyl complex and 10% of the corresponding metallafuran complex (see complex **10**). The corrected yield for the η^2-vinyl complex is 27%.

Tp′(CO)$_2$W(η^2(*C,O*)-C(CH$_3$)CHC(=O)CH=CHCH$_3$) (10). This complex was produced as a side product (ca. 10%) in the photolysis of Tp′(CO)$_3$WH with propyne (above). Separation from the major product (**9**) was not achieved. ^{1}H NMR (CDCl$_3$, δ): 7.12 (−C(CH$_3$)C*H*−), 6.40 (dq, $^3J_{HH}$ = 15.6 Hz, $^4J_{HH}$ = 1.6 Hz, −C*H*=CHCH$_3$), 6.13 (dq, $^3J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 7.2 Hz, −CH=C*H*CH$_3$), 5.95, 5.78 (1:2, Tp′ C*H*), 3.57 (−C(C*H*$_3$)−), 2.58, 2.41, 2.38, 1.61 (3:3:6:6, Tp′ C*H*$_3$), 1.89 (dd, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.6 Hz, =CHC*H*$_3$). ^{13}C NMR (CDCl$_3$, δ): 238.1 (−*C*(CH$_3$)−), 233.6 (*C*O), 177.3 (−*C*(O)−), 153.2, 151.6, 145.1, 143.5 (1:2:1:2, Tp′ *C*CH$_3$), 132.4 (d, $^1J_{CH}$ = 150 Hz, =*C*HCH$_3$), 126.0 (d, $^1J_{CH}$ = 150 Hz, −C(CH$_3$)CHC(O)*C*H=CHCH$_3$), 122.9 (d, $^1J_{CH}$ = 160 Hz, −*C*HC(O)−), 108.0, 106.5 (1:2, Tp′ *C*H), 37.7 (q, $^1J_{CH}$ = 130 Hz, −C(*C*H$_3$)−), 18.1 (=CH*C*H$_3$), 15.9, 13.6, 13.2, 12.6 (1:2:1:2, Tp′ C*C*H$_3$).

Tp′(CO)$_2$W(η^2-C(Bu^n)=CH$_2$) (11). The synthesis and characterization of **11** via LiHBEt$_3$ addition to [Tp′(CO)$_2$W(η^2-Bu^{n}C≡CH)][O$_3$SCF$_3$]has been reported.[55] Method a, using Tp′(CO)$_3$WH with 1-hexyne as the substrate and a 2.5 h photolysis time, yielded reasonably clean **11** in 46% yield following alumina chromatography. Photochemical synthesis of **11** invariably results in traces of **12**.

Tp′(CO)$_2$W(η^2(*C,O*)-C(Bu^n)CHC(=O)CH=CHBu^n) (12). A solution containing 2.00 g (3.53 mmol) of Tp′(CO)$_3$WH and 1.0 mL (8.7 mmol) of 1-hexyne in 150 mL of THF was prepared. The yellow solution was irradiated for 17 h, producing a dark green-yellow solution. Solvent was evaporated from this solution to produce an oil. The oily residue was dissolved in 11 mL of methanol. After 1.5 h of stirring, a color change to dark red-orange was evident. Solvent was again evaporated, and the residue was then chromatographed on alumina (hexanes−CH$_2$Cl$_2$, 3:1). An orange band was collected. After solvent evaporation, 6 mL of methanol was used to wash the oil, forming a bright orange precipitate. The solid was filtered and placed under vacuum to dry. The ^{1}H NMR spectrum of this solid revealed a 2:1 mixture of products (**12**:**11**). The orange solid was then chromatographed on weakly acidic alumina with hexanes−CH$_2$Cl$_2$ (1:1) as the eluent. An orange band was collected. Evaporation of solvent yielded 0.350 g (14%) of analytically pure **12**. IR (KBr, cm^{-1}); ν_{BH} 2550; ν_{CO} 1942, 1854; ν_{CN} 1547. ^{1}H NMR (CDCl$_3$, δ, not all *n*-Bu signals reported): 7.32 (s, −C(Bu^n)C*H*−), 6.38 (d (br), $^3J_{HH}$ = 15.6 Hz, −C*H*=CHBu^n), 6.12 (dt, $^3J_{HH}$ = 15.6 Hz, $^3J_{HH}$ = 7.0 Hz, =C*H*Bu^n), 5.94, 5.78 (1:2, Tp′ C*H*), 3.90 (m, −C(C*H*$_2$Pr^n)), 2.57, 2.40, 2.38, 1.61 (3:3:6:6, Tp′ C*H*$_3$), 2.20 (dt, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 6.6 Hz, =CHC*H*$_2$Pr^n). ^{13}C NMR (CDCl$_3$, δ, not all *n*-Bu signals reported): 238.9 (−*C*(Bu^n)−), 238.5 ($^1J_{WC}$ = 154 Hz, *C*O), 178.0 (−C(Bu^n)CH*C*(O)CH=CHBu^n), 153.2, 151.7, 145.0, 137.6 (1:2:1:2, Tp′ *C*CH$_3$), 137.6 (d, $^1J_{CH}$ = 150 Hz, =*C*HBu^n), 124.9 (d, $^1J_{CH}$ = 150 Hz, −*C*H=CHBu^n), 120.4 (d, $^1J_{CH}$ = 150 Hz, −C(Bu^n)*C*H−), 108.1, 106.6 (1:2, Tp′*C*H), 51.1 (t, $^1J_{CH}$ = 127 Hz, −C(*C*H$_2$Pr^n)−), 15.9, 14.2, 13.9, 13.6, 13.2, 12.6 (1:1:1:2:1:2, Tp′ C*C*H$_3$, *C*H$_3$ of 2 *n*-Bu groups). Anal. Calcd for $WC_{30}H_{43}N_6BO_3$: C, 49.34; H, 5.93; N, 11.51. Found: C, 49.48; H, 6.00; N, 11.51.

Tp′(CO)$_2$W(η^3-CH$_2$CHCHSiMe$_3$) (13). A solution containing 1.00 g (1.77 mmol) of Tp(CO)$_3$WH and 0.54 mL of Me$_3$-SiC≡CCH$_3$ (3.65 mmol) in 200 mL of THF was prepared. Irradiation for 1.5 h produced a mixture containing **13** (ν_{CO} 1923, 1830 cm^{-1}), Tp′(CO)$_2$W(η^2-C(CH$_3$=CHSiMe$_3$) (ν_{CO} 1945, 1843 cm^{-1}), and Tp′(CO)$_2$W≡CEt (ν_{CO} 1960, 1868 cm^{-1}). Stirring of the mixture for 10 h promoted conversion of the vinyl complex to a mixture containing only **13** and the carbyne product. Isolation of 0.600 g of the mixed allyl and carbyne products was accomplished by chromatography on alumina. Rinsing of the solid with CH$_2$Cl$_2$ produced a small amount of **13x** as a residue. Separate spectroscopic characterizations of **13x** and the mixed products allowed characterization of all components in the mixture. IR (THF, cm^{-1}): ν_{CO} 1923, 1823; ν_{CN} 1545. ^{1}H NMR (CDCl$_3$, δ): **13x**, 5.80, 5.78, 5.66 (Tp′ *H*), 3.22 (dt, $^3J_{ca} = {}^3J_{ca'}$ = 9.4 Hz, $^3J_{cs}$ = 6.8 Hz, η^3-CHHC*H*CHSi-(CH$_3$)$_3$), 3.13 (dd, $^3J_{cs}$ = 6.2 Hz, $^2J_{as}$ = 3.2 Hz, η^3-C*H*HCHCHSi-(CH$_3$)$_3$), 2.90, 2.52, 2.47, 2.34, 2.34, 2.06 (Tp′ C*H*$_3$), 2.83 (dd, $^3J_{ca}$ = 9.2 Hz, $^2J_{as}$ = 3.2 Hz, η^3-CH*H*CHCHSi(CH$_3$)$_3$), 2.11 (dd, $^3J_{ca'}$ = 9.6 Hz, $^4J_{sa'}$ = 0.6 Hz, η^3-CHHCHC*H*Si(CH$_3$)$_3$), 0.09 ($^2J_{SiH}$ = 6.1 Hz, Si(C*H*$_3$)$_3$); **13s**, 5.88, 5.80, 5.78 (Tp′ *H*), 5.15 (dt, $^3J_{ca} = {}^3J_{ca'}$ = 8.2 Hz, $^3J_{cs}$ = 5.2 Hz, η^3-CHHC*H*CHSi(CH$_3$)$_3$), 2.13 (d, $^3J_{sc}$ = 4.8 Hz, η^3-C*H*HCHCHSi(CH$_3$)$_3$) 1.92, 1.59 (d each, $^1J_{ca} \approx {}^1J_{ca'}$ = 8 Hz, η^3-CH*H*CHC*H*Si(CH$_3$)$_3$), 0.34 ($^2J_{SiH}$ = 6.8 Hz, Si(C*H*$_3$)$_3$). ^{13}C NMR (CDCl$_3$, δ): **13x**, 223.7 ($^1J_{WC}$ = 150 Hz, *C*O), 220.4 (d, $^1J_{WC}$ = 160 Hz, $^3J_{CH}$ = 10 Hz, *C*O), 154.9, 154.1, 153.6, 146.4, 145.9, 143.4 (Tp′*C*CH$_3$), 108.4, 108.3, 106.2 (Tp′*C*H), 73.5 (dd, $^1J_{CH}$ = 168 Hz, $^3J_{CH}$ = 4.6 Hz, η^3-CHH*C*H-CHSi(CH$_3$)$_3$), 58.5 (t, $^1J_{CH}$ = 159 Hz, η^3-*C*HHCHCHSi(CH$_3$)$_3$), 55.6 (d, $^1J_{CH}$ = 130 Hz, η^3-CHHCH*C*HSi(CH$_3$)$_3$), 17.3, 17.0, 15.8, 12.8, 12.7 (1:1:1:1:2, Tp′*C*H$_3$), 2.07 (q, $^1J_{CH}$ = 118 Hz, $^1J_{SiC}$ = 51.3 Hz, Si(*C*H)$_3$)$_3$); **13s**, 231.4, 228.9 (*C*O), 153.1, 151.2, 149.7, 144.8, 144.0, 143.9 (Tp′ *C*CH$_3$), 107.7, 107.3, 107.2 (Tp′ *C*H), 85.1 (d, $^1J_{CH}$ = 173 Hz, η^3-CHH*C*HCHSi(CH$_3$)$_3$), 60.1 (t, $^1J_{CH}$ = 160 Hz, η^3-*C*HHCHCHSi(CH$_3$)$_3$), 48.61 (d, $^1J_{CH}$ =

Table 4. Crystallographic Data and Data Collection Parameters for 2 and 12

	2	12
	Crystallographic Data	
empirical formula	$WC_{31}H_{33}N_7OB\cdot 2CH_2Cl_2$	$WC_{30}H_{43}BN_6O_2$
fw	886.16	730.36
cryst dimens, mm	0.40 × 0.40 × 0.20	0.30 × 0.30 × 0.15
space group	$P2_1/n$	$P2_1/n$
cell params		
a, Å	10.7356(8)	17.8657(20)
b, Å	10.8007(6)	10.2112(13)
c,. Å	31.0408(16)	18.083(3)
β, deg	93.318(12)	93.982(12)
V, Å^3	3593.2(4)	3290.9(8)
Z	4	4
calcd density, g/cm^3	1.638	1.474
	Collection and Refinement Parameters	
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
monochromator	graphite	graphite
μ, cm^{-1}	36.2	36.1
scan type	Ω	$\theta/2\theta$
2θ limit, deg	50.0	46.0
quadrants collected	$\pm h,+k,+l$	$\pm h,+k,+l$
total no. of rflns	6144	4577
no. of data with $I \geq 2.5\sigma(I)$	4448	3333
R,[a] %	3.9	3.3
R_w,[a] %	5.2	4.1
GOF	1.56	1.33
no. of params	425	370
largest parameter shift (shift/error ratio)	0.050	0.063

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

129 Hz, η^3-CHHCHCHSi(CH$_3$)$_3$), 0.81 (q, $^1J_{CH}$ = 118 Hz, $^1J_{SiC}$ = 51.3 Hz, Si(*C*H)$_3$)$_3$). Anal. Calcd for $WC_{23}H_{37}N_6BO_2Si$ (the sample contained a mixture of allyl (**13**) and carbyne (**14**) isomers): C, 42.48; H, 5.42; N, 12.92. Found: C, 41.66; H, 5.33; N, 13.01.

Tp′(CO)$_2$W≡CCHMeSiMe$_3$ (14). A sample of **13x** was heated in toluene-d_8 for 9 h. Isolation of **14** was accomplished by flash chromatography with hexanes/CH$_2$Cl$_2$ on dried alumina. Partial hydrolysis to Tp′(CO)$_2$W≡CEt accompanied isomerization and isolation. IR (cm^{-1}): ν_{CO} 1964, 1867 (CDCl$_3$); ν_{CO} 1968, 1871 ν_{CN} 1545 (THF). ^{1}H NMR (CDCl$_3$, δ, ppm): 5.84, 5.71 (2:1, Tp′ *H*), 2.48 (q, $^3J_{HH}$ = 7.2 Hz, ≡CC*H*MeSiMe$_3$), 2.54, 2.51, 2.42, 2.34, 2.29 (3:3:3:6:3), 1.28 (d, $^3J_{HH}$ = 7.2 Hz, ≡CCH*Me*SiMe$_3$), 0.19 ($^2J_{SiH}$ = 6.8 Hz, ≡CCHMeSi*Me*$_3$). ^{13}C NMR (CDCl$_3$, δ, ppm): 301.4 (≡*C*CHMeSiMe$_3$), 225.7, 224.8 ($^1J_{WC}$ = 140 Hz each, *C*O), 152.1, 151.9, 151.5, 144.5, 144.4, 144.1 (Tp′ *C*CH$_3$), 106.4, 106.2, 106.1 (Tp′*C*H), 49.7 (d, $^1J_{CH}$ = 119 Hz, $^2J_{WC}$ = 35 Hz, ≡C*C*HMeSiMe$_3$), 17.2, 16.3, 15.2, 13.6, 12.8, 12.7, 12.5 (Tp′ *C*H$_3$, ≡CCH*Me*SiMe$_3$), −1.82 (q, $^1J_{CH}$ = 119 Hz, $^1J_{SiC}$ = 50 Hz, ≡CCHMeSi*Me*$_3$).

Crystal Structure Determinations. Crystal structure determinations were performed by Dr. Peter S. White (UNC−CH) under the conditions listed in Table 4.

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Supporting Information Available: Crystallographic data for **2** and **12** and NMR spectra for **4**, **5**, **7**, **8**, **9**, **10** and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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