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

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 $CpW(CO)_2[\eta^3-2-(phenylethynyl)allyl]$  (2) was prepared from the reaction between CpW-(CO)<sub>3</sub>Na and 2-methylene-4-phenyl-3-butyn-1-yl tosylate, followed by decarbonylation with Me<sub>3</sub>NO. Treatment of **2** with  $CF_3SO_3H$  in cold  $CDCl_3$  produced a mixture of  $[CpW(CO)_2 (\eta^{4}-1-(benzylidene)trimethylenemethane)]X$  (**3a**) and CpW(CO)<sub>2</sub> $(\eta^{3}-2-CH_{2}X-4-phenyl-2,3$ butadien-1-yl) (**3b**) ( $X = CF_3SO_3$ ), which were characterized with <sup>1</sup>H and <sup>13</sup>C NMR spectra. Treatment of this mixture (**3a**,**b**) with a variety of nucleophiles gave compounds of the type  $CpW(CO)_2(\eta^3-2-CH_2X-4-phenyl-2,3-butadien-1-yl)$  (X = OH (4a), OMe (4b), iBuNH (4c), Me (4d), Ph (4e), CCPh (4f), H (4g)). In the presence of  $Bu_4NI$ , protonation of 4d-e with  $CF_{3}$ -SO<sub>3</sub>H in cold CH<sub>2</sub>Cl<sub>2</sub> produced CpW(CO)I[ $\eta^4$ -(2-PhCH<sub>2</sub>-3-XCH<sub>2</sub>)vinylketene] (X = Me (**6a**), Ph (6b)), the structural identity of which was established from an X-ray diffraction study of the analogous complex  $CpW(CO)I[\eta^4-(2-PhCH_2-3-ICH_2)vinylketene]$  (6c). Treatment of 2 with a mixture of acetaldehyde and BF<sub>3</sub>·Et<sub>2</sub>O in cold CH<sub>2</sub>Cl<sub>2</sub>, followed by reduction of NaBH<sub>3</sub>-CN gave  $CpW(CO)_2(\eta^3-2-methyl-4-phenyl-5-methyl-2,4-pentadien-1-yl)$  (7), which was characterized by X-ray structural analysis.

# Introduction

Protonation<sup>1</sup> and electrophilic alkylation<sup>2</sup> of CpM- $(CO)_2(\eta^3-2\text{-vinylallyl})$  produced isolable  $CpM(CO)_2(\eta^4$ trimethylenemethane)<sup>+</sup> precipitates (M = Mo, W) which were reactive toward attack of various nucleophiles to vield difunctionalized  $\pi$ -allyl complexes<sup>2a</sup> as depicted in Scheme 1. Demetalations of these trimethylenemethane cations with Me<sub>3</sub>NO gave functionalized 1,3-diene complexes.<sup>2a</sup> 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.<sup>3</sup> One can reasonably anticipate that formation of a  $\eta^4$ -1-(methylene)trimethylenemethane (Scheme 1, eq 2) cation is more difficult than that of a  $\eta^4$ -trimethylenemethane species. In this work, we report protonation of CpW(CO)<sub>2</sub>[ $\eta^3$ -2-(phenylethynyl)allyl] (2) to yield a tungsten  $\eta^4$ -1-(benzylidene)trimethylenemethane cation, an unprecedented case of  $\eta^4$ -1-(methylene)trimethylenemethane; the reaction chemistry of this cation is also described.

### **Results and Discussion**

Synthesis, Structure, and Protonation of Com**pound 2**. According to a conventional method,<sup>4</sup> the reaction between CpW(CO)<sub>3</sub>Na and 2-methylene-4phenyl-3-butyn-1-yl tosylate gave air-stable CpW(CO)<sub>3</sub>-

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Scheme 1



M = CpMo(CO)<sub>2</sub>, CpW(CO)<sub>2</sub>; E = H, RCHO, CH<sub>2</sub> =CHCOR; Nu = H, carbanion



 $\eta^4$ -1-(methylene)trimethylenemethane η<sup>4</sup>-trimethylenemethane



 $(\eta^{1}-2-\text{methylene-4-phenyl-3-butyn-1-yl})$  (1) as a vellow oil; the yield was 68%. Further stirring of 1 with anhydrous Me<sub>3</sub>NO (2.0 equiv) in CH<sub>2</sub>Cl<sub>2</sub> led to decarbonylation<sup>5</sup> to produce CpW(CO)<sub>2</sub>[ $\eta^3$ -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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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  $\pi$ -electron delocalization through the phenyl, alkyne, and allyl groups.

The reaction between 2 and CF<sub>3</sub>SO<sub>3</sub>H 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  $\eta^4$ -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  $\eta^3$ -2,3-butadien-1-yl structure<sup>6-10</sup> in which the CF<sub>3</sub>CO<sub>2</sub> group is linked to the  $C_{\alpha}$ carbon. The two low-field signals at  $\delta$  8.20 and 7.74 ppm were assigned to the CHPh protons of 3a,b, respectively. The <sup>1</sup>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<sub>3</sub>CO<sub>2</sub> group of **3b** (vide infra). <sup>13</sup>C NMR signals of the two cations (**3a**:**3b** = 1:3) were assigned from  ${}^{1}\text{H}$ -<sup>13</sup>C NMR correlation spectra. Compared to spectral data<sup>1,9–10</sup> of CpMo(CO)<sub>2</sub>( $\eta^4$ -trimethylenemethane)BF<sub>4</sub> and CpMo(CO)<sub>2</sub>( $\eta^3$ -2,3-butadienyl) complexes, we assigned the two low-field signals at  $\delta$  155.8 and 160.6 ppm to the quaternary C<sub>3</sub> carbons of **3a**,**b**, respectively, and the signals at  $\delta$  96.2 and 93.5 ppm to the C<sub>2</sub> carbons of **3a**,**b**, respectively. The two W–CO carbonyls were equivalent for **3a** but inequivalent for **3b**. The  $C_{\alpha}$ carbon of **3b** resonated at  $\delta$  64.7 ppm. For both **3a** and **3b**, we could not deduce the orientation of the phenyl group with respect to the CpW(CO)<sub>2</sub> 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<sub>4</sub>Cl solution added. Scheme 3 summarizes the types of nucleophiles and the corresponding isolated vields. 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  $\eta^3$ -2,3-butadienyl complexes  $6^{-10}$  **4a**-g were obtained in 48-60% yields. In entry 1, Bu<sub>4</sub>NOH replaced water because the latter was not reactive enough at -20 °C to yield the desired  $\eta^3$ -2,3-butadienyl product; in this case CpW(CO)<sub>2</sub>( $\eta^3$ -2benzoylallyl) (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  $\eta^{1}$ -2,3-butadienyl structure. Similar to  $CpMo(CO)_2(\eta^3-2,3-butadienyl)$  complexes, the CHPh protons of 4a-g show signals at  $\delta$  7.50–7.70 ppm, whereas the two C = CHPh olefin carbons show signals at  $\delta$  160–165 and 120–125 ppm, respectively. The *cis* or trans relationship between CHPh and CpW(CO)<sub>2</sub> 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  $\eta^3$ -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<sub>3</sub>CO<sub>2</sub>H (2.0 equiv) in CDCl<sub>3</sub> 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<sub>3</sub> 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<sub>a</sub> carbon of **3a** or **3b** is kinetically favorable and reversible in the presence of acid. The attack at the quaternary

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**Figure 2.** <sup>1</sup>H NMR spectra of **3a**,**b** in CDCl<sub>3</sub> at -10 °C.







C<sub>3</sub> 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 C3 carbon opposite CpW(CO)2, as depicted in Scheme 4.

Synthesis and Characterization of Tungsten- $\eta^4$ -Vinylketene Complexes. In the presence of iodide, compounds 4d, e were protonated with CF<sub>3</sub>SO<sub>3</sub>H to yield tungsten $-\eta^4$ -vinylketene complexes<sup>11-14</sup> **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  $\delta$  250 and 210 ppm, respectively, and two sets of NMR signals of nonequivalent methylene protons were observed in the region  $\delta$  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]<sup>9a</sup> 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 $-\eta^3$ -vinylcarbene intermediate9a 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<sup>15,16</sup> 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<sub>3</sub>SO<sub>3</sub>H

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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<sub>4</sub>NI (2.3 equiv) in cold CH<sub>2</sub>Cl<sub>2</sub>; the yield was 40%. Here, the  $\eta^3$ -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  $\eta^4$ vinylketene structure; the coordination geometry about the tungsten center approximates a piano-stool geometry if vinylketene is considered two-coordinate. The  $\eta^4$ -butadiene moiety is almost planar, as indicated by the small dihedral angle  $1.1(1)^\circ$  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  $\eta^4$ 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 $-\eta^4$ -vinylketene moiety is best described by an  $\sigma$ , $\eta^3$ -acylallyl bonding, represented by **B** in Scheme 5. In this formalism, the C(2) atom becomes sp<sup>2</sup>-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



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

C(2) atom; this diastereomer is expected to be more stable than the other isomer possibly present in the reaction.

Alkylation of 2 with Acetaldehyde. We carried out preliminary tests on the alkylation of 2 with acetaldehyde in the presence of BF<sub>3</sub>·Et<sub>2</sub>O. Treatment of 2 with a mixture of BF<sub>3</sub>·Et<sub>2</sub>O (1.2 equiv) and CH<sub>3</sub>-CHO (10 equiv) in cold diethyl ether produced a brownish yellow precipitate, and further addition of Bu<sub>4</sub>NOH 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<sub>3</sub>CN (5-6 equiv) in acetonitrile produced only one product, 7, in 65% yield after workup. Complex 7 has a  $\eta^3$ -pentadienyl structure containing a vinyl PhC=CHMe group, as indicated by the <sup>1</sup>H and <sup>13</sup>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  $\eta^3$ -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  $\eta^3$ -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<sub>3</sub>CN (95% deuterium content) as a reducing reagent to understand the formation mechanism of **7**. In this reaction, <sup>1</sup>H NMR spectra of **7** showed deuterium content at C<sub>2</sub> methyl and C<sub>3</sub>H 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<sub>1</sub> position to yield  $\eta^{1}$ -2,3-butadienyl species **D**. A second hydride attack at the allyl C<sub>3</sub>-carbon of **D** led to S<sub>N</sub>2' displacement of the OBF<sub>3</sub><sup>-</sup> group to yield **7**.

In conclusion, we have demonstrated the existence of a CpW(CO)<sub>2</sub>( $\eta^4$ -1-(methylene)trimethylenemethane)<sup>+</sup> cation, which was generated on protonation of CpW(CO)<sub>2</sub>-

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

|  | · 0/                   |  |                        |
|--|------------------------|--|------------------------|
| 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)                |
| $C(1_{0})$ W(1_{0}) $C(2_{0})$                 | 77 1(11)               | $W(1_{0}) = C(5_{0}) = C(6_{0})$               | 110 1(17)              |
| C(1a) = W(1a) = C(2a)<br>C(1a) = W(1a) = C(2a) | 77.1(11)<br>99.2(10)   | C(4a) = C(5a) = C(6a)                          | 119.1(17)<br>192.9(94) |
| C(1a) = W(1a) = C(3a)<br>C(1a) = W(1a) = C(4a) | 82.3(10)<br>87.7(11)   | C(4a) = C(5a) = C(6a)                          | 120.2(24)              |
| C(1a) = W(1a) = C(4a)<br>C(1a) = W(1a) = C(5a) | 07.7(11)               | C(5a) = C(0a) = C(7a)                          | 129 (3)                |
| C(1a) = W(1a) = C(3a)<br>C(2a) = W(1a) = C(3a) | 120.0(11)<br>121.0(11) | C(0a) = C(7a) = C(6a)<br>C(1b) = W(1b) = C(2b) | 129 (3)<br>76 9(19)    |
| C(2a) = W(1a) = C(3a)<br>C(2a) = W(1a) = C(4a) | 227(11)                | C(1b) = W(1b) = C(2b)                          | 70.0(12)<br>91 5(11)   |
| C(2a) = W(1a) = C(4a)<br>C(2a) = W(1a) = C(5a) | 86 0(10)               | C(1b) = W(1b) = C(3b)                          | 01.3(11)               |
| C(2a) = W(1a) = C(3a)<br>C(2a) = W(1a) = C(4a) | 30.0(10)<br>25 4(0)    | C(1b) = W(1b) = C(4b)<br>C(2b) = W(1b) = C(2b) | 91.9(11)<br>191 5(11)  |
| C(3a) = W(1a) = C(4a)<br>C(3a) = W(1a) = C(5a) | 50 2(0)                | C(2b) = W(1b) = C(3b)                          | 121.3(11)<br>00 6(11)  |
| C(3a) = W(1a) = C(3a)<br>C(4a) = W(1a) = C(5a) | 35.2(9)                | C(2b) = W(1b) = C(4b)                          | 30.0(11)               |
| U(4a) = W(1a) = C(3a)<br>W(1a) = C(1a) = C(3a) | 50 2(0)                | W(1b) = C(1b) = O(1b)                          | 30.3(10)<br>174.9(92)  |
| W(1a) = C(1a) = C(2a)<br>W(1a) = C(1a) = O(1a) | 1747(94)               | W(1b) = C(1b) = O(1b)<br>W(1b) = C(2b) = O(2b) | 174.2(23)<br>174.0(24) |
| C(2a) = C(1a) = O(1a)                          | 174.7(24)              | W(1b) = C(2b) = O(2b)<br>W(1b) = C(2b) = C(4b) | 71.2(15)               |
| $W(1_2) = C(2_2) = C(1_2)$                     | 525(0)                 | W(1b) = C(4b) = C(4b)                          | 72 9(16)               |
| W(1a) = C(2a) = C(1a)                          | 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(0b)                          | 116 7(16)              |
| W(1a) = C(3a) = C(4a)                          | 71 7(16)               | C(3h) - C(4h) - C(5h)                          | 191 (3)                |
| W(1a) = C(3a) = C(4a)                          | 72 9(16)               | C(3b) = C(4b) = C(3b)                          | 110 2(23)              |
| W(1a) = C(4a) = C(5a)                          | 74 3(16)               | C(5b) - C(4b) - C(9b)                          | 127(3)                 |
| W(1a) = C(4a) = C(0a)                          | 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)                         | 1135(24)               |
| C(5a) - C(4a) - C(9a)                          | 129 5(24)              | C(7b) - C(6b) - C(10b)                         | 1204(24)               |
| W(1a) - C(5a) - C(4a)                          | 70 7(15)               | C(6b) - C(6b) - C(8b)                          | 127(3)                 |
| (1)  | 10.111.01              |  | 101001                 |

### Scheme 6



[2-(phenylethynyl)allyl] (2). Nucleophilic attack at this cation produced a CpW(CO)<sub>2</sub>( $\eta^{3}$ -2,3-butadienyl) complex that in the presence of HI underwent protonation to yield cations of the type CpW(CO)I( $\eta^{4}$ -vinylketene)<sup>+</sup>. Electrophilic alkylation of 2 with acetaldehyde/BF<sub>3</sub>·Et<sub>2</sub>O yielded the corresponding CpW(CO)<sub>2</sub>( $\eta^{4}$ -1-(methylene)-trimethylenemethane)<sup>+</sup> precipitate that upon NaBH<sub>3</sub>-CN reduction gave an  $\eta^{3}$ -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)<sub>6</sub>, phenylacetylene, and cyclopentadiene were obtained commercially and used without purification. Anhydrous Me<sub>3</sub>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 <sup>1</sup>H NMR (400 and 300 MHz) and <sup>13</sup>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 <sup>1</sup>H and <sup>13</sup>C NMR spectra are reported relative to tetramethylsilane ( $\delta$  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)<sub>3</sub>( $\eta^{1}$ -2-methylene-4-phenyl-**3-butyn-1-yl) (1).** W(CO)<sub>6</sub> (5.00 g, 14.2 mmol) was refluxed with  $NaC_5H_5$  (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  $\times$  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<sup>-1</sup>): v(CO) 2011 (vs), 1916 (vs); v(C=C) 2004 (m). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.44–7.28 (5H, m, Ph), 5.52 (5H, s, Cp), 5.12 (2H, s, =CH<sub>2</sub>), 2.52 (2H, s, W-CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  228.6, 217.1 (2 W–CO), 138.8, 131.2, 128.3, 128.0 (Ph), 123.4 (C2), 116.8 (=CH2), 92.2 (Cp), 92.1, 88.3 (C≡C), -7.1 (W-C<sub>1</sub>). Mass (75 eV, m/e): 474 (M<sup>+</sup>), 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)<sub>2</sub>[ $\eta^3$ -2-(phenylethynyl)allyl)] (2). To a CH<sub>2</sub>Cl<sub>2</sub> (30 mL) solution of 1 (4.00 g, 8.44 mmol) was added  $Me_3NO$  (1.26 g, 16.8 mmol), and the mixture was stirred at 23 °C for 12 h. To this solution was added H<sub>2</sub>O, and the product was extracted with diethyl ether ( $2 \times 20$  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<sup>-1</sup>): v(CO) 1951 (s), 1880 (s). <sup>1</sup>H NMR (400 MHz, -30 °C, CDCl<sub>3</sub>): *endo/exo* = 3/2, *endo* isomer,  $\delta$  7.40–7.19 (5H, m, Ph), 5.32 (5H, s, Cp), 2.88 (2H, s, H<sub>1s</sub>), 1.77 (2H, s, H<sub>1a</sub>); exo isomer, δ 7.40-7.19 (5H, m, Ph), 5.45 (5H, s, Cp), 2.97 (2H, s, H<sub>1s</sub>), 1.27 (2H, s, H<sub>1a</sub>). <sup>13</sup>C NMR (100 MHz, -30 °C, CDCl<sub>3</sub>): endo isomer,  $\delta$  225.9 (CO), 132.1, 127.9, 127.8, 122.3 (Ph), 88.4 (Cp), 89.9, 81.8 (C=C), 59.1 (C<sub>2</sub>), 29.0 (C<sub>1</sub>); exo isomer, & 223.4 (CO), 131.6, 128.3, 122.0 (Ph), 94.3 (Cp), 91.3, 81.5 (C≡C), 59.1 (C<sub>2</sub>), 35.2 (C<sub>1</sub>). Mass (75 eV, m/e): 446 (M<sup>+</sup>), 390 (M<sup>+</sup> - 2CO). Anal. Calcd for C<sub>18</sub>H<sub>14</sub>WO<sub>2</sub>: C, 48.46; H, 3.16. Found: C, 48.40; H, 3.16.

(3) Characterization of 3a,b. To compound 2 (22.6 mg,  $5.06 \times 10^{-2}$  mmol) in CDCl\_3 (0.35 mL) was added CF\_3SO\_3H (8.90 ul, 1.01  $\times$  10<sup>-1</sup> mmol) at -10 °C, and the yields of 3aand **3b** (**3a/3b** =1/3) were ca. 96% according to *in situ* NMR spectra. IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 2050 (s), 2030 (s), 2001 (s), 1988 (s). <sup>1</sup>H NMR (400 MHz, -10 °C, CDCl<sub>3</sub>): **3a**,  $\delta$  8.20 (1H, s, CHPh), 7.41-7.09 (5H, m, Ph), 5.82 (5H, s, Cp), 3.64 (2H, s, H<sub>1s</sub>), 3.13 (2H, s, H<sub>1a</sub>); 3b, 8 7.74 (1H, s, CHPh), 7.41-7.09 (5H, m, Ph), 5.50 (5H, s, Cp), 3.47 (1H, s, H<sub>1s</sub>), 3.11 (1H, d, J = 6.5 Hz, C<sub>a</sub>HH), 3.02 (1H, d, J = 6.5 Hz, C<sub>a</sub>HH), 2.89 (1H, s, H<sub>1a</sub>). <sup>13</sup>C NMR (100 MHz, -10 °C, CDCl<sub>3</sub>): 3a, 198.8 (W-CO), 155.8 (C<sub>3</sub>), 134.7, 129.8, 128.8, 127.2 (Ph), 122.1 (CHPh), 96.2 (C2), 86.7 (C5H5), 56.3 (C1); 3b, 200.3, 197.9 (2 W-CO), 160.6 (C<sub>3</sub>), 134.0, 130.8, 128.4, 127.0 (Ph), 122.2 (CHPh), 93.5  $(C_2)$ , 87.7  $(C_5H_5)$ , 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)<sub>2</sub>[ $\eta^{3-2}$ -(hydroxymethyl)-4phenyl-2,3-butadien-1-yl] (4a). To a diethyl ether solution (10 mL) of 2 (0.20 g, 0.45 mmol) was added CF<sub>3</sub>SO<sub>3</sub>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

<sup>(17)</sup> Sonogashira, K.; Tohda, Y.; Hagihara, N. Tetrahedron Lett. 1975, 4467.

precipitate at -20 °C were added a THF solution of 20% Bu<sub>4</sub>-NOH (1.17 mL, 0.90 mmol) and then H<sub>2</sub>O (4 mL); the mixture was stirred for 2 h before addition of an aqueous NH<sub>4</sub>OH (5 mL) solution. The solution was extracted with diethyl ether  $(2 \times 20 \text{ mL})$ , 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 (CH2Cl2, cm<sup>-1</sup>): v(CO) 1954 (s), 1881 (s). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.61 (1H, s, CHPh), 7.50-7.18 (5H, m, Ph), 5.26  $(5H, s, Cp), 4.24 (1H, d, J = 12.3 Hz, C\alpha HH), 4.12 (1H, d, J)$ = 12.3 Hz, C $\alpha$ *H*H'), 2.93 (1H, s, H<sub>1s</sub>), 2.59 (1H, s, H<sub>1a</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 225.1, 224.4 (2 W–CO), 159.5 (C<sub>3</sub>), 139.7, 128.2, 127.5, 126.6 (Ph), 122.7 (CHPh), 89.8 (Cp), 80.6  $(C_2)$ , 67.5  $(C_{\alpha})$ , 28.2  $(C_1)$ . Mass (75 eV, *m/e*): 464  $(M^+ - CO)$ , 408 (M<sup>+</sup> – 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)<sub>2</sub>[ $\eta^3$ -2-(methoxymethyl)-4phenyl-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<sup>-1</sup>): v(CO) 1955 (s), 1884 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  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 $_{\alpha}$ *HH*'), 3.60 (1H, d, J =10.6 Hz, C $\alpha$ H*H*'), 3.45 (3H, s, OMe), 2.90 (1H, s, H<sub>1s</sub>), 2.59 (1H, s, H<sub>1a</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  224.4, 221.9 (2 W–CO), 160.7 (C<sub>3</sub>), 139.8, 128.0, 127.4, 126.3 (Ph), 122.1 (*C*HPh), 89.6 (Cp), 78.0 (C<sub>2</sub>), 76.4 (OMe), 58.6 (C $_{\alpha}$ ), 29.6 (C<sub>1</sub>). Mass (75 eV, *m/e*): 478 (M<sup>+</sup>), 422 (M<sup>+</sup> – 2CO). Anal. Calcd for C<sub>19</sub>H<sub>18</sub>WO<sub>3</sub>: C, 47.72; H, 3.79. Found: C, 48.15; H, 3.41.

(6) Synthesis of CpW(CO)<sub>2</sub>[ $\eta^3$ -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<sup>-1</sup>): v(CO) 1953 (s), 1882 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  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, C $\alpha$ *HH'*), 3.02 (1H, d, J = 13.1 Hz, C $\alpha$ H*H*), 2.88 (1H, s, H<sub>1s</sub>), 2.64 (1H, s, H<sub>1a</sub>), 2.59 (2H, m, NCH<sub>2</sub>), 1.77 (1H, m, C*H*Me<sub>2</sub>), 0.93 (6H, d, J= 6.6 Hz, Me). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  222.8, 222.0 (2 W–CO), 161.4 (C<sub>3</sub>), 139.8, 127.9, 127.4, 126.3 (Ph), 121.6 (*C*HPh), 89.7 (Cp), 57.1 (C<sub>2</sub>), 56.6 (C<sub>a</sub>), 30.2 (C<sub>1</sub>), 28.3 (NCH<sub>2</sub>), 20.6 (CH), 20.4 (Me). Mass (75 eV, *m/e*): 519 (M<sup>+</sup>), 463 (M<sup>+</sup> – 2CO). Anal. Calcd for C<sub>22</sub>H<sub>25</sub>WO<sub>2</sub>N: C, 50.88; H, 4.85. Found: C, 51.16; H, 4.67.

(7) Synthesis of CpW(CO)<sub>2</sub>( $\eta^3$ -2-ethyl-4-phenyl-2,3butadien-1-yl) (4d). This compound was similarly prepared according to the procedure for synthesis of 4a, except that Me<sub>2</sub>-CuLi (5.0 equiv) was used; the yield was 55%. IR (Nujol, cm<sup>-1</sup>): v(CO) 1953 (s), 1883 (s). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.55 (1H, s, C*H*Ph), 7.54–7.19 (5H, m, Ph), 5.52 (5H, s, Cp), 2.85 (1H, s, H<sub>1s</sub>), 2.61 (1H, s, H<sub>1a</sub>), 2.23 (2H, m, C<sub>α</sub>*HH*), 1.19 (3H, t, *J* = 7.5Hz, CH<sub>2</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  224.3, 226.9 (2 W–CO), 161.8 (C<sub>3</sub>), 140.1, 127.9, 127.4, 126.1 (Ph), 121.5 (*C*HPh), 89.8 (Cp), 86.3 (C<sub>2</sub>), 30.8 (C<sub>1</sub>), 29.6 (Cα), 15.5 (Me). Mass (75 eV, *m/e*): 462 (M<sup>+</sup>), 406 (M<sup>+</sup> – 2CO). Anal. Calcd for C<sub>19</sub>H<sub>18</sub>WO<sub>2</sub>: C, 49.37, H, 3.93. Found: C, 49.66; H, 3.88.

(8) Synthesis of CpW(CO)<sub>2</sub>( $\eta^3$ -2-benzyl-4-phenyl-2,3butadien-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<sup>-1</sup>): v(CO) 1955 (s), 1886 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.60–7.17 (11H, m, Ph+ CHPh), 5.26 (5H, s, Cp), 3.39 (1H, d, J = 13.8 Hz, CHH), 3.26 (1H, d, J = 13.8, CHH'), 2.91 (1H, s, H<sub>1s</sub>), 2.62 (1H, s, H<sub>1a</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  226.2, 223.5 (2 W–CO), 161.6 (C<sub>3</sub>), 141.5, 139.5, 132.3, 130.0, 129.0, 128.4, 127.1, 126.5, 122.2 (2 Ph + C<sub>4</sub>), 89.8 (Cp), 81.8 (C<sub>2</sub>), 44.3 (C<sub>a</sub>), 30.1 (C<sub>1</sub>). Mass (75 eV, *m/e*): 524 (M<sup>+</sup>), 468 (M<sup>+</sup> – 2CO). Anal. Calcd for C<sub>24</sub>H<sub>20</sub>WO<sub>2</sub>: C, 54.98; H, 3.85. Found: C, 55.32; H, 3.64.

(9) Synthesis of CpW(CO)<sub>2</sub>[ $\eta^3$ -2-(phenylethynyl)-4phenyl-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<sup>-1</sup>): v(CO) 1955 (s), 1884 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>1s</sub>), 2.68 (1H, s, H<sub>1a</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  225.1, 224.4 (2 W–CO), 160.5 (C<sub>3</sub>), 141.0, 138.5, 132.0, 131.0, 129.0, 128.0, 127.6, 126.9, 123.2 (2 Ph + C<sub>4</sub>), 89.7 (Cp), 87.0, 83.4 (C=C), 79.1 (C<sub>2</sub>), 28.8 (C<sub>a</sub>), 27.8 (C<sub>1</sub>). Mass (75 eV, *m/e*): 548 (M<sup>+</sup>), 492 (M<sup>+</sup> – 2CO). Anal. Calcd for C<sub>26</sub>H<sub>20</sub>WO<sub>2</sub>: C, 56.96; H, 3.68. Found: C, 57.12; H, 3.02.

(10) Synthesis of CpW(CO)<sub>2</sub>( $\eta^{3}$ -2-methyl-4-phenyl-2,3butadien-1-yl) (4g). This compound was similarly prepared according to the procedure for synthesis of 4a, except that NaBH<sub>3</sub>CN (3.0 equiv) was used; the yield was 52%. IR (Nujol, cm<sup>-1</sup>): v(CO) 1955 (s), 1884 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.53 (1H, s, CHPh), 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<sub>1s</sub>), 2.64 (1H, s, H<sub>1a</sub>), 2.27 (3H, s, Me). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): 226.8, 223.7 (2 W–CO), 162.5 (C<sub>3</sub>), 140.1, 127.9, 127.2, 126.1 (Ph), 121.9 (C<sub>4</sub>), 89.8 (Cp), 81.4 (C<sub>2</sub>), 31.3 (C<sub>1</sub>), 22.5 (Me). Mass (75 eV, m/e): 448 (M<sup>+</sup>). Anal. Calcd for C<sub>18</sub>H<sub>16</sub>WO<sub>2</sub>: C, 48.24; H, 3.60. Found: C, 48.04; H, 3.55.

(11) Synthesis of CpW(CO)<sub>2</sub>( $\eta^3$ -2-benzoylallyl) (5). To a THF/H<sub>2</sub>O solution (1/1, 5 mL) of **3a** (0.22 g, 0.48 mmol) was added p-toluenesulfonic acid (4.1 mg, 2.4  $\times$  10  $^{-2}$  mmol), and the mixture was stirred for 6 h at 23 °C. To this solution was added an aqueous NaHCO<sub>3</sub> 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 (Rf 0.54) that gave 5 (0.12 g, 0.26 mmol, 55%). IR (cm<sup>-1</sup>): v(CO) 1962 (s), 1887 (s), 1658 (vs). <sup>1</sup>H NMR (400 MHz, -10 °C, CDCl<sub>3</sub>):  $\delta$  7.32–7.22 (5H, m, Ph), 5.34 (5H, s, Cp), 3.69 (2H, s, COCH<sub>2</sub>), 3.12 (2H, s, H<sub>1s</sub>), 1.59 (2H, s, H<sub>1a</sub>). <sup>13</sup>C NMR (100 MHz, -10 °C, CDCl<sub>3</sub>):  $\delta$  222.3 (2 W-CO), 198.1 (PhCOCH<sub>2</sub>), 135.1, 129.5, 128.4, 126.6 (Ph), 87.9 (Cp), 86.7 (C2), 42.6 (CH2), 25.4 (C1). 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[ $\eta^4$ -2-benzyl-3-(ethylvinyl)ketene] (6a). To a dichloromethane (10 mL) solution of 4d (0.10 g, 0.22 mmol) and Bu<sub>4</sub>NI (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<sub>3</sub> solution (10 mL). The product was extracted with diethyl ether (2  $\times$ 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<sup>-1</sup>): v(CO) 1999 (s), 1942 (s), 1650 (vs). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.39-7.21 (5H, m, Ph), 5.27 (5H, s, Cp), 3.64 (2H, ABq, J = 4.0 Hz, PhCH<sub>2</sub>), 3.61 (1H, d, J = 3.4 Hz,  $C_4H_s$ ), 2.77 (1H, m, CHHMe), 2.72 (1H, d, J = 3.4Hz, C<sub>4</sub>H<sub>a</sub>), 2.65 (1H, m, CHH'Me), 0.73 (3H, t, J = 7.6 Hz, Me). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  259.4 (C<sub>1</sub>=O), 219.7 (CO), 147.4 (C<sub>3</sub>), 139.0, 128.7, 128.6, 126.6 (Ph), 90.4 (Cp), 74.3 (C<sub>2</sub>), 39.2 (C<sub>4</sub>), 33.6 (PhCH<sub>2</sub>), 29.4 (CH<sub>2</sub>Me), 14.7 (Me). Mass (75 eV, m/e: 562 (M<sup>+</sup> – CO). Anal. Calcd for C<sub>19</sub>H<sub>19</sub>WO<sub>2</sub>I: C, 38.67; H, 3.25. Found: C, 38.21; H, 3.15.

(13) Synthesis of CpW(CO)I[ $\eta^{4}$ -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<sup>-1</sup>): v(CO) 2002 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>4s</sub>), 2.73 (1H, d, J = 3.2 Hz, H<sub>4a</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  253.7 (C<sub>1</sub>=O), 210.0 (W–CO), 143.9 (C<sub>3</sub>), 138.7, 138.4, 129.4, 128.9, 128.6, 128.2, 126.7, 126.4 (Ph), 90.4 (Cp), 76.4 (C<sub>2</sub>), 41.1, 40.7, 33.7 (C<sub>4</sub> + 2 CH<sub>2</sub>Ph). Mass (75 eV, *m/e*) 624: (M<sup>+</sup> – CO). Anal. Calcd for C<sub>24</sub>H<sub>21</sub>WO<sub>2</sub>I: C, 44.20; H, 3.25. Found: C, 43.98; H, 3.11.

# Table 4. Crystal Data and Conditions for Crystallographic Data Collection and Structure Refinement<sup>a</sup>

|   | 2   | 6c                               | 7                                 |
|---|---|----------------------------------|-----------------------------------|
| formula                                   | WC <sub>18</sub> H <sub>14</sub> O <sub>2</sub> | $W_{12}O_2C_{18}H_{16}$          | WC20H21O2                         |
| fw  | 446.15  | 701.97                           | 477.23                            |
| diffractometer used                       | nonius  | nonius                           | nonius                            |
| space group                               | monoclinic, $P_{21}/c$                          | monoclinic, $P_{21}/c$           | orthorhombic, Pca <sub>21</sub>   |
| 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)                         |
| $\beta$ (deg)                             | 100.952(20)                                     | 91.327(16)                       | 3510.3(19)                        |
| $V(Å^3)$                                  | 1509.5(7)                                       | 1935.8(12)                       |                                   |
| Z   | 4   | 4                                | 8                                 |
| $D_{\rm calc} \ ({\rm g \ cm^{-3}})$      | 1.963   | 2.409                            | 1.806                             |
| λ (Å)                                     | 0.7107  | 0.7107                           | 0.7107                            |
| F(000)                                    | 844.  | 1270.                            | 1840.                             |
| unit cell detn: no; $2\theta$ 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 $\theta$ )                     | 2 ( $0.80 + 0.35 \tan \theta$ )  | 2 ( $0.65 \pm 0.35 \tan \theta$ ) |
| scan speed (deg/min)                      | 2.06 - 8.24                                     | 3.30-8.24                        | 2.06 - 8.24                       |
| $2\theta_{\rm max}$ (deg)                 | 50.0  | 45.0                             | 50.0                              |
| hkl ranges                                | (-20, +19) (0-7) (0-17)                         | (-8, +8) $(0-12)$ $(0-22)$       | (0-21) $(0-7)$ $(0-25)$           |
| $\mu$ (cm <sup>-1</sup> )                 | 78.162  | 92.568                           | 67.199                            |
| cryst size (mm)                           | 0.10	imes 0.30	imes 0.45                        | $0.20\times0.30\times0.40$       | 0.20 	imes 0.25 	imes 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                         | $\sum (W F_{\rm o}-F_{\rm c} ^2)$               | $\sum (W F_{ m o}-F_{ m c} ^2)$  | $\sum (W F_{ m o}-F_{ m c} ^2)$   |
| weighting scheme                          | $(1/\sigma^2) (F_0)$                            | $(1/\sigma^2)$ (F <sub>o</sub> ) | $(1/\sigma^2)$ (F <sub>o</sub> )  |
| $q$ (2nd ext. coeff) $	imes$ 10 $^4$      | 0.61(3)   | 0.71(3)                          | 1.42(13)                          |
| $(\Delta/\sigma)_{\rm max}$               | 0.0188  | 0.0110                           | 0.0550                            |
| (D map) min, max (e/ų)                    | -1.020, 0.780                                   | -1.030, 0.900                    | -1.230; 3.850                     |
|   |   |                                  |                                   |

 ${}^{a}R_{F} = \sum (F_{\sigma} - F_{c}) / \sum F_{\sigma}; R_{w} = [\sum (w(F_{\sigma} - F_{c})^{2}) / \sum (wF_{\sigma}^{2})]^{1/2}; \text{GOF} = [\sum (w(F_{\sigma} - F_{c})^{2}) / (\text{NO} - \text{NP})]^{1/2}.$ 

(14) Synthesis of CpW(CO)I[ $\eta^{4}$ -2-benzyl-3-((iodomethyl)vinyl)ketene) (6c). This compound was similarly prepared from the reaction between 2, CF<sub>3</sub>SO<sub>3</sub>H, and Bu<sub>4</sub>NI according to the procedure for the synthesis of **6a**. IR (cm<sup>-1</sup>): v(CO) 2003 (s), 1648 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  7.36–7.20 (5H, m, Ph), 5.31 (5H, s, Cp), 4.48 (1H, d, J = 9.4 Hz, CHH'Ph), 3.85 (1H, d, J = 9.4 Hz, CHHPh), 3.69 (1H, d, J = 14.9 Hz, CHH'I), 3.62 (1H, d, J = 14.9 Hz, CHH'I), 3.59 (1H, d, J = 3.2 Hz, H<sub>4</sub>s), 2.66 (1H, d, J = 3.2 Hz, H<sub>4</sub>a). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  253.7 (C<sub>1</sub>=O), 211.4 (CO), 137.1 (C<sub>2</sub>), 136.9, 129.8, 128.9 (Ph), 90.1 (Cp), 75.6 (C<sub>3</sub>), 39.7 (C<sub>4</sub>), 33.9 (CHH'Ph), 4.0 (CHH'I). Anal. Calcd for C<sub>18</sub>H<sub>16</sub>WO<sub>2</sub>I<sub>2</sub>: C, 30.80; H, 2.30. Found: C, 30.92; H, 2.42.

(15) Synthesis of CpW(CO)<sub>2</sub>( $\eta^{3}$ -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 BF3·Et2O (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<sub>3</sub>CN (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<sub>4</sub>Cl 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<sup>-1</sup>): v(CO) 1935 (s), 1856 (s). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  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<sub>3</sub>H), 2.51 (1H, s, H<sub>1s</sub>), 2.35 (3H, s, Me), 1.56 (3H, d, J = 13.1 Hz, Me), 1.51 (1H, s, H<sub>1a</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  230.8, 229.8 (2 W–CO), 143.3 (C<sub>4</sub>), 141.5, 129.0, 128.1, 126.4 (Ph), 122.3 (C<sub>5</sub>), 97.8 (C<sub>2</sub>), 89.7 (Cp), 54.8 (C<sub>3</sub>), 27.7 (C<sub>1</sub>), 21.5 (Me), 15.0 (Me). Mass (75 eV, *m/e*): 476 (M<sup>+</sup>), 416 (M<sup>+</sup> – 2CO). Anal. Calcd for C<sub>20</sub>H<sub>20</sub>WO<sub>2</sub>: 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 K $\alpha$  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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