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Synthesis, Protonation, and Electrophilic Alkylation of CpW(CO)$_2$[η^3-2-(phenylethynyl)allyl]

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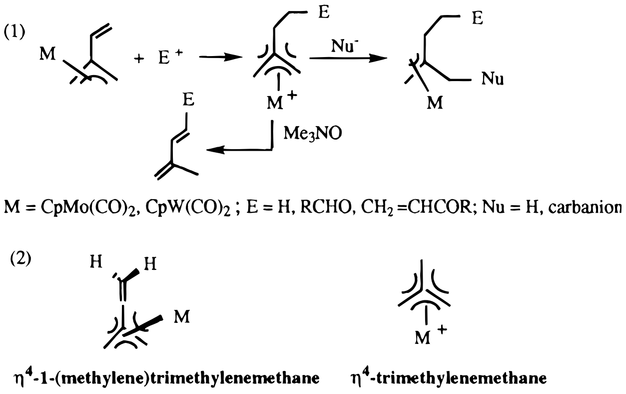
CpW(CO)$_2$[η^3-2-(phenylethynyl)allyl] (**2**) was prepared from the reaction between CpW(CO)$_3$Na and 2-methylene-4-phenyl-3-butyn-1-yl tosylate, followed by decarbonylation with Me$_3$NO. Treatment of **2** with CF$_3$SO$_3$H in cold CDCl$_3$ produced a mixture of [CpW(CO)$_2$(η^4-1-(benzylidene)trimethylenemethane)]X (**3a**) and CpW(CO)$_2$(η^3-2-CH$_2$X-4-phenyl-2,3-butadien-1-yl) (**3b**) (X = CF$_3$SO$_3$), which were characterized with ^{1}H and ^{13}C NMR spectra. Treatment of this mixture (**3a**,**b**) with a variety of nucleophiles gave compounds of the type CpW(CO)$_2$(η^3-2-CH$_2$X-4-phenyl-2,3-butadien-1-yl) (X = OH (**4a**), OMe (**4b**), iBuNH (**4c**), Me (**4d**), Ph (**4e**), CCPh (**4f**), H (**4g**)). In the presence of Bu$_4$NI, protonation of **4d**−**e** with CF$_3$SO$_3$H in cold CH$_2$Cl$_2$ produced CpW(CO)I[η^4-(2-PhCH$_2$-3-XCH$_2$)vinylketene] (X = Me (**6a**), Ph (**6b**)), the structural identity of which was established from an X-ray diffraction study of the analogous complex CpW(CO)I[η^4-(2-PhCH$_2$-3-ICH$_2$)vinylketene] (**6c**). Treatment of **2** with a mixture of acetaldehyde and BF$_3$·Et$_2$O in cold CH$_2$Cl$_2$, followed by reduction of NaBH$_3$CN gave CpW(CO)$_2$(η^3-2-methyl-4-phenyl-5-methyl-2,4-pentadien-1-yl) **(7)**, which was characterized by X-ray structural analysis.

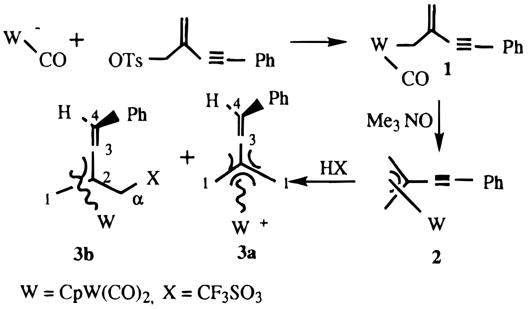
Introduction

Protonation[1] and electrophilic alkylation[2] of CpM(CO)$_2$(η^3-2-vinylallyl) produced isolable CpM(CO)$_2$(η^4-trimethylenemethane)$^+$ precipitates (M = Mo, W) which were reactive toward attack of various nucleophiles to yield difunctionalized π-allyl complexes[2a] as depicted in Scheme 1. Demetalations of these trimethylenemethane cations with Me$_3$NO gave functionalized 1,3-diene complexes.[2a] In organic reactions, electrophilic protonation and alkylation of organic alkynes are more difficult than those of olefins because the vinyl cation generated in the former is an energetically unstable species.[3] One can reasonably anticipate that formation of a η^4-1-(methylene)trimethylenemethane (Scheme 1, eq 2) cation is more difficult than that of a η^4-trimethylenemethane species. In this work, we report protonation of CpW(CO)$_2$[η^3-2-(phenylethynyl)allyl] (**2**) to yield a tungsten η^4-1-(benzylidene)trimethylenemethane cation, an unprecedented case of η^4-1-(methylene)-trimethylenemethane; the reaction chemistry of this cation is also described.

Scheme 1



Scheme 2



Results and Discussion

Synthesis, Structure, and Protonation of Compound 2. According to a conventional method,[4] the reaction between CpW(CO)$_3$Na and 2-methylene-4-phenyl-3-butyn-1-yl tosylate gave air-stable CpW(CO)$_3$(η^1-2-methylene-4-phenyl-3-butyn-1-yl) (**1**) as a yellow oil; the yield was 68%. Further stirring of **1** with anhydrous Me$_3$NO (2.0 equiv) in CH$_2$Cl$_2$ led to decarbonylation[5] to produce CpW(CO)$_2$[η^3-2-(phenylethynyl)allyl] **(2)** in 60% yield as an air-stable yellow solid. The molecular structure of **2** is provided in Figure 1; selected

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(1) Allen, S. R.; Barnes, S. G.; Green, M.; Moran, G.; Murrall, N. M.; Welch, A. *J. Chem. Soc., Dalton Trans.* **1984**, 1175.

(2) (a) Yang, G.- M.; Su, G.-M.; Liu, R.-S. *Organometallics* **1992**, *11*, 3444. (b) Yang, G.-M.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *Organometallics* **1991**, *10*, 2531. (c) Yang, G.-M.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Chem. Soc., Chem. Commun.* **1991**, 478.

(3) Kohler, H. J.; Lischka, H. *J. Am. Chem. Soc.* **1979**, *101*, 3479.

(4) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.

(5) Lawson, R. J.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 7433.

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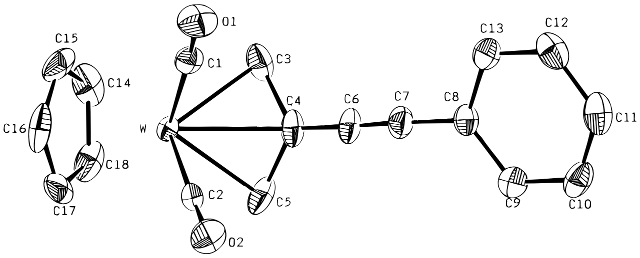

Figure 1. ORTEP drawing of compound **2**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2

W−C(1)	1.965(6)	C(2)−O(2)	1.155(6)
W−(C2)	1.967(5)	C(3)−C(4)	1.410(9)
W−C(3)	2.267(6)	C(4)−C(5)	1.409(10)
W−C(4)	2.286(6)	C(4)−C(6)	1.443(8)
W−C(5)	2.286(6)	C(6)−C(7)	1.183(8)
C(1)−O(1)	1.144(7)	C(7)−C(8)	1.433(8)
C(1)−W−C(2)	76.85(21)	W−C(2)−O(2)	178.3(5)
C(1)−W−C(3)	82.77(23)	W−C(3)−C(4)	72.7(3)
C(1)−W−C(4)	88.46(23)	W−C(4)−C(5)	71.2(3)
C(2)−W−C(5)	120.69(23)	W−C(4)−C(6)	72.0(4)
C(2)−W−C(3)	119.50(21)	W−C(4)−C(6)	122.5(4)
C(2)−W−C(4)	86.63(21)	C(3)−C(4)−C(5)	114.6(5)
C(2)−W−C(4)	86.63(21)	C(3)−C(4)−C(5)	121.7(6)
C(2)−W−C(5)	80.44(22)	C(3)−C(4)−C(6)	121.7(6)
C(3)−W−C(4)	36.07(23)	C(5)−C(4)−C(6)	123.6(6)
C(3)−W−C(5)	62.8(3)	W−C(5)−C(4)	72.1(3)
C(4)−W−C(5)	35.9(3)	C(4)−C(6)−C(7)	174.6(6)
W−C(1)−O(1)	176.0(5)	C(6)−C(7)−C(8)	175.1(6)

bond distances and angles appear in Table 1. The molecule clearly possesses a plane of symmetry across the tungsten−allyl plane. The tungsten−allyl bonding is symmetric with essentially equal lengths for the C(3)−C(4) (1.410(9) Å) and C(4)−C(5) (1.409(10) Å) bonds as well as for the W−C(3) (2.267(6) Å) and W−C(5) (2.286(6) Å) bonds. The phenyl group is parallel to the C(3)−C(4)−C(5) allyl plane; this orientation is favorable for π-electron delocalization through the phenyl, alkyne, and allyl groups.

The reaction between **2** and CF_3SO_3H was examined in an NMR experiment *in situ*. Shortly after **2** was treated with CF_3SO_3H (2.0 equiv) in $CDCl_3$ at −10 °C, the proton NMR spectra, as depicted in Figure 2, showed signals of the two solution species **3a**,**b** in 1:3 molar ratio, respectively. When the same sample was cooled to −60 °C, **3a**,**b** were observed to be in the molar ratio 2:3; these two species appear to be in a state of equilibrium with each other. Figure 2 shows the assignment of proton NMR signals for the two cations. Only three proton NMR signals were observed for the nonaromatic protons of **3a**, consistent with a η^4-1-(benzylidene)trimethylenemethane cation. In contrast, five NMR signals were observed for the nonaromatic protons of **3b**, and the AB quartet pattern of the $C_\alpha H_2$ proton signals suggested an η^3-2,3-butadien-1-yl structure[6−10] in which the CF_3CO_2 group is linked to the C_α carbon. The two low-field signals at δ 8.20 and 7.74 ppm were assigned to the C*H*Ph protons of **3a**,**b**, respectively. The ^{1}H NMR pattern of **3b** resembles those of the analogous complexes **4a**−**f**, in which OH, OMe, iBuNH, Ph, and other substituents replace the CF_3CO_2 group of **3b** (*vide infra*). ^{13}C NMR signals of the two cations (**3a**:**3b** = 1:3) were assigned from ^{1}H−^{13}C NMR correlation spectra. Compared to spectral data[1,9−10] of $CpMo(CO)_2(\eta^4$-trimethylenemethane)BF_4 and $CpMo(CO)_2(\eta^3$-2,3-butadienyl) complexes, we assigned the two low-field signals at δ 155.8 and 160.6 ppm to the quaternary C_3 carbons of **3a**,**b**, respectively, and the signals at δ 96.2 and 93.5 ppm to the C_2 carbons of **3a**,**b**, respectively. The two W−CO carbonyls were equivalent for **3a** but inequivalent for **3b**. The C_α carbon of **3b** resonated at δ 64.7 ppm. For both **3a** and **3b**, we could not deduce the orientation of the phenyl group with respect to the $CpW(CO)_2$ fragment by proton-NOE difference spectra. Compounds **3a** and **3b** are unstable near 23 °C, at which temperature the NMR signals of **3a** and **3b** quickly disappear within 1 h accompanied by formation of an unknown black precipitate.

Reactions of 3a and 3b with Nucleophiles. Complexes **3a**,**b** were reactive toward various nucleophiles under ambient conditions. In a typical reaction, a mixture of **3a** and **3b** generated *in situ* was treated with excess nucleophile in cold diethyl ether (−20 °C); the reaction mixture was slowly warmed to 23 °C and aqueous NH_4Cl solution added. Scheme 3 summarizes the types of nucleophiles and the corresponding isolated yields. Although starting materials consisted of **3a** and **3b** each in significant composition (**3a**:**3b** = (1:2)−(1:3)), for every case in Scheme 3, only η^3-2,3-butadienyl complexes[6−10] **4a**−**g** were obtained in 48−60% yields. In entry 1, Bu_4NOH replaced water because the latter was not reactive enough at −20 °C to yield the desired η^3-2,3-butadienyl product; in this case $CpW(CO)_2(\eta^3$-2-benzoylallyl) (**5**) was obtained in 35% yield after stirring the water mixture at 23 °C for 6 h (*vide infra*). NMR spectral data of **4a**−**g** were consistent with those expected for a η^1-2,3-butadienyl structure. Similar to $CpMo(CO)_2(\eta^3$-2,3-butadienyl) complexes, the C*H*Ph protons of **4a**−**g** show signals at δ 7.50−7.70 ppm, whereas the two *C*=*C*HPh olefin carbons show signals at δ 160−165 and 120−125 ppm, respectively. The *cis* or *trans* relationship between CHPh and $CpW(CO)_2$ fragments was not deducible from proton-NOE difference spectra. Although **4a,d,e** were obtained as yellow solids, the quality of single crystals was poor.

Compounds **4a**,**b** undergo an acid-catalyzed hydrolysis to the η^3-benzoyl complex **5** at 23 °C (Scheme 4). Stirring of wet THF solutions of **4a**,**b** at 23 °C with the catalyst *p*-toluenesulfonic acid (10 mol %) for 24 h gave **5** in 55% and 52% yields, respectively. In a separate NMR experiment, treatment of **4a** with CF_3CO_2H (2.0 equiv) in $CDCl_3$ regenerated the two cations **3a**,**b** in the a ratio **3a**:**3b** = 1:3. Formation of **5** was apparently generated from hydroxy attack at the C_3 carbon of **3a** or **3b**. In connection with the results in Scheme 3, we concluded that attack of OR (OR = OH, OMe) at the C_α carbon of **3a** or **3b** is kinetically favorable and reversible in the presence of acid. The attack at the quaternary

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(6) (a) Bruce, M. I.; Rogers, J. R.; Snow, M. R.; Swincer, A. G. *J. Chem. Soc., Chem. Commun.* **1981**, 271. (b) Bruce, M. I.; Hambley, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* **1985**, *4*, 494.

(7) Nesmeyanov, A. N.; Kolobova, N. E.; Zlotina, I. B.; Lokshin, B. V.; Lescheva, I. F.; Znobina, G. K.; Anisimov, K. N. *J. Organomet. Chem.* **1976**, *110*, 339.

(8) Hughes, R. P.; Lambert, J. M. J.; Rheingold, A. L. *Organometallics* **1985**, *4*, 2055.

(9) (a) Benyunes, S. A.; Deeth, R. J.; Fries, A.; Green, M.; Mapartlin, M.; Nation, C. B. M. *J. Chem. Soc., Dalton Trans.* **1992**, 3453. (b) Benyunes, S. A.; Green, M.; Deeth, R. J.; Mapartlin, M.; Nation, C. B. M. *J. Chem. Soc., Chem. Commun.* **1989**, 1998.

(10) Brisdon, B. J.; Deeth, R. J.; Hodson, A. W. G.; Kemp, C. W.; Mahon, M. F.; Molloy, K. C. *Organometallics* **1991**, *10*, 1107.

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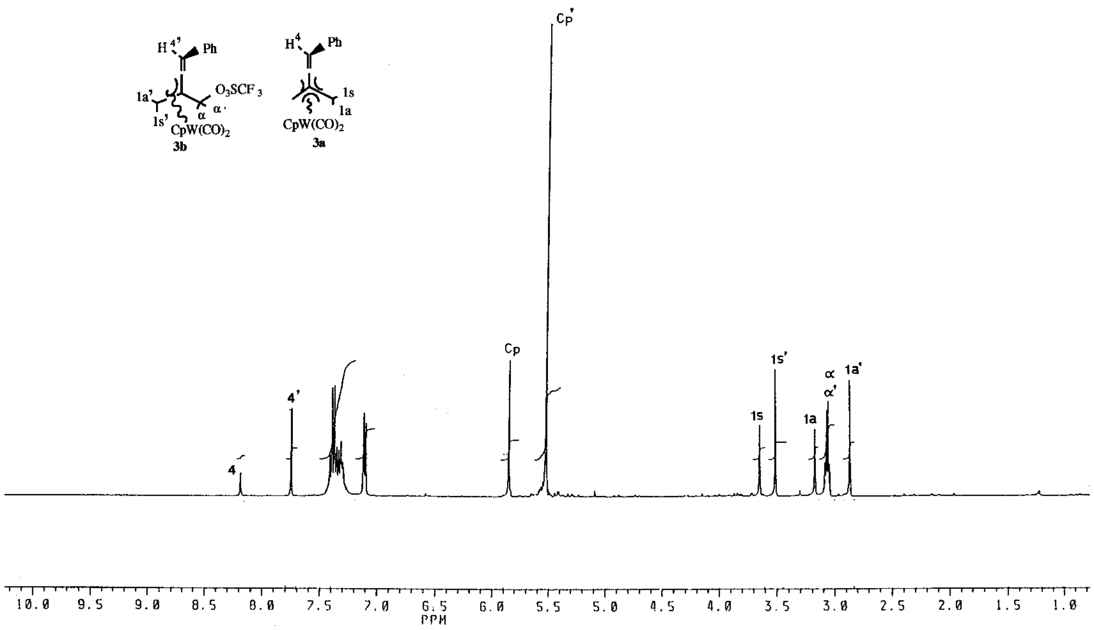
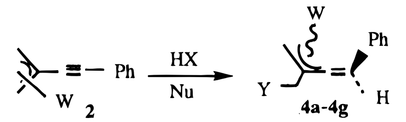


Figure 2. ^1H NMR spectra of **3a,b** in $CDCl_3$ at −10 °C.

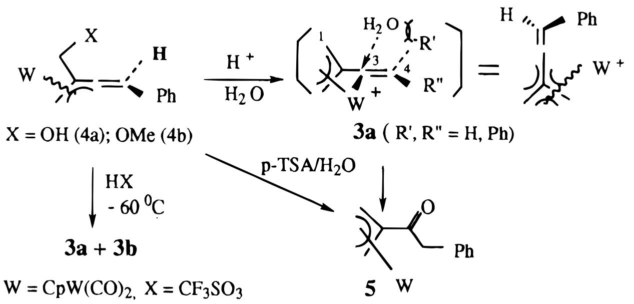
Scheme 3



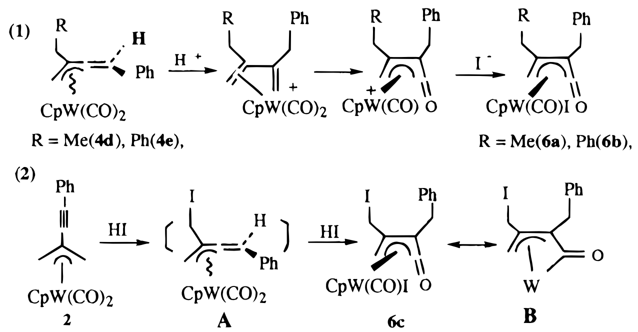
Entry	Nucleophile	Y	Yields
1	Nu_4NOH	OH	**4a** (53 %)
2	MeOH	OMe	**4b** (55 %)
3	$iBuNH_2$	iBuNH	**4c** (48 %)
4	Me_2CuLi	Me	**4d** (58 %)
5	PhLi	Ph	**4e** (58 %)
6	PhCCLi	PhCC	**4f** (60 %)
7	$NaBH_3CN$	H	**4g** (52 %)

W = $CpW(CO)_2$, HX = CF_3SO_3H

Scheme 4



Scheme 5



C_3 carbon of **3a** or **3b** appears to be kinetically slower, probably because of additional steric hindrance between the parallel C−OH and C−R bonds (R = H, Ph) as OH approaches the C_3 carbon opposite $CpW(CO)_2$, as depicted in Scheme 4.

Synthesis and Characterization of Tungsten−η^4-Vinylketene Complexes. In the presence of iodide, compounds **4d,e** were protonated with CF_3SO_3H to yield tungsten−η^4-vinylketene complexes[11−14] **6a,b** (Scheme 5). The red products were purified on a short alumina column; the yields were 35−40%. IR spectra of **6a,b** revealed one W−CO terminal absorption band at 2000 cm^{-1} and a second CO band at 1650 cm^{-1}. In the NMR spectra, two carbon signals appeared at δ 250 and 210 ppm, respectively, and two sets of NMR signals of nonequivalent methylene protons were observed in the region δ 2.50−4.00. The structures of **6a,b** are likely similar to that of $(C_5Me_5)MoI(CO)[\eta^4$-(2-methylvinyl)-ketene][9a] because of close resemblance of their spectra data. If this is the case, the formation of **6a,b** from **4d,e** is believed to involve a tungsten−η^3-vinylcarbene intermediate[9a] generated from protonation at the CHPh carbon of **4d-4e**, as depicted in Scheme 5. Further insertion of a coordinated carbonyl into the W=C bond[15,16] of this intermediate, followed by capture of iodide ion, produced the observed products. To ascertain the correct structure, we synthesized the analogue **6c** (Scheme 5), which has better crystallinity than **6a,b** for X-ray structural analysis. Compound **6c** was readily synthesized by treatment of complex **2** with CF_3SO_3H

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(11) (a) Wulff, W. D.; Gilberson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520. (b) Templeton, J. L.; Herrick, R. S.; Rusik, C. A.; McKenna, C. E.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1985**, *24*, 1383.

(12) (a) Newton, M. G.; Pantaleo, N. S.; King, R. B.; Chu, C. K. *J. Chem. Soc., Chem. Commun.* **1979**, 10. (b) Binger, P.; Cetinkaya, B.; Kruger, C. *J. Organomet. Chem.* **1978**, *159*, 63.

(13) Alcock, N. W.; Danks, T. N.; Richards, C. J.; Thomas, S. E. *J. Chem. Soc., Chem. Commun.* **1989**, 21.

(14) Jens, K. J.; Weiss, E. *Chem. Ber.* **1984**, *117*, 2469.

(15) Mayr, A.; Asaro, M. F.; Glines, T. L. *J. Am. Chem. Soc.* **1987**, *109*, 2215.

(16) Garrett, K. E.; Sheridan, J. B.; Pourreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383.

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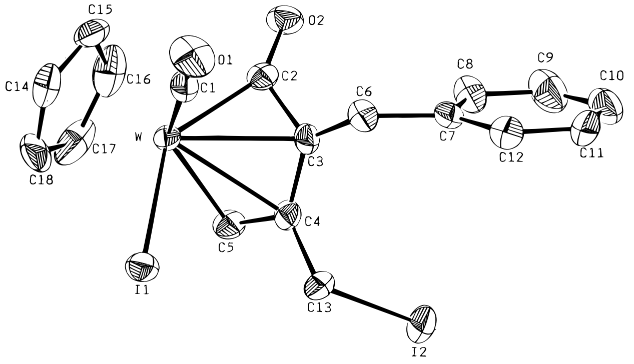

Figure 3. ORTEP drawing of compound **6c**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 6c

W−I(1)	2.8498(17)	C(2)−C(3)	1.503(12)
W−C(1)	1.997(9)	C(2)−O(2)	1.203(10)
W−C(2)	2.071(8)	C(3)−C(4)	1.386(12)
W−C(3)	2.381(7)	C(3)−C(6)	1.500(12)
W−C(4)	2.468(7)	C(4)−C(5)	1.425(12)
W−C(5)	2.279(8)	C(6)−C(7)	1.522(11)
C(1)−C(1)	1.140(10)		
I(1)−W−C(1)	79.0(3)	W−C(1)−O(1)	178.3(7)
I(1)−W−C(2)	136.62(23)	W−C(2)−C(3)	81.9(5)
I(1)−W−C(3)	98.04(20)	W−C(2)−O(2)	146.7(6)
I(1)−W−C(4)	78.88(20)	C(3)−C(2)−O(2)	131.2(7)
I(1)−W−C(5)	86.93(23)	W−C(3)−C(2)	59.4(4)
C(1)−W−C(2)	89.1(3)	W−C(3)−C(4)	76.8(4)
C(1)−W−C(3)	81.8(3)	W−C(3)−C(6)	129.6(5)
C(1)−W−C(4)	104.3(3)	C(2)−C(3)−C(4)	113.9(7)
C(1)−W−C(5)	138.9(3)	C(2)−C(3)−C(6)	119.8(7)
C(2)−W−C(3)	38.7(3)	C(4)−C(3)−C(6)	126.3(8)
C(2)−W−C(4)	63.8(3)	W−C(4)−C(3)	70.0(4)
C(2)−W−C(5)	75.0(3)	W−C(4)−C(5)	65.4(4)
C(3)−W−C(4)	33.2(3)	C(3)−C(4)−C(5)	117.5(8)
C(3)−W−C(5)	62.0(3)	W−C(5)−C(4)	79.9(4)
C(4)−W−C(5)	34.6(3)	C(3)−C(6)−C(7)	113.8(7)

and Bu_4NI (2.3 equiv) in cold CH_2Cl_2; the yield was 40%. Here, the η^3-2,3-butadienyl complex **A** is presumably the reaction intermediate that reacted further with HI to **6c** as the final product.

The molecular structure of **6c** is shown in Figure 3, and the selected bond distances and angles are provided in Table 2. The ORTEP drawing confirms the η^4-vinylketene structure; the coordination geometry about the tungsten center approximates a piano-stool geometry if vinylketene is considered two-coordinate. The η^4-butadiene moiety is almost planar, as indicated by the small dihedral angle 1.1(1)° between the C(2)−C(3)−C(4) and C(3)−C(4)−C(5) planes; however, the O(2) atom lies 0.72(1) Å from the diene plane. In this η^4-diene moiety, the W−C(2) distance (2.071(8) Å) is much shorter than the other W−C(3) (2.381(7) Å), W−C(4) (2.468(7) Å), and W−C(5) (2.279(8) Å) bonds; likewise, the C(2)−C(3) length (1.503(12) Å) is longer than the C(3)−C(4) (1.386(12) Å) and C(4)−C(5) (1.425(12) Å) bonds. According to these structural parameters, the tungsten−η^4-vinylketene moiety is best described by an σ,η^3-acylallyl bonding, represented by **B** in Scheme 5. In this formalism, the C(2) atom becomes sp^2-hybridized to distort the ketene O(2)−C(2)−C(3) fragment (131.2(7)°) from linearity. The long W−C(2) bond reflects the electronic effect of the C(2)−O(2) carbonyl, which makes the C(2) atom more significant than the other carbons in the metal−diene back-bonding. Consequently, the W−I bond (2.8498(17) Å) is favored to be *trans* to the C(2) atom; this diastereomer is expected to be more stable than the other isomer possibly present in the reaction.

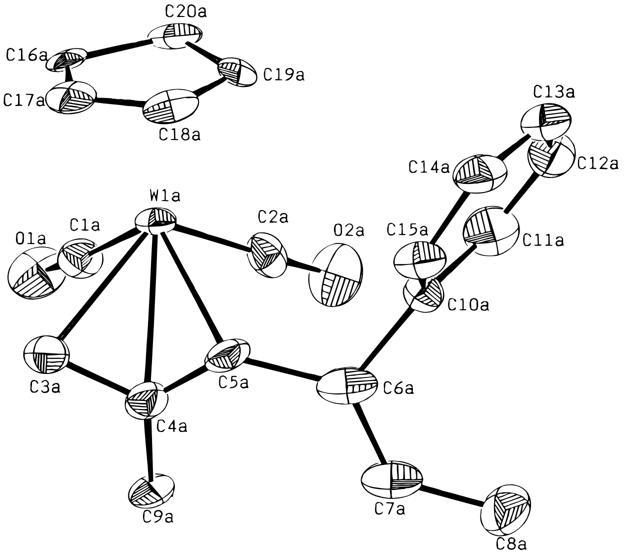

Figure 4. ORTEP drawing of one independent molecule of compound **7.**

Alkylation of 2 with Acetaldehyde. We carried out preliminary tests on the alkylation of **2** with acetaldehyde in the presence of $BF_3{\cdot}Et_2O$. Treatment of **2** with a mixture of $BF_3{\cdot}Et_2O$ (1.2 equiv) and CH_3CHO (10 equiv) in cold diethyl ether produced a brownish yellow precipitate, and further addition of Bu_4NOH or MeOH led to disappearance of this cation. The resulting products consisted of three diastereomers for each case, due to generation of three asymmetric carbon centers. Separations of the mixtures with fractional crystallization or column chromatography were unsuccessful. Treatment of this salt with $NaBH_3CN$ (5−6 equiv) in acetonitrile produced only one product, **7**, in 65% yield after workup. Complex **7** has a η^3-pentadienyl structure containing a vinyl PhC═CHMe group, as indicated by the ^1H and ^{13}C NMR data. The structure of **7** was confirmed with an X-ray diffraction study to provide the molecular structure in Figure 4 and the selected bond distances and angles in Table 3. The ORTEP drawing shows a η^3-pentadienyl ligand with a *trans* PhC═CH double bond and a methyl group on the central allyl carbon. The phenyl group is essentially orthogonal to the allyl plane presumably because of steric hindrance. The η^3-pentadienyl fragment is nearly planar, as indicated by the dihedral angle 27(4)° between the C(3a)−C(4a)−C(5a) and C(6a)−C(7a)−C(8a) planes.

We used $NaBD_3CN$ (95% deuterium content) as a reducing reagent to understand the formation mechanism of **7**. In this reaction, ^1H NMR spectra of **7** showed deuterium content at C_2 methyl and C_3H positions: ca. 30% and 92%, respectively. These data indicate that intermediate **C** is likely an alkylated (methylene)trimethylenemethane cation that underwent hydride attack at the C_1 position to yield η^1-2,3-butadienyl species **D**. A second hydride attack at the allyl C_3-carbon of **D** led to S_N2' displacement of the OBF_3^- group to yield **7**.

In conclusion, we have demonstrated the existence of a $CpW(CO)_2(\eta^4$-1-(methylene)trimethylenemethane$)^+$ cation, which was generated on protonation of $CpW(CO)_2$-

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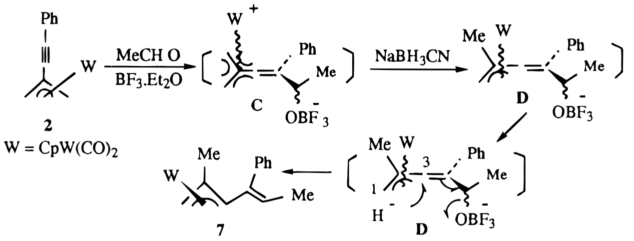
Table 3. Selected Bond Distances (Å) and Angles (deg) for 7

W(1a)−C(1a)	1.93(3)	W(1b)−C(1b)	1.83
W(1a)−C(2a)	1.87(3)	W(1b)−C(1b)	1.83(3)
W(1a)−C(2a)	1.87(3)	W(1b)−C(2b)	1.88(3)
W(1a)−C(3a)	2.32(3)	W(1b)−C(3b)	2.28(3)
W(1a)−C(4a)	2.31(3)	W(1b)−C(4b)	2.26(3)
W(1a)−C(5a)	2.351(25)	C(1b)−O(1b)	1.25(3)
C(1a)−C(2a)	2.37(4)	C(2b)−O(2b)	1.25(4)
C(1a)−O(1a)	1.15(3)	C(3b)−C(4b)	1.42(4)
C(2a)−O(2a)	1.18(3)	C(4b)−C(5b)	1.33(4)
C(3a)−C(4a)	1.41(4)	C(4b)−C(9b)	1.70(4)
C(4a)−C(5a)	1.40(4)	C(5b)−C(6b)	1.44(4)
C(4a)−C(9a)	1.45(4)	C(6b)−C(7b)	1.38(4)
C(5a)−C(6a)	1.55(4)	C(6b)−C(10b)	1.52(4)
C(6a)−C(7a)	1.36(4)	C(7b)−C(8b)	1.47(4)

C(1a)−W(1a)−C(2a)	77.1(11)	W(1a)−C(5a)−C(6a)	119.1(17)
C(1a)−W(1a)−C(3a)	82.3(10)	C(4a)−C(5a)−C(6a)	123.2(24)
C(1a)−W(1a)−C(4a)	87.7(11)	C(5a)−C(6a)−C(7a)	129 (3)
C(1a)−W(1a)−C(5a)	120.8(11)	C(6a)−C(7a)−C(8a)	129 (3)
C(2a)−W(1a)−C(3a)	121.0(11)	C(1b)−W(1b)−C(2b)	76.8(12)
C(2a)−W(1a)−C(4a)	88.7(11)	C(1b)−W(1b)−C(3b)	81.5(11)
C(2a)−W(1a)−C(5a)	86.0(10)	C(1b)−W(1b)−C(4b)	91.9(11)
C(3a)−W(1a)−C(4a)	35.4(9)	C(2b)−W(1b)−C(3b)	121.5(11)
C(3a)−W(1a)−C(5a)	59.2(9)	C(2b)−W(1b)−C(4b)	90.6(11)
C(4a)−W(1a(−C(5a)	35.0(10)	C(3b)−W(1b)−C(4b)	36.5(10)
W(1a)−C(1a)−C(2a)	50.3(9)	W(1b)−C(1b)−O(1b)	174.2(23)
W(1a)−C(1a)−O(1a)	174.7(24)	W(1b)−C(2b)−O(2b)	174.0(24)
C(2a)−C(1a)−O(1a)	128.6(22)	W(1b)−C(3b)−C(4b)	71.3(15)
W(1a)−C(2a)−C(1a)	52.5(9)	W(1b)−C(4b)−C(3b)	72.2(16)
W(1a)−C(2a)−O(2a)	177.8(22)	W(1b)−C(4b)−C(5b)	75.8(17)
C(1a)−C(2a)−O(2a)	125.8(20)	W(1b)−C(4b)−C(9b)	116.7(16)
W(1a)−C(3a)−C(4a)	71.7(16)	C(3b)−C(4b)−C(5b)	121 (3)
W(1a)−C(4a)−C(3a)	72.9(16)	C(3b)−C(4b)−C(9b)	110.2(23)
W(1a)−C(4a)−C(5)	74.3(16)	C(5b)−C(4b)−C(9b)	127(3)
W(1a)−C(4a)−C(9a)	125.9(20)	C(4b)−C(5b)−C(6b)	130(3)
C(3a)−C(4a)−C(5a)	110(3)	C(5b)−C(5b)−C(7b)	125(3)
C(3a)−C(4a)−C(9a)	119.4(25)	C(5b)−C(6b)−C(10b)	113.5(24)
C(5a)−C(4a)−C(9a)	129.5(24)	C(7b)−C(6b)−C(10b)	120.4(24)
W(1a)−C(5a)−C(4a)	70.7(15)	C(6b)−C(6b)−C(8b)	127(3)

Scheme 6



[2-(phenylethynyl)allyl] (**2**). Nucleophilic attack at this cation produced a CpW(CO)$_2$(η^3-2,3-butadienyl) complex that in the presence of HI underwent protonation to yield cations of the type CpW(CO)I(η^4-vinylketene)$^+$. Electrophilic alkylation of **2** with acetaldehyde/BF$_3$·Et$_2$O yielded the corresponding CpW(CO)$_2$(η^4-1-(methylene)-trimethylenemethane)$^+$ precipitate that upon NaBH$_3$CN reduction gave an η^3-pentadienyl derivative.

Experimental Section

All operations were carried out under argon in a Schlenk apparatus or in a glove box. The solvents benzene, diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane was dried over calcium hydride and distilled. W(CO)$_6$, phenylacetylene, and cyclopentadiene were obtained commercially and used without purification. Anhydrous Me$_3$NO was obtained by sublimation of its dihydrate form at 110 °C. 2-Methylene-4-phenyl-3-butyn-1-yl tosylate was prepared from phenylacetylene and 2-bromo-2-propen-1-ol according to the procedures described in the literature.[17]

All ^{1}H NMR (400 and 300 MHz) and ^{13}C NMR (100 and 75 MHz) spectra were obtained on either a Bruker AM-400 or a Varian Gemini-300 spectrometer; the chemical shifts in ^{1}H and ^{13}C NMR spectra are reported relative to tetramethylsilane (δ 0 ppm). Elemental analyses were performed at National Cheng Kung University, Tainan, Taiwan. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. High-resolution mass spectra were recorded on a JEOL HX 110 spectrometer.

(1) Synthesis of CpW(CO)$_3$(η^1-2-methylene-4-phenyl-3-butyn-1-yl) (1). W(CO)$_6$ (5.00 g, 14.2 mmol) was refluxed with NaC$_5$H$_5$ (1.17 g, 15.0 mmol) in THF (40 mL) for 72 h, and to this solution was added 2-methylene-4-phenyl-3-butyn-1-yl tosylate (4.58 g, 14.2 mmol) at 23 °C. The mixture was stirred for 4 h, evaporated to dryness, and extracted with diethyl ether (2 × 20 mL). The extract was concentrated and eluted through a silica column (diethyl ether/hexane 1/1) to give **1** as a yellow oil (R_f 0.88, 4.60 g, 9.70 mmol, 68%) IR (Nujol, cm^{-1}): υ(CO) 2011 (vs), 1916 (vs); υ(C≡C) 2004 (m). ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.44−7.28 (5H, m, Ph), 5.52 (5H, s, Cp), 5.12 (2H, s, =CH$_2$), 2.52 (2H, s, W−CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 228.6, 217.1 (2 W−CO), 138.8, 131.2, 128.3, 128.0 (Ph), 123.4 (C$_2$), 116.8 (=CH$_2$), 92.2 (Cp), 92.1, 88.3 (C≡C), −7.1 (W−C$_1$). Mass (75 eV, *m/e*): 474 (M$^+$), 446 (M$^+$ − CO), 390 (M$^+$ − 3CO). Anal. Calcd for C$_{19}$H$_{14}$WO$_3$: C, 48.13; H, 2.98. Found: C, 49.28; H, 2.06.

(2) Synthesis of CpW(CO)$_2$[η^3-2-(phenylethynyl)allyl)] (2). To a CH$_2$Cl$_2$ (30 mL) solution of **1** (4.00 g, 8.44 mmol) was added Me$_3$NO (1.26 g, 16.8 mmol), and the mixture was stirred at 23 °C for 12 h. To this solution was added H$_2$O, and the product was extracted with diethyl ether (2 × 20 mL). The extract was concentrated and eluted through a silica column (diethyl ether/hexane 1/1, R_f 0.58) to produce a yellow band that yielded **2** as a yellow solid (2.26 g, 5.06 mmol, 60%). IR (neat, cm^{-1}): υ(CO) 1951 (s), 1880 (s). ^{1}H NMR (400 MHz, −30 °C, CDCl$_3$): *endo*/*exo* = 3/2, *endo* isomer, δ 7.40−7.19 (5H, m, Ph), 5.32 (5H, s, Cp), 2.88 (2H, s, H$_{1s}$), 1.77 (2H, s, H$_{1a}$); *exo* isomer, δ 7.40−7.19 (5H, m, Ph), 5.45 (5H, s, Cp), 2.97 (2H, s, H$_{1s}$), 1.27 (2H, s, H$_{1a}$). ^{13}C NMR (100 MHz, −30 °C, CDCl$_3$): *endo* isomer, δ 225.9 (CO), 132.1, 127.9, 127.8, 122.3 (Ph), 88.4 (Cp), 89.9, 81.8 (C≡C), 59.1 (C$_2$), 29.0 (C$_1$); *exo* isomer, δ 223.4 (CO), 131.6, 128.3, 122.0 (Ph), 94.3 (Cp), 91.3, 81.5 (C≡C), 59.1 (C$_2$), 35.2 (C$_1$). Mass (75 eV, *m/e*): 446 (M$^+$), 390 (M$^+$ − 2CO). Anal. Calcd for C$_{18}$H$_{14}$WO$_2$: C, 48.46; H, 3.16. Found: C, 48.40; H, 3.16.

(3) Characterization of 3a,b. To compound **2** (22.6 mg, 5.06 × 10^{-2} mmol) in CDCl$_3$ (0.35 mL) was added CF$_3$SO$_3$H (8.90 ul, 1.01 × 10^{-1} mmol) at −10 °C, and the yields of **3a** and **3b** (**3a**/**3b** =1/3) were ca. 96% according to *in situ* NMR spectra. IR (CH$_2$Cl$_2$, cm^{-1}): 2050 (s), 2030 (s), 2001 (s), 1988 (s). ^{1}H NMR (400 MHz, −10 °C, CDCl$_3$): **3a**, δ 8.20 (1H, s, CHPh), 7.41−7.09 (5H, m, Ph), 5.82 (5H, s, Cp), 3.64 (2H, s, H$_{1s}$), 3.13 (2H, s, H$_{1a}$); **3b**, δ 7.74 (1H, s, CHPh), 7.41−7.09 (5H, m, Ph), 5.50 (5H, s, Cp), 3.47 (1H, s, H$_{1s}$), 3.11 (1H, d, J = 6.5 Hz, C$_\alpha$H*H′*), 3.02 (1H, d, J = 6.5 Hz, C$_\alpha$H*H′*), 2.89 (1H, s, H$_{1a}$). ^{13}C NMR (100 MHz, −10 °C, CDCl$_3$): **3a**, 198.8 (W−CO), 155.8 (C$_3$), 134.7, 129.8, 128.8, 127.2 (Ph), 122.1 (*C*HPh), 96.2 (C$_2$), 86.7 (C$_5$H$_5$), 56.3 (C$_1$); **3b**, 200.3, 197.9 (2 W−CO), 160.6 (C$_3$), 134.0, 130.8, 128.4, 127.0 (Ph), 122.2 (*C*HPh), 93.5 (C$_2$), 87.7 (C$_5$H$_5$), 64.7 (C$_\alpha$), 56.2 (C$_1$). Both **3a** and **3b** were not stable at 23 °C in solid form, and elemental analyses of the two samples were not successful.

(4) Synthesis of CpW(CO)$_2$[η^3-2-(hydroxymethyl)-4-phenyl-2,3-butadien-1-yl] (4a). To a diethyl ether solution (10 mL) of **2** (0.20 g, 0.45 mmol) was added CF$_3$SO$_3$H (0.040 mL, 0.90 mmol) at −20 °C, and the mixture was stirred for 1 h to produce dark yellow precipitates of **3a** and **3b**. To the

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[17] Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

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precipitate at −20 °C were added a THF solution of 20% Bu_4NOH (1.17 mL, 0.90 mmol) and then H_2O (4 mL); the mixture was stirred for 2 h before addition of an aqueous NH_4OH (5 mL) solution. The solution was extracted with diethyl ether (2 × 20 mL), concentrated and eluted through a silica column (diethyl ether/hexane = 1/1) to produce a yellow band (R_f 0.40) that gave **4a** as a yellow solid (0.11 g, 0.24 mmol, 53%). IR (CH_2Cl_2, cm^{-1}): υ(CO) 1954 (s), 1881 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 7.61 (1H, s, C*H*Ph), 7.50−7.18 (5H, m, Ph), 5.26 (5H, s, Cp), 4.24 (1H, d, *J* = 12.3 Hz, Cα*H*H′*)*, 4.12 (1H, d, *J* = 12.3 Hz, CαH*H*′), 2.93 (1H, s, H_{1s}), 2.59 (1H, s, H_{1a}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 225.1, 224.4 (2 W−CO), 159.5 (C_3), 139.7, 128.2, 127.5, 126.6 (Ph), 122.7 (*C*HPh), 89.8 (Cp), 80.6 (C_2), 67.5 (C_α), 28.2 (C_1). Mass (75 eV, *m*/*e*): 464 (M^+ − CO), 408 (M^+ − 2CO). Anal. Calcd for $C_{18}H_{16}WO_3$: C, 46.58; H, 3.47. Found: C, 46.36; H, 3.35.

(5) Synthesis of $CpW(CO)_2[\eta^3$-2-(methoxymethyl)-4-phenyl-2,3-butadien-1-yl] (4b). This compound was similarly prepared according to the procedure for synthesis of **4a**, except that excess MeOH (5 mL) was used; the yield was 55%. IR (neat, cm^{-1}): υ(CO) 1955 (s), 1884 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (1H, s, C*H*Ph), 7.48−7.14 (5H, m, Ph), 5.25 (5H, s, Cp), 3.95 (1H, d, *J* = 10.6 Hz, C_α*H*H′), 3.60 (1H, d, *J* = 10.6 Hz, CαH*H*′), 3.45 (3H, s, OMe), 2.90 (1H, s, H_{1s}), 2.59 (1H, s, H_{1a}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.4, 221.9 (2 W−CO), 160.7 (C_3), 139.8, 128.0, 127.4, 126.3 (Ph), 122.1 (*C*HPh), 89.6 (Cp), 78.0 (C_2), 76.4 (OMe), 58.6 (C_α), 29.6 (C_1). Mass (75 eV, *m*/*e*): 478 (M^+), 422 (M^+ − 2CO). Anal. Calcd for $C_{19}H_{18}WO_3$: C, 47.72; H, 3.79. Found: C, 48.15; H, 3.41.

(6) Synthesis of $CpW(CO)_2[\eta^3$-2-((isobutylamino)methyl)-4-phenyl-2,3-butadien-1-yl] (4c). This compound was prepared according to the procedure for synthesis of **4a**, except that excess isobutylamine (2 mL) was used; the yield was 48%. IR (Nujol, cm^{-1}): υ(CO) 1953 (s), 1882 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (1H, s, C*H*Ph), 7.50−7.17 (5H, m, Ph), 5.23 (5H, s, Cp), 3.30 (1H, d, *J* = 13.1 Hz, Cα*H*H′), 3.02 (1H, d, *J* = 13.1 Hz, CαH*H*′), 2.88 (1H, s, H_{1s}), 2.64 (1H, s, H_{1a}), 2.59 (2H, m, NCH_2), 1.77 (1H, m, C*H*Me_2), 0.93 (6H, d, *J* = 6.6 Hz, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 222.8, 222.0 (2 W−CO), 161.4 (C_3), 139.8, 127.9, 127.4, 126.3 (Ph), 121.6 (*C*HPh), 89.7 (Cp), 57.1 (C_2), 56.6 (C_α), 30.2 (C_1), 28.3 (NCH_2), 20.6 (CH), 20.4 (Me). Mass (75 eV, *m*/*e*): 519 (M^+), 463 (M^+ − 2CO). Anal. Calcd for $C_{22}H_{25}WO_2N$: C, 50.88; H, 4.85. Found: C, 51.16; H, 4.67.

(7) Synthesis of $CpW(CO)_2(\eta^3$-2-ethyl-4-phenyl-2,3-butadien-1-yl) (4d). This compound was similarly prepared according to the procedure for synthesis of **4a**, except that Me_2CuLi (5.0 equiv) was used; the yield was 55%. IR (Nujol, cm^{-1}): υ(CO) 1953 (s), 1883 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 7.55 (1H, s, C*H*Ph), 7.54−7.19 (5H, m, Ph), 5.52 (5H, s, Cp), 2.85 (1H, s, H_{1s}), 2.61 (1H, s, H_{1a}), 2.23 (2H, m, C_α*HH*′), 1.19 (3H, t, *J* = 7.5Hz, CH_2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 224.3, 226.9 (2 W−CO), 161.8 (C_3), 140.1, 127.9, 127.4, 126.1 (Ph), 121.5 (*C*HPh), 89.8 (Cp), 86.3 (C_2), 30.8 (C_1), 29.6 (Cα), 15.5 (Me). Mass (75 eV, *m*/*e*): 462 (M^+), 406 (M^+ − 2CO). Anal. Calcd for $C_{19}H_{18}WO_2$: C, 49.37, H, 3.93. Found: C, 49.66; H, 3.88.

(8) Synthesis of $CpW(CO)_2(\eta^3$-2-benzyl-4-phenyl-2,3-butadien-1-yl) (4e). This compound was prepared according to the procedure for synthesis of **4a** except that PhLi (5.0 equiv) was used; the yield was 58%. IR (Nujol, cm^{-1}): υ(CO) 1955 (s), 1886 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.60−7.17 (11H, m, Ph+ C*H*Ph), 5.26 (5H, s, Cp), 3.39 (1H, d, *J* = 13.8 Hz, CH*H*′), 3.26 (1H, d, *J* = 13.8, C*H*H′), 2.91 (1H, s, H_{1s}), 2.62 (1H, s, H_{1a}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 226.2, 223.5 (2 W−CO), 161.6 (C_3), 141.5, 139.5, 132.3, 130.0, 129.0, 128.4, 127.1, 126.5, 122.2 (2 Ph + C_4), 89.8 (Cp), 81.8 (C_2), 44.3 (C_α), 30.1 (C_1). Mass (75 eV, *m*/*e*): 524 (M^+), 468 (M^+ − 2CO). Anal. Calcd for $C_{24}H_{20}WO_2$: C, 54.98; H, 3.85. Found: C, 55.32; H, 3.64.

(9) Synthesis of $CpW(CO)_2[\eta^3$-2-(phenylethynyl)-4-phenyl-2,3-butadien-1-yl] (4f). This compound was prepared according to the procedure for synthesis of **4a**, except that lithium phenylacetylide (5.0 equiv) was used; the yield was 60%. IR (Nujol, cm^{-1}): υ(CO) 1955 (s), 1884 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.62 (1H, s, C*H*Ph), 7.31−7.17 (10H, m, Ph), 5.27 (5H, s, Cp), 3.86 (1H, d, *J* = 17.6 Hz, CH*H*′), 3.27 (1H, d, *J* = 17.6Hz, C*H*H′), 3.16 (1H, s, H_{1s}), 2.68 (1H, s, H_{1a}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 225.1, 224.4 (2 W−CO), 160.5 (C_3), 141.0, 138.5, 132.0, 131.0, 129.0, 128.0, 127.6, 126.9, 123.2 (2 Ph + C_4), 89.7 (Cp), 87.0, 83.4 (C≡C), 79.1 (C_2), 28.8 (C_α), 27.8 (C_1). Mass (75 eV, *m*/*e*): 548 (M^+), 492 (M^+ − 2CO). Anal. Calcd for $C_{26}H_{20}WO_2$: C, 56.96; H, 3.68. Found: C, 57.12; H, 3.02.

(10) Synthesis of $CpW(CO)_2(\eta^3$-2-methyl-4-phenyl-2,3-butadien-1-yl) (4g). This compound was similarly prepared according to the procedure for synthesis of **4a**, except that $NaBH_3CN$ (3.0 equiv) was used; the yield was 52%. IR (Nujol, cm^{-1}): υ(CO) 1955 (s), 1884 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (1H, s, C*H*Ph), 7.50 (2H, d, *J* = 5.0 Hz, Ph), 7.38 (2H, t, *J* = 5.0 Hz, Ph), 7.16 (1H, *J* = 5.0 Hz, Ph), 5.25 (5H, s, Cp), 2.84 (1H, s, H_{1s}), 2.64 (1H, s, H_{1a}), 2.27 (3H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): 226.8, 223.7 (2 W−CO), 162.5 (C_3), 140.1, 127.9, 127.2, 126.1 (Ph), 121.9 (C_4), 89.8 (Cp), 81.4 (C_2), 31.3 (C_1), 22.5 (Me). Mass (75 eV, *m*/*e*): 448 (M^+). Anal. Calcd for $C_{18}H_{16}WO_2$: C, 48.24; H, 3.60. Found: C, 48.04; H, 3.55.

(11) Synthesis of $CpW(CO)_2(\eta^3$-2-benzoylallyl) (5). To a THF/H_2O solution (1/1, 5 mL) of **3a** (0.22 g, 0.48 mmol) was added *p*-toluenesulfonic acid (4.1 mg, 2.4 × 10 $^{-2}$ mmol), and the mixture was stirred for 6 h at 23 °C. To this solution was added an aqueous $NaHCO_3$ solution (5 mL), and the product was extracted with ether, concentrated, and eluted through a silica column (diethyl ether/hexane) to yield a yellow band (R_f 0.54) that gave **5** (0.12 g, 0.26 mmol, 55%). IR (cm^{-1}): υ(CO) 1962 (s), 1887 (s), 1658 (vs). ^1H NMR (400 MHz, −10 °C, $CDCl_3$): δ 7.32−7.22 (5H, m, Ph), 5.34 (5H, s, Cp), 3.69 (2H, s, $COCH_2$), 3.12 (2H, s, H_{1s}), 1.59 (2H, s, H_{1a}). ^{13}C NMR (100 MHz, −10 °C, $CDCl_3$): δ 222.3 (2 W−CO), 198.1 ($PhCOCH_2$), 135.1, 129.5, 128.4, 126.6 (Ph), 87.9 (Cp), 86.7 (C_2), 42.6 (CH_2), 25.4 (C_1). Mass (75 eV, *m*/*e*): 464 (M^+), 436 (M^+ − CO), 408 (M^+ − 2CO). Anal. Calcd for $C_{18}H_{16}WO_3$: C, 46.58; H, 3.47. Found: C, 46.36; H, 3.35.

(12) Synthesis of CpW(CO)I[η^4-2-benzyl-3-(ethylvinyl)ketene] (6a). To a dichloromethane (10 mL) solution of **4d** (0.10 g, 0.22 mmol) and Bu_4NI (0.11 g, 0.30 mmol) was added CF_3SO_3H (0.011 mL, 0.11 mmol) at −60 °C; the mixture was stirred for 2 h before addition of an aqueous $NaHCO_3$ solution (10 mL). The product was extracted with diethyl ether (2 × 10 mL), concentrated, and eluted through a short alumina column (dichloromethane/diethyl ether = 1/1) to produce a red band that yielded **6a** as a red solid (R_f 0.45, 40 mg, 0.080 mmol, 35%). IR (Nujol, cm^{-1}): υ(CO) 1999 (s), 1942 (s), 1650 (vs). ^1H NMR (400 MHz, $CDCl_3$): δ 7.39−7.21 (5H, m, Ph), 5.27 (5H, s, Cp), 3.64 (2H, ABq, *J* = 4.0 Hz, PhC*H*$_2$), 3.61 (1H, d, *J* = 3.4 Hz, C_4H_s), 2.77 (1H, m, CH*H*′Me), 2.72 (1H, d, *J* = 3.4 Hz, C_4H_a), 2.65 (1H, m, C*H*H′Me), 0.73 (3H, t, *J* = 7.6 Hz, Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 259.4 (C_1=O), 219.7 (CO), 147.4 (C_3), 139.0, 128.7, 128.6, 126.6 (Ph), 90.4 (Cp), 74.3 (C_2), 39.2 (C_4), 33.6 ($PhCH_2$), 29.4 (CH_2Me), 14.7 (Me). Mass (75 eV, *m*/*e*): 562 (M^+ − CO). Anal. Calcd for $C_{19}H_{19}WO_2I$: C, 38.67; H, 3.25. Found: C, 38.21; H, 3.15.

(13) Synthesis of CpW(CO)I[η^4-2-benzyl-3-(benzylvinyl)ketene] (6b). This compound was prepared according to the procedure for synthesis of **6a**, except that compound **4e** was used; the yield was 38%. IR (neat, cm^{-1}): υ(CO) 2002 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.30−6.79 (10H, m, Ph), 5.26 (5H, s, Cp), 4.25 (1H, d, *J* = 15.5 Hz, C*H*H′Ph), 4.02 (1H, d, *J* = 15.5 Hz, CH*H*′Ph), 3.78 (1H, d, *J* = 14.9 Hz, C*H*H′Ph), 3.71 (1H, d, *J* = 14.9 Hz, CH*H*′Ph), 3.61 (1H, d, *J* = 3.2 Hz, H_{4s}), 2.73 (1H, d, *J* = 3.2 Hz, H_{4a}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 253.7 (C_1=O), 210.0 (W−CO), 143.9 (C_3), 138.7, 138.4, 129.4, 128.9, 128.6, 128.2, 126.7, 126.4 (Ph), 90.4 (Cp), 76.4 (C_2), 41.1, 40.7, 33.7 (C_4 + 2 CH_2Ph). Mass (75 eV, *m*/*e*) 624: (M^+ − CO). Anal. Calcd for $C_{24}H_{21}WO_2I$: C, 44.20; H, 3.25. Found: C, 43.98; H, 3.11.

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Table 4. Crystal Data and Conditions for Crystallographic Data Collection and Structure Refinement[a]

	2	6c	7
formula	$WC_{18}H_{14}O_2$	$W_{12}O_2C_{18}H_{16}$	$WC_{20}H_{21}O_2$
fw	446.15	701.97	477.23
diffractometer used	nonius	nonius	nonius
space group	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	orthorhombic, $Pca2_1$
a (Å)	17.047(5)	8.1337(18)	18.169(6)
b (Å)	6.1126(20)	11.173(6)	8.964(3)
c (Å)	14.755(3)	21.306(4)	21.553(6)
β (deg)	100.952(20)	91.327(16)	3510.3(19)
V (Å^3)	1509.5(7)	1935.8(12)	
Z	4	4	8
D_{calc} (g cm^{-3})	1.963	2.409	1.806
λ (Å)	0.7107	0.7107	0.7107
F(000)	844.	1270.	1840.
unit cell detn: no; 2θ range (deg)	25; 19.66−32.00	25; 28.60−39.65	25; 15.18−19.00
scan type	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
scan width (deg)	2 (0.65 0.35 tan θ)	2 (0.80 + 0.35 tan θ)	2 (0.65 + 0.35 tan θ)
scan speed (deg/min)	2.06−8.24	3.30−8.24	2.06−8.24
2θ_{max} (deg)	50.0	45.0	50.0
hkl ranges	(−20, +19) (0−7) (0−17)	(−8, +8) (0−12) (0−22)	(0−21) (0−7) (0−25)
μ (cm^{-1})	78.162	92.568	67.199
cryst size (mm)	0.10 × 0.30 × 0.45	0.20 × 0.30 × 0.40	0.20 × 0.25 × 0.45
transmissn	0.335; 1.000	0.570; 1.000	0.757; 1.000
temp (K)	298.00	298.00	298.00
no. of measd rflns	2649	2518	2769
no. of obsd rflns ($I > 2.0\sigma(I)$)	2346	2237	2057
no. of unique rflns	2649	2518	2769
R_F; R_w	0.022; 0.020	0.028; 0.028	0.048; 0.050
GOF	2.39	2.21	2.04
refinement program	NRCVAX	NRCVAX	NRCVAX
no. of atoms	35	39	88
no. of refined params	191 (2346 out of 2649 rflns)	209 (2237 out of 2518 rflns)	416 (2057 out of 2769 rflns)
minimize function	$\Sigma(w\|F_o - F_c\|^2)$	$\Sigma(w\|F_o - F_c\|^2)$	$\Sigma(w\|F_o - F_c\|^2)$
weighting scheme	$(1/\sigma^2)$ (F_o)	$(1/\sigma^2)$ (F_o)	$(1/\sigma^2)$ (F_o)
q (2nd ext. coeff) × 10^4	0.61(3)	0.71(3)	1.42(13)
$(\Delta/\sigma)_{max}$	0.0188	0.0110	0.0550
(D map) min, max (e/Å^3)	−1.020, 0.780	−1.030, 0.900	−1.230; 3.850

[a] $R_F = \Sigma(F_\sigma - F_c)/\Sigma F_\sigma$; $R_w = [\Sigma(w(F_\sigma - F_c)^2)/\Sigma(wF_\sigma{}^2)]^{1/2}$; GOF $= [\Sigma(w(F_\sigma - F_c)^2)/(\mathrm{NO} - \mathrm{NP})]^{1/2}$.

(14) Synthesis of CpW(CO)I[η^4-2-benzyl-3-((iodomethyl)vinyl)ketene) (6c). This compound was similarly prepared from the reaction between **2**, CF_3SO_3H, and Bu_4NI according to the procedure for the synthesis of **6a**. IR (cm^{-1}): υ(CO) 2003 (s), 1648 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.20 (5H, m, Ph), 5.31 (5H, s, Cp), 4.48 (1H, d, J = 9.4 Hz, C*H*H′Ph), 3.85 (1H, d, J = 9.4 Hz, CH*H*′Ph), 3.69 (1H, d, J = 14.9 Hz, C*H*H′I), 3.62 (1H, d, J = 14.9 Hz, CH*H*′I), 3.59 (1H, d, J = 3.2 Hz, H_{4s}), 2.66 (1H, d, J = 3.2 Hz, H_{4a}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 253.7 (C_1=O), 211.4 (CO), 137.1 (C_2), 136.9, 129.8, 128.9 (Ph), 90.1 (Cp), 75.6 (C_3), 39.7 (C_4), 33.9 (*C*HH′Ph), 4.0 (*C*HH′I). Anal. Calcd for $C_{18}H_{16}WO_2I_2$: C, 30.80; H, 2.30. Found: C, 30.92; H, 2.42.

(15) Synthesis of CpW(CO)$_2$(η^3-2,5-dimethyl-4-phenyl-2,4-pentadien-1-yl) (7). To a diethyl ether solution of compound **2** (0.20 g, 0.45 mmol) was added acetaldehyde (0.37 mmol, 4.50 mmol) and $BF_3{\cdot}Et_2O$ (0.13 mL, 0.68 mmol) at −40 °C, and the solution was stirred for 3 h to produce an insoluble precipitate. The diethyl ether layer was decanted away, and the precipitate was washed with diethyl ether at −40 °C. This precipitate in diethyl ether (5 mL) was treated with an acetonitrile solution of $NaBH_3CN$ (0.12 g, 1.35 mmol) at −40 °C to cause disappearance of the precipitate. The solution was stirred for 1 h at −40 °C before addition of an aqueous NH_4Cl solution. The product was extracted with diethyl ether, concentrated, and eluted through a silica column (diethyl ether/hexane = 1/1) to yield a yellow band of **7** (R_f 0.81, 0.13 g, 0.27 mmol, 60%). IR (Nujol, cm^{-1}): υ(CO) 1935 (s), 1856 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55−7.07 (5H, m, Ph), 5.93 (1H, q, J = 6.3 Hz, =CHMe), 4.91 (5H, s, Cp), 3.22 (1H, s, C_3H), 2.51 (1H, s, H_{1s}), 2.35 (3H, s, Me), 1.56 (3H, d, J = 13.1 Hz, Me), 1.51 (1H, s, H_{1a}). ^{13}C NMR (100 MHz, $CDCl_3$): δ 230.8, 229.8 (2 W−CO), 143.3 (C_4), 141.5, 129.0, 128.1, 126.4 (Ph), 122.3 (C_5), 97.8 (C_2), 89.7 (Cp), 54.8 (C_3), 27.7 (C_1), 21.5 (Me), 15.0 (Me). Mass (75 eV, *m/e*): 476 (M$^+$), 416 (M$^+$ − 2CO). Anal. Calcd for $C_{20}H_{20}WO_2$: C, 50.44; H, 4.23. Found: C, 49.98; H, 4.20.

X-ray Diffraction Studies of 2, 6c, and 7. Single crystals of **2, 6c,** and **7** were sealed in glass capillaries under an inert atmosphere. Data for **2, 6c,** and **7** were collected on a Nonius CAD 4 using graphite-monochromated Mo Kα radiation, and the structures were solved by the heavy-atom method; all data reduction and structural refinements were performed with the NRCCSDP package. Crystal data, details of data collection, and structural analysis are summarized in Table 4. For all structures, all non-hydrogen atoms were refined with anisotropic parameters, and all hydrogen atoms included in the structure factors were placed in idealized positions.

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Supporting Information Available: Tables of atomic coordinates, bond distances, bond angles, and thermal parameters for **2, 6c,** and **7** (13 pages). Ordering information is given on any current masthead page.

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