Tungsten η^1-Five-Membered Oxygenated Heterocycles Derived from Tungsten η^1-Propargyl Compounds: Systematic Syntheses, Structural Rearrangement, Electrophilic Alkylations, and Oxidative Demetalations

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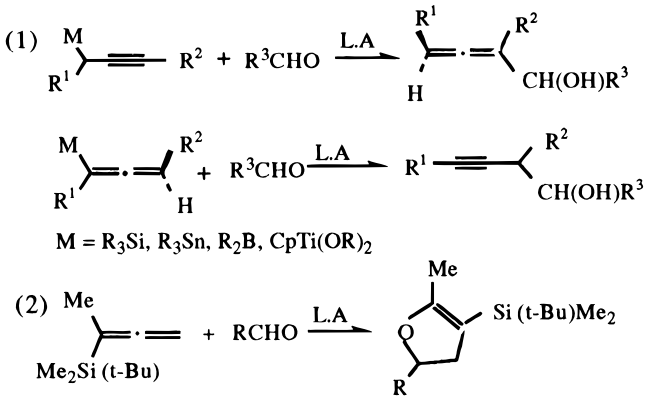
Received June 9, 1995[⊗]

Abstract: In the presence of $BF_3{\cdot}Et_2O$, tungsten η^1-propargyl complexes reacted smoothly with aldehydes to give tungsten η^1-2,5-dihydro-3-furyl complexes **1**−**3**. Treatment of **1**−**3** with Ph_3CBF_4 in CH_2Cl_2 (−60 °C, 1 h) delivered tungsten η^1-3-furylidene complexes **4**−**6** which underwent skeletal rearrangement to η^1-2-furylidene **13**−**15** isomers when warmed to 5 °C. Treatment of **4**−**6** with Et_3N at −60 °C produced tungsten η^1-3-furyl complexes **7**−**9** which were isomerized to η^1-2-furyl isomers **10**−**12** by a strong Bronsted acid. Protonation of **10**−**12** by CF_3CO_2H yielded η^1-2-furylidene complexes **13**−**15**. The two exceptional isomerizations were examined by *in situ* ^1H NMR studies. Further oxidation of η^1-2-furyl compounds **10**−**12** with *m*-chloroperbenzoic acid gave tungsten η^1-Δ^3-butenolides **16**−**18**. Tungsten η^1-3-furyl complexes **7** and **9** underwent alkylation with trimethoxymethane and aldehydes at −60 °C to yield η^1-3-furylidene cationic precipitates that were subsequently reduced with $NaBH_3CN$ to yield complex η^1-2,5-dihydro-3-furyl compounds in good diastereoselectivity; the stereochemical courses were distinct for **7** and **9**. Tungsten η^1-2,5-dihydro-3-furyl, η^1-2-furyl, η^1-3-furyl, and η^1-Δ^3-butenolide complexes were decomplexed with appropriate reagents to liberate 2,5-dihydrofurans, furans, and Δ^3- and Δ^2-butenolides in reasonable yields.

Introduction

Condensation of metal η^1-propargyl and η^1-allenyl complexes[1−3] with aldehydes and ketones promoted by Lewis acid is an important reaction in organic synthesis. In this reaction, there often exits an equilibrium between η^1-propargyl and η^1-allenyl species (typically two alcohols). The selectivity problem can be circumvented by selecting metals of covalent type (M = R_3Si, R_3Sn, R_2B, $CpTi(OR)_2$) where R^1 and R^2 are of suitable sizes.[1,2] Overwhelmingly, the products are either homopropargyl or allenyl alcohols (Scheme 1, eq 1). Effective annulation of these compounds with aldehydes to form a five-membered heterocycle is rare and known only for (*tert*-butyldimethylsilyl)-allene[4] that furnishes 2,3-dihydrofurans in good yields (eq 2). Lewis acid-promoted cyclizations of propargyltrimethylsilanes with ketals or acetals are reported[4d] to yield 2,5-dihydrofurans in 20−35% yields.

Scheme 1



Five-membered oxygenated heterocycles including dihydrofurans, furans, and butenolides are important structural units in

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1995.

(1) For the application of metal allenyl and propargyl compounds in organic synthesis, see the review paper: (a) Yamamoto, H. In *Comprehensive Organic Synthesis: Addition to C-X p bonds Part II*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, Chapter 1.3, p 81. (b) Fleming, I. In *Comprehensive Organic Synthesis: Addition to C-X p bonds, Part I*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, Chapter 2.2, p 575. (c) Panek, J. S. In *Comprehensive Organic Synthesis: Addition to C-X p bonds Part II*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Chapter 2.5, p 580. (d) Epsztein, R. In *Comprehensive Carbanion Chemistry*; Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1984; Part B, p 107.

(2) For main-group metal allenyl and propargyl compounds, see representative examples: (a) Seyferth, D.; Son, D. Y.; Shah, S. *Organometallics* **1994**, *13*, 2105. (b) Brown, H. C.; Khire, U. R.; Racherla, U. S. *Tetrahedron Lett.* **1993**, *34*, 15. (c) Brown, H. C.; Khire, U. R.; Narla, G.; Racherla, U. S. *J. Org. Chem.* **1995**, *60*, 544. (d) Danheiser, R. L.; Carini, D. J. *J. Org. Chem.* **1980**, *45*, 3925. (e) Boaretto, A.; Marton, D.; Tagliavini, G. *J. Organomet. Chem.* **1985**, *297*, 149. (f) Marshall J. A.; Wang, X.-J. *J. Org. Chem*. **1991**, *56*, 3212. (g) Marshall, J. A.; Wang, X. J. *J. Org. Chem.* **1991**, *56*, 6264.

(3) For chemistry of transition-metal propargyl and allenyl compounds, see representative examples: (a) Bell, P. B.; Wojcicki, A. *Inorg. Chem.* **1981**, *20*, 1585. (b) Raghu, S.; Rosenblum, M. *J. Am. Chem. Soc.* **1973**, *95*, 3060. (c) Pu, J.; Peng, T. S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 3232. (d) Blosser, P. W.; Shimpff, D. G.; Gallucci, J. C.; Wojcicki, A. *Organometallics* **1993**, *12*, 1393. (e) Benaim, J.; Merour, J.-Y.; Roustan, J. L. C. R. *Acad. Sci. Paris, Ser. C* **1971**, *272*, 789.

(4) (a) Danheiser, R. L.; Fink, D. M. *Tetrahedron Lett.* **1985**, *26*, 2513. (b) Danheiser, R. L.; Kwasigroch, C. A.; Tsai, Y. M. *J. Am. Chem. Soc.* **1985**, *107*, 7233. (c) Danheiser, R. L.; Becker, D. A. *Heterocycles* **1987**, *25*, 277. (d) Pornet, J.; Miginiac, L.; Jaworski, K.; Randrianoelina, B. *Organometallics* **1985**, *4*, 333.

(5) (a) Donnelly, D. M. X.; Meegan, M. J. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Reese, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 4, Part 3, p 657. (b) Bolvin, T. L. B. *Tetrahedron* **1987**, *43*, 3309. (c) Katritzky, A. R. *Adv. Heterocycl. Chem.* **1982**, *30*, 167. (d) Lipshutz, B. H. *Chem. Rev.* **1986**, *86*, 795. (e) Padwa, A.; Murphree, S. S. *Org. Prep. Proced.* **1991**, *23*, 545.

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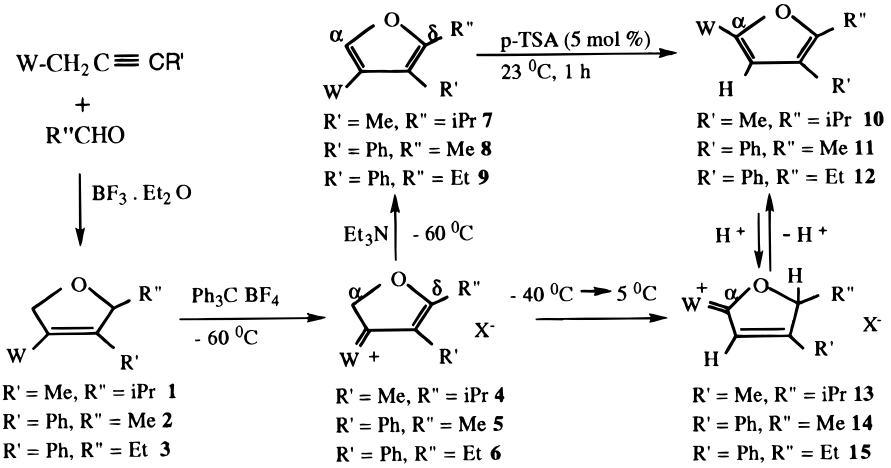
Scheme 2[a]



[a] W = $CpW(CO)_3$. X = BF_4.

organic molecules.[5,6] Numerous papers on metal-η^1-propargyl and η^1-allenyl complexes are reported, yet none aim at the systematic synthesis of these oxygenated heterocycles. We hereby report[7] an effective annulation of tungsten η^1-propargyl compounds with aldehydes to yield η^1-2,5-dihydro-3-furyl compounds that are subsequently transformed into η^1-heterocycles of various classes including η^1-2-furyl, η^1-3-furyl, η^1-2-furylidene, η^1-3-furylidene, η^1-Δ^3-butenolide and complex η^1-2,5-dihydro-3-furyl complexes. During the syntheses, we enconter some unusual organometallic reactions of which the mechanism will be discussed in details.

Results

Syntheses of Tungsten η^1-3-Furylidene, η^1-3-Furyl, η^1-2-Furyl, and η^1-2-Furylidene Compounds. As shown in Scheme 2, treatment of $CpW(CO)_3(\eta^1$-3-R′-propargyl) (R′ = Me, Ph) with aldehydes (2−3 equiv) in the presence of BF_3·Et_2O produced η^1-2,5-dihydro-3-furyl complexes **1**−**3** in good yields (>90%); the reaction mechanism followed a typical [3 + 2] cyclization pathway[8,9] involving an allene cationic intermediate. Organic 2,3- and 2,5-dihydrofurans can be oxidized to furans by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ);[10] the reaction intermediate is proposed to be an unstable 2-hydrofurylium cation. We have discovered that Ph_3CBF_4 effects the oxidation of **1**−**3** satisfactorily, and the resulting cationic intermediates can be isolated and fully characterized.

Treatment of **1**−**3** with Ph_3CBF_4 (0.98−1.00 equiv) in cold CH_2Cl_2 (−60 °C, 1 h) followed by a slow addition of excess cold pentane produced orange precipitates of η^1-3-furylidenes **4**−**6**; the yields exceeded 85%. Diagnostic for the η^1-3-furylidene structure are the ^{1}H and ^{13}C NMR spectra (−40 °C, CD_2Cl_2) that show the absence of $C_\delta H$ hydrogen. In this oxidation, hydride abstraction of the $C_\alpha H_2$ protons of **1**−**3** is not operative because the corresponding intermediate is envisaged to be an unstable η^2-allene cation of a five-membered ring.[11] Deprotonation of **4**−**6** with Et_3N (2−3 equiv) in cold CH_2Cl_2 (−60 °C, 0.5 h) afforded η^1-3-furyl complexes **7**−**9**[12,13] quantitatively (>95% yield).

Scheme 2 shows further syntheses of tungsten η^1-2-furyl and η^1-2-furylidene compounds. In the presence of catalysts (ca. 5 mol %), 4-toluenesulfonic acid, or CF_3CO_2H, compounds **7**−**9** underwent a novel isomerization to η^1-2-furyl isomers **10**−**12** at 23 °C and completely within 1 h. Compounds **7**−**9** and their η^1-2-furyl isomers **10**−**12** were easily distinguished by their ^{1}H and ^{13}C NMR spectra in $CDCl_3$. For **10**−**12**, the loss of aromaticity is achieved with a protonation reaction[14] to give Fischer-type carbenes. Slow addition of excess CF_3CO_2H (ca. 15 equiv) to **10**−**12** in anhydrous diethyl ether at 0 °C produced red precipitates of η^1-2-furylidenes **13**−**15**; the yields exceeded 60% upon addition of excess hexane. Measurement of NMR spectra of **13**−**15** was best performed on treatment of **10**−**12** with excess CF_3CO_2H (ca. 15 equiv) in an NMR tube (yields > 96%, CD_2Cl_2, 0 °C). The reason is that these salts easily lose one proton to regenerate η^1-2-furyl compounds in the absence of acid. The 2-furylidene structure of **10**−**12** is supported by ^{1}H and ^{13}C NMR data; the W=C_α carbon signals appear at δ 270−280 (J_{WC_α} = 110−120 Hz). In the case of **13**, the magnitude of the coupling constant J_{HCHMe_2} = 2.9 Hz indicates that the site of protonation is the C_δ carbon.

NMR Studies on Isomerizations of Tungsten η^1-3-Furylidene and Tungsten η^1-2-Furyl Compounds. The tungsten alkylidene cation[15] $CpW(CO)_3(=CH_2)^+$ decomposes quickly to ethylene at 23 °C. On the contrary, η^1-3-furylidene cations **4**−**6**

(6) For metal-mediated synthesis of furans and butenolides, see representative examples: (a) Davies, Hwu M. L.; Romines, K. R. *Tetrahedron* **1988**, *44*, 3343. (b) Padwa, A.; Kinder, F. R. *J. Org. Chem.* **1993**, *58*, 21. (c) Wulff, W. D.; Gilberstson, S. R.; Springer, J. P. *J. Am. Chem. Soc.* **1986**, *108*, 520. (d) Danheiser, R. L.; Stoner, E. J.; Koyama, H.; Yamashita, D. S.; Klade, C. A. *J. Am. Chem. Soc.* **1989**, *111*, 4407.

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(10) Anderson, J. C.; Lindsay, D. G.; Reese, C. B. *Tetrahedron* **1964**, 2091.

(11) Stable metal η^2-allene compounds of six- and seven-membered rings are reported; see the representative examples: (a) Oons, S. M.; Jones, W. M. *Organometallics* **1988**, *7*, 2172. (b) Yin, J.; Abboud, K. A.; Jones, W. A. *J. Am. Chem. Soc.* **1993**, *115*, 3810.

(12) For transition-metal η^1-furyl compounds, see: (a) Jones, W. D.; Dong, L.; Myers, A. W. *Organometallics* **1995**, *14*, 855. (b) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 1583. (c) Selnau, H. E.; Merola, J. S. *Organometallics* **1993**, *12*, 3800. (d) Pannell, K. H.; Cea-Olivares, R.; Toscano, R. A.; Kapoor, R. N. *Organometallics* **1987**, *6*, 1821.

(13) Only one example of transition-metal η^1-3-furyl compounds was reported; see ref 12a.

(14) For transition-metal η^1-pyrrolyl and η^1-thienyl compounds, see: (a) Johnson, T. D.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4728. (b) Robertson, M. J.; White, C. J.; Angelici, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 5190. (c) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151. (d) Ng, M. M. P.; Roper, W. R.; Wright, L. J. *Organometallics* **1994**, *13*, 2563. (e) Erker, G.; Petrenz, R.; Kruger, C.; Lutz, F.; Weiss, A.; Werner, S. *Organometallics* **1992**, *11*, 1646.

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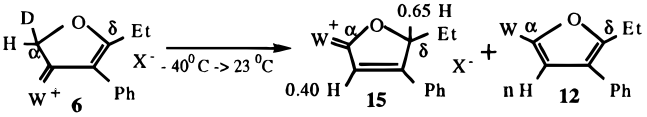
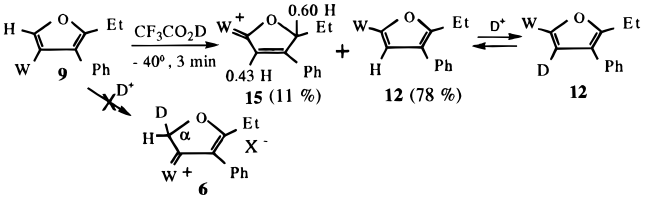
Scheme 3[a]



[a] W = CpW(CO)$_3$. X = BF_4.

Scheme 4[a]



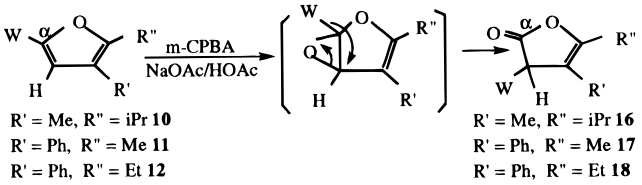
[a] W = CpW(CO)$_3$. X = CF_3CO_2.

undergo an irreversible transformation to their η^1-2-furylidene isomers **13**−**15** above 0 °C as shown in Scheme 2. When an NMR sample of **6** (BF_4 salt, CD_2Cl_2, −40 °C) was immediately warmed to 5 °C, the ^{1}H NMR spectra of solution species were recorded for a period of 20 min, 45 min, and 4 h. These spectra[16] clearly indicated that compound **6** underwent a steady isomerization to its 2-furylidene isomer **15** at 5 °C without formation of any detectable intermediate. Only NMR signals of **15** were observed after a long period (5 °C, t = 4 h); the yield was quantitative (>96%) based on the internal CD_2Cl_2 standard.

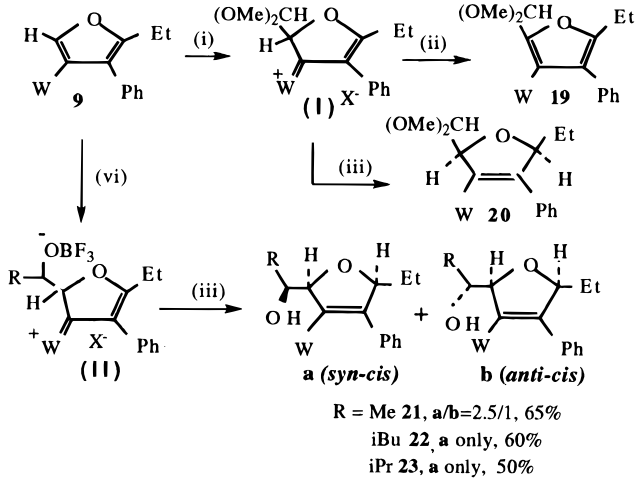
To assist understanding this structural rearrangement, we prepared a deuterated sample of **6** in which one of the $C_\alpha H_2$ protons was completely deuterated. Measurements of the rate constants of isomerization for **6** and its deuterated sample showd a kinetic isotopic effect, k_{CH}/k_{CD} = 6.0 (k_{CH} = 2.6 × 10^{-4} s^{-1}, k_{CD} = 4.3 × 10^{-5} s^{-1}, 23 °C). As depicted in Scheme 3, 4 h after isomerization of the deuterated sample **6**, a mixture of deuterated species including **6**, η^1-2-furylidene **15**, and η^1-2-furyl complex **12** was obtained with the molar ratio 1.45:1.25:1, respectively; in this case, the proton NMR intensity ratio of C_βH, C_δH, and C*H*H′Me of **15** was 0.40:0.65:1, respectively. Here, the $C_\delta H/C_\beta H$ = 1.60 value of **15** is near an equilibrium ratio ($C_\delta H/C_\beta H$ = 1.50) determined by a separate NMR experiment.[17]

We further examined the isomerization of η^1-3-furyl complex **9** with CF_3CO_2D by low-temperature ^{1}H NMR spectra.[18] The results are briefly summarized in Scheme 4. Shortly after **9** was treated with CF_3CO_2D (1.0 equiv, 0.055 M) in CD_2Cl_2 at −40 °C (t = 3 min), the ^{1}H NMR spectra revealed that η^1-2-furyl complex **12** was the dominant solution species (ca. 78%) in addition to unreacted **9** (ca. 12%), η^1-2-furylidene **15** (ca. 11%), and a trace of 3-furylidene **6** (<1%). On the basis of the NMR integral, the C_βH of newly generated **12** has a proton content exceeding 95%; the complex **15** here is likely produced from further protonation (D^+) of **12**.[17] When the same NMR sample was warmed to 23 °C for 4 h, the NMR signal of the C_β-H proton of **12** gradually decreased until a 50% proton content (a statistical distribution) was attained. A decreasing proton content here is attributed to an exchange between D^+ and the C_β-H proton of **12** that is slower than η^1-3-furyl isomerization.

Scheme 5



Scheme 6[a]



[a] W = CpW(CO)$_3$. X^- = Sn(OMe)Cl_4^-. (i) $CH(OMe)_3/SnCl_4$, −60 °C; (ii) Et_3N, −60 °C; (iii) $NaBH_4CN$, −60 °C; (vi) $RCHO/BF_3{\cdot}Et_2O$, −60 °C.

***m*-CPBA Oxidation of η^1-2-Furyl Complexes.** Scheme 5 shows the oxidation of **10**−**12** with *m*-chloroperbenzoic acid (*m*-CPBA, 1.2 equiv) in hexane (5 °C, 1 h) over a HOAc/NaOAc mixture, yielding the products **16**−**18** in 65−70% yields. Spectral data reveal that **16**−**18** are related to **10**−**12** by incorporation of an oxygen atom to form a η^1-lactone species (ν(CO) 1775−1765 cm^{-1}). The ORTEP drawing[19] of **18** confirms the η^1-Δ^3-butenolide structure with a 1,2-shift of CpW(CO)$_3$ to the C_β carbon. The oxidation mechanism here is straightforward;[20] *m*-CPBA preferentially oxidizes the furyl $WC_\alpha{=}C_\beta$ double bond due to the electron-donating ability of the CpW(CO)$_3$ fragment. Rearrangement of the epoxide intermediate is expected to give the η^1-Δ^3-butenolide compound.

1,4-Addition Reactions on η^1-3-Furyl Compounds. Shown in Scheme 6 is the reaction between **9** and a mixture of $HC(OMe)_3$ (2.0 equiv) and $SnCl_4$ (1.0 equiv) in cold CH_2Cl_2 (−60 °C), yielding a precipitate (**I**) that upon deprotonation with Et_3N gave tetrasubstituted η^1-furyl complex **19** in good yield (83%); one important feature here is the isolation of an η^1-3-furylidene precipitate **(I)**. Reduction of this salt **(I)** with $NaBH_3CN$ at −60 °C led to hydride addition rather than deprotonation, yielding η^1-*cis*-2,5-dihydro-3-furyl complex **20** as one single diastereomer in 86% yield; the ORTEP drawing of **20** appears in Figure 1a.

Alkylation of **9** with a mixture of $RCHO/BF_3{\cdot}Et_2O$ (R = Me, iBu, iPr) in cold toluene (−40 °C) likewise led to a 3-furylidene

(16) Variable-temperature spectra showing the isomerization of **6** to **15** were prepared as supporting information.

(17) When a NMR sample of η^1-2-furyl complex **12** was treated with CF_3CO_2D (1.0 equiv, 0.22 M) in CD_2Cl_2 at −40 °C, after a brief period (t = 10 min), the solution species consisted of **12** (86%) and η^1-2-furylidene **15** (14%); in this case the C_βH of **12** retained one unit of proton intensity, whereas the C_βH and C_δH positions of **15** were scrambled with deuterium with $C_\delta H/C_\beta H$ = 1.50 ($C_\delta H + C_\beta H$ = 1 H) like those in Scheme 3. After the temperature was raised to 23 °C for 24 h, the proton content of C_βH of **12** was decreased to 50%, whereas the proton (deuterium) distribution of **15** remained unaltered; a new equilibrium, [**12**]/[**15**] = 30, was attained.

(18) ^{1}H NMR spectra monitoring the isomerization of **9** with CF_3CO_2D (1.0 equiv) in CD_2Cl_2 were prepared was supporting information.

(19) The ORTEP drawing and related structural parameters of compound **21** were prepared as supporting information.

(20) (a) Kuwajima, I.; Urabe, H. *Tetrahedron Lett.* **1981**, *22*, 5191. (b) Takeda, K.; Minato, H.; Ishikawa, M.; Miyawaki, M. *Tetrahedron* **1964**, *20*, 2655.

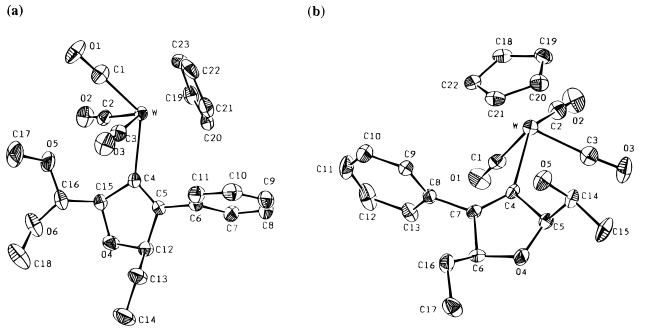


Figure 1. (a) ORTEP drawing of compound **20**. Selected bond lengths (Å): W−C(4) = 2.264(4), C(4)−C(5) = 1.327(5), C(5)−C(12) = 1.512(5), C(12)−O(4) = 1.430(5), C(15)−O(4) = 1.440(5), and C(4)−C(15) = 1.534(5). (b) ORTEP drawing of compound **21a**. Selected bond lengths (Å): W−C(4) = 2.259(6), C(4)−C(7) = 1.329(9), C(4)−C(5) = 1.530(7), C(5)−O(4) = 1.438(8), and C(6)−O(4) = 1.423(7).

precipitate (**II**) that was subsequently reduced with $NaBH_3CN$ (3.0 equiv) to yield 2,5-dihydro-3-furyl complexes **21**−**23**. Although this reaction simultaneously created three asymmetric carbon centers, the reactions proceeded diastereoselectively such that only one diastereomer was found for **22** and **23**, whereas two diastereomers (**a**/**b** = 2.5:1) were isolated for **21**. The stereochemistry of the dominant isomer was determined to be the *cis* configuration at the ring structure and the *syn* configuration at the *C*H(OH) and C_α carbons according to an X-ray diffraction study of **21a**; an ORTEP drawing of **21a** appears in Figure 1b. The minor isomer **21b** also adopts a *cis* configuration according to 2D NOESY correlation spectra; hence, we assign an *anti-cis* structure to **21b**.

The stereochemical chemistry in 1,4-addition reactions of compound **7** is summarized in Scheme 7; the outcome is distinct from those observed for **9**. Treatment of **7** with $CH(OMe)_3$/$SnCl_4$ in cold CH_2Cl_2 at −60 °C followed by deprotonation with Et_3N gave **24** in 75% yield. Reduction of the same salts (**III**) with $NaBH_3CN$ delivered **25** as a single isomer in 88%, which has a *trans* configuration according to proton NOE difference spectra. With the same procedure, the reaction between **7** and RCHO/BF_3·Et_2O (R = Me, iBu) followed by $NaBH_3CN$ reduction afforded **26** and **27**, respectively. Three diastereomers were formed for each of **26** and **27**, separable on a silica gel column; the respective isolated yields are depicted in Scheme 7. The crystal quality of major diastereomers **26c** and **27c** was poor; hence, the two compounds were converted to their acetyl derivatives **28a**,**b** in 86−88% yields. The ORTEP drawing of **28a** in Figure 2a reveals that the molecule adopts an *anti-trans* structure.

Further structural assignment of the other two minor diastereomers relies on comparison of proton NMR spectra. A common feature of the two minor isomers **27a**,**b** is the C*H*(OH) proton that appears as a dd pattern (d = doublet; $J_{HCHH'}$ = 10.5 Hz, $J_{HC_\alpha H}$ = 4.5 Hz, $J_{HCHH'}$ = 0 Hz), in contrast with a doublet pattern ($J_{HCHH'}$ = 10.7 Hz, $J_{HC_\alpha H}$ = $J_{HCHH'}$ = 0 Hz) for the corresponding proton of the major isomer **27c**. We therefore conclude that **27a**,**b** have identical *syn* configurations for the two asymmetric C_αH and RCH(OH) carbons. In 2D NOESY correlation spectra, the C_αH and C_δH protons of **27a** show a pronounced NOE relationship, whereas the C_αH proton of **27b** shows no NOE correlation with the C_δH proton but with the methyl group of the isopropyl substituent. These data indicate that **27a** has a *cis* configuration whereas **27b** has a *trans* configuration.

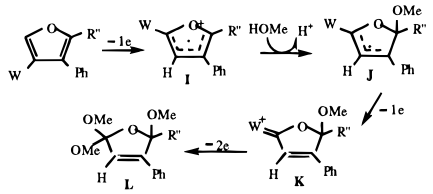
Applications to Five-Membered Oxygenated Hetrocycles. It is imperative to demetalate the η^1-heterocycles chemoselectively to substantiate organic syntheses. Chart 1 summarizes five-membered oxygenated heterocycles of types that can be produced from tungsten η^1-propargyl complexes. Treatment of **2** and **3** with $(NH_4)_2Ce(NO_3)_6$ in CH_2Cl_2/MeOH mixture under flowing CO (1 atm) produced only one organic component, **29** and **30**, in 60−63% yields. Ce(IV) oxidation of **11** and **12** generated **31** and **32** in 54−59% yields, analyzed as Δ^2-butenolide[21] according to NMR and mass spectral data. The generation of **31** and **32** from **11** and **12** involves a four-electron oxidation; it is not difficult to deduce the mechanism.[22,23] Under nitrogen, demetalation of **11** and **12** by I_2 in CH_2Cl_2/CH_3OH afforded **33** and **34** in 60−63% yields in addition to byproducts **31** and **32** (8−10% yields). η^1-Δ^3-Butenolides **17** and **18** were demetalated with Me_3NO (4.0 equiv, 30 °C, 2 h) in CH_2Cl_2 to give **35** and **36** in 53−58% yields together with η^3-Δ-butenolide compounds **37** and **38** in small yields (20−21%). The molecular structure of **38** was determined by X-ray diffraction study; an ORTEP drawing appears in Figure 2b. Ce(IV) oxidation of **21a** in CH_2Cl_2 under flowing CO led to an intramolecular lactonization to give bicyclic lactone **39** as a single diastereomer (40%). Ce(IV) oxidation of **28b** under the same conditions gave **40** in 46% yield.

Dicussion

Proposed Mechanism for Isomerization of η^1-3-Furylidene. Isomerization of the two furylidene cations is unprecedented in transition-metal carbene chemistry;[24] it involves a switch of three atom positions. In this isomerization, a large value of kinetic isotopic effect (k_{CH}/k_{CD} = 6.0) for the 50% deuterated η^1-3-furylidene sample **6** implies that a hydrogen shift is important for the reaction mechanism. The oxonium resonance of η^1-3-furylidene represented by **A** in Scheme 8 resembles a metalated cyclopentadiene group in which a 1,2-shift of hydrogen or metal is known to be feasible.[25] We propose a mechanism that the isomerization is initiated with a 1,2-shift of $C_\alpha H_2$ hydrogen of **A** to give **B** that subsequently undergoes a 1,2-tungsten shift to bring the $CpW(CO)_3$ fragment away from the CγR′ substituent, yielding η^1-2-furyl oxonium species **C**. For the state **B**, a 1,2-hydrogen shift of C_βH to the Cγ carbon is considered less important because the forming intermediate suffers steric hindrance between R′ and neighboring $CpW(CO)_3$. Formation of η^1-2-furylidene can be accomplished by a consecutive 1,2-hydrogen shift of **C** via intermediates **D** and **E**. All these elementary processes are reversible, but thermodynamic equilibrium favors η^1-2-furylidene complex. According to this process, the $C_\beta D/C_\delta D$ content ratio of η^1-2-furylidene **15** derived from 50% deuterated η^1-3-furylidene **6** is expected to be near the equilibrium value 1.50 because of

(21) Binger, P.; Weintz, H. J. *Chem. Ber.* **1984**, *117*, 654.

(22) We propose that η^1-2-furyl complexes **11** and **12** undergo one-electron oxidation to give a cationic radical (**I**) that reacts with MeOH to give a radical species (**J**).[25,26] Further oxidation of **J** by Ce(IV) oxidation produces 2-furylidene species **K** that subsequently loses two electrons to the precursor **L** of Δ^2-butenolide.

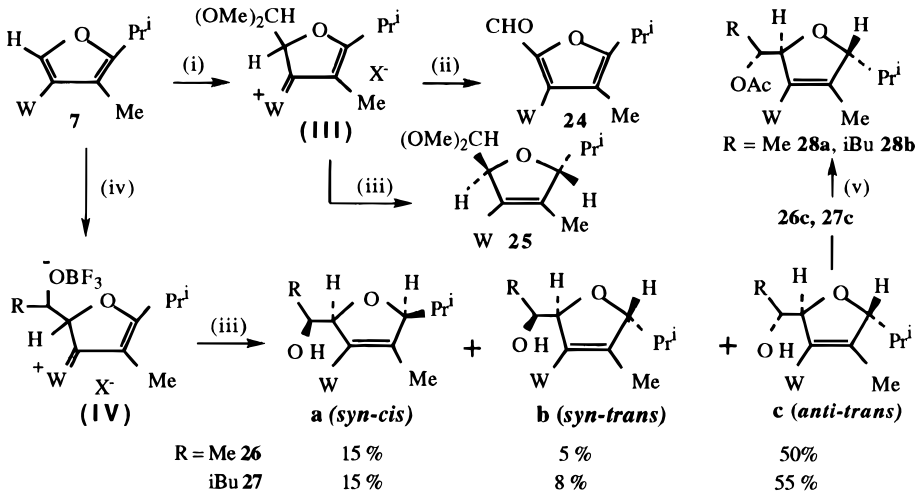


(23) (a) Weinberg, N. L.; Weinberg, H. R. *Chem. Rev.* **1968**, *68*, 449. (b) Elming, N. *Adv. Org. Chem.* **1960**, *2*, 67.

(24) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 16, p 784.

(25) Mann, B. E. In *Compresensive Organometallics Chemistry*; Wilkenson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 3, Chapter 20, p 173.

Scheme 7[a]



[a] W = $CpW(CO)_3$. X^- = $Sn(OMe)Cl_4^-$. (i) $CH(OMe)_3/SnCl_4$, −60 °C; (ii) Et_3N, −60 °C; (iii) $NaBH_4CN$, −60 °C; (iv) $RCHO/BF_3{\cdot}Et_2O$, −60 °C; (v) Ac_2O/DMAP, 0 °C.

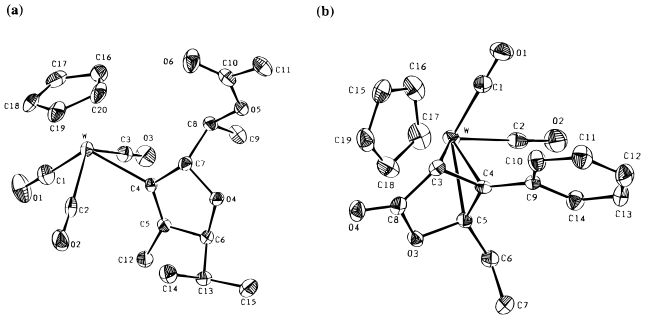
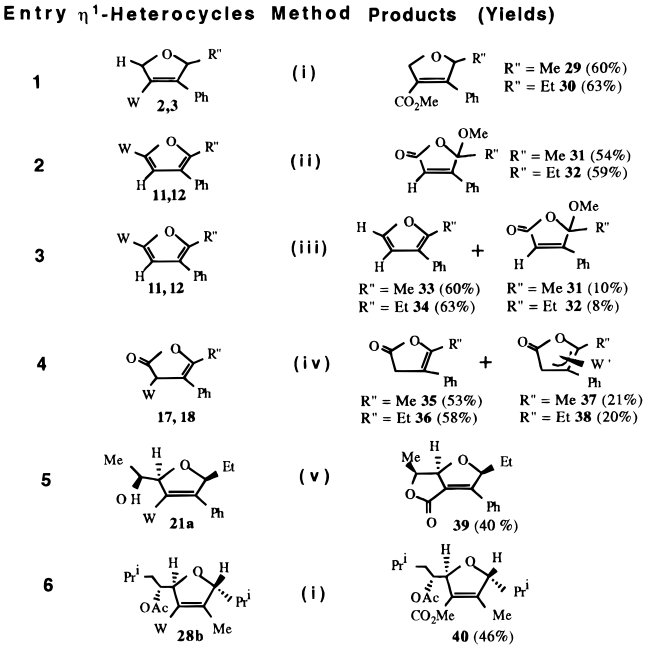


Figure 2. (a) ORTEP drawing of compound **28a**. Selected bond lengths (Å): W−C(4) = 2.289(5), C(4)−C(7) = 1.516(7), C(7)−O(4) =1.447-(6), C(6)−O(4) = 1.427(6), C(5)−C(6) = 1.517(7), and C(4)−C(5) = 1.317(7). (b) ORTEP drawing of compound **38**. Selected bond distances (Å): W−C(3) = 2.286(6), W−C(4) = 2.239(5), W−C(5) = 2.292(6), C(3)−C(4) = 1.443(8), C(4)−C(5) = 1.463(8), C(5)−O(3) = 1.454-(7), C(8)−O(3) = 1.368(7), and C(8)−O(4) = 1.216(7).

multiple reversible steps, consistent with our isotopic result $C_\beta D/C_\delta D = 1.60$.

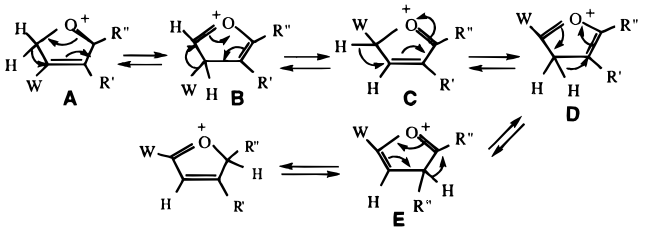
Proposed Mechanism for Isomerization of η^1-3-Furyl Complex. Several η^1-3-metalated aromatic heterocycles are known,[12a,13,14b] most of which have two methyl groups at the heterocyclic 2,5-carbons. Treatment of these compounds with strong Bronsted acid cleaves the metal−carbon σ bond. Isomerization of η^1-3-furyl compounds to their η^1-2-furyl isomers deserves special attention because the mechanism is atypical. In the isomerization of **9** with CF_3CO_2D, the NMR results in Scheme 4 reveal two important features. (i) The C_β-H proton of newly generated η^1-2-furyl complex **12** is virtually all protonated rather deuterated, indicative of a 1,2-mutual switch of C_α-H and $CpW(CO)_3$ positions during the isomerization reaction. (ii) Only a trace of η^1-3-furylidene **6** was detected even though it was shown to be a stable species at this temperature and in the presence of excess CF_3CO_2H (4−5 equiv). The latter information indicates that the isomerization does not proceed *via* the expected 3-furylidene → 2-furylidene pathway. We propose a plausible mechanism which involves a ring-opening process through protonation at the furan oxygen as depicted in Scheme 9; the driving force for this process is the formation of a tungsten η^2-alkyne cationic species (**F**) that

Chart 1. Yields and Products for Oxidative Demetalation of η^1-Heterocycles[a]



[a] W = $CpW(CO)_3$, W′ = $CpW(CO)_2$. (i) $(NH_4)_2Ce(NO_3)_6$ (3.0 equiv), CO (1 atm), $MeOH/CH_2Cl_2$, −78 → 23 °C, 3 h; (ii) $(NH_4)_2Ce(NO_3)_6$ (5.0 equiv), $MeOH/CH_2Cl_2$, −78 → 23 °C, CO (1 atm); (iii) I_2 (2.0 equiv), $MeOH/CH_2Cl_2$, −78 → 23 °C, 3 h; (iv) Me_3NO (4.0 equiv), H_2O (2.0 equiv), 30 °C, 4 h; (v) $(NH_4)_2Ce(NO_3)_6$ (3.0 equiv), CO (1 atm), CH_2Cl_2, −78 → 23 °C.

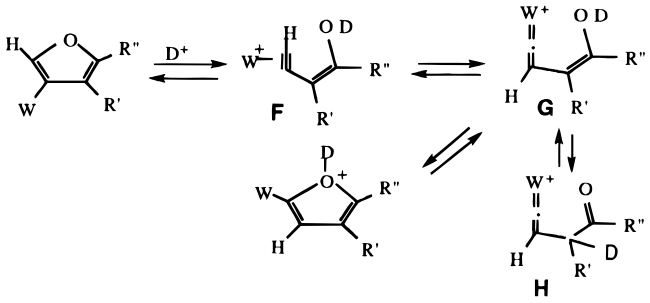
Scheme 8



subsequently undergoes a known facile η^2-alkyne → η^1-allene rearrangement[26,27] to yield **G**. Further attack of the enol group of **G** on the allenylidene W=C_α=C carbon results in ring closure to yield η^1-2-furyl isomer as the primary product.[29b,c]

(26) (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Pombeiro, A. J. L.; Richards, R. L. *Coord. Chem. Rev.* **1990**, *104*, 13. (c) Bullock, R. M. *J. Chem. Soc., Chem. Commun.* **1989**, 165. (d) Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1077.

Scheme 9[a]



[a] W = $CpW(CO)_3$.

One major concern with this mechanism is a possible enol **G**−ketone **H** tautomerization. Very likely, this enolization rate is slower than the intramolecular annulation of **G** because the former requires protonation at the enol CγR carbon of **G** to break its stable conjugated structure, yielding ketone species **H**. Acid-catalyzed ketone−enol tautomerization is known to be a slow step according to halogenation of ketones.[28]

The thermodynamic equilibriums in the two isomerizations strongly favor η^1-2-metalated species. Electronic effects are certainly important because the furan oxygen of 2-metalated isomers can stabilize the electron-deficient WC_α carbon center.[29] We believe that a steric effect is equally important because 3-metalated isomers suffer additional steric hindrance between the neighboring $CpW(CO)_3$ and Cγ-R substituents.

Stereochemical Course in 1,4-Addition Reactions on η^1-3-Furyl Compounds. No electrophilic alkylations have been reported for any transition-metal η^1-aromatic heterocycle including furyl,[11] thienyl,[14] or pyrrolyl[14] compounds. η^1-3-Furyl complexes in our system are capable of undergoing 1,4-addition reactions, *via* electrophilic alkylation and sequential reduction; the intermediate involves an alkylated η^1-3-furylidene cation. This process represents a breakthrough in organic furan chemistry because furans only undergo electrophilic substitution.[30,31] The results in Schemes 6 and 7 clearly show the different stereochemical outcomes for addition of aldehydes to the two η^1-3-furyl compounds **7** and **9**, and sequential $NaBH_3CN$ reduction of the two furylidene intermediates proceeds in different stereochemistry. We first rationalize the issue in hydride addition. For intermediates **III** and **IV** derived from **7**, the methyl group is too small to be a stereotemplate; $NaBH_3CN$ addition at the C_δ carbons occurs equally from the same or other side with the C_α-alkylated substituent. Therefore, the stereoselectivity in this case favors *trans* products because the *cis* form suffers the steric hindrance between $CH(OBF_3)R$ and isopropyl groups. While in **I** and **II**, the bulky phenyl group is envisaged to be quite nonplanar with the furylidene ring, particularly as W-C_α becomes a double bond to enhance steric hindrance between $CpW(CO)_3$ and the phenyl group. In this manner, limited space is available for the hydride addition from the same side as the C_α-alkylated substituent; this kinetic effect favors the *cis* product.

Scheme 10 shows models to rationalize the stereochemistry in the aldehyde reaction.[1ab,32−36] In an open transition-state mechanism,[1a,b,32−36] antiperiplanar (**V**) and synclinal (**VI**) states are considered the most important among six possible conformations because of less steric hindrance. *Syn* selectivity of **9** represents a more common case as for most allylsilanes[32,33] and allylstannanes[32,33] including 3-alkoxyallyl compounds;[34] this stereoselection commonly arises from antiperiplanar conformation with a staggered conformation between the C═C and C═O double bonds. The *anti* selectivity of **7** is exceptional because few such cases[36] are reported in an open transition-state mechanism. The fact that **7** behaves distinctly from **9** leads us to consider the roles of C_δ substituents of the two η^1-3-furyl complexes, i.e., ethyl versus isopropyl; the Cγ substituents are too remote from the reaction center. In the case of **7**, the isopropyl group is considerably larger than the ethyl substituent, in this case synclinal conformation **VI** becomes important to yield *anti* stereoselection because antiperiplanar **V** suffers steric interactions between the coordinated BF_3 and isopropyl groups.

Conclusions

In this work, we elaborated tungsten η^1-propargyl compounds for systematic syntheses of tungsten η^1-oxygenated heterocycles including 2,5-dihydrofuryl, η^1-2-furyl, η^1-3-furyl, η^1-2-furylidene, η^1-3-furylidene, and η^1-Δ^3-butenolide complexes. During syntheses of these compounds, we discovered atypical organometallic reactions involving skeletal rearrangement of η^1-3-furylidene to η^1-2-furylidene and of η^1-3-furyl to η^1-2-furyl compounds. The η^1-3-furyl complexes in this system underwent diastereoselective 1,4-addition reactions to yield complex η^1-2,5-dihydrofuryl compounds; this process greatly enhances organic furan chemistry. Oxidative demetalations of representative η^1-heterocyclic compounds were performed to yield useful 2,5-dihydrofurans, furans, Δ^3-butenolides, Δ^3-butenolides, and complex 2,5-dihydrofurans.

Experimental Section

All operations were carried out under argon in a Schlenk apparatus or 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. Ph_3CBF_4 was crystallized from CH_2Cl_2 and hexane at −40 °C before use; tungsten hexacarbonyl, $BF_3{\cdot}Et_2O$, dicyclopentadiene, 3-phenylpro-

(27) (a) Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1991**, *10*, 1079. (b) Trost, B. M.; Dyker, G.; Kulawiec, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 7809. (c) Trost, B. M.; Martinez, J. A.; Kulawiec, R. J.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 10402.

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(29) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, CA, 1994; Chapter 6, p 151.

(30) Bird, C. W.; Cheeseman, G. W. H. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Reese, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 4, Part 3, p 39.

(31) Sargent, M. V.; Dean, F. M. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R., Reese, C. W., Eds.; Pergamon Press: Oxford, 1984; Vol. 4, Part 3, p 599.

(32) For discussion concerning the mechanism and stereochemistry of antiperiplanar and synclinal transition states in organic reactions, see refs 1a,b and (a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (b) Roush, W. R. In *Comprehensive Organic Synthesis: Addition to C-X p bonds, Part II*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Chapter 1.1, p 1. (c) Denmark, S. E.; Weber, E. J.; Wilison, T. M. *Tetrahedron* **1989**, *45*, 1053.

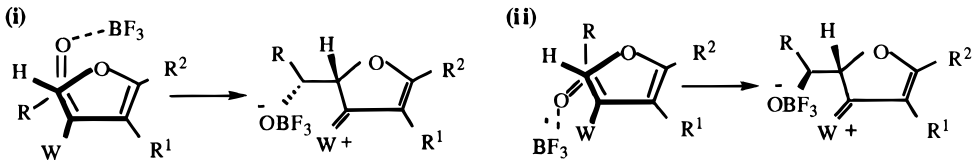
(33) (a) Denmark, S. E.; Weber, E. J. *J. Am. Chem. Soc.* **1984**, *106*, 7970. (b) Denmark, S. E.; Henke, B. R.; Weber, E. *J. Am. Chem. Soc.* **1987**, *109*, 2512. (c) Marshall, J. A.; Wang, X.-J. *J. Org. Chem.* **1991**, *56*, 3211. (d) Marshall, J. A.; Crooks, S. L.; DeHoff, B. S. *J. Org. Chem.* **1988**, *53*, 1616. (e) Panek, J. S.; Cirillo, P. F. *J. Org. Chem.* **1993**, *59*, 999. (f) Panek, J. S.; Beresis, R. *J. Org. Chem.* **1993**, *58*, 809. (g) Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 556.

(34) (a) Korreda, M.; Tanaka, Y. *Tetrahedron Lett.* **1987**, *28*, 143. (b) Keck, G. E.; Abbot, D. E.; Wiley, M. R. *Tetrahedron Lett.* **1987**, *28*, 139.

(35) Denmark, S. E.; Almstead, N. G. *J. Org. Chem.* **1994**, *59*, 5130.

(36) Only a few cases of *anti* selectivity are observed for allylation of aldehydes in an open transition-state mechanism.[34,35] For tributyltin allyl compounds, several cases of *anti* selectivity derive from a closed transition-state mechanism without catalysts or with $SnCl_4$ or $MgCl_2$ as catalyst; see representative examples: (a) Keck, G. E.; Abbott, D. A. *Tetrahedron Lett.* **1984**, *25*, 1883. (b) Mikami, K.; Kawamoto, K.; Loh, T.-P.; Nakai, T. *J. Chem. Soc., Chem. Commun.* **1990**, 1359. (c) Hull, C.; Mortlock, S. V.; Thomas, E. J. *Tetrahedron* **1989**, *45*, 1007. (d) Koreeda, M.; Tanaka, Y. *Chem. Lett.* **1982**, 1299.

Scheme 10



pargyl alcohol, 2-butyn-1-ol, aldehydes, and trimethoxymethane were obtained commercially and used without purification. $CpW(CO)_3(\eta^1$-3-phenylpropargyl) and $CpW(CO)_3(\eta^1$-3-methylpropargyl) were prepared according to the procedures described in the literature.[3a]

All ^{1}H NMR (400 and 300 MHz) and ^{13}C NMR (100 and 75 MHz) spectra were obtained on either a Bruker AM-400 or a Varian Gemini-300 spectrometer; the chemical shifts of ^{1}H and ^{13}C NMR are reported relative to tetramethylsilane ($\delta = 0$ ppm). Elemental analyses were performed at National Cheng Kung University, Tainan; solid samples of **10**−**15** were kept at −20 °C until analyses. Infrared spectra were recorded on a Perkin-Elmer 781 spectrometer. High-resolution mass spectra were recorded on a JEOL HX 110 spectrometer.

Synthesis of $CpW(CO)_3(\eta^1$-4-methyl-5-isopropyl-2,5-dihydro-3-furyl) (1). To a CH_2Cl_2 solution (40 mL) of $CpW(CO)_3(\eta^1$-3-methylpropargyl) (4.00 g, 10.4 mmol) at −40 °C were added $BF_3{\cdot}Et_2O$ (1.38 mL, 11.0 mmol) and iPrCHO (1.49 g, 20.7 mmol), and the mixture was stirred for 2 h at the same temperature before addition of a saturated $NaHCO_3$ solution (15 mL). The organic layer was separated, washed with water (2 × 10 mL), dried over $MgSO_4$, and evaporated under vacuum. The residue was eluted through a silica gel column (diethyl ether/hexane = 1/1) to produce a yellow band ($R_f = 0.50$) that yielded **1** as a yellow solid (4.43 g, 9.67 mmol, 93%). IR (Nujol, cm^{-1}): ν(CO) 2005 (s), 1934 (s), ν(C═C) 1630 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.51 (5H, s, Cp), 4.37 (3H, m, $C_\alpha HH' + C_\delta H$), 1.81 (1H, m, $J = 6.9$, 1.1 Hz, CH), 1.58 (3H, s, Me), 0.95 and 0.63 (6H, d, d, $J = 6.9$ Hz, 2 Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 227.7, 215.3, 214.9, 144.5, 108.9, 93.1, 90.6, 89.1, 31.8, 20.0, 15.7, 14.4. MS (75 eV, *m*/*e*): 458 (M^+). Anal. Calcd for $C_{16}H_{18}WO_4$: C, 41.94; H, 3.96. Found: C, 41.76; H, 4.20.

Synthesis of $CpW(CO)_3(\eta^1$-4-phenyl-5-methyl-2,5-dihydro-3-furyl) (2). This compound was similarly prepared from $CpW(CO)_3(\eta^1$-3-phenylpropargyl), acetaldehyde, and $BF_3{\cdot}Et_2O$ in cold CH_2Cl_2; the yield was 90%. IR (Nujol, cm^{-1}): ν(CO) 2012 (s), 1910 (s), ν(C═C) 1610 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10−7.42 (5H, m, Ph), 5.28 (5H, s, Cp), 5.00 (1H, m, C_δH), 4.70 (1H, dd, $J = 6.9$, 2.2 Hz, $C_\alpha HH'$), 4.70 (1H, dd, $J = 6.9$, 3.2 Hz, $C_\alpha HH'$), 1.07 (3H, d, $J = 6.2$ Hz, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 227.0, 217.3, 216.3, 153.0, 139.6, 129.2, 128.0 and 126.6, 111.4, 90.7, 89.8, 85.9, 20.9 (Me). MS (75 eV, *m*/*e*): 492 (M^+). Anal. Calcd for $C_{19}H_{16}WO_4$: C, 46.37; H, 3.28. Found: C, 46.39; H, 3.37.

Synthesis of $CpW(CO)_3(\eta^1$-4-phenyl-5-ethyl-2,5-dihydro-3-furyl) (3). This compound was similarly prepared from $CpW(CO)_3(\eta^1$-3-phenylpropargyl), propionaldehyde, and $BF_3{\cdot}Et_2O$ in cold CH_2Cl_2; the yield was 94%. IR (Nujol, cm^{-1}): ν(CO) 2009 (s), 1914 (s), ν(C═C) 1615 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.50 (5H, m, Ph), 5.25 (5H, s, Cp), 4.99 (1H, m, C_δH), 4.78 (1H, dd, $J = 14.3$, 4.3 Hz, $C_\alpha HH'$), 4.72 (1H, dd, $J = 14.3$, 3.3 Hz, $C_\alpha HH'$), 1.55 (1H, m, CHH'), 1.35 (1H, m, CHH'), 0.84 (3H, t, $J = 6.5$ Hz, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 227.2, 217.5, 216.3, 151.1, 139.7, 129.1, 128.1, 126.6, 115.1, 90.7, 90.5, 77.2, 27.6, 8.4. MS (75 eV, *m*/*e*): 506 (M^+). Anal. Calcd for $C_{20}H_{18}WO_4$: C, 47.42; H, 3.58. Found: C, 47.64; H, 3.64.

Synthesis of $[CpW(CO)_3(\eta^1$-4-methyl-5-isopropyl-3-furylidene)]BF_4 (4). To a CH_2Cl_2 (10 mL) solution of **1** (2.00 g, 4.37 mmol) was slowly added Ph_3CBF_4 (1.41 g, 4.30 mmol) in CH_2Cl_2 (3 mL) at −60 °C during a period of 30 min; the mixture was stirred for 20 min. At −60 °C, cold pentane (ca. 100 mL) was slowly added to yield an orange precipitate, and the solution layer was removed. The precipitate was redissolved in cold CH_2Cl_2 (5 mL, −60 °C) and reprecipitated with pentane (55 mL), and the organic layer was discarded again to leave **4** in vacuo at −30 °C. The sample (2.10 g, 3.86 mmol, 88%) was kept at −30 °C before spectral measurement and elemental analysis. IR (Nujol, cm^{-1}): ν(CO) 2054 (vs), 1991 (vs). ^{1}H NMR (400 MHz, CD_2Cl_2, −40 °C): δ 6.01 (5H, s, Cp), 5.93 (2H, s, C_αH), 3.21 (1H, hept, $J = 7.1$ Hz, CH), 2.14 (3H, s, Me), 1.29 (6H, d, $J = 7.1$ Hz, Me). ^{13}C NMR (100 MHz, CD_2Cl_2, −40 °C): δ 235.0 (W═C_β, $J_{WC} = 110$ Hz), 220.1, 212.9, 203.4, 143.5, 98.6, 94.6, 30.6, 18.8, 18.7, 14.3. Anal. Calcd for $C_{16}H_{17}O_4WBF_4$: C, 35.33; H, 3.15. Found: C, 34.96; H, 3.40.

Synthesis of $[CpW(CO)_3(\eta^1$-4-phenyl-5-methyl-3-furylidene)]BF_4 (5). This compound was similarly prepared from **2** and Ph_3CBF_4 (1.0 equiv) in cold CH_2Cl_2; the yield was 91%. IR (Nujol): ν(CO) 2054 (vs), 1990 (vs). ^{1}H NMR (400 MHz, CD_2Cl_2, −40 °C): δ 7.20−7.60 (5H, m, Ph), 6.18 (2H, s, $C_\alpha H_2$), 5.80 (5H, s, Cp), 2.51 (3H, s, Me). ^{13}C NMR (100 MHz, CD_2Cl_2, −40 °C): δ 231.1 (W═C_β, $J_{WC} = 112$ Hz), 216.1, 211.5, 196.0, 149.1, 128.5, 128.2, 127.1, 126.6, 96.7, 90.8, 22.3. Anal. Calcd for $C_{19}H_{15}WO_4BF_4$: C, 39.48; H, 2.62. Found: C, 39.04; H, 2.88.

Synthesis of $[CpW(CO)_3(\eta^1$-4-phenyl-5-ethyl-3-furylidene)]BF_4 (6). This compound was similarly prepared from **3** and Ph_3CBF_4 (1.0 equiv) in cold CH_2Cl_2; the yield was 90%. IR (Nujol, cm^{-1}): ν(CO) 2056 (vs), 1992 (vs). ^{1}H NMR (400 MHz, CD_2Cl_2, −40 °C): δ 7.20−7.60 (5H, m, Ph), 6.19 (2H, s, $C_\alpha H_2$), 5.82 (5H, s, Cp), 2.81 (2H, q, $J = 7.2$ Hz, CH_2), 1.28 (3H, q, $J = 7.2$ Hz, Me). ^{13}C NMR (100 MHz, CD_2Cl_2, −40 °C): δ 231.3 (W═C_β, $J_{WC} = 119$ Hz), 218.7, 214.6, 201.6, 150.8, 130.7, 129.0, 128.5, 128.3, 99.0, 93.1, 24.3, 7.8. Anal. Calcd for $C_{20}H_{17}WO_4BF_4$: C, 40.58; H, 2.89. Found: 40.08; H, 3.12.

Synthesis of $CpW(CO)_3(\eta^1$-4-methyl-5-isopropyl-3-furyl) (7). Et_3N (1.10 g, 11.0 mmol) was added to **4** (2.00 g, 3.68 mmol) in CH_2Cl_2 (8 mL) at −60 °C, and the resulting yellow solution was stirred for 20 min before it was warmed to 23 °C. After addition of water (20 mL), the organic layer was extracted with diethyl ether (2 × 10 mL), washed with water, and dried in vacuo to give **7** as a yellow solid (1.51 g, 3.31 mmol, 90%). IR (Nujol, cm^{-1}): ν(CO) 2019 (s), 1918 (s), ν(C═C) 1617 (w). ^{1}H NMR (400 MHz, C_6D_6): δ 7.11 (1H, s, C_βH), 4.62 (5H, s, Cp), 3.08 (1H, m, C*H*), 2.01 (3H, s, Me), 1.41 (6H, d, $J = 7.0$ Hz, 2 Me). ^{13}C NMR (100 MHz, C_6D_6): δ 229.5, 216.3, 155.9, 147.2, 129.9, 122.1, 90.4, 26.9, 21.7, 27.6, 12.8. MS (12 eV, *m*/*e*): 456 (M^+). Anal. Calcd for $C_{16}H_{16}WO_4$: C, 42.13; H, 3.54. Found: C, 41.23; H, 3.53.

Synthesis of $CpW(CO)_3(\eta^1$-4-phenyl-5-methyl-3-furyl) (8). This compound was similarly prepared from **5** and Et_3N (2.5 equiv) in cold CH_2Cl_2; the yield was 93%. IR (Nujol, cm^{-1}): ν(CO) 2018 (s), 1917 (s), ν(C═C) 1618 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.50 (5H, m, Ph), 6.92 (1H, s, C_αH), 5.18 (5H, s, Cp), 2.12 (3H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 228.1, 216.1, 149.1, 147.1, 138.1, 132.1, 131.2, 128.1, 126.3, 91.3, 12.3. MS (75 eV, *m*/*e*): 490 (M^+). Anal. Calcd for $C_{19}H_{14}WO_4$: C, 46.56; H, 2.88. Found: C, 46.32; H, 3.14.

Synthesis of $CpW(CO)_3(\eta^1$-4-phenyl-5-ethyl-3-furyl) (9). This compound was similarly prepared from **6** and Et_3N (3.0 equiv) in cold CH_2Cl_2; the yield was 93%. IR (Nujol, cm^{-1}): ν(CO) 2017 (s), 1910 (s), ν(C═C) 1614 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.40 (5H, m, Ph), 6.89 (1H, s, C_αH), 5.13 (5H, s, Cp), 2.40 (2H, q, $J = 7.4$ Hz, CH_2), 1.07 (3H, t, $J = 7.4$ Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 228.5, 216.0, 154.0, 147.0, 143.8, 138.1, 131.7, 131.2, 127.6, 126.6, 91.2, 20.1, 13.3. MS (75 eV, *m*/*e*): 504 (M^+). Anal. Calcd for $C_{20}H_{18}WO_4$: C, 47.61; H, 3.20. Found: C, 47.51; H, 3.15.

Synthesis of $CpW(CO)_3(\eta^1$-4-methyl-5-isopropyl-2-furyl) (10). To a CH_2Cl_2 (20 mL) solution of **7** (1.66 g, 3.64 mmol) was added

p-TSA (31 mg, 0.18 mmol) in CH_2Cl_2 (3 mL) at 23 °C; the solution was stirred for 1 h before the reaction was quenched with a saturated $NaHCO_3$ solution. The organic layer was separated, dried over $MgSO_4$, and evaporated to dryness under vacuum. The residue was eluted through a silica gel column under nitrogen to produce a yellow band (diethyl ether/hexane = 1/1, $R_f = 0.87$) that yielded **10** as a yellow oil (1.58 g, 3.49 mmol, 96%). IR (Nujol, cm^{-1}): ν(CO) 2011 (s), 1910 (s), ν(C═C) 1605 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.25 (1H, s, $C_\beta H$), 5.49 (5H, s, Cp), 2.93 (1H, m, $J = 6.9$ Hz, CH), 1.19 (6H, d, d, $J = 6.9$ Hz, 2 Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 228.3, 215.6, 163.3, 133.3, 132.8, 114.4, 91.6, 26.6, 21.8, 9.6. MS (75 eV, *m*/*e*): 456 (M^+). Anal. Calcd for $C_{16}H_{16}WO_4$: C, 42.13; H, 3.54. Found: C, 42.24; H, 3.66.

Synthesis of CpW(CO)$_3$(η^1-4-phenyl-5-methyl-2-furyl) (11). This compound was prepared from **8** and *p*-TSA (5.0 mol %) in CH_2Cl_2 at 23 °C; the yield was 94%. IR (Nujol, cm^{-1}): ν(CO) 2007 (s), 1911 (s), ν(C═C) 1607 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.40 (5H, m, Ph), 6.64 (1H, s, $C_\beta H$), 5.56 (5H, s, Cp), 2.48 (3H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 227.7, 215.8, 155.2, 135.9, 134.9, 131.4, 131.3, 128.4, 127.3, 125.6, 91.8, 13.5. MS (75 eV, *m*/*e*): 490 (M^+). Anal. Calcd for $C_{19}H_{14}WO_4$: C, 46.56; H, 2.88. Found: C, 46.77; H, 2.89.

Synthesis of CpW(CO)$_3$(η^1-4-phenyl-5-ethyl-2-furyl) (12). This compound was similarly prepared from **9** and *p*-TSA (5.0 mol %) in CH_2Cl_2 at 0 °C; the yield was 93%. IR (Nujol, cm^{-1}): ν(CO) 2007 (s), 1911 (s), ν(C═C) 1607 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30−7.40 (5H, m, Ph), 6.59 (1H, s, $C_\beta H$), 5.54 (5H, s, Cp), 2.80 (1H, q, $J = 7.2$ Hz, C*H*$_2$CH$_3$), 1.25 (1H, t, $J = 7.2$ Hz, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 227.8, 215.7, 160.4, 135.2, 135.1, 131.3, 131.2, 128.4, 127.3, 125.7, 91.7, 20.9, 13.4. MS (75 eV, *m*/*e*): 504 (M^+). Anal. Calcd for $C_{20}H_{16}WO_4$: C, 47.64; H, 3.20. Found: C, 47.87; H, 3.33.

Synthesis of [CpW(CO)$_3$(η^1-4-methyl-5-isopropyl-2-furylidene)]-CF_3CO_2 (13). To **10** (0.20 g, 0.44 mmol) in diethyl ether (3 mL) at 0 °C was slowly added CF_3CO_2H (0.70 g, 6.6 mmol) to yield a red precipitate. The solution was concentrated to ca. 1.5 mL; then hexane (2 mL) was added to yield further solid. The solvent was removed to leave **13** as a red solid (0.17 g, 0.29 mmol, 67%). IR (Nujol, cm^{-1}): ν(CO) 2060 (s), 1988 (s), ν(C═C) 1607 (w). ^{1}H NMR (400 MHz, CD_2Cl_2, 0 °C): δ 7.32 (1H, s, $C_\beta H$), 6.02 (5H, s, Cp), 5.67 (1H, d, $J = 2.9$ Hz, $C_\delta H$), 2.52 (1H, m, $J = 6.9, 2.9$ Hz, CH), 2.43 (3H, s, Me), 1.47 and 0.68 (d, d, $J = 6.9$ Hz, 2 Me). ^{13}C NMR (100 MHz, CD_2Cl_2, 0 °C): δ 278.4 (W═C$_\alpha$, $J_{WC} = 114$ Hz), 213.6, 212.6, 179.0, 163.0 (q, $J_{CF} = 43.7$ Hz), 130.1, 115.0 (q, $J_{CF} = 284.0$ Hz), 110.1, 95.8, 38.2, 30.4, 21.4, 14.2. Anal. Calcd for $C_{18}H_{17}WO_6F_3$: C, 37.92; H, 3.01. Found: C, 37.77; H, 3.23.

Synthesis of [CpW(CO)$_3$(η^1-4-phenyl-5-methyl-2-furylidene)]-CF_3CO_2 (14). This compound was similarly prepared from **11** and CF_3CO_2H (15 equiv) in diethyl ether; the yield was 70%. IR (Nujol, cm^{-1}): ν(CO) 2068 (s), 1988 (s), ν(C═C) 1610 (w). ^{1}H NMR (400 MHz, CD_2Cl_2, 0 °C): δ 7.74 (1H, s, $C_\beta H$), 7.50−7.70 (5H, m, Ph), 6.40 (1H, q, $J = 7.1$ Hz, $C_\delta H$), 6.06 (5H, s, Cp), 1.80 (3H, d, $J = 7.1$ Hz, Me). ^{13}C NMR (75 MHz, CD_2Cl_2, 0 °C): δ 273.3 (W═C$_\alpha$, $J_{WC} = 118$ Hz), 213.7, 212.6, 176.0, 163.0 (q, $J_{CF} = 43.7$ Hz), 139.3, 130.4, 129.0, 128.9, 128.7, 115.0 (q, $J_{CF} = 284.0$ Hz), 101.1, 95.8, 20.9. Anal. Calcd for $C_{21}H_{15}WO_6F_3$: C, 41.75; H, 2.50. Found: C, 41.66; H, 2.77.

Synthesis of [CpW(CO)$_3$(η^1-4-phenyl-5-ethyl-2-furylidene)]CF_3CO_2 (15). This compound was prepared from **12** and CF_3CO_2H (15 equiv) in diethyl ether; the yield was 65%. IR (Nujol, cm^{-1}): ν(CO) 2069 (s), 1996 (s), ν(C═C) 1610 (w). ^{1}H NMR (400 MHz, $CDCl_3$, 0 °C): δ 7.78 (1H, s, $C_\beta H$), 7.60−7.70 (5H, m, Ph), 6.43 (1H, dd, $J = 5.0, 3.6$ Hz, $C_\delta H$), 6.08 (5H, s, Cp), 2.57 (1H, ddq, $J = 20.1, 7.2, 3.6$ Hz, C*H*H′), 1.97 (1H, ddq, $J = 20.1, 7.2, 5.0$ Hz, CH*H*′), 0.91 (3H, t, $J = 7.2$ Hz, Me). ^{13}C NMR (100 MHz, CD_2Cl_2, 0 °C): δ 273.5 (W═C$_\alpha$, $J_{WC} = 110$ Hz), 213.9, 212.7, 176.3, 163.0 (q, $J_{CF} = 43.7$ Hz), 140.3, 133.4, 129.1, 128.8, 128.6, 115.0 (q, $J_{CF} = 284.0$ Hz), 106.1, 95.1, 27.9, 8.3. Anal. Calcd for $C_{22}H_{17}WO_6F_3$: C, 42.74; H, 2.77. Found: C, 42.88; H, 2.88.

Synthesis of CpW(CO)$_3$(η^1-2(3*H*)-oxo-4-methyl-5-isopropylfuran-3-yl) (16). To a hexane solution (5 mL) of **10** (0.80 g, 1.76 mmol) was added NaOAc (0.20 g, 2.4 mmol) and HOAc (0.20 mL, 3.5 mmol); to this stirred mixture was added dropwise *m*-CPBA (0.34 g, 1.95 mmol) at 0 °C. After stirring for 20 min, the solution was treated with a Na_2CO_3 solution, and the organic layer was extracted with diethyl ether, washed with $NaHCO_3$ (5 mL), and dried in vacuo. The residues were chromatographed through a silica gel column (diethyl ether/hexane = 1/1) to yield an orange band of **16** ($R_f = 0.25$; orange solid, 0.55 g, 1.17 mmol, 67%). IR (Nujol, cm^{-1}): ν(CO) 2012 (s), 1914 (s), 1768 (s), ν(C═C) 1640 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.44 (5H, s, Cp), 3.80 (1H, s, $C_\beta H$), 2.73 (1H, hept, $J = 6.9$ Hz, CH), 1.67 (3H, s, Me), 1.13, 1.10 (6H, d, d, $J = 6.9$ Hz, 2 Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 227.7, 218.1, 188.2, 145.8, 117.8, 92.9, 29.5, 21.3, 20.1, 12.1, 8.7. MS (12 eV, *m*/*e*): 472 (M^+). Anal. Calcd for $C_{16}H_{16}WO_5$: C, 40.70; H, 3.42. Found: C, 40.54; H, 3.49.

Synthesis of CpW(CO)$_3$(η^1-2(3*H*)-oxo-4-phenyl-5-methylfuran-3-yl) (17). This compound was similarly prepared from **11** and *m*-CPBA over a HOAc/NaOAc mixture; the yield of **17** was 69% after chromatographic elution (SiO_2, diethyl ether/hexane = 1/1, $R_f = 0.26$). IR (Nujol, cm^{-1}): ν(CO) 2016 (s), 1915 (s), 1775 (s), ν(C═C) 1638 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00−7.40 (5H, m, Ph), 5.41 (5H, s, Cp), 4.23 (1H, s, $C_\beta H$), 1.99 (3H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 227.7, 217.7, 217.2, 187.3, 138.7, 134.3, 129.1, 128.0, 127.3, 126.4, 92.5, 11.5, 8.1. MS (75 eV, *m*/*e*): 506 (M^+). Anal. Calcd for $C_{19}H_{14}WO_5$: C, 45.05; H, 2.79. Found: C, 45.03; H, 2.81.

Synthesis of CpW(CO)$_3$(η^1-2(3*H*)-oxo-4-phenyl-5-ethylfuran-3-yl) (18). This compound was similarly prepared from **12** and *m*-CPBA over a HOAc/NaOAc mixture; the yield of **18** was 70% after chromatographic elution (SiO_2, diethyl ether/hexane = 1/1, $R_f = 0.27$). IR (Nujol, cm^{-1}): ν(CO) 2018 (s), 1914 (s), 1768 (s), ν(C═C) 1640 w); IR (Nujol, cm^{-1}): ν(CO) 2027 (s), 1932 (s), 1770 (s), ν(C═C) 1618 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.00−7.30 (5H, m, Ph), 4.69 (5H, s, Cp), 4.15 (1H, s, $C_\beta H$), 2.28 (1H, dq, $J = 11.4, 7.4$ Hz, CH*H*′), 2.16 (1H, dq, $J = 11.4, 7.4$ Hz, C*H*H′), 1.11 (3H, t, $J = 7.4$ Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 229.4, 218.9, 217.7, 186.3, 144.2, 135.0, 128.9, 128.4, 128.3, 126.2, 92.6, 19.7, 12.9, 8.4. MS (75 eV, *m*/*e*): 520 (M^+). Anal. Calcd for $C_{20}H_{16}WO_5$: C, 46.15; H, 3.10. Found: C, 46.13; H, 3.12.

Synthesis of CpW(CO)$_3$[η^1-2-(dimethoxymethyl)-4-phenyl-5-ethyl-3-furyl] (19). To **9** (0.20 g, 0.40 mmol) in CH_2Cl_2 (10 mL) at −40 °C were added trimethoxymethane (80 mg, 0.80 mmol) and then $SnCl_4$ (1.0 M in heptane, 0.48 mL); the mixture was stirred for 1 h before addition of Et_3N (0.12 g, 1.20 mmol). The solution was warmed to 23 °C and added with H_2O (10 mL). The mixture was extracted with diethyl ether (2 × 10 mL). The organic layer was washed with water (2 × 10 mL), dried over $MgSO_4$, and evaporated under vacuum to give a yellow solid. Crystallization of this solid from a saturated diethyl ether/hexane solution at −40 °C yielded **19** as a yellow crystalline material (0.15 g, 0.26 mmol, 65%). A second crystallization of the mother liquor gave **19** in 18% yield (40 mg, 0.070 mmol). IR (Nujol, cm^{-1}): ν(CO) 2014 (s), 1915 (s), ν(C═C) 1612 (w). ^{1}H NMR (300 MHz, toluene-d_8): δ 7.25−7.44 (5H, m, Ph), 5.77 (1H, s, C*H*), 4.98 (5H, s, Cp), 3.61 (3H, s, OMe), 2.63 (2H, q, $J = 7.6$ Hz, CH_2), 1.27 (3H, t, $J = 7.6$ Hz, Me). ^{13}C NMR (75 MHz, toluene-d_8): δ 228.5, 217.4, 157.0, 156.4, 141.2, 142.3, 135.4, 131.5, 129.1, 128.0, 103.5, 94.2, 56.1, 23.2, 18.1. MS (12 eV): 578 (M^+). Anal. Calcd for $C_{23}H_{22}WO_6$: C, 47.77; H, 3.83. Found: C, 47.69; H, 3.82.

Synthesis of CpW(CO)$_3$[η^1-2-(dimethoxymethyl)-4-phenyl-5-ethyl-*cis*-2,5-dihydro-3-furyl] (20). This compound was prepared from **9**, $CH(OMe)_3$, and $SnCl_4$ in cold CH_2Cl_2 except that $NaBH_3CN$ replaced Et_3N; the yield of **20** (yellow solid) was 86% after elution through a silica gel column (diethyl ether/hexane = 1/1, $R_f = 0.20$). IR (Nujol, cm^{-1}): ν(CO) 2011 (s), 1911 (s), ν(C═C) 1618 (w). ^{1}H NMR (300 MHz, toluene-d_8): δ 7.22−7.51 (5H, m, Ph), 5.49 (1H, br d, $J = 3.8$ Hz, $C_\alpha H$), 5.19 (1H, br t, $J = 6.8$ Hz, $C_\delta H$), 4.84 (5H, s, Cp), 4.67 (1H, d, $J = 3.8$ Hz, CH), 3.63 (3H, s, OMe), 3.60 (3H, s, OMe), 1.75 (1H, m, CH*H*′), 1.62 (1H, m, C*H*H′), 1.21 (3H, t, $J = 7.3$ Hz, Me). ^{13}C NMR (75 MHz, toluene-d_8): δ 228.0, 216.8, 158.1, 143.5, 132.8, 131.1, 129.3, 117.4, 109.0, 101.8, 95.0, 94.4, 56.9, 56.8, 31.7, 13.7. MS (12 eV): 580 (M^+). Anal. Calcd for $C_{23}H_{24}WO_6$: C, 47.61; H, 4.17. Found: C, 47.55; H, 4.12

Synthesis of CpW(CO)$_3$[η^1-2-(1′-hydroxyethyl)-4-phenyl-5-ethyl-*cis*-2,5-dihydro-3-furyl] (21a,b). To **9** (0.30 g, 0.60 mmol) in toluene (10 mL) at −40 °C were added CH_3CHO (40 mg, 0.89 mmol) and then $BF_3{\cdot}Et_2O$ (0.09 mL, 0.71 mmol). A red oil was gradually deposited when the solution was stirred for 1 h at −40 °C; to this

mixture was added a CH_3CN solution (5 mL) of $NaBH_3CN$ (0.19 g, 2.95 mmol) that caused immediate disappearance of the oil. After stirring for 1 h, a saturated $NaHCO_3$ solution was added to the resulting yellow solution; the organic layer was extracted with diethyl ether (2 × 15 mL), washed with H_2O, and then dried in vacuo. Elution of residues through a silica gel column (diethyl ether/hexane = 1/1) produced two yellow bands of **21a** (R_f = 0.80; yellow solid, 0.15 g, 0.28 mmol, 46.4%) and **21b** (R_f = 0.21; yellow solid, 60 mg, 0.11 mmol, 18.6%).

Spectral Data for 21a. IR (Nujol, cm^{-1}): ν(CO) 2015 (s), 1910 (s), ν(C═C) 1610 (w). ^{1}H NMR (400 MHz, toluene-d_8): δ 7.36−7.12 (5H, m, Ph), 5.12 (1H, br s, C_αH), 5.07 (1H, br t, J = 4.7 Hz, C_δH), 4.73 (5H, s, Cp), 4.39 (1H, q, J = 4.2 Hz, C*H*(OH)), 1.62 (3H, d, J = 4.2 Hz, Me), 1.52 (1H, m, CH*H*′), 1.44 (1H, m, C*H*H′), 1.04 (3H, t, J = 7.8 Hz, Me). ^{13}C NMR (100 MHz, toluene-d_8): δ 228.1, 218.7, 157.0, 141.6, 130.6, 128.8, 126.3, 117.9, 102.7, 92.5, 92.2, 68.6, 30.3, 22.9, 11.6. MS (12 eV): 550 (M^+). Anal. Calcd for $C_{22}H_{22}WO_5$: C, 48.02; H, 4.03. Found: C, 48.27; H, 4.15.

Spectral Data for 21b. IR (Nujol, cm^{-1}): ν(CO) 2018 (s), 1911 (s), ν(C═C) 1605 (w). ^{1}H NMR (300 MHz, C_6D_6): δ 6.82−7.01 (5H, m, Ph), 5.15 (1H, br d, J = 3.4 Hz, C_αH), 4.85 (1H, br t, J = 4.6 Hz, C_δH), 4.16 (5H, s, Cp), 4.04 (1H, dq, J = 6.3, 3.4 Hz, C*H*(OH)), 1.22 (2H, m, C*HH*′), 1.13 (3H, d, J = 6.3 Hz, Me), 0.79 (3H, t, J = 7.4 Hz, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 227.8, 219.9, 154.0, 139.9, 129.1, 128.4, 126.8, 114.8, 103.5, 91.4, 91.2, 69.7, 28.3, 17.4, 10.7. MS (12 eV): 550 (M^+). Anal. Calcd for $C_{22}H_{22}WO_5$: C, 48.02; H, 4.03. Found: C, 48.22; H, 4.14.

Synthesis of CpW(CO)$_3$[η^1-2-(*syn*-1′-hydroxy-4′-methylbutyl)-4-phenyl-5-ethyl-*cis*-2,5-dihydro-3-furyl] (22a). This compound was similarly prepared from **9**, isovaleraldehyde, and BF_3·Et_2O in cold toluene followed by $NaBH_3CN$ reduction; the yield of **22a** was 60% after elution through a silica gel column (yellow solid; diethyl ether/hexane = 1/1, R_f = 0.82). IR (Nujol, cm^{-1}): ν(CO) 2014 (s), 1910 (s), ν(C═C) 1605 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17−7.36 (5H, m, Ph), 5.20 (5H, s, Cp), 4.85 (1H, d, J = 3.5 Hz, C_αH), 4.80 (1H, dt, J = 4.1, 3.5 Hz, C_δH), 3.95 (1H, d, J = 8.4 Hz, C*H*(OH)), 1.70 (2H, m, CH*H*′), 1.64 (2H, m, C*H*H′), 1.65 (1H, m, C*H*), 1.30, 1.24 (2H, m, C*HH*′), 0.92 and 0.95 (6H, d, d, J = 6.8 Hz, 2 Me), 0.83 (3H, t, J = 7.4 Hz, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 228.2, 218.9, 155.1, 140.1, 129.3, 128.3, 127.3, 117.3, 101.5, 91.6, 91.1, 69.4, 28.8, 24.6, 23.8, 21.8, 10.4. MS: 592 (M^+). Anal. Calcd for $C_{25}H_{28}WO_5$: C, 50.69; H, 4.76. Found: C, 50.55; H, 4.88.

Synthesis of CpW(CO)$_3$[η^1-2-(*syn*-1′-hydroxy-3′-methylpropyl)-4-phenyl-5-ethyl-*cis*-2,5-dihydro-3-furyl] (23a). This compound was similarly prepared from **9**, isobutyraldehyde, and BF_3·Et_2O in cold toluene followed by $NaBH_3CN$ reduction; the yield of **23a** was 50% after elution through a silica gel column (yellow solid; diethyl ether/hexane = 1/1, R_f = 0.82). IR (Nujol, cm^{-1}): ν(CO) 2011 (s), 1918 (s), ν(C═C) 1605 (w). ^{1}H NMR (300 MHz, toluene-d_8): δ 7.26−7.39 (5H, m, Ph), 5.48 (1H, d, J = 2.9 Hz, C_αH), 5.10 (1H, m, C_δH), 4.82 (5H, s, Cp), 3.89 (1H, d, J = 7.7 Hz, C*H*(OH)), 2.36 (1H, m, CH), 1.58 (1H, m, CH*H*′), 1.28 (1H, m, C*H*H′), 1.48 and 1.43 (6H, d, d, J = 5.0 Hz, 2 Me), 1.10 (3H, t, J = 5.5 Hz, Me). ^{13}C NMR (75 MHz, toluene-d_8): δ 229.2, 218.7, 157.1, 142.0, 130.8, 129.7, 128.5, 118.7, 99.93, 91.8, 92.5, 77.9, 34.6, 30.5, 21.4, 21.1, 11.6. MS (12 eV, *m*/*e*): 578 (M^+). Anal. Calcd for $C_{24}H_{26}WO_5$: C, 49.85; H, 4.53. Found: C, 49.66; H, 4.47.

Synthesis of CpW(CO)$_3$(η^1-2-formyl-4-methyl-5-isopropyl-3-furyl) (24). This compound was similarly prepared from **16**, $CH(OMe)_3$, and $SnCl_4$ in cold CH_2Cl_2 followed by Et_3N deprotonation; the yield of **24** was 75% after crystallization from diethyl ether/hexane. IR (Nujol, cm^{-1}): ν(CO) 2012 (s), 1918 (s), ν(C═C) 1615 (w). ^{1}H NMR (300 MHz, toluene-d_8): δ 10.05 (1H, s, CHO), 4.96 (5H, s, Cp), 3.07 (1H, m, CH), 2.15 (3H, s, Me), 1.09 (6H, d, d, J = 6.5 Hz, 2 Me). ^{13}C NMR (75 MHz, toluene-d_8): δ 228.4, 217.6, 182.3, 164.1, 159.9, 149.9, 132.7, 94.7, 29.7, 23.2, 23.3, 17.3. MS (12 eV, *m*/*e*): 484 (M^+). Anal. Calcd for $C_{17}H_{16}WO_5$: C, 42.26; H, 3.13. Found: C, 42.30; H, 3.11.

Synthesis of CpW(CO)$_3$[η^1-2-(dimethoxymethyl)-4-methyl-5-isopropyl-*trans*-2,5-dihydro-3-furyl] (25). This compound was similarly prepared from **7**, $CH(OMe)_3$, and $SnCl_4$ in cold CH_2Cl_2 followed by $NaBH_3CN$ reduction; the yield was 85% after elution from a silica gel column (yellow solid; R_f = 0.20, diethyl ether/hexane = 1/1). IR (Nujol, cm^{-1}): ν(CO) 2016 (s), 1918 (s), ν(C═C) 1645 (w). ^{1}H NMR (300 MHz, toluene-d_8): δ 5.12 (5H, s, Cp), 4.99 (1H, dd, J = 3.8, 2.8 Hz, C_αH), 4.68 (1H, d, J = 2.8 Hz, C_δH), 4.52 (1H, d, J = 3.8 Hz, CH), 3.47 (3H, s, OMe), 3.45 (3H, s, OMe), 2.06 (1H, m, CH), 1.91 (Me), 1.39 and 1.11 (6H, d, d, J = 7.0 Hz, 2 Me). ^{13}C NMR (75 MHz, toluene-d_8): δ 228.5, 217.8, 151.5, 112.8, 99.4, 96.0, 94.2, 57.6, 57.4, 34.7, 22.8, 20.0, 18.8. MS: 532 (M^+). Anal. Calcd for $C_{19}H_{24}WO_6$: C, 42.88; H, 4.55. Found: C, 42.89; H, 4.50.

Synthesis of CpW(CO)$_3$[η^1-2-(1′-hydroxyethyl)-4-methyl-5-isopropyl-2,5-dihydro-3-furyl] (26a−c). These compounds were similarly prepared from **7**, acetaldehyde, and BF_3·Et_2O in cold CH_2Cl_2 before $NaBH_3CN$ reduction; the three diastereomers were separated on a silica gel column (diethyl ether/hexane = 1/1) with the following R_f values and yields: **26a** (R_f = 0.50; yellow solid, 0.08 g, 0.17 mmol, 15%), **26b** (R_f = 0.20; yellow solid, 30 mg, 0.060 mmol, 5%), and **26c** (R_f = 0.12; yellow solid, 0.27 g, 0.55 mmol, 50%).

Spectral Data for 26a (*syn-cis*). IR (Nujol, cm^{-1}): ν(CO) 2014 (s), 1911 (s), ν(C═C) 1610 (w). ^{1}H NMR (300 MHz, C_6D_6): δ 4.84 (5H, s, Cp), 4.63 (1H, d, J = 3.8 Hz, C_αH), 4.43 (1H, d, J = 3.8 Hz, C_δH), 4.37 (1H, q, J = 6.5 Hz, CH), 1.80 (1H, hept, J = 6.8 Hz, CH), 1.58 (3H, s, Me), 1.52 (3H, d, J = 6.5 Hz, Me), 1.10 and 0.76 (6H, d, d, J = 6.8 Hz, 2 Me). MS (75 eV, *m*/*e*): 502 (M^+). Anal. Calcd for $C_{18}H_{22}WO_5$: C, 43.05; H, 4.42. Found: C, 43.32; H, 4.40.

Spectral Data for 26b (*syn-trans*). IR (Nujol, cm^{-1}): ν(CO) 2014 (s), 1910 (s), ν(C═C) 1638 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.50 (5H, s, Cp), 4.52 (1H, d, J = 5.3 Hz, C_αH), 4.43 (1H, d, J = 5.3 Hz, C_δH), 4.03 (1H, q, J = 6.5 Hz, C*H*(OH)), 1.78 (1H, hept, J = 6.8Hz, CH), 1.76 (3H, s, Me), 1.27 (3H, d, J = 6.5 Hz, Me), 0.98, 0.62 (3H, 3H, d, d, J = 6.8 Hz, 2 Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 228.4, 217.5, 142.8, 109.2, 100.4, 94.4, 91.5, 69.5, 32.5, 21.5, 19.8, 17.0, 14.5. MS (12 eV, *m*/*e*): 502 (M^+). Anal. Calcd for $C_{18}H_{22}WO_5$: C, 43.05; H, 4.42. Found: C, 43.33; H, 4.51.

Spectral Data for 26c (*anti-trans*). IR (Nujol, cm^{-1}): ν(CO) 1948 (s), 1850 (s), ν(C═C) 1645 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.06 (5H, s, Cp), 4.98 (1H, d, J = 3.3 Hz, C_αH), 4.61 (1H, d, J = 3.3 Hz, C_δH), 4.15 (1H, q, J = 6.5 Hz, C*H*(OH)), 2.00 (1H, hept, J = 7.0 Hz, C*H*), 1.75 (3H, s, Me), 1.32 (3H, d, J = 6.5 Hz, Me), 1.30, 1.01 (3H, 3H, d, d, J = 7.0 Hz, CH). ^{13}C NMR (75 MHz, $CDCl_3$): δ 229.3, 217.5, 148.1, 112.5, 103.1, 94.7, 92.3, 71.6, 33.2, 21.3, 18.3, 17.4, 15.7. MS (12 eV): 502 (M^+). Anal. Calcd for $C_{18}H_{22}WO_5$: C, 43.05; H, 4.42. Found: C, 43.24; H, 4.55.

Synthesis of CpW(CO)$_3$[η^1-2-(1′-hydroxy-3′-methylpropyl)-4-ethyl-5-isopropyl-2,5-dihydro-3-furyl] (27a−c). This compound was similarly prepared from **7**, isovaleraldehyde, and BF_3·Et_2O and sequential $NaBH_3CN$ reduction in cold CH_2Cl_2; three diastereomers were separated on a silica gel column (diethyl ether/hexane = 1/1) with the following R_f values and yields: **27a** (R_f = 0.50; yellow solid, 15%), **27b** (R_f = 0.20; yellow solid, 8%), and **27c** (R_f = 0.12; yellow solid, 55%).

Spectral Data for 27a (*syn-cis*). IR (Nujol, cm^{-1}): ν(CO) 2010 (s), 1911 (s), ν(C═C) 1640 (w). ^{1}H NMR (300 MHz, toluene-d_8): δ 5.07 (5H, s, Cp), 4.71 (1H, dd, J = 4.8, 2.3 Hz, C_αH), 4.55 (1H, d, J = 2.3 Hz, C_δH), 4.39 (1H, dd, J = 10.0, 4.8 Hz, C*H*OH), 2.26 (1H, m, CH), 2.08 (1H, m, C*H*H′), 1.58 (1H, m, CH*H*′), 2.00 (1H, m, C*H*), 1.79 (3H, s, Me), 1.29, 1.21 (3H, 3H, d, d, J = 6.6 Hz, 2 Me), 1.29, 0.92 (6H, d, d, J = 6.9 Hz, 2 Me). ^{13}C NMR (75 MHz, toluene-d_8): δ 228.9, 214.0, 150.8, 114.2, 99.0, 93.1, 91.6, 71.3, 46.6, 32.2, 26.1, 25.0, 23.1, 21.6, 18.1, 17.0. MS (12 eV, *m*/*e*): 544 (M^+). Anal. Calcd for $C_{21}H_{28}WO_5$: C, 46.34; H, 5.19. Found: C, 46.68; H, 5.23.

Spectral Data for 27b (*syn-trans*). IR (Nujol, cm^{-1}): ν(CO) 2010 (s), 1911 (s), ν(C═C) 1640 (w). ^{1}H NMR (300 MHz, toluene-d_8): δ 5.07 (5H, s, Cp), 4.91 (1H, dd, J = 4.4, 3.5 Hz, C_αH), 4.60 (1H, dd, J = 6.4, 3.5 Hz, C_δH), 4.23 (1H, dd, J = 10.3, 4.4 Hz, C*H*OH), 2.23 (1H, m, C*H*Me$_2$), 2.10 (1H, m, C*H*H′), 1.97 (1H, m, C*H*Me$_2$), 1.79 (3H, s, C_γMe), 1.54 (1H, m, CH*H*′), 1.34, 0.98 (6H, d, d, J = 6.6 Hz, C_δCH*Me*$_2$), 1.26, 1.22 (6H, d, d, J = 6.9 Hz, CH*Me*$_2$). ^{13}C NMR (75 MHz, toluene-d_8): δ 228.4, 219.7, 150.7, 111.8, 101.9, 95.8, 92.5, 71.5, 46.5, 34.0, 26.0, 25.1, 22.7, 21.3, 18.0, 15.7. MS (12 eV, *m*/*e*): 544 (M^+). Anal. Calcd for $C_{21}H_{28}WO_5$: C, 46.34; H, 5.19. Found: C, 46.47; H, 5.34.

Spectral Data for 27c (*anti-trans*). IR (Nujol, cm^{-1}): ν(CO) 2014 (s), 1915 (s), ν(C═C) 1645 (w). ^{1}H NMR (300 MHz, toluene-d_8): δ

5.05 (5H, s, Cp), 4.97 (1H, d, J = 2.5 Hz, C$_\alpha$H), 4.63 (1H, d, J = 2.5 Hz, C$_\delta$H), 3.85 (1H, d, J = 10.7 Hz, C*H*OH), 2.23 (1H, m, C*H*H′), 2.20 (1H, m, CH), 1.73 (1H, m, CH), 1.76 (3H, s, Me), 1.39 (1H, m, C*H*H′), 1.34, 1.04 (6H, d, d, J = 6.7 Hz, 2 Me), 1.24, 1.22 (6H, d, d, J = 6.5 Hz, 2 Me). ^{13}C NMR (75 MHz, toluene-d_8): δ 229.4, 217.8, 146.4, 111.4, 102.3, 93.1, 90.7, 72.6, 39.2, 31.8, 24.6, 24.1, 21.6, 20.0, 15.9, 14.4. MS (12 eV, *m*/*e*): 544 (M$^+$). Anal. Calcd for $C_{21}H_{28}WO_5$: C, 46.34; H, 5.19. Found: C, 46.55; H, 5.34.

Synthesis of CpW(CO)$_3$[η^1-2-(*anti*-1′-acetoxyethyl)-4-methyl-5-isopropyl-*trans*-2,5-dihydro-3-furyl] (28a). To **26c** (0.27 g, 0.54 mmol) in CH_2Cl_2 (4 mL) and DMAP (0.11 g, 0.92 mmol) was added acetic anhydride (0.080 mL, 0.81 mmol), and the mixture was stirred for 2 h before addition of a saturated NH_4Cl solution. The organic layer was extracted with diethyl ether (2 × 15 mL), washed with water, and dried in vacuo. The residue was chromatographed through a silica gel column (diethyl ether/hexane = 1/1) to develop a yellow band of **28a** (R_f = 0.55; yellow solid, 0.25 g, 0.46 mmol, 86%). IR (Nujol, cm^{-1}): ν(CO) 2015 (s), 1811 (s), 1710 (s), ν(C═C) 1637 (w). ^{1}H NMR (300 MHz, toluene-d_8): δ 5.35 (1H, q, J = 6.3 Hz, C*H*(OAc)), 5.15 (5H, s, Cp), 4.98 (1H, d, J = 3.3 Hz, C$_\alpha$H), 4.68 (1H, d, J = 3.3 Hz, C$_\delta$H), 2.03 (1H, m, C$_\delta$C*H*Me$_2$), 1.99 (3H, s, CO*Me*), 1.83 (3H, s, C$_\gamma$Me), 1.48 (3H, d, J = 6.3 Hz, (OAc)CH*Me*), 1.35, 1.05 (6H, d, d, J = 6.8, CH*Me*$_2$). ^{13}C NMR (75 MHz, toluene-d_8): δ 229.5, 217.3, 171.7, 149.0, 112.4, 99.9, 95.3, 92.2, 74.8, 33.1, 24.0, 20.8, 17.6, 15.2, 14.1. MS (12 eV, *m*/*e*): 546 (M$^+$). Anal. Calcd for $C_{20}H_{26}WO_6$: C, 43.97; H, 4.80. Found: C, 43.89; H, 4.75.

Synthesis of CpW(CO)$_3$[η^1-1-(*anti*-1′-acetoxy-3′-methylpropyl)-4-ethyl-5-isopropyl-*trans*-2,5-dihydro-3-furyl] (28b). This compound was similarly prepared from **27c**, acetyl anhydride, and DMAP; the yield of **28b** (yellow solid) was 88% after chromatographic elution (R_f = 0.58, silica gel, diethyl ether/hexane = 1/1). IR (Nujol, cm^{-1}): ν(CO) 2014 (s), 1914 (s), 1712 (s), ν(C═C) 1640 (w). ^{1}H NMR (300 MHz, toluene-d_8): δ 5.37 (1H, dd, J = 11.2, 1.8 Hz, C*H*OAc), 5.30 (5H, s, Cp), 4.94 (1H, dd, J = 4.8, 1.8 Hz, C$_\alpha$H), 4.71 (1H, d, J = 4.8 Hz, C$_\delta$H), 2.21 (1H, m, C*H*H′), 1.57 (1H, m, CH*H*′), 2.05 (1H, m, C*H*), 1.97 (3H, s, Me), 1.92 (1H, m, CH), 1.86 (3H, s, Me), 1.35, 1.07 (6H, d, d, J = 6.7 Hz, 2 Me), 1.20, 1.05 (6H, d, d, J = 6.5 Hz, 2 Me). ^{13}C NMR (75 MHz, toluene-d_8): δ 229.7, 218.3, 172.3, 148.6, 112.8, 100.4, 95.0, 92.3, 77.2, 36.6, 33.3, 26.1, 25.0, 22.8, 21.4, 21.0, 17.7, 15.7. MS (12 eV, *m*/*e*): 558 (M$^+$). Anal. Calcd for $C_{23}H_{30}WO_6$: C, 47.12; H, 5.16. Found: C, 47.24; H, 5.14.

Synthesis of 3-Carbomethoxy-4-phenyl-5-methyl-2,5-dihydrofuran (29). Carbon monoxide was bubbled through a solution (5 mL) of **2** (0.20 g, 0.41 mmol) in CH_2Cl_2/CH_3OH (1/1) at −78 °C for 20 min, and $(NH_4)_2Ce(NO_3)_6$ (0.67 g, 1.23 mmol) in CH_3OH (1 mL) was added dropwise. The solution was stirred at −78 °C for 1 h before it was warmed to 23 °C, and the solution was kept stirring for 1 h. The dark red mixture was filtered through a short silica gel bed, and the residue was eluted on a preparative silica gel TLC plate to produce an organic component (R_f = 0.44, diethyl ether/hexane = 1/1; 50 mg, 0.25 mmol, 60%). IR (Nujol, cm^{-1}): ν(CO) 1720 (s), ν(C═C) 1618 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.40 (m, 5H, Ph), 5.31 (1H, m, C$_\delta$H), 4.94 (1H, dd, J = 16.9, 3.7 Hz, C$_\alpha$H*H*′), 4.86 (1H, dd, J = 16.9, 3.2 Hz, C$_\alpha$*H*H′), 3.63 (1H, s, OMe), 1.22 (3H, d, J = 6.4 Hz, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.3, 154.0, 132.4, 128.7, 128.5, 128.1, 128.0, 86.1, 75.1, 51.3, 20.1. MS (75 eV, *m*/*e*): 218 (M$^+$). HRMS: calcd for $C_{13}H_{14}O_3$, 218.0943; found, 218.0946.

Synthesis of 3-Carbomethoxy-4-phenyl-5-ethyl-2,5-dihydrofuran (30). This compound was similarly prepared from **3** and $(NH_4)_2Ce(NO_3)_6$ under flowing CO in CH_2Cl_2/CH_3OH (1/1, 3 mL); the yield of **30** was 63% as a colorless oil (R_f = 0.46, diethyl ether/hexane = 1/1). IR (Nujol, cm^{-1}): ν(CO) 1700 (s), ν(C═C) 1610 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.27 (1H, dt, J = 4.0, 3.3 Hz, C$_\delta$H), 4.99 (1H, dd, J = 16.3, 3.3 Hz, C$_\alpha$H*H*′), 4.93 (1H, dd, J = 16.3, 3.3 Hz, C$_\alpha$*H*H′), 1.63 (1H, m, C*H*H′), 1.45 (1H, m, CH*H*′), 0.86 (3H, t, J = 7.2 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.3, 152.6, 132.6, 128.7, 128.2, 128.1, 125.3, 90.8, 75.9, 51.5, 26.7, 8.6. MS (75 eV, *m*/*e*): 232 (M$^+$). HRMS: calcd for $C_{14}H_{16}O_3$, 232.1099 (M$^+$); found, 232.1094.

Synthesis of 2(5*H*)-4-Phenyl-5-methyl-5-methoxyfuranone (31). This compound was similarly prepared from the reaction between **11** and $(NH_4)_2Ce(NO_3)_6$ (5.0 equiv) under flowing CO in CH_2Cl_2/CH_3OH (1/1); the yield was 54% as a colorless oil (R_f = 0.45, diethyl ether/hexane = 1/1). IR (Nujol, cm^{-1}): ν(CO) 1750, ν(C═C) 1618. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40−7.80 (5H, m, Ph), 6.39 (1H, s, C$_\beta$H), 3.23 (3H, s, OMe), 1.75 (3H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 163.5, 131.7, 129.2, 128.9, 127.7, 116.3, 109.4, 50.9, 24.8. MS (75 eV, *m*/*e*): 204 (M$^+$). HRMS: calcd for $C_{12}H_{12}O_3$, 204.0786; found, 204.0788.

Synthesis of 2(5*H*)-4-Phenyl-5-ethyl-5-methoxyfuranone (32). This compound was similarly prepared from **12** and $(NH_4)_2Ce(NO_3)_6$ under flowing CO; the yield was 59% as a colorless oil (R_f = 0.49, diethyl ether/hexane = 1/1). IR (Nujol, cm^{-1}): ν(CO) 1760 (s), ν(C═C) 1617 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40−7.80 (5H, m, Ph), 6.42 (1H, s, C$_\beta$H), 3.25 (3H, s, OMe), 2.21 (1H, dq, J = 18.0, 7.6 Hz, C*H*H′), 1.92 (1H, m, J = 18.0, 7.6 Hz, CH*H*′), 0.81 (3H, t, J = 7.6 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.7, 162.4, 131.7, 129.1, 127.5, 127.3, 117.3, 111.9, 50.8, 30.4, 7.2. MS (75 eV, *m*/*e*): 218 (M$^+$). HRMS: calcd for $C_{13}H_{14}O_3$, 218.0943; found, 218.0945.

Demetalation of 11 with I_2. This reaction was conducted similarly from the reaction between **11** and I_2 (2.0 equiv) under a nitrogen atmosphere according to the synthesis of **29** except that I_2 replaced $(NH_4)_2Ce(NO_3)_6$; the yields of **33** and **31** were 60% and 10%, respectively.

Spectral Data for 33. IR (Nujol, cm^{-1}): ν(C═C) 1618 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.40 (5H, m, Ph), 7.35 (1H, d, J = 2.0 Hz, C$_\alpha$H), 6.55 (1H, d, J = 2.0 Hz, C$_\beta$H), 2.47 (3H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): 144.2, 140.2, 134.5, 129.5, 128.5, 127.7, 126.3, 11.2, 20.4. MS (75 eV, *m*/*e*): 158 (M$^+$). HRMS: calcd for $C_{11}H_{10}O$, 158.0732; found, 158.0734.

Demetalation of 12 with I_2. This reaction was conducted similarly from the reaction between **12** and I_2 (2.0 equiv); the yields of **34** and **32** were 63% and 8%, respectively.

Spectral Data for 34. IR (Nujol, cm^{-1}): ν(C═C) 1600 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (1H, d, J = 2.3 C$_\alpha$H), 7.40−7.27 (5H, m, Ph), 6.50 (1H, d, J = 2.3 Hz, C$_\beta$H), 2.82 (2H, q, J = 5.4 Hz, CH_2), 1.29 (3H, t, J = 5.4 Hz, Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 140.2, 134.5, 129.5, 128.5, 127.7, 126.3, 111.2, 20.4, 12.9. MS (12 eV, *m*/*e*): 172 (M$^+$). HRMS: calcd for $C_{12}H_{12}O$, 172.0888; found, 172.0892.

Demetalation of 17 with Me_3NO. To a solution of **17** (0.20 g, 0.40 mmol) in CH_2Cl_2 (5 mL) were added anhydrous Me_3NO (0.12 g, 1.60 mmol) and H_2O (14.4 mg, 0.80 mmol), and the solution was stirred at 28 °C for 2 h. The residue was treated with H_2O (5 mL); the organic layer was extracted with diethyl ether, dried in vacuo, and eluted through a silica gel column (diethyl ether/hexane = 1/1) to produce two bands that gave **35** (R_f = 0.49; 36 mg, 0.21 mmol) and **37** (R_f = 0.33; 40 mg, 0.084 mmol) in 53% and 21% yields, respectively.

Spectral Data for 35. IR (Nujol, cm^{-1}): ν(CO) 1760 (s), ν(C═C) 1618 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.20−7.50 (5H, m, Ph), 3.52 (2H, s, C$_\beta$H$_2$), 2.20 (3H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.9, 147.8, 132.4, 129.2, 128.7, 127.2, 126.8, 36.3, 13.0. MS (75 eV, *m*/*e*): 174 (M$^+$). HRMS: calcd for $C_{11}H_{10}O_2$, 174.0681 (M$^+$); found, 174.0689.

Spectral Data for 37. IR (Nujol, cm^{-1}): ν(CO) 1987 (s), 1920 (s), 1730 (s), ν(C═C) 1618 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10−7.50 (5H, m, Ph), 5.45 (5H, s, Cp), 3.83 (1H, s, C$_\beta$H), 2.42 (3H, s, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 221.0, 219.1, 178.1, 137.5, 128.6, 128.5, 127.7, 125.5, 94.3, 92.4, 30.2, 22.9. MS (75 eV, *m*/*e*): 478 (M$^+$). Anal. Calcd for $C_{18}H_{14}WO_4$: C, 45.18; H, 2.95. Found: C, 44.87; H, 3.03.

Demetalation of 18 with Me_3NO. This reaction was conducted similarly from **18** and Me_3NO in the presence of water; the yields of **36** and **38** were 58% and 20%, respectively.

Spectral Data for 36. IR (Nujol, cm^{-1}): ν(CO) 1785 (s), ν(C═C) 1617 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30−7.60 (5H, m, Ph), 3.54 (2H, s, C$_\beta$H$_2$), 2.57 (2H, m, J = 7.5 Hz, CH_2), 1.22 (3H, t, J = 1.6, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.5, 152.7, 131.3, 129.3, 128.7, 127.2, 126.8, 36.6, 20.3, 11.3. MS (75 eV, *m*/*e*): 188 (M$^+$). HRMS: calcd for $C_{12}H_{12}O_2$, 188.0837; found, 188.0844.

Spectral Data for 38. IR (Nujol, cm^{-1}): ν(CO) 1988 (s), 1921 (s), 1722 (s), ν(C═C) 1617 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.10−7.50 (5H, m, Ph), 5.48 (5H, s, Cp), 3.88 (1H, s, C$_\beta$H), 2.78 (1H, m, J = 18.5, 7.5 Hz, C*H*H′), 2.51 (1H, m, J = 18.5, 7.5 Hz, CH*H*′), 1.13 (3H, t, J = 7.5 Hz, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 221.3, 218.5,

178.7, 137.3, 130.0, 128.5, 127.6, 125.4, 99.8, 91.9, 30.0, 29.5, 13.1. MS (75 eV, *m*/*e*): 492 (M^+). Anal. Calcd for $C_{19}H_{16}WO_4$: C, 46.37; H, 3.28. Found: C, 46.17; H, 3.15.

Demetalation of 21a by Ce(IV) Salt. This reaction followed the synthesis of **29** except that reactants **21a** and $(NH_4)_2Ce(NO_3)_6$ were treated in CH_2Cl_2 rather than in CH_3OH/CH_2Cl_2; the yield of bicyclic lactone **39** was 40%. IR (neat, cm^{-1}): ν(CO) 1767 (s), ν(C═C) 1622 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62−7.23 (5H, m, Ph), 5.73 (1H, dq, J = 7.9, 6.5Hz, CH), 5.65 (1H, dd, J = 7.9, 5.1 Hz, C_αH), 4.78 (1H, m, C_δH), 1.98 (1H, m, C*H*H′), 1.72 (1H, m, CH*H*′), 1.35 (3H, d, J = 6.5 Hz, Me), 0.96 (3H, t, J = 7.3 Hz, Me). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.9, 149.8, 134.2, 130.0, 128.7, 128.0, 128.5, 96.0, 86.5, 77.7, 28.1, 15.0, 9.4. MS (12 eV, *m*/*e*): 244 (M^+). HRMS: calcd for $C_{15}H_{16}O_3$, 244.1099; found, 244.1103.

Demetalation of 28b by Ce(IV) Salt. This reaction followed the synthesis of **29** involving the use of CH_2Cl_2/CH_3OH as solvent; the yield of **40** was 46%. IR (neat, cm^{-1}): ν(CO) 1712 (s), ν(C═C) 1615 (w). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.38 (1H, dd, J = 11.2, 1.8 Hz, C*H*OAc), 5.06 (1H, dd, J = 4.0, 1.8 Hz, C_αH), 4.66 (1H, d, J = 4.0 Hz, C_δH), 3.75 (3H, s, OMe), 2.06 (3H, s, Me), 2.02 (3H, s, Me), 1.88 (1H, m, CH*H*′), 1.54 (1H, m, C*H*H′), 1.62 (1H, m, CH), 1.09 (1H, m, CH), 1.04, 0.72 (6H, d, d, J = 6.7 Hz, 2 Me), 0.85, 0.79 (6H, d, d, J = 6.5 Hz, CH). ^{13}C NMR (75 MHz, toluene-d_8): δ 170.6, 163.8, 154.7, 124.5, 94.0, 87.5, 74.1, 51.3, 36.7, 31.3, 24.4, 23.5, 21.5, 21.2, 19.6, 14.7, 12.3. MS (12 eV, *m*/*e*): 312 (M^+). HRMS: calcd for $C_{17}H_{28}O_5$, 312.1937; found, 312.1934.

X-ray Diffraction Studies of 18, 20, 21a, 28a, and 38. Single crystals of **18**, **20**, **21a**, **28a**, and **38** were sealed in glass capillaries under an inert atmosphere. Data for **20**, **21a**, **28a**, and **38** were collected on a Nonius CAD 4 instrument using graphite-monochromated Mo Kα radiation, and the structures were solved by the heavy atom method; all data reduction and structural refinements were performed with the NRCCSDP package. Data for **18** were collected on a Nicolet R_3M/V diffractometer using graphite-monochromated Mo Kα radiation, and the structure was solved by the Patterson superposition method; all data reduction and structural refinement were performed with the SHELXTL Plus package. Crystal data, details of data collection, and structural analysis of these seven compounds are prepared as supporting information. For all structures, all non-hydrogen atoms were refined with anisotropic parameters, and all hydrogen atoms included in the structure factor were placed in idealized positions.

Acknowledgment. The authors wish to thank the National Science Council and National Institute of Health, Taiwan, for financial support of this work; the authors also thank reviewers of this manuscript for their valuable comments and suggestions.

Supporting Information Available: Variable-temperature ^{1}H NMR spectra showing the isomerization of **6** to **15** in CD_2Cl_2, ^{1}H NMR spectra monitoring the isomerization of **9** to **12** with CF_3CO_2D (1.0 equiv) in CD_2Cl_2 (−40 °C), tables of crystal data, atomic coordinates, bond distances, bond angles, and thermal parameters, and ORTEP drawings for **18**, **20**, **21a**, **28a**, and **38** (39 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JA9518888