Nucleophilic Addition to Tungsten η^4-2-(Methoxycarbonyl)-1,3-pentadiene Cations: Control of Nucleophilic Regiochemistry by the Diene Conformation

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Received May 23, 1994[⊗]

Treatment of $CpW(CO)_3(\eta^1$-vinylpropargyl) (**1**) with CF_3SO_3H in 1.2 equimolar proportion in Et_2O at −78 °C, followed by addition of CH_3OH, produced $CpW(CO)_2(\eta^3$-2-(methoxycarbonyl)-2,4-pentadien-1-yl) (**2**) in good yield. Further treatment of **2** with CF_3SO_3H in cold diethyl ether (−78 °C) generated an orange precipitate of [$CpW(CO)_2(\eta^4$-*s-trans*-2-(methoxycarbonyl)-1,3-pentadiene)]BF_4 (**3a**), which was characterized by ^1H and ^{13}C NMR spectra. Above −10 °C, this cation underwent an irreversible isomerization to the more stable *s-cis*-η^4-diene conformer **3b**. The sites of nucleophilic addition to these two conformers are distinct for most nucleophiles. For **3a**, hard nucleophiles such as water, alcohols, thiols, and amines added exclusively at the $=C_\delta HMe$ carbon, whereas organocopper reagents preferred the $C_\alpha H_2$ carbon to give Michael reaction products. For **3b**, nucleophiles regardless of their natures all add unambiguously at the $C_\alpha H_2$ carbon. The distinct nucleophilic regiochemistries of these two η^4-diene conformers are discussed. To demonstrate the synthetic utility of these nucleophilic additions, we performed demetalation of several allyl products derived from **3a** and **3b**.

Introduction

Nucleophilic addition on transition-metal−η^4-diene complexes has been widely studied.[1-3] This reaction has been investigated for various metal systems,[4-8] including Pd(II), Ni(II), Co(I), Rh(I), Fe(II), Fe(0), and Mo(II), and the importance of this reaction in organic synthesis is well recognized. So far, all reported chemistry has been performed exclusively on metal complexes of the *s-cis* conformational form **A** (Chart 1). The first metal−*s-trans*-η^4-diene conformer **B** was reported by Erker[9] in 1980, and considerable progress in its chemistry has been achieved.[10] Green[11] reported that protonation of $CpMo(CO)_2(\eta^3$-pentadienyl) gave a molybdenum−*s-trans*-η^4-diene cation in CH_2Cl_2 at low temperature (−78 °C), which underwent an irreversible isomerism to the more stable *s-cis*-η^4 conformer as the temperature was raised above −20 °C. We[12] found that $CpMo(CO)_2$(*s-trans*-η^4-diene)$^+$ is much more reactive than its *s-cis*-diene conformer toward nucleophilic attack. So far, there has been no comparison of the regiochemistry for nucleophilic attack of these two conformers. Control of the nucleophilic regiochemistry by the diene conformation of $CpM(CO)_2(\eta^4$-diene)$^+$ (M = W, Mo) is significant in organic synthesis because these complexes produce varied products after demetalation of the resulting π-allyl compounds.

Chart 1

To choose a more meaningful system, we noted that the 2-carboxylated 1,3-diene is unstable and undergoes facile dimerization even at ambient temperature.[13a,b] Conjugated addition (Michael reaction) on 2-carboxylated 1,3-dienes is not at all operable. One method to circumvent this problem is to complex such an unstable

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[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

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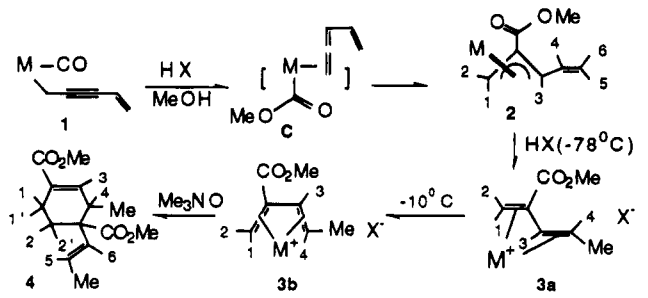
Scheme 1[a]



[a] M = $CpW(CO)_2$; X = CF_3SO_3.

monomer with a suitable metal cationic fragment,[13c,d] which is subject to nucleophilic attack. In this full paper,[14] we report the generation of $CpW(CO)_2(\eta^4$-2-(methoxycarbonyl) 1,3-diene)$^+$ in both *s-trans* and *s-cis* conformations, and their reactions with various nucleophiles are described.

Results and Discussion

Synthesis and Characterization of the η^4 2-Carboxylated 1,3-Diene Cations. As shown in Scheme 1, the key compound $CpW(CO)_3(\eta^3$-2-(methoxycarbonyl)-penta-2,4-dien-1-yl) (**2**) is easily prepared by acidification of **1**[15] with CF_3SO_3H (1.2 molar equiv) in diethyl ether (−40 °C), followed by addition of excess MeOH; the yield was 65%. The formation of **2** is believed to proceed via intramolecular insertion[16,17] of an η^1-methoxycarbonyl group into the coordinated η^2-vinylallene ligand (**C**), which is presumably the reaction intermediate. Formation of metal η^3-2-carboxylated allyl (metal = $CoW(CO)_3$, $CpMo(CO)_3$) compounds by reaction of the corresponding η^1-propargyl ligands with alcohols, thiols, and water was previously documented.[16,17] Compound **2** exists in two conformational isomers in solution with an exo/endo ratio of 32/68. The two isomers are readily distinguishable by their ^{1}H NMR (−50 °C, $CDCl_3$) signals of the allyl protons;[18] the chemical shifts of the H^1 and H^3 protons of the exo conformer are smaller than those of the corresponding protons of the endo isomers. Slow addition of CF_3SO_3H (1.2 molar equiv) to **2** in cold diethyl ether (−40 °C) generated an air-sensitive orange precipitate, the η^4-*s-trans*-2-(methoxycarbonyl)-1,3-pentadiene cation **3a**, which was isolated in pure form and fully characterized. The *s-trans*-diene structure is assigned to **3a** from comparison of its four diene proton NMR signals (−60 °C, d_6-acetone) with reported molybdenum *s-trans*[11,12] and *s-cis* diene cations.[19] Generally, the diene protons of the *s-trans*-diene conformer usually have larger δ (ppm) values than those of the *s-cis*-diene conformer. This pattern is followed if one compares the proton NMR signals of **3a** with those of its *s-cis*-diene conformer (**3b**, Scheme 1). A characteristic feature here is the chemical shift of the H^4 signal (δ 6.23 ppm), which is much larger than those of the H^2 (δ 4.31 ppm) and H^3 (δ 4.54 ppm) proton signals. This character is inconsistent with that expected for a *s-cis*-diene cation,[19] because the two inner diene proton H^1 and H^4 signals of the *s-cis* isomer (**3b**) generally have small δ values (δ <3.0 ppm)[19] if the effect of the methoxycarbonyl group is neglected. Additional support of the *s-trans*-diene conformational structure relies on proton NOE difference spectra (−60 °C, d_6-acetone). Irradiation of the H^3 (δ 4.53 ppm) proton caused increased intensities of the H^1 (δ 3.82 ppm) and H^4 (δ 6.23 ppm) proton signals by 2.7% and 2.0%, respectively. Irradiation of the H^1 proton signal produced increased intensities of the H^2 (δ 4.31 ppm) and H^3 signals by 10.2% and 2.1%, respectively, and in this case the intensity of the H^4 proton signal was unaffected. For **3b**, the H^1 and H^3 protons are too far from each other to have an NOE effect. The cation **3a** was kept at −20 °C as the solid form without isomerization. Leaving the solid at 23 °C for 24 h caused partial isomerization (ca. 25%) to its *s-cis*-diene conformer, as indicated by NMR spectra (−60 °C, d_6-acetone). The cation **3a** is stable at −60 °C in d_6-acetone at least for a few hours without isomerization. When the temperature was raised above −10 °C, the NMR sample showed a new pattern of NMR signals assigned to *s-cis*-η^4-diene cation **3b**. The two inner diene protons H^1 (δ 1.78 ppm) and H^4 (δ 3.46 ppm) of **3b** have much smaller chemical shifts than the corresponding protons of **3a**, consistent with the literature report.[19] The observed coupling constant J_{34} = 10.6 Hz is smaller than that (J_{34} = 12.6 Hz) of **3a**. In the proton NOE difference spectra, irradiation of the H^4 proton signal showed increased intensities of the H^1 and H^3 signals by 3.9% and 1.6%, respectively, compatible with a η^4-*cis*-diene conformation. Treatment of **3b** with anhydrous Me_3NO in CH_2Cl_2 (23 °C) liberated its monomer, which quickly dimerized to give **4** in 75% yield as one isomer.

Nucleophilic Addition on 3a and 3b. The cations **3a** and **3b** represent two conformers, the formation of which can be controlled selectively by temperature. Previous work[12,20,21] revealed that nucleophilic attack on $CpMo(CO)_2(\eta^4$-diene)$^+$ in both *s-trans* and *s-cis* form occurs only at the two terminal carbons to give π-allyl compounds. In this manner, the reactions between the two cations and nucleophiles by no means give the same π-allyl products even if their sites of addition are the same. Generally, tungsten and molybdenum dicarbonyl π-allyl products are kinetically stable[19,22,23] at room temperature, and the *anti*−*syn* allyl isomerization is not feasible under experimental conditions (*vide infra*). The implication for organic chemistry is that organic compounds can be selectively generated after decomplex-

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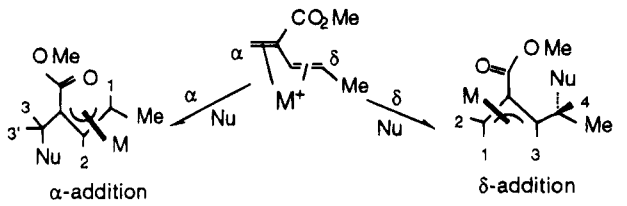
Scheme 2[a]



Nucleophiles	Product	Yield(%)	Product
H_2O	δ	89	5
MeOH	δ	91	6
$NaNH_2$	δ	63	7
Me_2CHNH_2	δ	84	8
$(Me_2CH)_2NH$	δ	69	9
EtSH	δ : α 72 : 28	74	10
PhSH	δ : α 68 : 32	62	11
Me_2CuLi	δ : α 32 : 68	57	12
$(PhCC)_2Cu$	δ : α 34 : 66	50	13

[a] M = $CpW(CO)_2$.

ation of the π-allyl products, assuming that nucleophilic attack on **3a** and **3b** is regioselective.

Similar to the case for the $CpMo(CO)_2$(*s-trans*-η^4-diene)$^+$ cation,[12] nucleophilic attack of **3a** by diverse nucleophiles such as water, methanol, amines, thiols, and organocopper reagents proceeds readily in cold diethyl ether (−40 °C), and the reaction is generally complete within 20 min. In a typical reaction, the cation **3a** was first isolated from its preparation and subsequently treated with appropriate bases in cold diethyl ether (−40 °C), quickly producing a clear yellow solution. Monitoring the solution on a SiO_2 TLC plate indicated that only one product was formed for water, methanol, and amine but two products were obtained for thiols and organocopper reagents. Scheme 2 tabulates the isolated yields and ratios of products of various nucleophiles. Despite the presence of the methoxycarbonyl group, nucleophiles can add at the diene δ-carbon in addition to the expected α-carbon, corresponding to the non-Michael and Michael reactions. Hard bases, e.g. water, methanol, and amines, including bulky isopropylamine and diisobutylamine, add highly regio- and stereoselectively at the δ-carbon to produce allyl compounds **5**−**9** as a single diastereomer; the nucleophiles presumably approach the diene moiety opposite to the tungsten fragment. Confirmation of this stereochemistry relies on an X-ray structural determination of γ-lactone **25** derived from **5** (Figure 1; vide infra). Less hard bases such as thiols slightly prefer a non-Michael reaction pathway with δ/α > 2. Addition of organocuprates to **3a** led to carbon−carbon bond forming reactions which alkylated preferentially at the α-diene carbon with δ/α = 1/2. Separation of the two α,δ-η^3-allyl complexes for **10**−**13** was conducted on a silica column. ^{1}H NMR spectroscopy is a useful tool to elucidate the structures of the two products. In the proton NMR spectra, the H^1 and H^3 proton resonances of the δ-addition products have chemical shifts of δ 1.0−1.2 ppm (J_{12} = 0 Hz) and 2.1−2.5 ppm, respectively, near those of the corresponding protons of **2** in the *endo* conformation. In the α-addition product, the coupling constant J_{12} = 10.0 Hz is characteristic of *trans* coupling between the *syn* and *anti* protons. The chemical shift of the H^1 proton (δ 2.64 ppm) of **10**α is close to reported values (δ 2.5−2.6 ppm) for common allylic *anti* protons

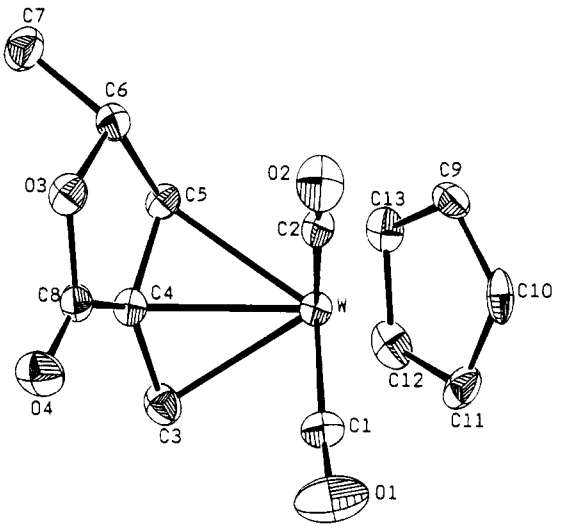


Figure 1. ORTEP drawing of **25**.

of the endo conformer but is smaller than those of **11**α−**13**α (3.5−3.6 ppm). The large δ values of the H^1 protons of **11**α−**13**α may be due to the deshielding of the adjacent carbonyl group. The H^3 and $H^{3'}$ protons of **10**α−**13**α show an AB quartet with geminal coupling $J_{33'}$ = 13−18 Hz, and their chemical shifts depend largely on the nature of the nucleophiles. In the particular case of **12**α, irradiation of the H^2 intensities of H^3 (δ 1.31 ppm) and $H^{3'}$ (δ 2.36 ppm) protons by 2.4% and 1.7%, respectively, consistent with the proposed structure. All compounds **5**−**13** in Scheme 2 are stable at 23 °C for a few hours in solution, and no isomerization was observed during this period. However, for **10**α−**13**α, further isomerization is possible if the NMR sample is kept at 23 °C for more than 3 days. In the case of **12**α, an NMR sample ($CDCl_3$) after standing for 75 h revealed the presence of the additional isomer **19**α (vide infra; Scheme 3) and an unknown species. The concentrations of these three species were approximately equal.

Figure 1 shows the X-ray structure of **25**, which was readily prepared from NaH-promoted intramolecular lactonization of **5** in THF (Scheme 4; vide infra). The selected bond distances and angles and atomic coordinates are shown in Tables 1 and 2, respectively. The ORTEP drawing confirms the stereochemistry of α-addition products shown in Scheme 2. The conformation of **25** is the endo form; i.e., the open mouth of the allyl group faces the cyclopentadienyl group. W−C3 (2.311(9) Å), W−C4 (2.263(9) Å), and W−C5 (2.292(8) Å) represent normal tungsten−η^3-allyl distances. The C3−C4 (1.411(11) Å) and C4−C5 (1.391(11) Å) lengths are between those of single and double bonds. The seven C3−C6, C8, O3, and O4 atoms are planar within a maximum deviation of 0.055(10) Å.

We examined the addition of various nucleophiles to the *s-cis*-diene cation **3b**; the results are summarized in Scheme 3. The cation is much less reactive than its *s-trans* conformer, and no reaction occurred for weak nucleophiles such as water and methanol at 23 °C. Regardless of the nature of the nucleophiles (hydroxide, methoxide, thiols, amine, and organocuprates), all added to the diene α-carbon to afford only one diastereomer; the yields were moderate (40−55%). Compounds **18**α, **19**α, and **21**α differ structurally from the related complexes **10**α, **12**α, and **13**α and are distinguishable

Table 1. Selected Bond Distances (Å) and Angles (deg) for 25

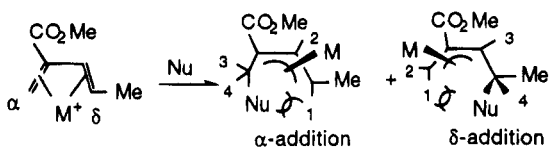
W—C1	1.958(9)	C4—C5	1.391(11)
W—C2	1.994(9)	C4—C8	1.463(12)
W—C3	2.311(9)	C5—C6	1.516(12)
W—C4	2.263(9)	C6—C7	1.509(13)
W—C5	2.292(8)	C6—O3	1.461(10)
C1—O1	1.145(11)	C8—O3	1.366(10)
C2—O2	1.144(11)	C8—O4	1.195(11)
C3—C4	1.411(11)		
C1—W—C2	77.5(3)	W—C4—C8	116.9(6)
C1—W—C3	81.7(3)	C3—C4—C5	124.0(8)
C1—W—C4	92.4(3)	C3—C4—C8	125.8(7)
C1—W—C5	123.8(3)	C5—C4—C8	109.4(7)
C2—W—C3	121.2(3)	W—C5—C4	71.1(5)
C2—W—C4	90.9(3)	W—C5—C6	124.7(6)
C2—W—C5	82.9(3)	C4—C5—C6	106.9(7)
C3—W—C4	35.9(3)	C5—C6—C7	114.0(7)
C3—W—C5	65.0(3)	C5—C6—O3	104.2(6)
C4—W—C5	35.6(3)	C7—C6—O3	109.3(7)
W—C1—O1	176.4(9)	C4—C8—O3	108.0(7)
W—C2—O2	178.4(7)	C4—C8—O4	131.6(8)
W—C3—C4	70.2(5)	O3—C8—O4	120.4(8)
W—C4—C3	73.9(5)	C6—O3—C8	110.7(6)
W—C4—C5	73.4(5)		

Table 2. Atomic Parameters *x*, *y*, and *z* and B_{iso} Values (Å²) for 25[a]

	x	*y*	*z*	B_{iso}[b]
W	0.21013(4)	0.09301(3)	0.19913(3)	2.025(16)
C1	0.1726(11)	0.2116(8)	0.0836(7)	3.3(5)
C2	0.2601(10)	0.2487(8)	0.2760(6)	2.9(5)
C3	0.3695(11)	0.0123(8)	0.0934(6)	3.1(4)
C4	0.4578(10)	0.0691(7)	0.1831(6)	2.3(4)
C5	0.4495(10)	0.0402(7)	0.2877(6)	2.3(4)
C6	0.5585(10)	0.1244(8)	0.3584(6)	2.9(4)
C7	0.6983(11)	0.0625(9)	0.4205(7)	4.0(5)
C8	0.5486(10)	0.1791(8)	0.1816(7)	2.8(4)
C9	0.0594(11)	0.0279(8)	0.3163(6)	3.0(4)
C10	−0.0364(10)	0.0790(8)	0.2290(8)	3.2(5)
C11	−0.0281(11)	0.0086(9)	0.1389(7)	3.7(5)
C12	0.0690(11)	−0.0893(8)	0.1730(7)	3.5(5)
C13	0.1227(10)	−0.0778(7)	0.2826(7)	3.0(4)
O1	0.1441(10)	0.2831(6)	0.0182(5)	6.6(5)
O2	0.2871(8)	0.3395(5)	0.3181(5)	4.5(4)
O3	0.6057(7)	0.2110(5)	0.2845(4)	3.1(3)
O4	0.5793(8)	0.2371(6)	0.1096(5)	4.4(3)

[a] Esd's refer to the last significant digit. [b] B_{iso} is the mean of the principal axes of the thermal ellipsoid.

Scheme 3[a]



Nucleophiles	Product	Yield(%)	Products
NaOH	α	46%	14
NaOMe	α	47%	15
$NaNH_2$	α	49%	16
Me_2CHNH_2	α	50%	17
EtSH	α	56%	18
Me_2CuLi	α	50%	19
$(n\text{-Bu})_2CuLi$	α	45%	20
$(PhCC)_2CuLi$	α	48%	21

[a] M = $CpW(CO)_2$.

by ^1H NMR spectroscopy. The chemical shift differences ($\Delta\delta$ >2 ppm) of the methylene protons CH^3H^4 of the former compounds are much larger than those of the $CH^3H^{3'}$ protons of the latter. The chemical shifts of the H^1 protons of **14α**–**21α** (δ 2.0–2.5 ppm, J_{23} = 10 Hz) are normal, compared to the values reported for π-crotyl compounds of the endo isomer (δ 2.5–2.6 ppm). In the NOE difference spectra, irradiation of the H^1 proton of **14α** showed increased intensities of the methylene protons H^3 (δ 2.03 ppm) and H^4 (δ 4.18 ppm) by 2.4% and 1.9%, respectively, consistent with the proposed structure.

From a comparison of the results of Schemes 2 and 3, nucleophilic additions on **3a** and **3b** may proceed with varied regiochemistry. We first rationalize the tendency of α-addition for attack of the hard base on **3a**. In our hypothesis, the *s-trans*-diene cation is generally highly reactive and its reaction with nucleophiles is expected to proceed via a small energy barrier. The relative energy states of the α- and δ-addition products determine the reaction selectivity if the reaction is reversible. We previously reported that hydroxy, alkoxy, and amino groups adjacent to an M–π-allyl group (M = Mo, W) are prone to ionization[12] because of the basicity of $CpM(CO)_2$ (M = Mo, W) that facilitates cleavage of the C–X (X = OH, ROH, R_2N) bond in an intramolecular S_N2 displacement. If the structures of the two products are compared, the δ-addition product is much more sterically favored because one of two *anti* positions in the α-addition product is the methoxycarbonyl group, which exerts strong steric hindrance with π-allylic electrons. Although the diene α-carbon is expected to be the most favorable site due to the influence of the methoxycarbonyl group, its influence is overwhelmed by the reversibility of the C–X group. For organocuprates, the α-addition site reflects its intrinsic preference for the enone α-carbon, and its carbon–carbon bond-forming reaction is considered irreversible.[24]

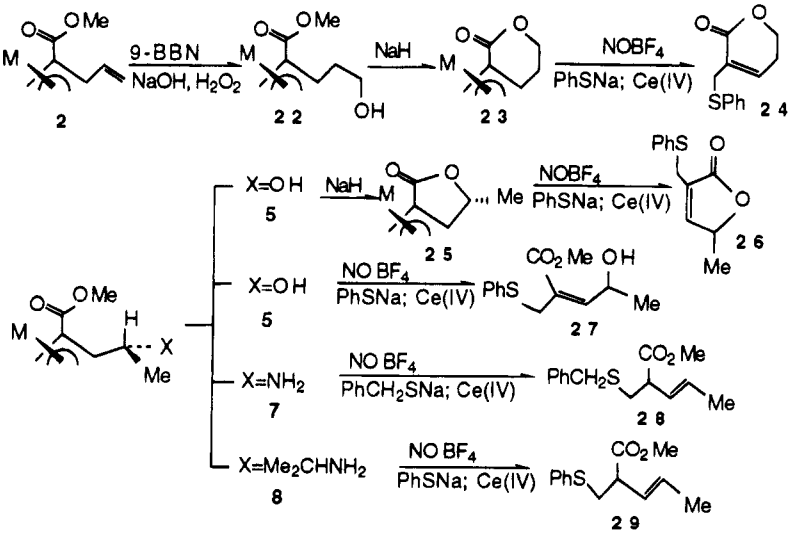
To test the reversibility of the C–X bond of **5δ**–**9δ**, we treated **6δ** with 20-fold excess CD_3OD in THF in the presence of 4-toluenesulfonic acid (0.15 molar equiv). After the mixture was stirred for 30 min at 23 °C, ^1H NMR of **6δ** shows a deuterium content of the methoxy group exceeding 90%, confirming an acid-catalyzed exchange process. Under our experimental conditions, the reaction of **3a** with water, alcohol, and amine (2–3 molar equiv) and thiols is expected to release 1 molar equiv of proton, which will accelerate the reaction to reach its equilibrium state.

In the addition of nucleophiles to *s-cis*-diene **3b**, both α- and δ-addition products have either CH_2Nu (α-isomer) or CHMeNu (β-isomer) substituents in the *anti* position, and the former is more sterically favorable than the latter in interaction with π-allyl electrons. Similar to **3a**, the diene α-carbon is the preferential site for Michael addition because of its more positive character compared to the δ-carbon. Despite formation of the C–X (X = OH, OR, NR_2)[12] bond being reversible, the fact that the α-carbon is the addition site for all nucleophiles is reasonable on both kinetic and thermodynamic grounds. To confirm the latter, we treated **14** and **15** with 4-toluenesulfonic acid (5 mol %) in wet THF (23 °C, 5 h), but no isomerization product was detectable by ^1H NMR spectra.

Demetalation of π-Allyl Compounds. As shown in Scheme 4, stirring of **2** with 9-BBN (3 equiv) in THF (48 h, 23 °C), followed by treatment with NaOH and

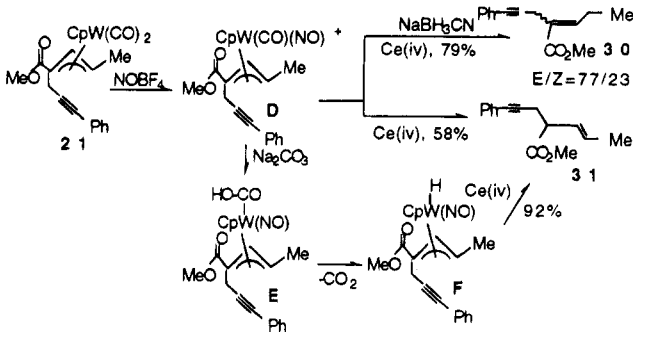
(24) Carey, F. A.; Sunderberg, R. A. In *Advanced Organic Chemistry, Part B: Reactions and Synthesis*; Plenum Press: New York, 1990; Chapter 8, p 408.

Scheme 4[a]



[a] M = $CpW(CO)_2$.

Scheme 5



oxidation with H_2O_2 (5 molar equiv) produced the 5-hydroxy allyl compound **22** in 70% yield. Further treatment of **22** with NaH induced intramolecular cyclization to give **23** in 94% yield. The reaction between **23** and $NOBF_4$ generated an electrophilic cation,[25,26] which reacted with benzenethiolate to give, after oxidation with Ce(IV), the unsaturated δ-lactone **24** in 66% yield. Likewise, compound **5** underwent facile NaH-promoted intramolecular cyclization to afford the allyl γ-lactone compound **25** as a single diastereomer (95%). The structure of **25** (Figure 1) clarifies the proposed stereochemistry of δ-addition products given in Scheme 1. Similarly, treatment of the NO cation of **25** with PhSNa, followed by Ce(IV) oxidation, delivered the furanone **26** in 58% yield. By a similar method, the pentenoate **27** was produced in 57% yield from the NO cation of **5**. We attempted the same demetalations on **7** and **8**, which failed to give the analogous 1,3-difunctionalized products. Instead, the reaction proceeded by an unusual hydrodenitrogenation pathway to produce the pentenoates **28** and **29** in yields of 53% and 58%, respectively. A detailed mechanism of the hydrodenitrogenation is not available at present.

To demonstrate the synthetic utility of allyl products derived from **3b**, we treated the NO cation of **21** with $NaBH_3CN$ to give, after oxidation with Ce(IV), 4-(methoxycarbonyl)-1-phenylhept-4-en-1-yne (**30**; 79%) with a *Z/E* ratio of ca. 23/77. In the *E* isomer, irradiation of the CH_2CH_3 (δ 2.29 ppm) protons produced a 1.2% Overhauser increase of the intensity of the $PhCC-CH_2$ (δ 3.36 ppm) protons. Direct Ce(IV) oxidation of this NO cation induced cleavage of W—C(allyl) bonds to give 4-(methoxycarbonyl)-1-phenylhept-5-en-1-yne (**31**) in 58% yield in addition to several unknown organic components. Treatment of the NO cation with an aqueous Na_2CO_3 solution, followed by Ce(IV) oxidation gave **31** in excellent yields (92%). The latter possibly involves the W—hydride species **F**, generated from the OH^- attack on the W—CO group of **D**, followed by a decarboxylation reaction. Further reductive elimination of **F** is expected to liberate the olefin **31**.

The objective of this work has to show the synthetic utility of unstable 2-carboxylated dienes. Nucleophilic attack of tungsten η^4 2-carboxylated 1,3-dienes is regarded as an alternative to the Michael reaction. We report here that α-addition is not the only route that one might anticipate; instead, the diene δ-carbon is the exclusive reaction site for attack of most nucleophiles on **3a**. Schemes 2 and 3 show that the nucleophilic regiochemistries correlate well with conformations of dienes and types of nucleophiles. The selectivities are explained on the basis of the steric hindrance of the resulting C—X bond formation. The data in the two schemes should be useful for employing the two cations in organic synthesis.

Experimental Section

All operations were carried out under argon in a Schlenk apparatus or in a glovebox. 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. Compounds **1** were prepared according to the procedures in our previous paper.[15]

All ^1H NMR (400 and 300 Hz) and ^{13}C NMR (75 MHz) spectra were recorded on either a Bruker AM-400 or a Varian Gemini-300 spectrometer; the chemical shifts of ^1H and ^{13}C NMR were measured 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 100 spectrometer.

Synthesis of $CpW(CO)_2(\eta^3$-2-(methoxycarbonyl)penta-2,4-dien-1-yl) (2). To **1** (0.30 g, 0.75 mmol) in diethyl ether

(25) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2570.
(26) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1976**, *98*, 3388.

(30 mL, −40 °C) was added CF_3SO_3H (0.080 mL, 0.90 mmol), and the mixture was stirred for 1 h, yielding a yellow precipitate. MeOH (10 mL) was slowly added to the mixture at the same temperature to give a clear orange solution, to which was quickly added a saturated Na_2CO_3 solution for neutralization. The solution was concentrated to half its volume, and the remaining solution was extracted with diethyl ether (2 × 20 mL). The ether layer was concentrated and eluted with a silica column (diethyl ether/hexane, 1/1) to give a yellow band (R_f 0.58). Removal of the solvent gave **2** as a yellow solid (0.21 g, 0.49 mmol, 65%). IR (Nujol): ν(CO) 1962 (vs), 1891 (vs), 1700 (s) cm^{-1}. ^1H NMR (400 MHz, −50 °C, $CDCl_3$): endo conformer (68%), δ 1.23 (1H, s, H^1), 2.84 (1H, s, H^2), 2.89 (1H, d, J = 10.6 Hz, H^3), 3.70 (3H, s, OMe), 4.74 (1H, d, J = 10.1 Hz, H^6), 5.00 (1H, d, J = 17.0 Hz, H^5), 5.31 (5H, s, Cp), 7.04 (1H, ddd, J = 17.0, 10.6, 10.1 Hz, H^4); exo conformer (32%), δ 0.79 (1H, d, J = 2.0 Hz, H^1), 1.96 (1H, d, J = 10.4 Hz, H^3), 2.99 (1H, d, J = 2.0 Hz, H^5), 5.35 (5H, s, Cp), 6.43 (1H, ddd, J = 16.0, 11.8, 10.4 Hz, H^4). ^{13}C NMR (100 MHz, −50 °C, $CDCl_3$): endo conformer, δ 22.0 (CH_3), 50.7 (CH^1H^2), 51.7 (OMe), 76.3 (*C*—CO), 89.2 (Cp), 112.3 (CH^4), 140.6 (CH^5H^6), 171.8 (*C*OOMe), 223.6, 223.5 (2 (W—CO); exo conformer, δ 30.1 (CH_3), 52.2 (CH^1H^2), 58.7 (OMe), 61.1 (*C*—CO), 93.3 (Cp), 112.9 (CH^4), 136.6 (CH^5H^6), 174.2 (*C*OOMe), 219.5, 223.1 (2 W—CO). Mass (72 eV, *m/e*): 430 (M^+), 402 (M^+ − CO), 374 (M^+ − 2CO), 346 (M^+ − 3CO). Anal. Calcd for $C_{14}H_{14}WO_4$: C, 39.10; H, 3.28. Found: C, 39.30; H, 3.34.

Synthesis of [CpW(CO)$_2$(η^4-*s-trans*-2-(methoxycarbonyl)-1,3-pentadiene)]CF_3SO_3 (3a). To a solution of **2** (0.20 g, 0.46 mmol) in diethyl ether (10 mL) at −40 °C was added CF_3SO_3H (0.040 mL, 0.46 mmol), and the mixture was stirred for 1 h to yield an orange precipitate. While the temperature was maintained at −40 °C, the ether layer was removed by syringe tube, and the precipitate was washed with diethyl ether (3 × 10 mL) before it was dried in vacuo (0.25 g, 0.43 mmol, 93%) at −30 °C. IR (Nujol): ν(CO) 2062 (vs), 2014 (vs), 1718 (s) cm^{-1}. ^1H NMR (400 MHz, −60 °C, d_6-acetone): δ 2.08 (3H, d, J = 6.4 Hz, Me), 3.66 (s, 3H, OMe), 3.82 (1H, s, H^1), 4.31 (1H, s, H^2), 4.54 (1H, d, J = 12.6 Hz, H^3), 6.23 (1H, dq, J = 12.6, 6.4 Hz, H^4), 6.27 (5H, s, Cp). ^{13}C NMR (100 MHz, −60 °C, d_6-acetone): δ 19.6 (Me), 45.5 (CH^1H^2), 52.7 (OMe), 77.8 (CH^3), 82.3 (*C*—CO), 95.9 (Cp), 99.1 (CH^4), 169.3 (*C*OOMe), 210.5, 216.5 (2 W—CO). Anal. Calcd for $C_{15}H_{15}WO_7SF_3$: C, 31.03; H, 2.61. Found: C, 31.14; H, 2.78.

Synthesis of [CpW(CO)$_2$(η^4-*s-cis*-2-(methoxycarbonyl)-1,3-pentadiene)]CF_3SO_3 (3b). The precipitate **3a** (0.25 g, 0.43 mmol) was dissolved in acetone (2 mL) at 23 °C, and the solution was stirred for 5 min before being precipitated with diethyl ether (20 mL). The resulting orange solid was collected by filtration and dried in vacuo. Recrystallization from CH_3CN/ether afforded a dark orange crystalline solid (0.24 g, 0.42 mmol, 98%). IR (Nujol): ν(CO) 2065 (vs), 2015 (vs), 1718 (s) cm^{-1}. ^1H NMR (400 MHz, −60 °C, CD_3COCD_3): δ 1.78 (1H, d, J = 1.5 Hz, H^1), 1.91 (3H, d, J = 6.2 Hz, Me), 3.01 (1H, d, J = 1.5 Hz, H^2), 3.46 (1H, dq, J = 10.6, 6.2 Hz, H^4), 3.81 (3H, s, OMe), 6.60 (1H, d, J = 10.6 Hz, H^3). ^{13}C NMR (100 MHz, −60 °C, d_6-acetone): δ 18.9 (Me), 48.9 (CH^1H^2), 53.4 (OMe), 66.8 (CH^4), 68.5 (*C*—CO), 89.8 (CH^3), 93.4 (Cp), 169.1 (*C*OOMe), 199.3, 202.4 (2 W—CO). Anal. Calcd for $C_{15}H_{15}WO_7SF_3$: C, 31.03; H, 2.61. Found: C, 31.24; H, 2.86.

Demetalation of 3b. To a solution of **3b** (0.28 g, 0.48 mmol) in CH_2Cl_2 (3 mL) was added Me_3NO (0.23 g, 3.0 mmol) at 23 °C, and the mixture was stirred for 8 h. During this period, the reaction was monitored by a SiO_2 TLC plate (UV), which showed the organic component **4** (R_f 0.34; diethyl ether/hexane, 1/1). To the solution was added water (5 mL) and diethyl ether (10 mL), and the organic layer was separated and evaporated in vacuo. The residues were chromatographed on a SiO_2 TLC plate with diethyl ether/hexane (1/1), which gave **4** as a colorless oil (45 mg, 0.18 mmol, 75%). NR (Nujol): ν(CO) 1720 (s), 1690 (s) cm^{-1}; ν(C=C) 1645 (m), 1600 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 0.94 (3H, d, J = 5.6 Hz, Me), 1.67−1.69 (4H, m, Me + CH^2), 2.10 (1H, m, $CH^{2'}$), 2.25−2.38 (2H, m, $CH^1H^{1'}$), 2.97 (1H, dq, J = 5.6, 4.7 Hz, H^4), 3.63, 3.68 (6H, s, s, 2 MeO), 5.37 (1H, d, J = 15.8 Hz, H^6), 5.52 (1H, dq, J = 15.8, 6.2 Hz, H^5), 6.90 (1H, d, J = 4.7 Hz, H^3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0, 18.1 (2 Me), 22.0, 24.5 (CH^2 + CH^1), 35.4 (CH^4), 50.1 (*C*—CO), 51.5, 52.0 (2 MeO), 126.6, 131.6 (CH^5 + CH^6), 128.2 (=*C*—CO), 146.0 (CH^9), 168.0, 175.4 (2 *C*OOMe). Mass (12 eV, *m/e*): 252 (M^+). HRMS: calcd for $C_{14}H_{20}O_4$ 252.1361, found 252.1368.

Synthesis of CpW(CO)$_2$(η^3-2-(methoxycarbonyl)-4-hydroxypent-2-en-1-yl) (5). To **3a** (0.27 g, 0.46 mmol) in diethyl ether (10 mL) at −40 °C was added water/THF (1/1, 10 mL), which resulted in the complete disappearance of **3a**. The clear dark yellow solution was brought to 23 °C, and additional ether (20 mL) was added. The organic layer was washed with water (5 mL), dried over $MgSO_4$, and concentrated. The residues were chromatographed through a SiO_2 column (diethyl ether/hexane, 1/1) to produce a yellow band of **5** (R_f 0.29, yellow solid, 0.18 g, 0.41 mmol, 89%). IR (Nujol): ν(OH) 3400 (br s) cm^{-1}; ν(CO) 1965 (vs), 1897 (vs), 1698 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.24 (3H, d, J = 6.4 Hz, Me), 1.30 (1H, s, H^1), 2.05 (1H, d, J = 7.8 Hz, H^3), 2.88 (1H, s, H^2), 3.71 (3H, s, OMe), 4.57 (1H, dq, J = 7.8, 6.4 Hz, H^4), 5.28 (5H, s, Cp). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.9 (Me), 24.0 (CH^1H^2), 51.5 (OMe), 55.1 (CH^3), 69.7 (CH^4), 88.3 (Cp), 90.6 (*C*—COOMe), 173.7 (*C*OOMe), 221.9, 223.4 (2 W—CO). Mass (12 eV, *m/e*): 448 (M^+). Anal. Calcd for $C_{14}H_{16}WO_5$: C, 37.50; H, 3.57. Found: C, 37.52; H, 3.65.

Synthesis of CpW(CO)$_2$(η^3-2-(methoxycarbonyl)-4-methoxypent-2-en-1-yl) (6). To **3a** (0.25 g, 0.48 mmol) in diethyl ether (10 mL) at −40 °C was added MeOH (5 mL), and the resulting clear yellow solution was brought to 23 °C. The solution was concentrated to half-volume before addition of diethyl ether, and the organic layer was washed with water. This organic solution was concentrated and eluted through a long silica column (ether/hexane, 1/1) to give a yellow band (R_f 0.30) that produced **6** as a yellow solid (0.20 g, 0.43 mmol, 91%). IR (Nujol): ν(CO) 1964 (vs), 1894 (vs), 1695 (s). ^1H NMR (300 MHz, $CDCl_3$): δ 1.28 (3H, d, J = 5.5 Hz, Me), 1.30 (1H, s, H^1), 1.97 (1H, d, J = 9.4 Hz, H^3), 3.01 (1H, s, H^2), 3.42 (3H, s, OMe), 3.70 (3H, s, OMe), 4.54 (1H, dq, J = 9.4, 5.5 Hz, H^4), 5.31 (5H, s, Cp). ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.2 (Me), 24.4 (CH^1H^2), 51.0 (OMe), 52.7 (CH^3), 55.9 (OMe), 76.7 (CH^4), 77.9 (*C*—COOMe), 88.5 (Cp), 171.1 (*C*OOMe), 222.4, 233.2 (2 W—CO). Mass (12 eV, *m/e*): 462 (M^+). Anal. Calcd for $C_{15}H_{18}WO_5$: C, 38.96; H, 3.93. Found: C, 38.88; H, 3.86.

Synthesis of CpW(CO)$_2$(η^3-2-(methoxycarbonyl)-4-aminopent-2-en-1-yl) (7). To **3a** (0.24 g, 0.42 mmol) in diethyl ether (10 mL) at −40 °C was added $NaNH_2$ (50 mg, 1.25 mmol), and the solution was stirred for 30 min before water (5 mL) was added. The solution was brought to 23 °C and extracted twice with diethyl ether (20 mL). After removal of the solvent in vacuo, the residues were eluted with a silica column (ether/hexane, 1/1) to develop a yellow band (R_f 0.030) that afforded **7** as a yellow solid (0.17 g, 0.26 mmol, 62%). IR (Nujol): ν(N—H) 3540 (s) cm^{-1}; ν(CO) 1963 (vs), 1878 (vs), 1698 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.17 (1H, s, H^1), 1.21 (3H, d, J = 6.4 Hz), 2.09 (1H, d, J = 9.2 Hz, H^3), 2.94 (1H, s, H^2), 3.20 (2H, br s, NH_2), 3.64 (3H, s, OMe), 4.00 (1H, dq, J = 9.2, 6.4 Hz, H^4), 5.27 (5H, s, Cp). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.8 (CH^1H^2), 25.0 (Me), 51.1 (OMe), 51.9 (CH^3), 56.6 (CH^4), 78.0 (*C*—COOMe), 88.4 (Cp), 170.8 (*C*OOMe), 222.5, 223.0 (2 W—CO). Mass (12 eV, *m/e*): 447 (M^+). Anal. Calcd for $C_{14}H_{17}WNO_4$: C, 37.61; H, 3.83; N, 3.13. Found: C, 37.77; H, 3.99; N, 3.33.

Synthesis of CpW(CO)$_2$(η^3-2-(methoxycarbonyl)-4-(isopropylamino)pent-2-en-1-yl) (8). To **3a** (0.24 g, 0.42 mmol) in diethyl ether (10 mL) at −40 °C was added isobutylamine (0.07 mL, 0.90 mmol), and the solution was stirred for 20 min. To the resulting yellow clear solution was added a saturated NH_4Cl solution (10 mL), and the organic layer was extracted with diethyl ether (2 × 10 mL). The ether layer was evapo-

rated in vacuo and eluted through a SiO_2 column to give a yellow band (ether/hexane, 1/1; R_f 0.31) that afforded **7** as a yellow solid (0.17 g, 0.35 mmol, 84%). IR (Nujol): ν(NH) 3512 (s) cm^{-1}; ν(CO) 1965 (vs), 1896 (vs), 1695 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 1.15 (3H, d, J = 6.4 Hz, Me), 1.19, 1.21 (3H, 3H, d, d, J = 6.4 Hz, $CHMe_2$), 1.27 (s, 1H, H^1), 2.12 (1H, d, J = 9.6 Hz, H^3), 2.91 (1H, s, H^2), 3.08 (1H, m, $CHMe_2$), 3.45 (1H, br s, NH), 3.67 (3H, s, OMe), 3.90 (1H, dq, J = 9.6, 6.4 Hz, H^4), 5.30 (5H, s, Cp). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8, 20.9 ($CHMe_2$), 23.6 (Me), 24.1 (CH^1H^2), 46.5 (CH^3), 51.3 (OMe), 52.7 ($CHMe_2$), 53.5 (CH^4), 71.8 (*C*—COOMe), 88.5 (Cp), 171.9 (*C*OOMe), 221.3, 231.0 (2 W—CO). Mass (12 eV, *m/e*): 489 (M^+). Anal. Calcd for $C_{17}H_{23}WO_4N$: C, 41.74; H, 4.74; N, 2.86. Found: C, 41.88; H, 4.88; N, 2.75.

Synthesis of CpW(CO)$_2$(η^3-2-(methoxycarbonyl)-4-(diisopropylamino)pent-2-en-1-yl) (9). This compound was similarly prepared from **3a** (0.24 g, 0.42 mmol) and diisopropylamine (0.080 g, 0.90 mmol) in cold diethyl ether (−40 °C, 20 min), and the yield of **9** (yellow solid, 0.15 g, 0.29 mmol) was 69%. IR (Nujol): ν(NH) 3500 (s) cm^{-1}; ν(CO) 1961 (vs), 1893 (vs), 1692 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 0.99 (12H, d, J = 6.2 Hz, $2CHMe_2$), 1.12 (1H, s, H^1), 1.20 (3H, d, J = 6.2 Hz, Me), 2.50 (1H, d, J = 9.5 Hz, H^3), 2.84 (1H, s, H^2), 3.16 (2H, m, $CHMe_2$), 3.63 (OMe), 4.26 (1H, dq, J = 9.5, 6.2 Hz, H^4), 5.26 (5H, s, Cp). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.8 (Me), 22.8, 23.2, 23.4, 23.8 (4 Me), 24.0 (CH^1H^2), 44.7, 45.0 (2 $CHMe_2$), 45.9 (CH^4), 51.0 (OMe), 52.7 (CH^3), 78.5 (*C*—COOMe), 89.1 (Cp), 173.8 (*C*OOMe), 224.5, 226.3 (2 W—CO). Mass (12 eV, *m/e*): 531 (M^+). Anal. Calcd for $C_{20}H_{29}WO_4N$: C, 45.21; H, 5.50; N, 2.64. Found: C, 45.44; H, 5.62; N, 2.77.

Synthesis of CpW(CO)$_2$(η^3-1-*anti*-(methoxycarbonyl)-1-*syn*-((ethylthio)methyl)-3-*syn*-methylallyl) (10α) and CpW(CO)$_2$(η^3-2-(methoxycarbonyl)-4-(thioethyl)pent-2-en-1-yl) (10δ). These two compounds were prepared similarly from **3a** (0.24 g, 0.42 mmol) and EtSH (0.050 mL, 0.80 mmol) in cold diethyl ether (−40 °C, 20 min). The mixtures were separated on a SiO_2 column (diethyl ether/hexane, 1/1; R_f 0.20 for **10**α and R_f 0.32 for **10**δ), and the isolated yields of **10**α (yellow oil, 0.042 g, 0.085 mmol) and **10**δ (yellow solid, 0.11 g, 0.23 mmol) were 20% and 54%, respectively. Data for **10**α: IR (Nujol) ν(CO) 1965 (vs), 1896 (vs), 1695 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, t, J = 7.4 Hz, Me), 1.84 (3H, d, J = 6.4 Hz, Me), 2.47 (1H, d, J = 13.1 Hz, H^3), 2.64 (1H, dq, J = 10.0, 7.4 Hz, H^1), 2.65 (2H, q, J = 7.4 Hz, S—CH_2), 3.54 (3H, s, OMe), 3.59 (1H, d, J = 13.1 Hz, $H^{3'}$), 4.07 (1H, J = 10.0 Hz, H^2), 5.44 (5H, s, Cp); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5 (Me), 21.5 (CH^1), 26.9 (S—CH_2), 40.8 ($CH^3H^{3'}$), 50.8 (OMe), 54.6 (*C*—COOMe), 57.1 (CH^1), 70.0 (CH^2), 92.2 (Cp), 174.2 (*C*OOMe), 226.3, 227.2 (2 W—CO); mass (12 eV, *m/e*) 431 (M^+ = SEt). Anal. Calcd for $C_{16}H_{20}WO_4S$: C, 39.02; H, 4.07. Found: C, 39.29; H, 4.10. Data for **10**δ: IR (Nujol) ν(CO) 1964 (vs), 1894 (vs), 1697 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (s, 1H, H^1), 1.23 (3H, t, J = 7.5 Hz, Me), 1.35 (3H, d, J = 6.8 Hz, Me), 2.15 (1H, d, J = 10.6 Hz, H^3), 2.64 (2H, q, J = 7.5 Hz, S—CH_2), 2.96 (1H, s, H^2), 3.67 (3H, s, OMe), 4.27 (1H, dq, J = 10.8, 6.8 Hz, H^4), 5.30 (5H, s, Cp); ^{13}C NMR (100 MHz) δ 14.4 (Me), 23.0 (CH^1H^2), 24.8 (Me), 25.2 (S—CH_2), 40.2 (CH^3), 51.0 (OMe), 56.5 (CH^4), 77.2 (*C*—COOMe), 88.4 (Cp), 168.0 (*C*OOMe), 222.7, 223.6 (2 W—CO); mass (12 eV, *m/e*) 492 (M^+). Anal. Calcd for $C_{16}H_{20}WO_4S$: C, 39.02; H, 4.10. Found: C, 39.38; H, 4.19.

Synthesis of CpW(CO)$_2$(η^3-1-*anti*-(methoxycarbonyl)-1-*syn*-((phenylthio)methyl)-3-*syn*-methylallyl) (11α) and CpW(CO)$_2$(η^3-2-(methoxycarbonyl)-4-(thiophenyl)pent-2-en-1-yl) (11δ). These two compounds were prepared similarly from **3a** (0.22 g, 0.42 mmol) and PhSH (0.050 mL, 0.50 mL) in cold diethyl ether (−40 °C, 20 min). The mixtures were separated on a SiO_2 column (ether/hexane, 1/1; R_f 0.38 for **11**α and R_f 0.44 for **11**δ), and the isolated yields of **11**α (yellow oil, 0.041 g, 0.083 mmol) and **11**δ (yellow solid, 0.090 g, 0.18 mmol) were 20% and 42%, respectively. Data for **11**α: IR (Nujol) ν(CO) 1946 (vs), 1862 (vs), 1695 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.72 (3H, d, J = 6.2 Hz, Me), 2.77 (1H, d, J = 12.7 Hz, H^3), 3.49 (3H, s, OMe), 3.58 (1H, dq, J = 10.0, 6.2 Hz, H^1), 3.71 (1H, d, J = 10.0 Hz, H^2), 3.92 (1H, d, J = 12.7 Hz, $H^{3'}$), 5.39 (5H, s, Cp), 7.30 (5H, m, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4 (Me), 45.6 (CH^1), 50.9 (OMe), 53.4 (*C*—COOMe), 57.2 (S—CH^3), 70.1 (CH^2), 92.0 (Cp), 127.2, 128.8, 132.5, 134.3 (Ph), 173.6 (*C*OOMe), 225.9, 226.7 (2 W—CO); mass (12 eV, *m/e*) 540 (M^+). Anal. Calcd for $C_{20}H_{20}WSO_4$: C, 44.46; H, 3.73. Found: C, 44.58; H, 3.88. Data for **11**δ: IR (Nujol) ν(CO) 1965 (vs), 1897 (vs), 1701 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (1H, s, H^1), 1.33 (3H, d, J = 6.7 Hz, Me), 2.94 (1H, s, H^2), 3.58 (3H, s, OMe), 4.59 (1H, dq, J = 10.8, 6.7 Hz, H^4), 5.29 (5H, s, Cp), 7.25−7.53 (5H, m, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.2 (CH^1H^2), 24.6 (Me), 45.4 (CH^3), 50.9 (OMe), 54.4 (CH^4), 88.3 (Cp), 93.5 (*C*—COOMe), 127.6, 128.7, 134.5, 134.8 (Ph), 170.4 (*C*OOMe), 222.3, 223.5 (2 W—CO); mass (12 eV, *m/e*) 540 (M^+). Anal. Calcd for $C_{20}H_{20}WSO_4$: C, 44.46; H, 3.73. Found: C, 44.53; H, 3.88.

Synthesis of CpW(CO)$_2$(η^3-1-*anti*-(methoxycarbonyl)-1-*syn*-ethyl-3-*syn*-methylallyl) (12α) and CpW(CO)$_2$(η^3-2-(methoxycarbonyl)-4-methylpent-2-en-1-yl) (12δ). To CuI (0.10 g, 0.53 mmol) in diethyl ether (20 mL) was added MeLi (1.6 M, 0.66 mL, 1.10 mmol) at −78 °C, and the mixtures were stirred for 2 h. This Me_2CuLi solution was transferred to a solution of **3a** (0.29 g, 0.51 mmol) in diethyl ether at −40 °C, and the mixtures were stirred for 20 min before addition of a saturated NH_4Cl solution (10 mL). The organic layer was extracted with diethyl ether (2 × 15 mL), washed with water (2 × 10 mL), and dried with $MgSO_4$. The residues were eluted with a SiO_2 column (diethyl ether/hexane, 1/1) to produce two yellow bands that give **12**α (R_f 0.46, yellow oil, 0.090 g, 0.20 mmol) and **12**δ (R_f 0.54, yellow solid, 0.041 g, 0.092 mmol) in 39% and 18% yields, respectively. Data for **12**α: IR (Nujol) ν(CO) 1941 (vs), 1856 (vs), 1696 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.09 (3H, t, J = 7.0 Hz, Me), 1.31 (1H, dq, J = 13.2, 7.0 Hz, CH^3), 1.83 (3H, d, J = 6.2 Hz, Me), 2.36 (1H, dq, J = 13.2, 7.0 Hz, $CH^{3'}$), 3.51 (3H, s, OMe), 3.52 (1H, dq, J = 10.0, 6.2 Hz, H^1), 4.00 (1H, d, J = 10.0 Hz, H^2), 5.41 (5H, s, Cp); ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.3, 21.5 (2 Me), 33.8 ($CH^3H^{3'}$), 50.6 (OMe), 56.7 (CH^1), 58.2 (*C*—COOMe), 70.9 (CH^2), 92.2 (Cp), 175.2 (*C*OOMe), 227.4, 228.0 (2 W—CO); mass (12 eV, *m/e*) 446 (M^+). Anal. Calcd for $C_{15}H_{18}WO_4$: C, 40.38; H, 4.07. Found: C, 40.55; H, 4.23. Data for **12**δ: IR (Nujol) ν(CO) 1960 (vs), 1889 (vs), 1703 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (3H, d, J = 6.9 Hz, Me), 1.06 (1H, s, H^1), 1.18 (3H, d, J = 7.2 Hz, Me), 1.95 (1H, d, J = 10.0 Hz, H^3), 2.95 (1H, s, H^2), 2.96 (1H, m, H^4), 3.67 (3H, s, OMe), 5.27 (5H, s, Cp); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0 (CH^1H^2), 25.7, 26.5 (2 Me), 30.4 (CH^3), 51.0 (OMe), 61.9 (CH^4), 65.9 (*C*—COOMe), 88.3 (Cp), 171.3 (*C*OOMe), 219.5, 224.4 (2 W—CO); mass (12 eV, *m/e*) 446 (M^+). Anal. Calcd for $C_{15}H_{18}WO_4$: C, 40.38; H, 4.07. Found: C, 40.44; H, 4.31.

Synthesis of CpW(CO)$_2$(η^3-1-*anti*-(methoxycarbonyl)-1-*syn*-(phenylethynyl)-3-*syn*-methylallyl) (13α) and CpW(CO)$_2$(η^3-2-(methoxycarbonyl)-4-(phenylethynyl)pent-2-en-1-yl) (13δ). These two compounds were similarly prepared from **3a** (0.22 g, 0.42 mmol) and $(PhCC)_2CuLi$ (ca. 0.50 mmol) [PhCCH (0.95 mmol), BuLi (1.6 M, 0.60 mL), CuI (0.090 g, 0.50 mmol)] in cold diethyl ether (−40 °C), and the two products were separated on a SiO_2 column (diethyl ether/hexane, 1/1) (**13**α, R_f 0.52, yellow oil, 0.080 g, 0.14 mmol, 33%; **13**δ, R_f 0.59, yellow solid, 0.040 g, 0.07 mmol, 17%). Data for **13**α: IR (Nujol) ν(CO) 1944 (vs), 1860 (vs), 1697 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.87 (3H, d, J = 6.3 Hz, Me), 3.00 (1H, d, J = 18.1 Hz, H^3), 3.45 (1H, d, J = 18.1 Hz, $H^{3'}$), 3.59 (3H, s, OMe), 3.67 (1H, dq, J = 10.0, 6.3 Hz, H^1), 4.44 (1H, d, J = 10.0 Hz, H^2), 5.53 (5H, s, Cp), 7.25−7.32 (5H, m, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5 (Me), 29.2 (CH^1), 50.9 (OMe), 51.6 (*C*—COOMe), 55.9 ($CH^3H^{3'}$), 70.8 (CH^2), 82.5, 91.0 (Ph*C*—*C*), 92.2 (Cp), 128.1, 128.4, 128.5, 131.6 (C_6H_5), 175.3 (*C*OOMe), 226.8, 228.0 (2 W—CO); mass (12 eV, *m/e*) 532 (M^+). Anal. Calcd for $C_{22}H_{20}WO_4$: C, 49.62; H, 3.76. Found: C, 49.78; H,

3.95. Data for **13**δ: IR (Nujol) ν (CO) 1966 (vs), 1896 (vs), 1701 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (1H, s, H^1), 1.34 (3H, d, J = 7.0 Hz, Me), 2.21 (1H, d, J = 10.1 Hz, H^3), 3.01 (1H, s, H^2), 3.73 (3H, s, OMe), 3.93 (1H, dq, J = 10.1, 7.0 Hz, H^4), 5.31 (5H, s, Cp), 7.30 (5H, m, C_6H_5); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6 (CH^{1}H^2), 24.2 (Me), 28.4 (CH^3), 51.2 (OMe), 55.2 (CH^4), 80.0 (*C*-COOMe), 88.2 (Cp), 93.2, 96.1 (Ph*CC*), 124.0, 127.3, 127.9, 131.5 (Ph), 170.9 (*C*OOMe), 221.7, 223.2 (2 W—CO); mass (12 eV, *m/e*) 532 (M$^+$). Anal. Calcd for $C_{22}H_{20}WO_4$: C, 49.62; H, 3.79. Found: C, 49.86; H, 3.85.

Synthesis of CpW(CO)$_2$(η^3-1-*anti*-(hydroxymethyl)-1-*syn*-(methoxycarbonyl)-3-*syn*-methylallyl) (14). To the cation **3b** (0.26 g, 0.50 mmol) in diethyl ether (20 mL) was added an aqueous NaOH (1M, 1 mL) solution, and the mixture was stirred for 1 h at 23 °C before addition of a saturated NH_4Cl solution (10 mL). The organic layer was extracted with diethyl ether (2 × 20 mL), dried over $MgSO_4$, and concentrated in vacuo. The residues were eluted through a SiO_2 column (diethyl ether/hexane, 2/1) to develop a yellow band (R_f 0.45) that afforded **14** (yellow solid, 0.10 g, 0.23 mmol) in 46% yield. IR (Nujol): ν(CO) 1941 (vs), 1852 (vs), 1692 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.85 (3H, d, J = 6.2 Hz, Me), 2.03 (1H, d, J = 12.2 Hz, H^3), 2.25 (1H, br s, OH), 2.50 (1H, dq, J = 10.2, 6.2 Hz, H^1), 3.69 (3H, s, OMe), 4.18 (1H, d, J = 12.2 Hz, H^4), 4.67 (1H, d, J = 10.2 Hz, H^2), 5.35 (5H, s, Cp). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.8 (Me), 47.1 (*C*—COOMe), 51.7 (OMe), 54.0 (CH^1), 63.8 (CH^{3}H^4), 66.9 (CH^2), 93.0 (Cp), 175.1 (*C*—OOMe), 225.4, 226.6 (2 W—CO). Mass (12 eV, *m/e*): 448 (M$^+$). Anal. Calcd for $C_{14}H_{16}WO_5$: C, 37.52; H, 3.60. Found: C, 37.77; H, 3.88.

Synthesis of CpW(CO)$_2$(η^3-1-*anti*-(methoxymethyl)-1-*syn*-(methoxycarbonyl)-3-*syn*-methylallyl) (15). This compound was similarly prepared from **3b** (0.29 g, 0.50 mmol) and NaOMe (0.038 g, 0.70 mmol) in CH_3OH (15 mL), and the yield of **15** (yellow solid, 0.11 g, 0.24 mmol) was 47%. IR (Nujol): ν(CO) 1955 (vs), 1878 (vs), and 1703 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.87 (3H, d, J = 6.1 Hz, Me), 1.91 (1H, d, J = 10.8 Hz, H^3), 2.45 (1H, dq, J = 10.3, 6.1 Hz, H^1), 3.17 (3H, s, OMe), 3.69 (3H, s, CO_2Me), 4.02 (1H, d, J = 10.8 Hz, H^4), 4.74 (1H, d, J = 10.3 Hz, H^2), 5.36 (5H, s, Cp). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.9 (Me), 47.5 (*C*—COOMe), 51.8 (OMe), 54.2 (CH^1), 58.0 (OMe), 66.4 (CH^2), 73.7 (CH^{3}H^4), 93.0 (Cp), 175.1 (*C*OOMe), 225.3, 227.0 (2 W—CO). Mass (12 eV, *m/e*): 462 (M$^+$). Anal. Calcd for $C_{15}H_{18}WO_5$: C, 38.98; H, 3.93. Found: C, 39.12; H, 4.10.

Synthesis of CpW(CO)$_2$(η^3-1-*anti*-(aminomethyl)-1-*syn*-(methoxycarbonyl)-3-*syn*-methylallyl) (16). This compound was similarly prepared from **3b** (0.29 g, 0.50 mmol) and $NaNH_2$ (0.050 g, 1.25 mmol), and the yield of **16** (0.11 g, 0.24 mmol) was 49%. IR (Nujol): ν (CO) 1946 (vs), 1863 (vs), 1695 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ −0.03 (1H, d, J = 13.6 Hz, H^3), 1.83 (3H, d, J = 6.3 Hz, Me), 2.25 (1H, dq, J = 10.4, 6.3 Hz, H^1), 3.56 (1H, d, J = 13.6 Hz, H^4), 3.58 (3H, s, OMe), 4.84 (1H, d, J = 10.4 Hz, H^2), 5.32 (5H, s, Cp). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0 (Me), 48.3 (*C*—COOMe), 51.8 (OMe), 53.8 (CH^1), 54.8 (CH^{3}H^4), 68.1 (CH^2), 93.2 (Cp), 175.4 (*C*OOMe), 227.5, 228.1 (2 W—CO). Mass (12 eV, *m/e*): 447 (M$^+$). Anal. Calcd for $C_{14}H_{17}WNO_4$: C, 37.61; H, 3.83; N, 3.13. Found: C, 37.77; H, 3.99; N, 3.33.

Synthesis of CpW(CO)$_2$(η^3-1-*anti*-(isopropylamino)-1-*syn*-(methoxycarbonyl)-3-*syn*-methylallyl) (17). This compound was similarly prepared from **3b** (0.26 g, 0.50 mmol) and isopropylamine (1 mL, 23.3 mmol) in diethyl ether (20 mL, 23 °C); the yield of **18** (yellow solid, 0.12 g, 0.25 mmol) was 50%. IR (Nujol): ν(CO) 1940 (vs), 1856 (vs), 1691 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *exo* isomer (88%), δ 0.46 (1H, d, J = 13.5 Hz, H^3), 0.47 (3H, d, J = 6.6 Hz, Me), 0.97 (3H, d, J = 6.6 Hz, Me), 1.81 (3H, d, J = 6.2 Hz, Me), 2.26 (1H, dq, J = 10.7, 6.2 Hz, H^1), 3.17 (1H, m, CHMe$_2$), 3.32 (1H, d, J = 13.5 Hz, H^3), 3.59 (3H, s, OMe), 4.72 (1H, d, J = 10.7 Hz, H^2), 5.29 (5H, s, Cp). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.6, 21.6 (CH*Me*$_2$), 21.0 (Me), 46.7 (*C*HMe$_2$), 48.4 (*C*—COOMe), 49.8 (CH^{3}H^4), 51.5 (OMe), 52.7 (CH^1), 66.8 (CH^2), 175.5 (*C*OOMe), 226.2, 228.0 (2 W—CO); *endo* isomer (12%), δ 0.90 (3H, d, J = 6.1 Hz, Me), 0.92 (3H, d, J = 6.1 Hz, Me), 1.05 (1H, d, J = 13.8 Hz, H^3), 1.86 (3H, d, J = 6.2 Hz, Me), 2.43 (1H, dq, J = 10.2, 6.2 Hz, H^1), 2.66 (1H, m, CHMe$_2$), 2.99 (1H, d, J = 13.8 Hz, H^4), 3.67 (3H, s, OMe), 4.66 (1H, d, J = 10.2 Hz, H^2), 5.35 (5H, s, Cp). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1 (Me), 22.4, 22.9 (CH*Me*$_2$), 47.9 (*C*HMe$_2$), 48.2 (*C*—COOMe), 48.7 (CH^{3}H^4), 51.3 (OMe), 53.4 (CH^1), 66.6 (CH^2), 175.8 (*C*OOMe), 219.0, 227.5 (2 W—CO). Mass (12 eV, *m/e*): 489 (M$^+$). Anal. Calcd for $C_{17}H_{23}NWO_4$: C, 41.74; H, 4.74; N, 2.86. Found: C, 41.88; H, 4.88; N, 2.99.

Synthesis of CpW(CO)$_2$(η^3-1-*anti*-((ethylthio)methyl)-1-*syn*-(methoxycarbonyl)-3-*syn*-methylallyl) (18). This compound was similarly prepared from **3b** (0.29 g, 0.50 mmol) and EtSH (0.060 mL, 0.80 mmol) in diethyl ether (23 °C, 6 h); the yield of **18** (0.13 g, 0.28 mmol) was 56%. IR (Nujol): ν-(CO) 1944 (vs), 1860 (vs), 1700 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.14 (3H, t, J = 7.2 Hz, Me), 1.40 (1H, d, J = 14.1 Hz, H^3), 1.87 (3H, d, J = 6.3 Hz, Me), 2.41 (2H, q, J = 7.2 Hz, S—CH$_2$), 2.46 (1H, dq, J = 10.1, 6.3 Hz, H^1), 3.37 (1H, d, J = 14.1 Hz, H^4), 3.69 (3H, s, OMe), 4.65 (1H, d, J = 10.1 Hz, H^2), 5.35 (5H, s, Cp). ^{13}C NMR (75 MHz, $CDCl_3$): 14.2 (Me), 20.6 (Me), 26.2 (S—CH$_2$), 34.4 (CH^{3}H$^{3'}$), 49.1 (*C*—COOMe), 51.6 (OMe), 52.9 (CH^1), 64.9 (CH^2), 93.1 (Cp), 175.0 (*C*OOMe), 226.7, 227.2 (2 W—CO). Mass (12 eV, *m/e*): 492 (M$^+$). Anal. Calcd for $C_{16}H_{20}WO_4S$: C, 39.02; H, 4.10. Found: C, 39.33; H, 4.26.

Synthesis of CpW(CO)$_2$(η^3-1-*anti*-ethyl-1-*syn*-(methoxycarbonyl)-3-*syn*-methylallyl) (19). This compound was similarly prepared from **3b** (0.29 g, 0.50 mmol) and Me_2CuLi [CuI (0.11 g, 0.58 mmol), MeLi (1.6 M, 0.73 mL, 1.2 mmol)] in diethyl ether (15 mL, 0 °C, 0.5 h); the yield of **19** (0.11 g, 0.25 mmol) was 50%. IR (Nujol): ν(CO) 1945 (vs), 1867 (vs), 1684 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.13 (1H, dq, J = 14.5, 7.3 Hz, H^3), 0.78 (3H, t, J = 7.3 Hz, Me), 1.92 (3H, d, J = 6.4 Hz, Me), 2.32 (1H, dq, J = 10.0, 6.4 Hz, H^1), 2.40 (1H, dq, J = 14.4, 7.3 Hz, H^4), 3.71 (3H, s, OMe), 4.61 (1H, d, J = 10.0 Hz, H^2), 5.43 (5H, s, Cp). ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.9 (Me), 25.2 (CH^{3}H^4), 51.6 (OMe), 52.1 (*C*—COOMe), 53.2 (CH^1), 65.9 (CH^2), 93.3 (Cp), 176.2 (*C*OOMe), 227.6, 228.6 (2 W—CO). Mass (12 eV, *m/e*): 446 (M$^+$). Anal. Calcd for $C_{15}H_{18}WO_4$: C, 40.35; H, 4.07. Found: C, 40.51; H, 4.22.

Synthesis of CpW(CO)$_2$(η^3-1-*anti*-pentyl-1-*syn*-(methoxycarbonyl)-3-*syn*-methylallyl) (20). This compound was similarly prepared from **3b** (0.29 g, 0.50 mmol) and Bu_2CuLi [CuI (0.11 g, 0.58 mmol), BuLi (1.6 M, 0.70 mL, 1.1 mmol)] in diethyl ether (15 mL, −40 to +23 °C, 4.5 h); the yield of **19** (0.11 g, 0.22 mmol) was 45%. IR (Nujol): ν (CO) 1942 (vs), 1858 (vs), 1684 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.05 (1H, m, H^3), 0.78 (3H, t, J = 7.2 Hz, Me), 1.16 (6H, m, (CH$_2$)$_3$), 1.86 (3H, d, J = 6.2 Hz, Me), 2.28 (1H, m, H^4), 2.39 (1H, dq, J = 10.2, 6.2 Hz, H^1), 3.64 (3H, s, OMe), 4.59 (1H, d, J = 10.2 Hz, H^2). ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.7 (Me), 20.9 (Me), 22.2 (CH^{3}H$^{3'}$), 31.3, 31.8, 33.5 ((CH$_2$)$_3$), 50.5 (*C*—COOMe), 51.5 (OMe), 53.0 (CH^1), 66.0 (CH^2), 93.2 (Cp), 176.3 (*C*OOMe), 227.7, 228.6 (2 W—CO). Mass (12 eV, *m/e*): 488 (M$^+$). Anal. Calcd for $C_{18}H_{24}WO_4$: C, 44.28; H, 4.95. Found: C, 44.40; H, 4.86.

Synthesis of CpW(CO)$_2$(η^3-1-*anti*-((phenylethynyl)-methyl)-1-*syn*-(methoxycarbonyl)-3-*syn*-methylallyl) (21). This compound was similarly prepared from **3b** (0.29 g, 0.50 mmol) and (PhCC)$_2$CuLi [CuI (0.11 g, 0.58 mmol), PhCCH (0.060 g, 0.58 mmol), BuLi (1.6 M, 0.70 mL, 1.1 mmol)] in diethyl ether (15 mL, −40 to 0 °C, 4.5 h); the yield of **21** was 48%. IR (Nujol): ν(CO) 1943 (vs), 1860 (vs), 1697 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 (1H, d, J = 17.5 Hz, H^3), 1.92 (3H, d, J = 6.2 Hz, Me), 2.60 (1H, dq, J = 10.1, 6.2 Hz, H^1), 3.34 (1H, d, J = 17.5 Hz, H^4), 3.73 (3H, s, Me), 4.71 (1H, d, J = 10.1 Hz, H^2), 5.39 (5H, s, Cp), 7.30 (5H, m, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0 (Me), 22.6 (CH^{3}H^4), 47.6 (*C*—COOMe), 51.1 (OMe), 54.2 (CH^1), 65.7 (CH^2), 80.0, 92.0 (Ph—*CC*), 93.3

(Cp), 123.8, 127.5, 128.1, 131.6 (Ph), 175.3 (*C*OOMe), 226.6, 227.0 (2 W—CO). Mass (12 eV, *m/e*): 532 (M^+). Anal. Calcd for $C_{22}H_{20}WO_4$: C, 49.62; H, 3.79. Found: C, 49.77; H, 3.88.

Synthesis of CpW(CO)$_2$(η^3-5-hydroxy-2-(methoxycarbonyl)pent-2-en-1-yl) (22). To **5** (0.30 g, 0.70 mmol) in THF (30 mL) was added 9-BBN (0.25 g, 2.05 mmol), and the solution was stirred for 2 days at 23 °C before addition of an aqueous NaOH solution (3 M, 3 mL). The mixture was further treated with H_2O_2 (35%, 0.3 mL) and heated to 30–35 °C for 0.5 h. The solution was concentrated to half its volume, and the organic layer was extracted with diethyl ether (2 × 20 mL). After removal of solvent in vacuo, the residues were chromatographed through a silica column (diethyl ether/hexane, 2/1) to give a yellow band (R_f 0.35) that afforded **22** as a yellow oil (0.22 g, 0.49 mmol, 70%). IR (Nujol): ν(CO) 1961 (vs), 1888 (vs), 1694 (s) cm^{-1}. ^{1}H NMR (75 MHz, $CDCl_3$): δ 1.15 (1H, s, H^1), 2.16 (1H, dd, J = 7.2, 6.8 Hz, H^3), 2.40 (1H, m, H^4), 2.88 (1H, s, H^2), 2.95 (1H, m, $H^{4'}$), 3.52 (1H, m, H^5), 3.64 (3H, s, OMe), 3.82 (1H, m, $H^{5'}$), 5.30 (5H, s, Cp). ^{13}C NMR (75 MHz, $CDCl_3$): δ 23.1 (CH^1H^2), 35.4 ($CH^4H^{4'}$), 46.9 ($CH^5H^{5'}$), 51.1 (CH^3), 65.1 (OMe), 78.1 (*C*—CO_2Me), 88.3 (Cp), 172.1 (CO_2Me), 223.1, 224.5 (2 W—CO). Mass (12 eV, *m/e*): 448 (M^+). Anal. Calcd for $C_{14}H_{16}WO_5$: C, 37.50; H, 3.60. Found: C, 37.77; H, 3.85.

Synthesis of CpW(CO)$_2$(η^3-*CH$_2$CCHCH$_2$CH$_2$OCO*) (23). To **22** (0.25 g, 0.56 mmol) in diethyl ether (30 mL) was added 50% NaH (0.060 g, 1.25 mmol), and the mixture was stirred for 1 h at 23 °C before addition of H_2O (10 mL). The organic layer was extracted with diethyl ether (2 × 10 mL), washed with water, dried over $MgSO_4$, and finally evaporated to dryness. Elution of residues through a SiO_2 column (diethyl ether/hexane, 1/1) produced a yellow band (R_f 0.51) that afforded **23** as a yellow solid (0.22 g, 0.53 mmol, 94%). IR (Nujol): ν(CO) 1947 (vs), 1868 (vs), 1706 (s) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.69 (1H, d, J = 2.8 Hz, H^1), 2.11 (1H, dd, J = 15.8, 2.2 Hz, H^4), 2.45 (1H, d, J = 2.2 Hz, H^3), 2.58 (1H, d, J = 2.8 Hz, H^2), 3.03 (1H, m, $H^{4'}$), 3.72 (1H, td, J = 10.8, 2.1 Hz, H^5), 4.32 (1H, ddd, J = 10.8, 5.5, 2.0 Hz, $H^{5'}$), 5.28 (5H, s, Cp). ^{13}C NMR (75 M
Hz, $CDCl_3$): δ 19.2 ($CH^4H^{4'}$),
25.0 (CH^1H^2), 61.2 (CH^3), 66.1 ($CH^5H^{5'}$), 88.8 (*C*—COOMe), 91.9 (Cp), 172.1 (CO_2Me), 217.2, 224.7 (2 W—CO). Mass (12 eV, *m/e*): 416 (M^+), 388 (M^+ − CO), 360 (M^+ − CO), 332 (M^+ − 2CO). Anal. Calcd for $C_{13}H_{12}WO_4$: C, 37.50; H, 2.91. Found: C, 37.67; H, 3.00.

Synthesis of 5,6-Dihydro-2*H*-3-((phenylthio)methyl)-pyran-2-one (24). To **23** (0.20 g, 0.48 mmol) in CH_3CN was added $NOBF_4$ (0.060 g, 0.51 mmol) at 0 °C, and the mixture was stirred for 10 min. To this red solution was added a solution of PhSNa [NaH, 0.0450 g (50%, 0.83 mmol), PhSH (0.090 mL, 0.88 mmol)] in diethyl ether (10 mL), and the suspension was stirred for 30 min before addition of $(NH_4)_2Ce(NO_3)_6$ (0.32 g, 0.67 mmol). After it was stirred for an additional 20 min, the solution was filtered and evaporated to leave a dark red residue. Elution on a preparative SiO_2 TLC plate (ether/hexane, 1/1) produced several UV-active bands, and the collection of the band with R_f 0.45 gave **24** as a colorless oil (0.070 g, 0.32 mmol, 66%). IR (Nujol): ν(CO) 1720 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (2H, td, J = 6.3, 4.0 Hz, =CH*C*H_2), 3.79 (2H, s, S—CH_2), 4.31 (2H, t, J = 6.3 Hz, O—CH_2), 6.65 (1H, d, J = 4.0 Hz, =CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.7 (—CH*C*H_2), 35.3 (S—CH_2), 67.8 (O—CH_2), 128.4, 130.6, 130.3, 132.2, 136.7 (C_6H_5 + *C*=CH), 142.8 (C=*C*H), 165.9 (CO_2). Mass (12 eV, *m/e*): 220 (M^+). HRMS: calcd for $C_{12}H_{12}SO_2$ 220.0558, found 220.0551.

Synthesis of CpW(CO)$_2$(η^3-*CH$_2$CCHCHMeOCO*) (25). This compound was similarly prepared from **5** (0.38 g, 0.84 mmol) with NaH (50 wt %, 0.10 g, 2.08 mmol) in diethyl ether (15 mL, 23 °C, 1 h), and the yield of **25** (0.33 g, 0.80 mmol) was 95%. IR (Nujol): ν(CO) 1960 (vs), 1885 (vs), 1748 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.48 (1H, d, J = 2.8 Hz, H^1), 1.60 (3H, d, J = 6.6 Hz, Me), 3.09 (1H, d, J = 2.8 Hz, H^2), 3.39 (1H, s, H^3), 4.72 (1H, q, J = 6.6 Hz, O—CH), 5.20 (5H, s, Cp). ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.0 (Me), 30.2 (CH^1H^2), 75.5 (CH^1H^2*C*), 77.2 (O—*C*H), 80.1 (CH^3), 95.0 (Cp), 176.6 (CO_2), 232.7, 237.8 (2 W—CO). Mass (12 eV, *m/e*): 416 (M^+). Anal. Calcd for $C_{13}H_{12}WO_4$: C, 37.50; H, 2.91. Found: C, 37.66; H, 3.10.

Synthesis of 2(5*H*)-5-methyl-3-((phenylthio)methyl)-furan-2-one (26). This compound was similarly prepared from **25** (0.27 g, 0.60 mmol), $NOBF_4$ (0.10 g, 0.84 mmol), and PhSNa [NaH, 0.045 g (50%, 0.83 mmol), PhSH (0.090 mL, 0.88 mmol)] according to the procedure described for **24**, and the yield of **26** (colorless oil, 0.091 mg, 0.35 mmol) was 58%. IR (Nujol): ν(CO) 1752 (vs) cm^{-1}; ν(C=C) 1620 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.29 (3H, d, J = 6.8 Hz, Me), 3.69 (2H, s, S—CH_2), 4.93 (1H, q, J = 6.8 Hz, OCH), 6.96 (1H, s, =CH), 7.30–7.35 (5H, m, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.7 (Me), 28.2 (S—CH_2), 77.6 (O—CH), 127.2, 129.2, 130.3, 130.7, 134.7 (Ph + *C*=CH), 151.8 (CH=), 172.7 (CO). Mass (12 eV, *m/e*): 220 (M^+). HRMS: calcd for $C_{12}H_{12}SO_2$ 220.0558, found 220.0550.

Synthesis of Methyl 2-((Phenylthio)methyl)-4-hydroxypent-2-enoate (27). This compound was similarly prepared from **5** (0.25 g, 0.56 mmol), $NOBF_4$ (0.070 g, 0.60 mmol), and PhSNa [NaH (50%, 0.040 g, 0.83 mmol), PhSH (0.090 mL, 0.88 mmol)] according to the procedure described for **24**, and the yield of **27** (colorless oil, 0.081 g, 0.32 mmol) was 58%. IR (neat): ν(CO) 1717 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07 (3H, d, J = 6.7 Hz, Me), 3.09 (1H, d, J = 12.8 Hz, S—CH*H'*), 3.30 (1H, d, J = 12.8 Hz, S—C*H*H'), 3.60 (1H, dq, J = 11.0, 6.7 Hz, C*H*(OH)), 3.73 (3H, s, OMe), 6.57 (1H, d, J = 11.0 Hz, =CH), 7.30 (5H, m, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.5 (Me), 30.9 (S—CH_2), 49.7 (*C*H(OH)), 52.1 (OMe), 129.1, 132.5, 133.2, 135.1, 137.5 (Ph + *C*CO_2Me), 145.0 (=CH), 167.3 (*C*O_2Me). Mass (12 eV, *m/e*): 252 (M^+). HRMS: calcd for $C_{13}H_{16}SO_3$ 252.0820, found 252.0824.

Synthesis of Methyl 2-((Benzylthio)methyl)pent-3-enoate (28). This compound was similarly prepared from **7** (0.20 g, 0.45 mmol), $NOBF_4$ (0.060 g, 0.51 mmol), $PhCH_2SNa$ [NaH (0.030 g, 0.63 mmol), $PhCH_2SH$ (0.080 mL, 0.68 mmol)], and $(NH_4)_2Ce(NO_3)_6$ (0.30 g, 0.55 mmol); the yield of **25** (0.060 g, 0.24 mmol) was 53%. IR (neat): ν(CO) 1732 (vs) cm^{-1}. ^{1}H NMR (75 MHz, $CDCl_3$): δ 1.65 (3H, d, J = 4.8 Hz, Me), 2.52 (1H, dd, J = 13.2, 6.6 Hz, CH*H'*), 2.74 (1H, dd, J = 13.2, 8.4 Hz, C*H*H'), 3.13 (1H, m, C*H*CH=), 3.69 (2H, s, CH_2), 4.35 (1H, dd, J = 16.5, 8.6 Hz, CH=), 5.56 (1H, dq, J = 16.5, 4.8 Hz, =C*H*Me), 7.25–7.38 (5H, m, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 17.7 (Me), 33.2, 36.4 (2 CH_2), 49.3 (*C*HC=), 51.9 (OMe), 127.3, 127.4, 128.7, 129.1, 129.7, 138.4 (Ph + CH=CH), 171.8 (CO_2Me). Mass (12 eV, *m/e*): 250 (M^+). HRMS: calcd for $C_{14}H_{18}SO_2$ 250.1027, found 250.1032.

Synthesis of Methyl 2-((Phenylthio)methyl)pent-3-enoate (29). This compound was similarly prepared from **8** (0.21 g, 0.43 mmol), $NOBF_4$ (0.050 g, 0.43 mmol), PhSNa [NaH (0.030 g, 0.63 mmol), PhSH (0.070 mL, 0.69 mmol)], and $(NH_4)_2Ce(NO_3)_6$ (0.27 g, 0.49 mmol); the yield of **29** (0.060 g, 0.25 mmol) was 58%. IR (neat): ν(CO) 1736 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.66 (3H, d, J = 4.8 Hz, Me), 3.01 (1H, dd, J = 12.2, 5.4 Hz, CH*H'*), 3.23 (2H, m, C*H*H'C*H*), 3.65 (3H, s, OMe), 5.40 (1H, J = 15.2, 8.1 Hz, CH=), 5.59 (1H, dq, J = 15.2, 4.8 Hz, =C*H*), 7.30–7.45 (5H, m, Ph). ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.1 (Me), 36.5, 49.5 (CHH' + *C*HCH=), 52.3 (OMe), 127.6, 127.8, 129.6, 130.2, 130.8, 136.2 (Ph + CH=CH), 174.1 (*C*O_2Me). Mass (12 eV, *m/e*): 236 (M^+). HRMS: calcd for $C_{13}H_{16}SO_2$ 236.0871, found 236.0872.

Synthesis of 4-(Methoxycarbonyl)-1-phenylhept-4-en-1-yne (30). To **21** (0.20 g, 0.38 mmol) in CH_3CN (10 mL) was added $NOBF_4$ (0.050 g, 0.40 mmol) at 0 °C; the mixture was stirred for 20 min before addition of $NaBH_3CN$ (0.040 g, 0.60 mmol). After the mixture was stirred for an additional 0.5 h, $(NH_4)_2Ce(NO_3)_6$ (0.48 g, 0.88 mmol) was added and this solution was evaporated to dryness in vacuo. Elution on a preparative SiO_2 TLC plate (diethyl ether/hexane, 1/6) pro-

duced several UV-active bands, and collection of the band (R_f 0.56) gave **30** as a colorless oil (0.070 g, 0.30 mmol, 79%). IR (neat): ν(C=C) 2214 (m) cm^{-1} ν(CO) 1713 (s) cm^{-1}; ν(C=C) 1655 (w) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): *E* (77%) form, δ 1.05 (3H, t, J = 7.6 Hz, Me), 2.29 (2H, quintet, J = 7.6 Hz, CH_2CH_3), 3.36 (2H, s, CH_2), 3.71 (3H, s, OMe), 6.82 (1H, t, J = 7.5 Hz, =$CHCH_2$), 7.19 (5H, m, C_6H_5); *Z* (23%) form, δ 1.08 (3H, t, J = 7.6 Hz, Me), 2.58 (1H, quintet, J = 7.6 Hz, CH_2-CH_3), 3.43 (2H, s, CH_2), 3.76 (3H, s, OMe), 6.44 (1H, d, J = 7.6 Hz, =CH), 7.37 (5H, m, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): *E* isomer, δ 12.8 (Me), 16.9, 22.8 (2 CH_2), 51.9 (OMe), 80.0, 87.0 (C≡C), 123.6 (=*C*−CO_2Me), 127.0, 127.5, 128.1, 131.5 (Ph), 146.5 (=CH), 167.2 (*C*OOMe); *Z* isomer, δ 13.6 (Me), 22.8, 24.0 (2 CH_2), 51.3 (OMe), 81.1, 86.2 (C≡C), 125.4 (=*C*CO_2Me), 127.1, 127.7, 128.1, 131.5 (Ph), 146.1 (=CH), 167.2 (*C*O_2Me). Mass (12 eV, *m/e*): 228 (M^+). HRMS: calcd for $C_{15}H_{16}O_2$ 228.1150, found 228.1154.

Synthesis of 4-(Methoxycarbonyl)-1-phenylhept-5-en-1-yne (31). Method A. To **21** (0.21 g, 0.39 mmol) in CH_3CN (10 mL) was added $NOBF_4$ (0.050 g, 0.40 mmol) at 0 °C, and the mixture was stirred for 30 min. To the yellow solution was added a saturated Na_2CO_3 solution (0.20 mL), and this mixture was stirred for 1 h. Monitoring the reaction by SiO_2 TLC plate (diethyl ether/hexane, 1/1) showed formation of a yellow component (R_f 0.59). To the solution was added $(NH_4)_2$-$Ce(NO_3)_6$ (0.48 g, 0.88 mmol) at 23 °C, and the mixture was stirred for 0.5 h, concentrated, and finally eluted on a preparative SiO_2 plate (diethyl ether/hexane, 1/2). Collection of the band with R_f 0.44 produced **31** as a colorless oil (0.082 g, 0.36 mmol, 92%). IR (Nujol): ν(C≡C) 2181 (s) cm^{-1}; ν(CO) 1730 (vs) cm^{-1}; ν(C=C) 1645 (m) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.66 (3H, dd, J = 6.3, 1.1 Hz, Me), 2.58 (1H, dd, J = 16.8, 7.2 Hz, CH*H'*), 2.73 (1H, dd, J = 16.8, 7.2 Hz, C*H*H'), 3.22 (1H, q, J = 7.2 Hz, C*H*COOMe), 3.66 (3H, s, OMe), 5.46 (1H, ddd, J = 15.3, 7.2, 1.1 Hz, CH=), 5.61 (1H, dq, J = 15.3, 6.3 Hz, C*H*Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9 (Me), 23.0 (CHH'), 48.4 (*C*HCOO), 52.0 (OMe), 82.0, 86.8 (C≡C), 123.2, 127.2, 127.8, 128.2 (Ph), 129.4 (CH=), 131.5 (=*C*HMe), 170.1 (*C*OOMe). Mass (12 eV, *m/e*): 228 (M^+). HRMS: calcd for $C_{15}H_{16}O_2$ 228.1150, found 228.1158.

Method B. This method is similar to method **A**, except that no Na_2CO_3 was used, and the nitroso salt of **21** was directly oxidized by $(NH_4)_2Ce(NO_3)_6$. The yield of **31** was 58% after purification on a preparative SiO_2 plate.

X-ray Diffraction Measurement of 25. A single crystal of **25** was sealed in a glass capillary under an inert atmosphere. Data for **25** were collected on a Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation, and the structure was solved by the heavy-atom method; all data reduction and structural refinement were performed with the NRCCSDP package. All non-hydrogen atoms were refined with anisotropic parameters, and their hydrogen atoms included in the structure factor calculations were placed in idealized positions. Crystal data and details of the data collection and structure analysis are summarized in Table 3.

Table 3. Crystal Data and Conditions for Crystallographic Data Collection and Structure Refinement for 25

formula	$WC_{13}H_{12}O_4$
fw	416.08
diffractometer used	Nonius
space group	monoclinic, $P2_1/c$
a(Å)	8.884(2)
b(Å)	11.071(2)
c(Å)	12.789(4)
β (deg)	100.71(2)
V (Å^3)	1235.9(5)
Z	4
D_{calc} (g/cm^3)	2.236
λ (Å)	0.7107
F(000)	780
unit cell detn: no.; 2θ range	25; 16.52−26.64°
scan type	$\theta/2\theta$
scan width (deg)	2(0.75 + 0.35 tan θ)
scan speed (deg/min)	1.64−8.24
2 θ(max) (deg)	45.0
hkl ranges	−9, to +9, 0−11, 0−13
μ (cm^{-1})	95.487
cryst size (nm)	0.05 × 0.10 × 0.50
transmissn: T_{min}; T_{max}	0.484; 1.000
temp (K)	298.00
no. of meas rflns	1721
no. of obs rflns ($I > 2.0\ \sigma(I)$)	1331
no. of unique rflns	1607
R_F; R_w[a]	0.023; 0.021
GOF	1.86
refinement program	NRCVAX
no. of atoms	30
no. of refined params	164 (1331 out of 1607 rlfns)
function minimized	$\sum(w\|F_o - F_c\|^2)$
wt scheme	$(1/\sigma^2)$ (F_o)
g (2nd ext. coeff) × 10^4	0.15(4)
max Δ/σ	0.0017
D map max; min (e/Å^3)	−0.700; 1.090

[a] $R_F = \sum(F_o - F_c)/\sum(F_o)$; $R_w = [\sum(w(F_o - F_c)^2/\sum)wF_o)^2]^{1/2}$. [b] GOF = $[\sum(w(F_o - F_c)^2/(N_{observns} - N_{params})]^{1/2}$.

Acknowledgment. We thank the National Science Council, Republic of China, for financial support of this work.

Supplementary Material Available: Tables of H atom atomic coordinates, all bond distances and angles, and thermal parameters for **25** (3 pages). Ordering information is given on any masthead page.

OM940396L