Transient Generation of the Reactive Carbene Complex $[Cp(CO)_2W{=}CH(Tol)]^+$ and Its Reactions with Alkynes To Form Vinylcarbene, Allyl, Naphthol, Diene, and Metallafuran Complexes

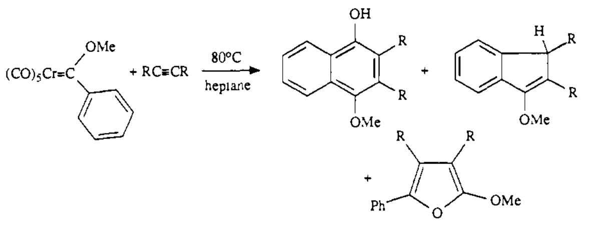
Kevin E. Garrett,[†] **John B. Sheridan,**[†] **Daniel B. Pourreau,**[†] **Wu Chang Feng,**[†] **Gregory L. Geoffroy,***[,†] **Donna L. Staley,**[‡] **and Arnold L. Rheingold**[‡]

Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802, and Department of Chemistry, The University of Delaware, Newark, Delaware 19716. *Received April 20, 1989*

Abstract: Although $Cp(CO)_2W{\equiv}CTol$, **9**, does not itself react with alkynes, protonation of −78 °C solutions of the complex with HBF_4 generates the transient carbene complex $[Cp(CO)_2W{=}CH(Tol)]^+$ which readily incorporates alkyne. Protonation of **9** in the presence of $PhC{\equiv}CPh$ gives the vinylcarbene complex $[Cp(CO)_2W{=}C(Ph)C(Ph){=}CH(Tol)]BF_4$, **14**, which results from insertion of the alkyne into the tungsten–carbene bond. Vinylcarbene complex **14** readily undergoes substitution of iodide for CO to give the neutral vinylcarbene complex $Cp(CO)(I)W{=}C(Ph)C(Ph){=}CH(Tol)$, **15**, which has been crystallographically characterized. The vinylcarbene ligand is coordinated to tungsten via the three carbon atoms (W–C = 1.999 (7), 2.305 (8), 2.293 (8) Å) with a 130.4° bend in the C–C–C linkage. The geometrical parameters indicate an sp^2 hybridization for each of the three carbons, but the substituents on this ligand are rotated such that π-bonding between the carbons is far from optimal. Vinylcarbene complex **14** also reacts with $[BH_4]^-$ and $P(Bu^n)_3$ to form the allyl complexes $Cp(CO)_2W\{\eta^3\text{-}PhCHC(Ph)CH(Tol)\}$ and $[Cp(CO)_2W\{\eta^3\text{-}(Bu^n{}_3P)(Ph)CC(Ph)CH(Tol)\}]BF_4$, respectively. Complex **14** also reacts with the nitrone $PhCH{=}N(O)Me$ to form the metallafuran complex $Cp(CO)_2W\{OC(Ph)C(Ph)C(Tol)\}$, **19**. This species results from oxygen-atom transfer from the nitrone to the carbene carbon of **14**, deprotonation of the vinyl group, and ring closure. The metallafuran complex **19** has been crystallographically characterized. It possesses a planar metallafuran ring with bond distances within the ring implying delocalized bonding. Protonation of $Cp(CO)_2W{\equiv}CTol$ in the presence of $MeC{\equiv}CMe$ and CO gives high yield formation of $[Cp(CO)_2W\{C_{13}H_{14}O\}]BF_4$, **20**, which possesses a coordinated naphthol ligand. The latter can be released from the metal by air oxidation, and the naphthol ligand undergoes deprotonation to form the allyl complex $Cp(CO)_2W\{C_{13}H_{13}O\}$. Reaction of the carbyne complex $Cp(CO)_2W{\equiv}C\{2,6\text{-}Me_2C_6H_3\}$ with HBF_4 in the presence of $MeC{\equiv}CMe$ led to the formation of $[Cp(CO)_2W\{C_{14}H_{16}O_2\}]^+$, **25**, which possesses a coordinated diene ligand assembled by a benzannulation reaction from the carbyne, alkyne, and a CO ligand. The relevance of these various reactions to the general mechanism of naphthol formation from metal carbenes and alkynes is discussed.

Introduction

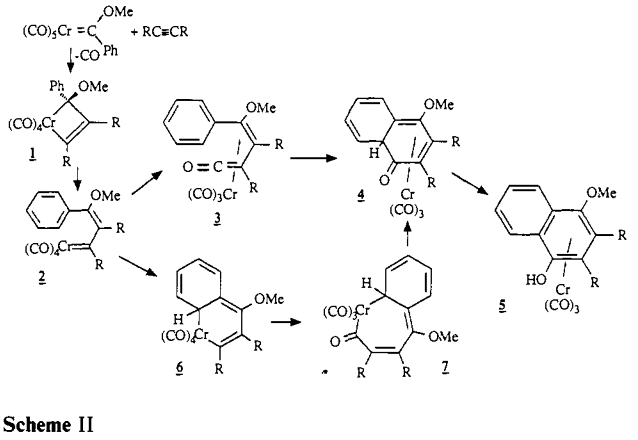
Transition-metal carbene complexes have found numerous applications in organic synthesis,[1,2] and one especially important class of reactions is one that occurs between carbene complexes and alkynes.[2,3] These reactions give a variety of products, depending upon the metal involved, its ligand set, the carbene substituents, and the nature of the alkyne employed. A typical set of organic products isolated after oxidative workup of such a reaction with $(CO)_5Cr{=}C(OMe)Ph$ is shown in eq 1.[2c]



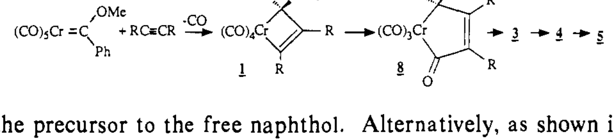
(1)

Even though the synthetic applications of these types of reactions are now well-established, the mechanism(s) by which they occur have never been fully elucidated.[2,3a] For the formation of naphthols from metal carbenes and alkynes, the mechanisms shown in Schemes I and II have been invoked, although there is no general agreement as to which specific path is followed.[3a] An early step common to each proposed path is the formation of the metallacyclobutene complex **1**. This species can ring open to yield the vinylcarbene complex **2** which would give the vinylketene complex **3** upon CO insertion. Electrocyclic ring closure to give **4** followed by a 1,3-hydrogen migration would yield complex **5**, the precursor to the free naphthol. Alternatively, as shown in Scheme I, metalation of the arene ring can occur from the vi-

Scheme I



Scheme II



[†] The Pennsylvania State University.

[‡] The University of Delaware.

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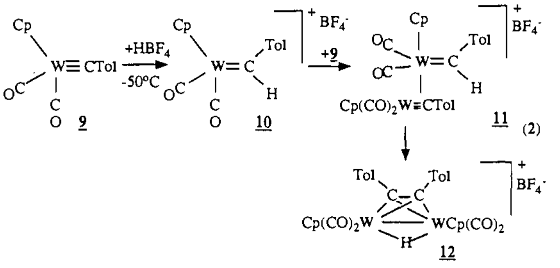
nylcarbene complex **2** to form the metallacycle **6**. This species would then yield **7** upon carbonylation, and reductive elimination from **7** would give intermediate **4** and from that **5**. A third suggested mechanism is shown in Scheme II and involves insertion of CO into the metallacyclobutene **1** to form a metallacyclopentenone **8** which could rearrange to give vinylketene complex **3** and from that **4** and **5**.[2,3a] Although a metallacyclobutene complex has generally been proposed as a common intermediate in the mechanisms of Schemes I and II, there is no direct evidence for its involvement. Indeed, the results described herein indicate that the reaction may well proceed directly from the carbene to the vinylcarbene stage without the intermediacy of a metallacyclobutene complex.

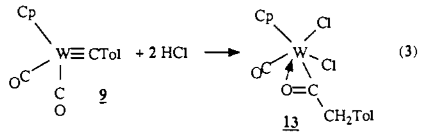
It has proven difficult to completely validate the mechanistic suggestions of Scheme I since the rate-limiting step typically involves ligand loss to open a coordination site for the alkyne to bind. Once bound, rapid ring closure occurs to give the observed products. No single reaction has been followed completely through the individual steps illustrated in Schemes I and II, although there are now several examples of the addition of alkynes to carbenes to form vinylcarbenes[5,6a–c] and the carbonylation of vinylcarbenes to yield vinylketenes.[4e,5e,k,6] However, to our knowledge the conversion of a well-characterized vinylcarbene or vinylketene complex into a naphthol or indene product has never been achieved.

One approach to investigating these mechanisms in more detail is to generate a coordinatively unsaturated carbene complex at a temperature sufficiently low to retard subsequent reactions so that they can be studied in detail. This can be achieved to some degree by opening a coordination site for the alkyne to bind through photoinduced ligand loss at low temperature as illustrated in our earlier study of the photosubstitution chemistry of $(CO)_5W{=}C(OMe)Ph$.[7] Irradiation of this complex in the presence of excess diphenylacetylene at −40 °C gave CO loss and formation of a carbene–alkyne complex that was isolated and was spectroscopically characterized.[7] Upon warmup to room temperature, this species rapidly underwent ring closure to yield an indenyl ether, but no intermediates could be detected in this conversion.

Another approach to generating coordinatively unsaturated carbene complexes is through the addition of electrophiles to nucleophilic carbyne ligands.[8-10] This is well illustrated by the work of Stone and co-workers summarized in eq 2.[8] Protonation of $Cp(CO)_2W{\equiv}CTol$, **9**, at −50 °C was proposed to give transient formation of the reactive carbene complex $[Cp(CO)_2W{=}C(H)Tol]^+$, **10**. Although this species was not detected, its intermediacy was inferred from the formation of **12** by the presumed mechanism of eq 2 and by the formation of $Cp(CO)_2(I)W{=}C(H)Tol$ when the protonation was conducted in the presence of iodide.[8] Also, protonation of $Cp(CO)_2W{\equiv}CTol$ with HCl instead of HBF_4 was shown by Kreissl and co-workers to result in double proton addition to the carbyne carbon to form an alkyl ligand that subsequently yields the η^2-acyl complex **13** upon CO insertion, eq 3.[9]



9 10 11 12 (2)



9 13 (3)

Protonation of these carbyne complexes in the presence of alkynes has never been reported, although the isolobal analogy between carbyne complex **9** and alkynes and the apparent intermediacy of **11** in reaction 2 suggests this to be a promising reaction. We have accordingly examined the reactivity of carbyne complex **9** with HBF_4 in the presence of alkynes, and those reactions are described herein. As expected, the chemistry is markedly sensitive to the alkyne employed and to the carbene substituents. Protonation of **9** in the presence of $MeC{\equiv}CMe$ results in formation of a naphthol complex analogous to **5** in Scheme I. By varying the carbene and alkyne substituents, vinylcarbene and diene complexes analogous to intermediates **2** and **4** have been isolated and crystallographically defined. New transformations of vinylcarbene complexes are also described, including their reactions with nucleophiles to form allyl and metallafuran derivatives.

Results

Protonation of $Cp(CO)_2W{\equiv}CTol$, 9, in the Presence of $PhC{\equiv}CPh$. Addition of HBF_4 to a solution of **9** in the presence of $PhC{\equiv}CPh$ was found to give rapid formation of the η^3-vinylcarbene complex **14**, eq 4. For simplicity, complex **14** is drawn in eq 4 with a metal–carbene double bond and with a

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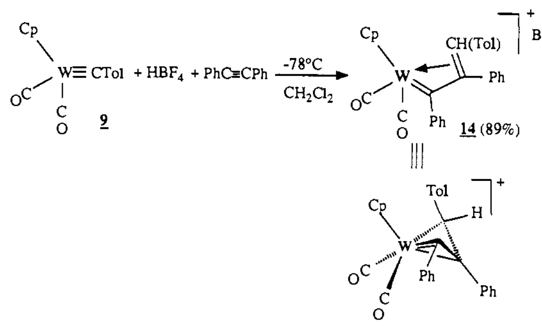
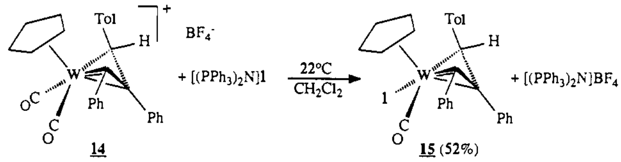


(4)

π-coordinated vinyl group, although the crystal structure of the derivative **15** discussed below indicates that the alternative drawing given in the equation is more accurate. Complex **14** was isolated in high yield as a thermally sensitive red solid and has been spectroscopically characterized. It has been further defined by its conversion to the crystallographically characterized vinylcarbene complex Cp(CO)(I)W=C(Ph)(Ph)C=CHTol, **15**, described below. Two ν(CO) bands at 2054 and 1975 cm^{-1} are present in the IR spectrum of **14**, indicating a dicarbonyl formulation, and its ^{1}H NMR spectrum shows characteristic Cp and vinyl proton resonances at δ 6.40 and 6.05, respectively. The ^{13}C{^{1}H} NMR spectrum of **14** shows a resonance at δ 269.3 ppm attributed to the carbene carbon and two resonances at δ 98.2 and 60.8 due to the vinyl carbons as well as Cp (δ 95.2) and aryl resonances. The δ 98.2 resonance splits into a doublet (J_{CH} = 184.6 Hz) upon recording the proton-coupled ^{13}C NMR spectrum, indicating its assignment to the terminal vinyl carbon bearing the hydrogen atom. The downfield δ 269.3 ppm resonance of **14** is in the region typical of metal carbenes and strongly indicates the η^3-vinylcarbene formulation drawn in eq 4 rather than a metallacyclobutene structure.

Iodide for CO Substitution in Vinylcarbene Complex 14. The vinylcarbene complex **14** rapidly undergoes substitution of CO by added iodide to give the neutral vinylcarbene complex **15**, eq 5. This complex was isolated as a yellow solid and has been crystallographically defined, Figures 1 and 2. Its spectroscopic data given in the Experimental Section are fully consistent with the determined structure. Furthermore, the similar positions of the vinylcarbene ^{13}C NMR resonances of complexes **14** and **15** [**14**, δ 269.3, 98.2, 60.8; **15**, δ 269.8, 91.1, 70.7] imply that the vinylcarbene ligand in **14** must be coordinated in a fashion similar to that which has been crystallographically established for **15**.



(5)

Crystal and Molecular Structure of Vinylcarbene Complex 15. Relevant crystallographic data for complex **15** are given in Tables I and II, and an ORTEP drawing is shown in Figure 1. An expanded view of the core of the molecule is drawn in Figure 2. The vinylcarbene ligand is coordinated to tungsten via three carbon atoms, although the W–C bond distances vary considerably. The W–C(10) distance of 1.999 (7) Å is a typical tungsten-carbon double bond value [compare to W(≡CBu^t)(=CHBu^t)(CH$_2$Bu^t)(1,2-dimethylphosphinoethane): W–C, 2.258 (9); W=C, 1.942 (9); W≡C, 1.785 (8) Å],[11] whereas the W–C(20) and W–C(30) distances of 2.305 (8) and 2.293 (8) are in the range of tungsten–carbon single bonds. Within the vinylcarbene ligand, the C(10)–C(20) and C(20)–(30) distances are nearly equal at 1.420 (11) and 1.443 (11) Å, respectively, and are midway between typical carbon–carbon single and double bond values. The C–C–C angles within the vinylcarbene ligand imply sp^2 hybridization about those carbons [C(10), 129.5°; C(20), 119.9° av; C(30), 124.2°]. As illustrated in Figure 2, the vinylcarbene ligand is bent with a hinge angle of 130.4° between the W–C(20)–C(10) and W–C(20)–C(30) planes. Other interplanar angles within this ligand

Table I. Crystallographic Data for Cp(CO)(I)W{=C(Ph)(Ph)C=CHTol}, **15**, and Cp(CO)$_2$W[OC(Ph)C(Ph)C(Tol)], **19**[a]

	15	**19**
(a) Crystal Parameters		
formula	$C_{28}H_{23}OIW\cdot{}^1/_2CH_2Cl_2$	$C_{29}H_{22}O_3W$
crystal system	monoclinic	monoclinic
space group	$I2/a$	$P2_1/n$
a, Å	16.383 (5)	12.130 (2)
b, Å	15.609 (5)	14.455 (3)
c, Å	20.935 (6)	13.572 (3)
β, deg	101.39 (2)	97.28 (2)
V, Å^3	5248 (3)	2360.5 (8)
Z	8	4
D(calcd)	1.84	1.695
μ(Mo Kα), cm^{-1}	59.35	52.0
temp, K	296	295
color	brown	deep red
size, mm	0.52 × 0.28 × 0.21	0.27 × 0.29 × 0.31
T_{max}/T_{min}	1.63	2.47
(b) Data Collection		
diffractometer	Nicolet R3m	
radiation	Mo Kα	
wavelength, Å	0.71073	
scan method	Wyckoff	
scan limits, deg	$4 \leq 2\theta \leq 50$	$4 \leq 2\theta \leq 55$
octants collected	$\pm h,+k,+l$	$\pm h,+k,+l$
rflns collected	4943	5881
indpdt rflns	4618	5429
obs rflns	3340 ($5\sigma F_o$)	4047 ($5\sigma F_o$)
R (merge)	0.032	0.023
std rflns	3 std/97 rflns	3 std/97 rflns
var in stds, %	<1	−2
(c) Refinement		
R(*F*), %	3.72	3.25
R(*wF*), %	3.95	4.23
GOF	1.017	0.99
Δ/σ (mean)	0.016	0.045
$\Delta(\rho)$, eÅ^{-3}	1.372	1.4 (near W)
N_o/N_v	10.3	14.7

[a] $R(F) = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R(wF) = \sum(w^{1/2}(|F_o| - |F_c|))/(w^{1/2}|F_o|)$; GOF $= [\sum w||F_o| - |F_c||/N_o - N_v]^{1/2}$.

Table II. Selected Bond Distances and Angles for the Vinylcarbene Complex Cp(CO)(I)W{=C(Ph)(Ph)C=CHTol}, **15**

(a) Bond Distances (Å)			
W–I	2.832 (1)	W–CNT[a]	2.010 (7)
W–C(1)	1.998 (10)	C(1)–O(1)	1.134 (13)
W–C(10)	1.999 (7)	C(10)–C(20)	1.420 (1)
W–C(20)	2.305 (8)	C(20)–C(30)	1.443 (11)
W–C(30)	2.293 (8)		

(b) Bond Angles (deg)			
I–W–C(1)	82.7 (3)	W–C(10)–C(16)	145.7 (5)
I–W–CNT[a]	112.7 (3)	W–C(10)–C(20)	82.9 (4)
I–W–C(10)	127.2 (2)	C(16)–C(10)–C(20)	129.5 (7)
I–W–C(20)	92.6 (2)	W–C(20)–C(30)	71.2 (4)
I–W–C(30)	81.0 (2)	W–C(20)–C(10)	59.4 (4)
C(1)–W–CNT	115.2 (3)	W–C(20)–C(26)	131.5 (5)
C(1)–W–C(10)	82.6 (3)	C(10)–C(20)–C(26)	126.1 (7)
C(1)–W–C(20)	91.6 (3)	C(26)–C(20)–C(30)	122.1 (6)
C(1)–W–C(30)	123.8 (4)	C(10)–C(20)–C(30)	111.4 (7)
C(10)–W–CNT	119.5 (4)	W–C(30)–C(36)	115.5 (5)
C(20)–W–CNT	144.5 (4)	W–C(30)–C(20)	72.2 (4)
C(30)–W–CNT	120.8 (4)	C(20)–C(30)–C(36)	124.2 (6)
W–C(1)–O(1)	177.9 (10)	C(36)–C(30)–H(30)	

(c) Interplanar angles (deg)	
W–C(10)–C(20)/W–C(30)–C(20)	130.4
C(30)–W–C(10)/C(30)–C(20)–C(10)	120.4
W–C(10)–C(16)/C(10)–C(20)–C(26)	117.8
C(36)–C(30)–H(30)/C(30)–C(20)–C(26)	135.0
C(36)–C(30)–H(30)/C(20)–C(10)–C(16)	96.1

[a] CNT denotes the centroid of the Cp ring.

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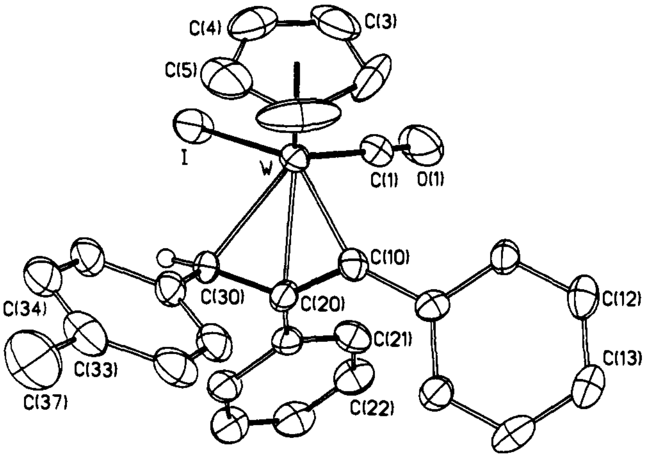


Figure 1. An ORTEP drawing of the vinylcarbene complex Cp(CO)(I)W{=C(Ph)C(Ph)CHTol}, **15**. Thermal ellipsoids are drawn at the 40% probability level, and hydrogen atoms have been omitted for clarity.

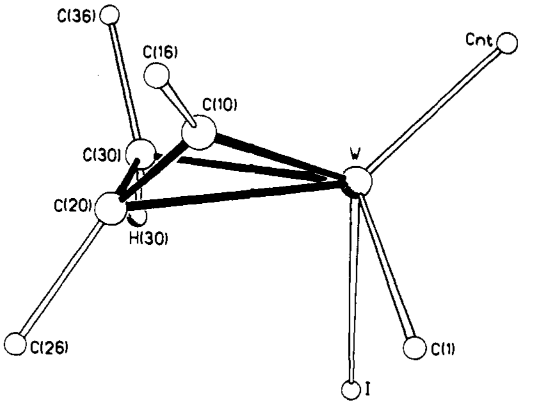


Figure 2. A drawing of the molecular core of the vinylcarbene complex Cp(CO)(I)W{=C(Ph)C(Ph)CHTol}, **15**. Cnt denotes the centroid of the cyclopentadienyl ring.

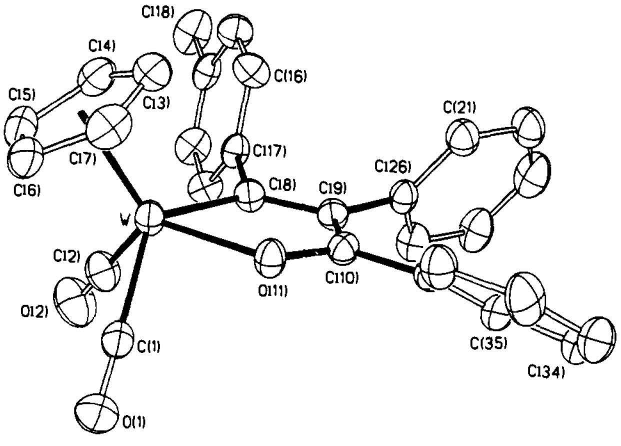


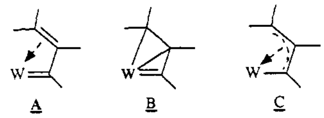
Figure 3. An ORTEP drawing for the metallafuran complex Cp(CO)$_2$W-[OC(Ph)C(Ph)C(Tol)], **19**.

are given in Table II. The structural details of the η^3-vinylcarbene ligand in complex **15** are similar to those found in all other crystallographically characterized complexes possessing ligands of this type.[5a,j,6f,12]

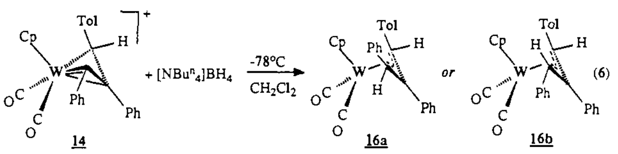
The interplanar angles and the drawing in Figure 2 show that the orientation of the vinylcarbene substituents is such that "normal" π-bonding between any of the three sp^2 carbon atoms would be difficult because none of the p orbitals are properly aligned for good orbital overlap. The electronic structure of η^3-vinylcarbene ligands and their orbital interaction with metal-based orbitals has never been fully addressed, although the classical resonance forms A–C have been drawn for these species.[3a,5a,j,6h,12] It is clear from the structural features of vinylcarbene complex **15** and the other structurally characterized η^3-vinylcarbene complexes[5a,j,6f,12] that none of the forms A–C provide an adequate description of the molecule. A full analysis of the bonding within this metal–ligand system will have to await the results of detailed electronic structure calculations.

Table III. Selected Bond Distances and Angles for the Metallafuran Complex Cp(W(CO)$_2$[OC(Ph)C(Ph)C(Tol)], **19**

(a) Bond Distances (Å)			
CNT–W	2.023 (5)	O(11)–W	2.100 (3)
C(1)–W	1.992 (5)	O(11)–C(10)	1.296 (6)
C(2)–W	1.962 (6)	C(8)–C(9)	1.393 (7)
C(8)–W	2.133 (5)	C(9)–C(10)	1.402 (7)
(b) Bond Angles (deg)			
CNT–W–C(1)	117.1 (3)	C(2)–W–C(8)	81.4 (2)
CNT–W–C(2)	116.7 (3)	C(2)–W–O(11)	125.5 (2)
CNT–W–C(8)	117.8 (3)	C(8)–W–O(11)	73.2 (2)
CNT–W–O(11)	118.9 (2)	W–C(8)–C(9)	117.5 (4)
C(1)–W–C(2)	78.5 (3)	C(8)–C(9)–C(10)	112.2 (5)
C(1)–W–C(8)	123.8 (2)	C(9)–C(10)–O(11)	117.1 (4)
C(1)–W–O(11)	77.2 (2)	C(10)–O(11)–W	120.0 (3)



Formation of Allyl Ligands via Addition of Nucleophiles to the Vinylcarbene Ligand of 14. The vinylcarbene ligand of complex **14** is susceptible to nucleophilic attack as indicated by its reaction with [NBu$^n_4$]BH$_4$ to form the allyl complex **16**, eq 6. This species was isolated as a yellow solid in 20% overall yield from **14**. It was spectroscopically characterized and is similar to the many well-known CpM(CO)$_2$(allyl) (M = Mo, W) complexes.[13] It shows a parent ion at m/z = 588 in its mass spectrum along with fragment ions corresponding to successive loss of two CO ligands. Its ^{1}H NMR spectrum shows resonances at δ 3.80 and 3.84 assigned to the two allyl protons, along with characteristic Cp and aromatic resonances. The ^{13}C{^{1}H} NMR spectrum of **16** shows resonances for the terminal allyl carbons at δ 47.1 and 47.6, and a resonance at δ 103.2 is assigned to the central allyl carbon. These are in the δ 42–86 ppm and δ 102–128 ranges typically found for terminal and central allyl carbons in other compounds.[14]



There are eight possible isomers of complex **16**, resulting from the endo and exo arrangements of the allyl ligand with respect to the Cp ligand in combination with the various syn and anti arrangements of the allyl substituents. The ^{1}H NMR data for complex **16** indicate the presence of only one isomer, although the data are not sufficient to determine exactly which isomer is formed. Faller and co-workers[13b–d] have shown that the endo/exo ratio in this family of complexes is very sensitive to the size and electronic properties of the allyl substituents, and it is not surprising that only one isomer is produced given the large size of the three aryl groups. On the basis of the crystal structure of the vinylcarbene complex **15** (Figure 2) and the presumed similar structure

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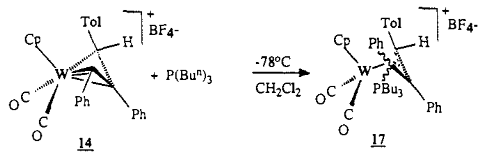
(12) Herrmann, W. A.; Fischer, R. A.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1263.

(13) (a) Faller, J. W.; Whitmore, B. C. *Organometallics* **1986**, *5*, 752. (b) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 3388. (c) Faller, J. W.; Adams, M. A. *J. Organomet. Chem.* **1979**, *170*, 71. (d) Faller, J. W.; Chen, C.-C.; Mattina, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361.

(14) Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257.

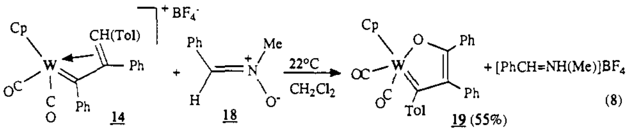
of **14**, the most logical isomers that would form are those sketched in eq 6 as **16a** and **16b**, with the all anti isomer **16a** more likely because of decreased steric interactions between the aryl substituents.

Tri(*n*-butyl)phosphine also adds to the vinylcarbene ligand of **14** to form the allyl complex **17** shown in eq 7. This species was isolated as a yellow solid and has been spectroscopically characterized. The two ν_{CO} bands (1965, 1892 cm^{-1}) in its IR spectrum indicate a dicarbonyl formulation, and their ~15-cm^{-1} shift to higher energy as compared to **16** is consistent with the positive charge on the complex. The ^{1}H NMR spectrum of **17** shows a single allylic resonance at δ 3.19 along with the Cp and the aryl resonances. A singlet at δ 49.6 is observed in the ^{31}P NMR spectrum of **17**, and the absence of ^{183}W satellites on this resonance indicates that the P(Bu^n)$_3$ ligand is not bound to tungsten. This conclusion is also indicated by the ^{13}C{^{1}H} NMR spectrum which shows a central allyl carbon resonance at δ 83.7 and terminal allyl carbon resonances at δ 57.9 and 91.9 with the latter appearing as a doublet (J_{PC} = 17.4 Hz) due to coupling to the attached phosphorus. The spectroscopic data thus rule out the possibility that the P(Bu^n)$_3$ ligand has coordinated to tungsten and displaced the coordinated vinyl group. However, as with complex **16**, the NMR data do not allow a determination of the syn/anti relationships of the allyl substituents.



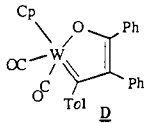
(7)

Formation of a Metallafuran from the Vinylcarbene Complex 14. In an attempt to couple a 1,3-dipolar reagent with the vinylcarbene ligand of complex **14**, this species was allowed to react with the nitrone **18**. The surprising product of this reaction was the metallafuran **19**, eq 8. This species was isolated in good yield and has been spectroscopically and crystallographically characterized, Figure 3. This reaction involves transfer of an oxygen atom from the nitrone to the carbene ligand of **14** and deprotonation of the vinyl substituent. The latter presumably occurs by the imine formed when the nitrone is deoxygenated, although the presence of the iminium salt which should form could not be verified in the reaction residue. The spectroscopic data for **19** are fully consistent with the determined structure. In particular, its ^{13}C NMR spectrum shows resonances at δ 254.2, 152.6, and 190.7, respectively, assigned to the α(W=C), β, and γ carbons of the metallafuran ring. These resonances are similar to those observed by other workers[15a] in a series of closely related metallfurans differing from **19** only in the organic substituents on the metallafuran ring. Those metallafurans were prepared by quite a different method involving the photoinduced reaction of Cp(CO)$_3$W–R complexes with alkynes, transformations which proceed via migration of the alkyl group to a CO ligand followed by insertion of the alkyne into the metal–acyl bond and ring closure to form the metallafuran.[15]



(8)

Crystal and Molecular Structure of Metallafuran 19. An ORTEP drawing of complex **19** is shown in Figure 3, and relevant crystallographic data are given in Tables I and III. The structure is quite similar to that of the metallafuran complex Cp(CO)$_2$W{OC(Me)C(Me)C(Me)} which was structurally characterized by Alt and co-workers[15a] which differs from **19** only by the presence of methyl substituents in place of the aryl groups. The bond distances and angles of **19** compare closely to those of Alt's compound.[15a] The metallafuran ring is flat, with a maximum deviation from the least-squares plane of 0.008 Å associated with O(11). The W–O(11) distance of 2.100 (3) Å is slightly longer than typical W–OR bond distances, whereas the W–C(8) distance of 2.133 (5) Å is a typical tungsten–carbon double bond value.[11,16] Similarly, the C(8)–C(9) and C(9)–C(10) distances of 1.393 (7) and 1.402 (7) Å imply bond orders between one and two. The data thus indicate the metallafuran ring to be a hybrid of the two resonance forms drawn in D and E below. This same conclusion was drawn by Alt for the analogous compound mentioned above.[15a] Other structurally characterized metallafuran complexes include (CO)$_4$Mn{OC(Me)C(H)C(Ph)}[17a] and *cis*-(CO)Cl$_2$Pt{OC(O^{i}Pr)C(Cl)C(CO$_2$Et)}.[17b]



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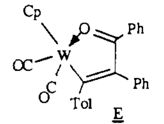
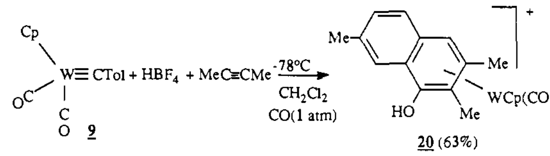


E

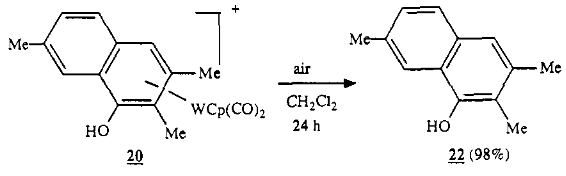
Protonation of Cp(CO)$_2$W≡CTol in the Presence of MeC≡CMe. In contrast to the above reaction 4 with PhC≡CPh which gave a vinylcarbene complex, protonation of Cp(CO)$_2$W≡CTol in the presence of MeC≡CMe gave instead the naphthol complex **20** shown in eq 9. This species apparently forms via one of the paths illustrated in Schemes I and II, and most likely through one of the two routes involving the intermediacy of a vinylcarbene complex, given the above-described formation of vinylcarbene complexes from **9** and PhC≡CPh. An attempt was made by low-temperature ^{1}H NMR monitoring to detect any intermediates in the synthesis of **20**, but those experiments showed no detectable intermediates between **9** and **20**.



(9)

Complex **20** was isolated in good yield as a thermally sensitive red solid and has been characterized spectroscopically by its release of the free naphthol upon oxidation and by its deprotonation to form the crystallographically characterized allyl complex described below. Solid samples of **20** are stable in the freezer for several months, but at room temperature they decompose within a few hours, even under an N$_2$ atm. The ^{1}H NMR spectrum of **20** shows a Cp resonance at δ 5.31 along with singlets at δ 2.27, 2.75, and 3.28 assigned to the three methyl groups. Also present is an OH resonance at δ 9.15 and resonances at δ 4.37, 6.70 (d, J_{HH} = 7 Hz), 6.82 (d), and 7.31 due to the aromatic protons. The high field resonance at δ 4.37 is assigned to the hydrogen para to the OH substituent, on the basis of a similar assignment established for the compound **21** described below.

The free naphthol **22** can easily be released from **20** by air oxidation, eq 10. It was obtained as a white solid in high yield from **20** and has been spectroscopically characterized. Its mass spectrum shows a parent ion at m/z = 186.1036 (calcd m/z = 186.1046), and its ^{1}H and ^{13}C{^{1}H} NMR spectra (see Experimental Section) are fully consistent with the indicated formulation.

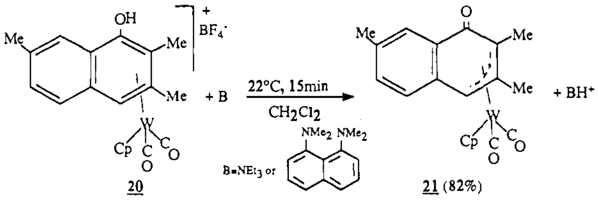


(10)

It is interesting that no evidence was obtained for a vinylcarbene complex in any of the reactions with MeC≡CMe, whereas the reaction of Cp(CO)$_2$W≡CTol/HBF$_4$ with PhC≡CPh stops completely at the vinylcarbene stage. The resulting vinylcarbene complex **14** (eq 4) proved completely resistant to carbonylation even under 4 atm of CO, and there is no indication that it reacts further to form a naphthol complex under any conditions yet examined. Given that MeC≡CMe forms a naphthol complex and that PhC≡CPh yields a vinylcarbene species from the Cp(CO)$_2$W≡CTol/HBF$_4$ reaction, the mixed substituent alkyne PhC≡CMe was of obvious interest. However, protonation of

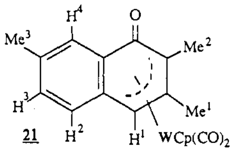
$Cp(CO)_2W{\equiv}CTol$ in the presence of either $PhC{\equiv}CMe$ or $PhC{\equiv}CH$ gave complex mixtures of products which proved impossible to characterize.

Reversible Deprotonation of the Naphthol Complex 20 To Form an Allyl Derivative. The naphthol complex **20** is readily deprotonated by 1,8-bis(dimethylamino)naphthalene or NEt_3 to form the neutral allyl complex **21**, eq 11. This complex was isolated

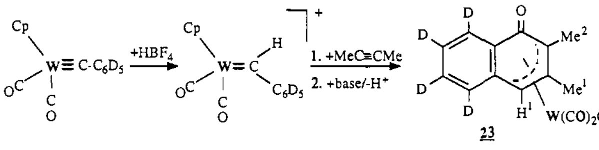


(11)

as an orange microcrystalline solid and has been spectroscopically characterized. It has also been defined by an X-ray crystal structure determination, although the structure is of relatively low accuracy because of a severe disorder problem (R = 10.5%).[18a] Nonetheless, the results confirm that the structure is that sketched in eq 11, and an ORTEP drawing of the molecule is given in the Supplementary Material. Also consistent with the assigned structure is the quantitative regeneration of the naphthol complex **20** upon protonation of **21**. The mass spectrum of allyl complex **21** shows a parent ion at m/z = 490 and ions corresponding to loss of the two CO's. Three methyl resonances are seen in its ^{1}H NMR spectrum at δ 1.97 (Me^3), 2.53 (Me^1), and 2.67 (Me^2) along with the Cp resonance at δ 4.29 and aromatic resonances at δ 4.22 (H^1), 6.43 (d, J_{HH} = 7.5 Hz, H^2 or H^3), 6.66 (d, H^3 or H^2), and 7.96 (H^4), with the labeling scheme given in the drawing below.



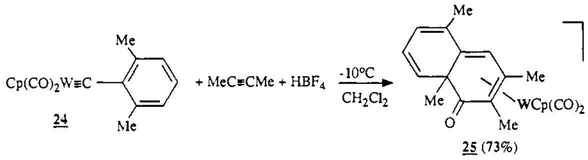
The specific assignments were made by comparison to those established for the derivative **23**, which was prepared as illustrated in eq 12. This latter species shows a Cp resonance at δ 4.27, methyl resonances at δ 2.49 and 2.66, and a single allyl resonance at δ 4.15. Irradiation of the δ 4.15 resonance of **23** in a difference



(12)

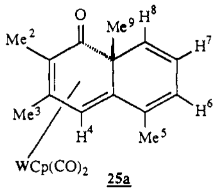
NOE ^{1}H NMR experiment gave enhancement of only the δ 2.66 signal, indicating the assignment of the latter to methyl Me^1 adjacent to H^1. Note that the allyl proton H^1 in **23** came from the HBF_4 used in the initial protonation step. Consistent with the mechanistic suggestions of Schemes I and II, it is an ortho proton on the aryl ring that migrates to the carbonyl oxygen in forming the naphthol complex, and it is this proton which is lost in the deprotonation step to form the allyl derivative **23** (and **21**).

Reaction of $Cp(CO)_2W{\equiv}C\{2,6\text{-}Me_2C_6H_3\}$, 24, with $MeC{\equiv}CMe$ To Form the Diene Complex 25. The results described above show that the course of the reaction of $Cp(CO)_2W{\equiv}CTol$ with alkynes in the presence of acid is markedly sensitive to the alkyne employed. Recall that the vinylcarbene complex **14** formed when $PhC{\equiv}CPh$ was used, whereas $MeC{\equiv}CMe$ gave instead the naphthol complex **20**. Next we wished to determine the effect of ortho substituents on the aryl-substituted carbyne carbon, and accordingly the reaction of $MeC{\equiv}CMe$ with the ortho disubstituted carbyne complex **24** was conducted. The product of this reaction proved to be the diene complex **25**, eq 13. This compound was isolated as a microcrystalline solid and was spectroscopically and crystallographically characterized. However, the structure is of relatively low accuracy because of a severe disorder problem,[18b] although the results clearly indicate the structure to be



(13)

that drawn in eq 13. An ORTEP drawing of the molecule is given as Figure B in the Supplementary Material. Its spectroscopic data are consistent with the determined structure. Its IR spectrum shows two ν_{CO} bands for the metal carbonyls as well as a ketonic ν_{CO} band at 1682 cm^{-1}. NMR data (see Experimental Section) indicate the presence of a 1.2:1 ratio of two diastereomers which result from the chiral nature of ring carbon C^9 (see below) and the tungsten atom, the latter because of the absence of a mirror plane through this center. The diastereomer shown in Figure B and the drawing below has the tungsten atom and the methyl group attached to C^9 on opposite sides of the pseudo plane of the dienone ring, an arrangement that would be reversed in the other diastereomer.



Discussion

The results reported herein show that the carbyne complex $Cp(CO)_2W{\equiv}CTol$, **9**, rapidly reacts with alkynes upon protonation to give a variety of products that depend markedly upon the carbyne and alkyne substituents. All evidence indicates that protonation initially occurs on the carbyne carbon to generate the highly reactive coordinatively unsaturated carbene derivative $[Cp(CO)_2W{=}CHTol]^+$, **10**, and that it is this species which incorporates the alkyne. This conclusion is strongly supported by (1) Stone and co-workers' reaction 2,[8] (2) their trapping of

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(15) (a) Alt, H. G.; Engelhardt, H. E.; Thewalt, U.; Riede, J. *J. Organomet. Chem.* **1985**, *288*, 165. (b) For an earlier report of the first member of this family of compounds, see: Green, M.; Nyathi, J. Z.; Scott, C.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1067. (c) Burkhardt, E. R.; Doney, J. J.; Bergman, R. G.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 2022.

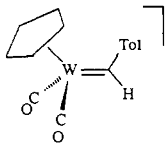
(16) **W=C**: $(CO)_5W{=}CPh_2$, W–C = 2.15 (2) Å; Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127. **W–C**: $W(Me)_2(PMe_3)_4$, W–C = 2.30 (5) Å; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Chem. Commun.* **1979**, 926. $Cp_2W(CH_2Ph)_2$, W–C = 2.276 (7), 2.291 (7) Å; Forder, R. A.; Jefferson, I. W.; Prout, K. *Acta Crystallogr.* **1975**, *B31*, 618. $[(CO)_5W{-}CH(OMe)Ph$, W–C = 2.34 (1) Å; Casey, C. P.; Polichnowski, S. W.; Tuinstra, H. E.; Albin, L. D.; Calabrese, J. C. *Inorg. Chem.* **1978**, *17*, 3045. **W–O**: $W_2(n\text{-}Pr)_2(C_2Me_2)_2(O\text{-}i\text{-}Pr)_4$, W–O = 1.88 (1) Å; Chisholm, M. H.; Eichhorn, B. W.; Huffman, J. C. *Organometallics* **1987**, *6*, 2264.

(17) (a) DeShong, P.; Sidler, D. R.; Rybczynski, P. J.; Slough, G. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 2575. (b) Canziani, F.; Albinati, A.; Garlaschelli, L.; Malatesta, M. C. *J. Organomet. Chem.* **1978**, *146*, 197.

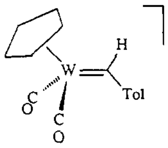
(18) (a) Crystal data for **21**: monoclinic, $P2/c$, a = 12.853 (4) Å, b = 13.066 (5) Å, c = 21.430 (8) Å, β = 106.67 (3)°, V = 3447 (2) Å^3, Z = 8. Two independent molecules are both distorted by disorder in the W-atom positions. Although R = 10.5% and several bond distances vary excessively (e.g., within the Cp ring the C–C distances vary from 1.35 to 1.50 Å), the structure is indisputedly that drawn in the text and illustrated in Figure A of the Supplementary Material. (b) Crystal data for **25**: orthorhombic, $P2_12_12_1$, a = 8.572 (2) Å, b = 16.737 (4) Å, c = 31.794 (7) Å, V = 4561 (2) Å^3, Z = 8, $R(F)$ = 5.42, $R(wF)$ = 5.33 for 4517 reflections with $F_o \geq 3\sigma(F_o)$. The asymmetric unit contains two independent cation/anion complexes and a chemically unidentified, isolated three-atom group (C(X), C(Y), and C(Z)) which was refined with full-occupancy carbon atoms. Inclusion of this group reduced $R(F)$ from 5.82 to 5.42%. The nearest intermolecular contact to this group is H(20F)···C(X) at 3.02 Å. Its inclusion appears warranted since its omission would create an unacceptably large void in the lattice. One of the two independent cations is disordered over two sites with a refined occupancy of 12.3 (2)% for the minor site. Only the W atom of the minor site was located. Additionally, one of the anions was disordered and could not be successfully modeled. The other anion was successfully constrained to a rigid tetrahedral geometry. Full experimental details of the structure refinement are given in the Supplementary Material.

the presumed carbene intermediate with added iodide to form the well-characterized carbene complex $Cp(CO)_2(I)W{=}CHTol$,[8] (3) Kreissl's protonation studies summarized in eq 3 which demonstrate double protonation at the carbyne cation,[9] and (4) the types of products observed in this study which are typical of species produced upon reaction of alkynes with well-characterized carbene complexes.[2,3] The $16e^-$ carbene intermediate **10** is similar to the *coordinatively saturated* $18e^-$ complexes $[Cp(CO)_2W{=}CHPh]^-$ and $[Cp(CO)_2(L)W{=}CHPh]^+$ (L = PPh_3, PEt_3) which have been respectively prepared by Winter[19] and Brookhart[20a,b] by quite different routes than that described herein for **10**. Neither of these latter compounds have been reported to react with alkynes, although styrene was shown to react with $[Cp(CO)_2(L)W{=}CHPh]^+$ to form phenylcyclopropane.[20b] Alkynes do react with the related carbene complex $[Cp(CO)_2Fe{=}CHPh]^+$ but to give cyclopropenes rather than the types of products reported herein.[20c]

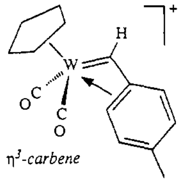
The carbene intermediate $[Cp(CO)_2W{=}CHTol]^+$, **10**, is a highly reactive species as indicated by the essentially instantaneous reaction that occurs at −78 °C upon addition of acid to mixtures of **9** and alkynes. Carbene complex **10** may be assumed to have a three-legged piano stool geometry with the plane of the carbene substituents bisecting the angle defined by the metal and the two carbonyl ligands, with both synclinal and anticlinal isomers possible.[21] This geometry has been shown to be adopted by a series of $Cp(CO)_2Mn{=}C(R)R'$ complexes[22] and has also been invoked for $[Cp(CO)_2Fe{=}CHR]^+$.[20a] However, unlike these latter compounds, carbene complex **10** is coordinatively unsaturated ($16e^-$), and one of the referees noted that it may have an η^3-carbene structure, like that depicted above, analogous to the η^3-vinylcarbene structures of **14** and **15**. We know of no precedence for benzylidene ligands adopting this bonding mode, although benzyl ligands have often been observed or proposed to bond in a similar η^3 fashion.[23]



synclinal

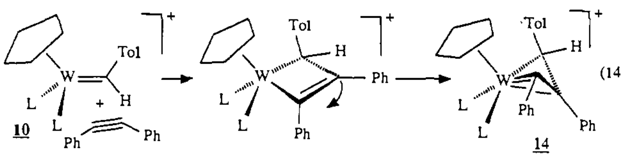


anticlinal



η^3*-carbene*

The initial product of coupling of the carbene ligand of **10** with an alkyne has generally been assumed to be a metallacyclobutene complex with a planar geometry as found for several crystallographically characterized examples.[24] Such metallacyclobutenes are postulated to undergo ring opening to yield vinylcarbenes (Scheme I). However, the crystal structure of vinylcarbene complex **15** and those of other vinylcarbene complexes[5a,j,6f,12] indicate that bond breaking is not required for the metallacyclobutene to vinylcarbene conversion, but instead the metallacyclobutene ring only has to bend to bring the central carbon to within bonding distance of the metal, eq 14. Moreover, these considerations raise the question of whether metallacyclobutenes need to be involved at all in the formation of vinylcarbenes. Indeed, there is no evidence that vinylcarbene complex **14** is produced from a discrete metallacyclobutene intermediate, and it is quite possible this complex is directly formed in the initial cycloaddition of the alkyne with carbene complex **10**.



(14)

As illustrated in Figure 2, the vinylcarbene complex **15** contains three chiral centers, W, C(30), and C(20) although only the first two are effective stereogenic centers. The *RR* stereoisomer is illustrated in the drawing, although the *SS* enantiomer is also present in the centrosymmetric crystal. NMR data imply that only the *RR,SS* pair is formed in the synthesis of **15** since no evidence was obtained for the presence of the other diastereomeric pair. This in turn implies a highly stereospecific substitution of iodide for the CO ligand trans to the carbene carbon in vinylcarbene complex **14**. Also, if the vinylcarbene ligand in complex **14** is coordinated similar to that in **15** as is indicated by the spectroscopic data, complex **14** can exist as a pair of diastereomers since the terminal vinyl carbon corresponding to C(30) in **15** and the tungsten atom are centers of chirality, the latter because of the absence of a mirror plane through the metal. As with complex **15**, the spectroscopic data for **14** show only the presence of a single pair of enantiomers, both of which presumably have the tolyl substituent and the Cp ligand on the same side of the plane defined by the metal atom and the terminal carbons of the vinylcarbene ligand, as found in **15** (Figure 2). Thus, the insertion of the alkyne into the tungsten–carbene bond is highly stereospecific and must occur with the synclinal isomer of carbene **10**, implying that this isomer is either predominant or that it is kinetically more reactive if synclinal and anticlinal isomers are equilibrated by rotation about the metal–carbene bond. The latter seems unlikely given the rapidity with which the coupling reaction occurs at −78 °C and the relatively high barrier to rotation about the metal–carbene bond found in the compound $[Cp(NO)(PPh_3)Re{=}CHPh]^+$ which also possesses a benzylidene ligand coordinated to a third-row metal atom.[25]

One of the objectives of this study was to try to distinguish the two mechanisms shown in Scheme I for the formation of naphthols from metal carbenes and alkynes. The key issue is whether or not the reaction proceeds through a vinylketene intermediate or instead via a metallacyclopentenone complex as illustrated in Scheme I. As noted in the Introduction, there is no general agreement as to which path is followed,[3a] although the isolation of several vinylketene complexes from the reactions of metal carbenes with alkynes[6d,g] and the knowledge that vinylketenes generated from organic precursors undergo benzannulation reactions to form naphthols[26] provides support for the vinylketene route. It was originally anticipated that this question could be addressed by generating the carbene complex $[Cp(CO)_2W{=}CHTol]^+$ at low temperature via protonation of $Cp(CO)_2W{\equiv}CR$, **9**, and then following by NMR its reaction with $MeC{\equiv}CMe$ to observe intermediates enroute to the naphthol complex **20**. However, this reaction is exceedingly fast even at −78 °C, and low-temperature NMR monitoring failed to detect any intermediates in the **9** to **20** conversion.

According to the mechanisms of Scheme I, the immediate precursor to the naphthol complex **20** is the diene species **28** which can be produced from either the vinylketene precursor **26** or from the metallacycle **27**, eq 15. We reasoned that it might be possible to intercept this reaction at the stage of one of these precursors to **20** by using a substituted aryl carbyne complex having ortho groups that would be less likely to undergo a 1,3-migration as in the **28** to **20** conversion. Under optimum circumstances, the reaction would stop at either the vinylcarbene **26** or the metallacycle **27**, thereby providing a basis for selecting one of the mechanistic paths of Scheme I over the other. The reaction of $MeC{\equiv}CMe$ with the ortho-disubstituted carbyne complex $Cp(CO)_2W{\equiv}C\{2,6\text{-}Me_2C_6H_3\}$ was examined for this purpose, but

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(19) Winter, M. J.; Woodward, S. *J. Organomet. Chem.* **1989**, *361*, C18.

(20) (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (b) Kegley, S. E.; Brookhart, M.; Husk, G. R. *Organometallics* **1982**, *1*, 760. (c) Brookhart, M.; Humphrey, M. B.; Kratzer, H. J.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802.

(21) Alternatively, a four-legged piano stool geometry with one unoccupied coordination site may be invoked, but this would not alter the conclusions drawn in the discussion.

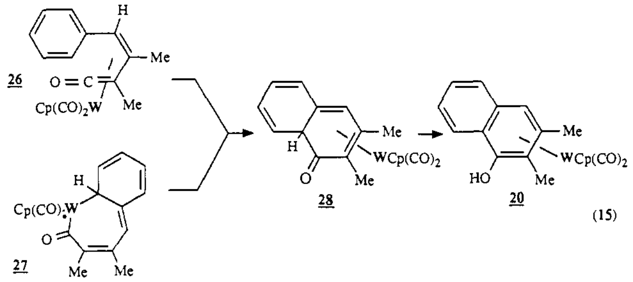
(22) Schubert, U. *Organometallics* **1982**, *1*, 1085.

(23) See, for example: Herrick, R. S.; Frederick, A. B.; Duff, R. R., Jr. *Organometallics* **1989**, *8*, 1120.

(24) (a) Tebbe, F. N.; Harlow, R. T. *J. Am. Chem. Soc.* **1980**, *102*, 6149. (b) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981**, *103*, 5584.

(25) McCormick, F. B.; Kiel, W. A.; Gladysz, J. A. *Organometallics* **1982**, *1*, 405.

(26) Moore, H. W.; Decker, O. H. W. *Chem. Rev.* **1986**, *86*, 821.



unfortunately this reaction proceeded directly to the diene complex **25** whose structure is analogous to that of **28** in eq 15, and thus no mechanistic distinction could be made from this experiment. An alternative strategy for achieving the same objective was to use an alkyl-substituted carbyne complex such as $Cp(CO)_2W\equiv CMe$ since the absence of an aryl group precludes the reaction from proceeding beyond the vinylketene or vinylcarbene stage depending upon which mechanism is important. However, protonation of $Cp(CO)_2W\equiv CMe$ in the presence of $MeC\equiv CMe$ took an entirely different course, giving the known compound $[CpW(CO)(MeC\equiv CMe)_2]^+$[27] as the only identifiable product. Thus, although the results described herein provide strong support for the overall mechanistic features of schemes I and II, they do not allow a distinction as to exactly which mechanist.c path is followed.

One final point to note is that the results described herein show that vinylcarbene complexes are susceptible to attack by nucleophiles at the carbene carbon. This is clearly demonstrated by the addition of hydride and tri(*n*-butyl)phosphine to this carbon to form allyl complexes as well as the reaction of vinylcarbene complex **14** with the nitrone **18** to form the metallafuran complex **19**. The latter reaction likely proceeds via initial nucleophilic attack of the oxygen atom of the nitrone on the carbene carbon. Formation of the allyl complex **17** (eq 7) upon addition of PBu_3 to vinylcarbene complex **14** strongly supports the suggestion recently made by Mitsudo et al. that phosphines add to the carbene carbon of a series of vinylcarbene complexes of iron to give undetected intermediates that rearrange to phosphine-substituted vinylketene complexes.[28] Vinylcarbene complexes **14** and **15** are obviously highly reactive species, and further studies of their chemistry with a variety of organic and inorganic substrates will be reported in due course.

Experimental Section

General Methods. The complex $Cp(CO)_2W\equiv CTol$ was prepared by the literature procedure.[29] The $Cp(CO)_2W\equiv C\{2,6\text{-}Me_2C_6H_3\}$ derivative was prepared in a similar fashion with use of $Li[2,6\text{-}Me_2C_6H_3]$ in place of $LiC_6H_4CH_3$. The salt $[(PPh_3)_2N]I$ was prepared from commercially available $[(PPh_3)_2N]Cl$ and KI by precipitation from H_2O followed by recrystallization from acetone/Et_2O. The nitrone PhCH-N{O}Me was synthesized by the literature method.[30] Solvents were dried by refluxing over Na/benzophenone ketyl (tetrahydrofuran (THF), Et_2O), or CaH_2 (CH_2Cl_2, pentane, hexane, toluene), or K_2CO_3 (acetone) and were freshly distilled prior to use. All manipulations were performed with standard Schlenk techniques. IR spectra were recorded on an IBM FTIR-32 spectrometer operated in the transmittance mode, NMR spectra were obtained on Brucker WP 200 and AM 300 FT NMR spectrometers, and mass spectra were recorded on AEI-MS9 (EI) and AFAB-MS9 (FAB) mass spectrometers. Elemental analyses were obtained from Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Reaction of $Cp(CO)_2W\equiv CTol$ with HBF_4 and $PhC\equiv CPh$ To Form $[Cp(CO)_2W=C(Ph)C(Ph)=CH(Tol)]BF_4$, 14. To a stirred −78 °C CH_2Cl_2 (20 mL) solution of $Cp(CO)_2W\equiv CTol$ (0.046 g, 0.109 mmol) and $PhC\equiv CPh$ (0.019 g, 0.109 mmol) maintained under a constant purge of CO was added 1 equiv (0.013 mL) of $HBF_4\cdot Et_2O$. The resultant red solution was slowly allowed to warm to 0 °C while stirring. The solvent was removed under vacuum, and the orange residue was washed three times with 10-mL portions of Et_2O, yielding an orange powder. This was recrystallized from layered CH_2Cl_2/Et_2O at −20 °C to give **14** as an orange microcrystalline solid in 89% yield (0.065 g, 0.097 mmol). The compound slowly decomposed at room temperature, even in the solid state under N_2, and a satisfactory elemental analysis was not obtained.

14: IR (CH_2Cl_2) ν(CO) = 2054 (s), 1975 (s) cm^{-1}; ^1H NMR (acetone-d_6) δ 2.34 (s, 3 H, CH_3), 6.05 (s, 1 H, $C=CH$(Tol)), 6.40 (s, 5 H, Cp), 6.77–7.81 (m, 14 H, aryl); ^{13}C NMR (acetone-d_6) δ 20.9 (TolCH_3), 60.8 (C(Ph)*C*(Ph)=CH(Tol)), 95.2 (Cp), 98.2 (C=*C*H(Tol)), 129.7, 130.2, 131.3, 133.6, 136.0, 137.1, 138.6, 139.7, 140.4 (aryl), 207.7, 210.0 (CO), 269.3 (W=*C*).

Reaction of Vinylcarbene Complex 14 with Iodide To Form the Vinylcarbene Complex Cp(CO)(I)W=C(Ph)C(Ph)=CHTol, 15. Complex **14** was prepared as described above from $Cp(CO)_2W\equiv CTol$ (0.107 g, 0.261 mmol). To the room temperature solution of this species was added $[(PPh_3)_2N]I$ (0.191 g, 0.288 mmol). This solution was stirred for 2.5 h, and the solvent was removed under vacuum to leave a brown residue. Chromatography of the latter at −30 °C on neutral alumina eluting with CH_2Cl_2 gave a single yellow band from which yellow microcrystalline **15** was obtained in 52% yield by solvent evaporation.

15: IR (CH_2Cl_2) ν(CO) = 1959 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 2.25 (s, 3 H, CH_3), 5.04 (s, 5 H, Cp), 6.59 (s, 1 H, $C=CH$(Tol)), 6.89–7.90 (m, 14 H, aryl); ^{13}C NMR (CD_2Cl_2) δ 20.8 (TolCH_3), 70.7 (C(Ph)*C*(Ph)=CH(Tol)), 91.1 (C=*C*H(Tol)), 94.4 (Cp), 123.4, 124.7, 126.2, 128.7, 128.8, 128.9, 129.2, 130.1, 130.4, 131.8, 132.0, 132.4, 134.8, 138.9, 142.2, 145.8 (aryl), 218.7 (*C*O), 269.8 (W=*C*); MS (EI) *m/z* = 658 [M^+ − CO], 528 [M^+ − CO − I]; MS (FAB) *m/z* = 686 [M^+], 658 [M^+ − CO], 559 [M^+ − I]. Anal. Calcd for $C_{28}H_{23}OIW\cdot 2CH_2Cl_2$ (%): C, 42.19; H, 3.19. Found: C, 42.77; H, 4.21.

Reaction of Vinylcarbene Complex 14 with $[Bu^n_4N]BH_4$ To Form $Cp(CO)_2W\{\eta^3\text{-}C(Ph)(H)C(Ph)C(Tol)(H)\}$, 16. To a −78 °C CH_2Cl_2 solution (20 mL) of complex **14**, prepared in situ from $Cp(CO)_2W\equiv CTol$ (0.065 g, 0.097 mmol) as described above, was added $[Bu^n_4N]BH_4$ (0.026 g, 0.10 mmol). The solution was stirred while allowed to warm to room temperature, and the solvent was removed under vacuum. The resulting yellow residue was purified by chromatography on neutral alumina, eluting with 20% CH_2Cl_2/hexane. The solvent was evaporated from the single yellow band which eluted to yield **16** as a yellow microcrystalline solid (0.012 g, 0.02 mmol; 20%).

16: IR (CH_2Cl_2) ν(CO) = 1950 (s), 1877 (s) cm^{-1}; ^1H NMR (CD_3CN) δ 2.16 (s, 3 H, CH_3), 3.80 (s, 1 H, C*H*), 3.84 (s, 1 H, C*H*), 5.49 (s, 5 H, Cp), 6.70–7.40 (m, 14 H, aryl); ^{13}C NMR ($CDCl_3$) δ 20.9 (TolCH_3), 47.1, 47.6 (*C*Ph, *C*Tol), 90.9 (Cp), 103.2 (*C*Ph), 124.9, 127.5, 127.6, 128.3, 128.4, 128.6, 133.7, 137.6 (aryl), 220.9, 219.8 (CO); MS: *m/z* = 588 (M^+), 560 (M^+ − CO), 532 (M^+ − 2CO). Anal. Calcd for $C_{29}H_{24}O_2W$ (%): C, 59.18; H, 4.08. Found: C, 59.43; H, 3.98.

Reaction of Vinylcarbene Complex 14 with $P(Bu^n)_3$ To Form $[Cp(CO)_2W\{\eta^3\text{-}PhC(PBu^n_3)C(Ph)CH(Tol)\}][BF_4]$, 17. To a −78 °C CH_2Cl_2 solution (20 mL) of complex **14**, prepared in situ from $Cp(CO)_2W\equiv CTol$ (0.058 g, 0.141 mmol) as described above, were added a few drops of $P(Bu^n)_3$ until no further lightening of the color occurred. The solvent was then removed under vacuum, and the yellow residue was purified by chromatography on neutral alumina, eluting first with 50 mL of CH_2Cl_2 and then with 10% acetone/CH_2Cl_2. The solvent was evaporated from the single yellow band which eluted to yield **17**. Recrystallization from CH_2Cl_2/hexane by slow cooling (24 h) to −78 °C gave **17** as a microcrystalline solid in 81% yield (0.077 g, 0.115 mmol).

17: IR (CH_2Cl_2) ν (CO) = 1965 (s), 1892 (s) cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.24 (t, 9 H, CH_3), 1.70 (m, 12 H, CH_2), 2.33 (m, 6 H, CH_2), 2.64 (s, 3 H, TolCH_3), 3.19 (s, 1 H, C*H*), 5.94 (s, 1 H, Cp), 6.12–7.84 (m, 14 H, aryl); ^{13}C NMR (CD_2Cl_2) δ 13.4 (Bu^nCH_3), 21.0 (Bu^nCH_2, J_{PC} = 15.3 Hz), 24.8 (TolCH_3), 25.4 (Bu^nCH_2, J_{PC} = 19.6 Hz), 57.9 (d, terminal allyl C), 83.7 (central allyl C), 91.9 (terminal allyl C, J_{PC} = 17.4 Hz), 98.5 (Cp), 127.9–140.1 (aryl), 206.1, 223.3 (*C*O); ^{31}P NMR (CD_2Cl_2) δ 49.6 (s). Anal. Calcd for $C_{41}H_{50}BF_4O_2PW$ (%): C, 56.16; H, 5.70. Found: C, 55.89; H, 5.59.

Reaction of Vinylcarbene Complex 14 with PhCH=N(O)Me To Form the Metallafuran 19. The vinylcarbene complex **14** was prepared in CH_2Cl_2 solution as described above from $Cp(CO)_2W\equiv CTol$ (0.050 g, 0.122 mmol). To this solution at 22 °C was added PhCH=N(O)Me (0.017 g, 0.122 mmol). The solution was stirred for 1 h, and the solvent was removed under vacuum to leave a red residue. This was chromatographed on neutral alumina, eluting with 3:1 pentane/CH_2Cl_2. A single red band eluted which gave microcrystalline red **19** in 55% yield (0.040 g, 0.066 mmol).

19: IR (CH_2Cl_2) ν(CO) = 1965 (s), 1887 (s) cm^{-1}; ^1H NMR (acetone-d_6) δ 2.20 (s, 3 H, TolCH_3), 5.72 (s, 5 H, Cp), 6.72–7.24 (m, 14 H, aryl); ^{13}C NMR (CD_2Cl_2) δ 21.0 (TolCH_3), 93.2 (Cp), 124.6, 126.1, 127.9, 128.7, 129.4, 129.7, 130.7, 131.9, 134.3, 138.0, 189.8 (aryl), 152.6 (C(Tol)*C*(Ph)CPh), 190.9 (C(Tol)C(Ph)*C*Ph), 237.6 (CO), 254.2 (*C*-

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(28) Mitsudo, T. A.; Watanabe, H.; Sasaki, T.; Takegami, Y.; Watanabe, Y. *Organometallics* **1988**, *8*, 368.

(29) McDermott, G. A.; Dorries, A. M.; Mayr, A. *Organometallics* **1987**, *6*, 925.

(30) Tsuge, O.; Sone, K.; Urano, S.; Matsuda, K. *J. Org. Chem.* **1982**, *47*, 5171.

(Tol)C(Ph)CPh); MS (FAB) m/z = 602 (M$^+$), 575 (M$^+$ − CO), 546 (M$^+$ − 2CO). Anal. Calcd for $C_{29}H_{22}O_3W$ (%): C, 57.86; H, 3.68. Found: C, 58.22; H, 4.33.

Reaction of Cp(CO)$_2$W$\equiv$CTol with HBF$_4$ and CH$_3$C$\equiv$CCH$_3$ To Form [Cp(CO)$_2$W(C$_{13}$H$_{14}$O)][BF$_4$], 20. A −78 °C CH_2Cl_2 (20 mL) solution of Cp(CO)$_2$W$\equiv$CTol (0.06 g, 0.16 mmol) and $CH_3C\equiv CCH_3$ (0.2 mL, 2.5 mmol) was stirred under a constant purge of CO, while 1 equiv (0.081 mL) of $HBF_4\cdot Et_2O$ was added. The orange solution immediately turned red, and stirring was continued for an additional 15 min. After warming to room temperature, hexane was added to induce precipitation of **20** which was isolated by filtration. The red precipitate was washed with hexane and recrystallized from CH_2Cl_2/hexane to give **20** in 63% yield (0.05 g, 0.10 mmol). Although spectroscopically pure, a satisfactory elemental analysis was not obtained due to the slow decomposition of **20** in the solid state even under an N_2 atm.

20: IR (CH_2Cl_2) ν(CO) = 2020 (s), 1954 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.27 (s, 3 H, CH_3), 2.75 (s, 3 H, CH_3), 3.28 (s, 3 H, CH_3), 4.37 (s, 1 H, aryl), 5.37 (s, 5 H, Cp), 6.70 (d, J = 7 Hz, 1 H, aryl), 6.82 (d, J = 7 Hz, 1 H, aryl), 7.31 (s, 1 H, aryl), 9.15 (s, 1 H, OH); ^{13}C NMR (CDCl$_3$) δ 14.7 (CH$_3$), 20.8 (CH$_3$), 23.5 (CH$_3$), 57.4 (aryl), 92.0 (aryl), 97.1 (Cp), 101.3, 102.6 (aryl), 122.1, 128.9, 130.3, 137.0, 143.8 (aryl), 212.7 (CO).

The free naphthol ($C_{13}H_{14}O$), **22**, was obtained in a separate experiment by stirring a red CH_2Cl_2 solution of **20**, prepared as described above, at room temperature in air for 24 h, during which time the color changed to green, and a black precipitate formed. Chromatography on a silica TLC plate using 40% CH_2Cl_2/hexanes as eluant gave a single colorless band of **22** which was isolated as a white microcrystalline solid in 98% yield (0.018 g, 0.10 mmol).

22: MS (high resolution) calcd for $C_{13}H_{14}O$ m/z = 186.1046 (M$^+$), found m/z = 186.1036 (M$^+$), 171.0805 (M$^+$ − CH$_3$), 143.0850 (M$^+$ − CH$_3$ − CO); IR (KBr) ν(OH) = 3370 (br) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.33 (s, 3 H, CH_3), 2.43 (s, 3 H, CH_3), 2.53 (s, 3 H, CH_3), 5.06 (br s, 1 H, OH), 7.23 (m, 2 H, aryl), 7.61 (d, J = 8 Hz, 1 H, aryl), 7.80 (s, 1 H, aryl); ^{13}C NMR (CDCl$_3$) δ 11.8 (CH$_3$), 20.9 (CH$_3$), 21.9 (CH$_3$), 116.7, 119.5, 120.1, 122.9, 126.9, 127.7, 130.9, 134.0, 134.8, 147.7 (aryl).

Deprotonation of [Cp(CO)$_2$W(C$_{13}$H$_{14}$O)][BF$_4$], 20, To Form Cp(CO)$_2$W(C$_{13}$H$_{13}$O), 21. An excess of 1,8-bis(dimethylamino)naphthalene was added to a freshly prepared solution of [Cp(CO)$_2$W(C$_{13}$H$_{14}$O)][BF$_4$], **20**, followed by stirring for 15 min. The solvent was then removed under vacuum, and the orange residue of Cp(CO)$_2$W(C$_{13}$H$_{13}$O), **21**, was extracted with pentane. The remaining tan residues were discarded, and complex **21** was purified by chromatography of the extracts on neutral alumina, eluting first with 50% CH_2Cl_2/pentane and then with 100% CH_2Cl_2. The solvent was removed from the combined red fractions to yield **21** as a red crystalline solid in 82% yield (0.016 g, 0.033 mmol).

21: IR (CH_2Cl_2) ν(CO) = 1966 (s), 1891 (s), 1626 (w) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.97 (s, 3 H, Me^3), 2.53 (s, 3 H, Me^1), 2.67 (s, 3 H, Me^2), 4.22 (s, 1 H, H^4), 4.29 (s, 5 H, Cp), 6.43 (d, J = 7.5 Hz, 1 H, H^2), 6.66 (d, J = 7.5 Hz, 1 H, H^3), 7.96 (s, 1 H, H^1); ^{13}C NMR (CDCl$_3$) δ 18.0 (CH$_3$), 20.8 (CH$_3$), 24.0 (CH$_3$), 49.7, 70.4 (aryl), 95.0 (Cp), 110.9, 122.5, 126.2, 127.1, 131.8, 134.7, 148.6, 189.3 (aryl), 225.9, 227.6 (CO); MS, m/z = 490 (M$^+$), 462 (M$^+$ − CO). Anal. Calcd for $C_{20}H_8O_3W$ (%): C, 48.97; H, 3.67. Found: C, 49.17; H, 3.88.

Preparation of Cp(CO)$_2$W(C$_{12}$H$_7$D$_4$O), 23. To a stirred −78 °C CH_2Cl_2 (20 mL) solution of Cp(CO)$_2$W$\equiv$CC$_6$D$_5$ (0.33 g, 0.8 mmol) and $CH_3C\equiv CCH_3$ (0.09 mL, 1.1 mmol) maintained under a constant purge of CO was added 1 equiv (0.11 mL) of $HBF_4\cdot Et_2O$. After warming the resultant red solution to 0 °C, an excess of 1,8-bis(dimethylamino)naphthalene was added followed by warming to room temperature and stirring for an additional 10 min. The solvent was removed under vacuum, and the orange Cp(CO)$_2$W(C$_{12}$H$_7$D$_4$O) was extracted with pentane and purified by chromatography on neutral alumina as described above.

23: IR (CH_2Cl_2) ν(CO) = 1967 (s), 1892 (s), 1616 (w) cm^{-1}; ^{1}H NMR (C_6D_6) δ 2.49 (s, 3 H, Me^2), 2.66 (s, 3 H, Me^1), 4.15 (s, 1 H, H^1), 4.27 (s, 5 H, Cp).

Reaction of Cp(CO)$_2$W$\equiv$C{2,6-Me$_2$C$_6$H$_3$}, 24, with MeC$\equiv$CMe To Form [Cp(CO)$_2$W{C$_{14}$H$_{16}$O}]BF$_4$, 25. To a −10 °C CH_2Cl_2 (15 mL) solution of Cp(CO)$_2$W$\equiv$C{2,6-Me$_2$C$_6$H$_3$} (0.067 g, 0.159 mmol) and MeC$\equiv$CMe (0.06 mL, 0.797 mmol) was added 1 equiv of $HBF_4\cdot Et_2O$ (0.022 mL) while stirring under a constant purge of CO. The resultant orange solution was warmed to room temperature and stirred for an additional hour. The solvent was removed to leave an orange oil which was washed with Et_2O (3 × 10 mL) and recrystallized from CH_2Cl_2/hexane to give [Cp(CO)$_2$W{C$_{14}$H$_{16}$O$_2$}]BF$_4$, **25**, as an orange microcrystalline solid in 73% yield (0.059 g, 0.117 mmol) containing a 1.2:1 mixture of diastereomers **25a** and **25b**. The labeling scheme for the following NMR data is given in the text.

25: IR (CH_2Cl_2) ν(CO) = 2046 (s), 1997 (s), 1682 (m) cm^{-1}. Anal. Calcd for $C_{21}H_{21}BF_4O_3W\cdot CH_2Cl_2$ (%): C, 39.10; H, 3.42. Found: C, 39.00; H, 3.62.

25a: ^{1}H NMR (CD$_2$Cl$_2$) δ 1.09 (s, 3 H, Me^5), 1.92 (s, 3 H, Me^9), 2.82 (s, 3 H, Me^3), 3.02 (s, 3 H, Me^2), 5.68 (br s, 5 H, Cp), 5.92 (s, 1 H, H^4), 6.35 (s, 1 H, H^6 or H^7), 6.36 (s, 1 H, H^6 or H^7), 6.41 (s, 1 H, H^8); ^{13}C NMR (CD$_2$Cl$_2$) δ 16.1 (Me^5), 16.7 (Me^3), 17.5 (Me^9), 20.4 (Me^2), 25.6 (C^4), 35.0 (C^2), 40.8 (C^{10}), 44.9 (C^9), 92.6 (C^3), 100.0 (Cp), 129.1 (C^5), 124.3 (C^6 or C^7), 134.8 (C^6 or C^7); 143.4 (C^8), 161.3 (C^{1}O), 209.3 (W-CO).

25b: ^{1}H NMR (CD$_2$Cl$_2$) δ (s, 3 H, Me^5), 1.93 (s, 3 H, Me^9), 2.82 (s, 3 H, Me^3), 3.05 (s, 3 H, Me^2), 5.68 (br s, 5 H, Cp), 5.92 (s, 1 H, H^4), 6.35 (s, 1 H, H^6 or H^7), 6.36 (s, 1 H, H^6 or H^7), 6.41 (s, 1 H, H^8); ^{13}C NMR (CD$_2$Cl$_2$) δ 16.1 (Me^5), 16.7 (Me^3), 19.0 (Me^9), 20.8 (Me^2), 25.6 (C^4), 35.0 (C^2), 40.8 (C^{10}), 44.9 (C^9), 92.6 (C^3), 100.0 (Cp), 129.1 (C^5), 124.3 (C^6 or C^7), 134.8 (C^6 or C^7), 143.4 (C^8), 161.3 (C^{1}O), 109.3 (W-CO).

Crystal Structure Determination for the Vinylcarbene Complex Cp(CO)(I)W{=C(Ph)(Ph)C=CHTol}, 15. Brown needles of the title compound were mounted on a glass fiber with epoxy cement. Unit-cell parameters were determined through a least-squares fit of 25 reflections ($20 \leq 2\theta \leq 25°$). An empirical absorption correction (six reflections, Ψ scan, 216 data, T_{max}/T_{min} = 1.63) was applied to the intensity data collected. Systematic absences in the diffraction data determined the possible space groups $I2/a$ and Ia for the structure. $I2/a$ was initially chosen due to the distribution of E values and was later verified by the chemically sensible results of refinement. Crystal and refinement data are collected in Table I. The structure was solved via a Patterson map which located the W atom. The remaining non-hydrogen atoms were located through subsequent Fourier syntheses and least-squares refinement. All non-hydrogen atoms were anisotropically refined; phenyl and tolyl rings were refined as rigid, regular hexagons (dC–C = 1.395 Å). All hydrogens were located from the difference map and refined isotropically. All computations used SHELXTL (5.1) software (Sheldrick, G., Nicolet XRD, Madison, WI).

Crystal Structure Determination of the Metallafuran Complex Cp(CO)$_2$W[OC(Ph)C(Ph)C(Tol)], 19. Data relating to the structural determination are given in Table I. Crystals of **19** were mounted on glass fibers in epoxy cement. Photographic evidence and systematic absences in the diffraction data unambiguously indicated the monoclinic space group $P2_1/n$. The data were empirically corrected for absorption and a small linear decay in intensity. The tungsten atom was located from a Patterson projection, and the remaining non-hydrogen atoms were found in a subsequent difference Fourier synthesis. All non-hydrogen atoms were anisotropically refined, and the hydrogen atoms were treated as idealized, updated isotropic contributions (dCH = 0.96 Å, U = 1.2 U for attached C).

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Supplementary Material Available: Tables of atomic positional parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **15**, **19**, and **25** and ORTEP drawings for **25** and the ordered molecule of **21** (26 pages); tables of observed and calculated structure factors (71 pages). Ordering information is given on any current masthead page.