Tungsten-Promoted Intramolecular Annulation of Propargyl Bromides with Ketones and Aldehydes for Synthesis of Fused 2,5-Dihydrofurans

Shwu-Ju Shieh,[†] Tze-Chin Tang,[†] Jien-Shiu Lee,[†] Gene-Hsian Lee,[‡] Shie-Ming Peng,[‡] and Rai-Shung Liu*[,†]

Department of Chemistry, National Tsinghua University, Hsinchu, 30043, Taiwan, Republic of China, and Department of Chemistry, National Taiwan University, Taipei, 10764, Taiwan, Republic of China

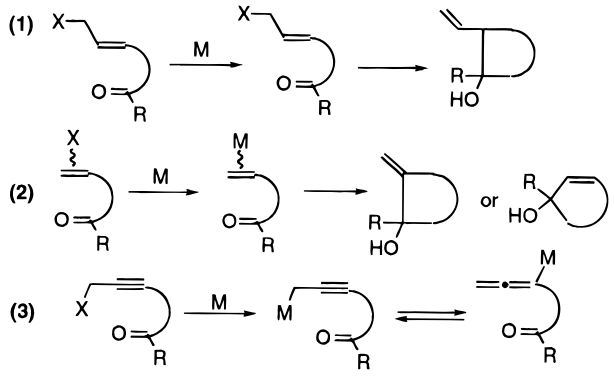
Received December 8, 1995[⊗]

Metal carbonyl salts $CpW(CO)_3Na$, $Re(CO)_5Na$, and $CpFe(CO)_2Na$ were used for intramolecular cyclization of 1-(3-bromo-1-propynyl)-2-(3-oxopropyl)benzene. Among these salts, $CpW(CO)_3Na$ was found to be the most effective in yielding a metalated fused η^1-2,5-dihydro-3-furyl complex. To generalize this cyclization, a number of organic substrates containing propargyl bromide and tethered aldehyde or ketone were prepared. Cyclizations of these substrates by $CpW(CO)_3Na$ proceeded with moderate yields (50%-65%), producing fused tungsten−η^1-2,5-dihydrofur-3-yl compounds of five-, six-, and seven-membered rings. Demetalations of these organometallic products by $(NH_4)_2Ce(NO_3)_6$ in CH_3OH/CH_2Cl_2 under flowing CO provided fused 3-(methoxycarbonyl)-2,5-dihydrofurans; the yields were 50−60% for most cases. Consecutive oxidations of the representative η^1-2,5-dihydrofur-3-yl complex **15** to its fused η^1-2-furyl and further to η^1-butenolide derivative were accomplished in good yields. Demetalations of these two fused η^1-heterocycles were successful for η^1-butenolide but not for the η^1-2-furyl derivative.

Introduction

Metal-mediated intramolecular annulation of unsaturated carbonyl halides (or pseudohalides) with ketones and aldehydes is useful for the synthesis of complex cyclic oxygenated molecules,[1−4] partially owing to the relatively easy synthesis of these organic substrates. Typically, low-valent metals initiate the reaction through oxidative displacement of halides, thereby yielding reactive organometallic anion equivalents to achieve a subsequent carbon−carbon bond-forming reaction with ketones and aldehydes. This synthetic method proceeds well with allyl[3] and vinyl halides[4] (Scheme 1, eqs 1 and 2) but not for propargyl halides for which the well-known allenic−propargyl equilibrium of the corresponding organometallic intermediates interferes (Seheme 1, eq 3).[5,6] A

Scheme 1



recent investigation[7] indicated that Pd(0)−SmI_2 allows the intramolecular coupling of propargyl acetate with a ketone to yield α-alkynylcycloalkanol smoothly; however, the coupling with aldehydes is unsatisfactory (<20%). No effective method is yet available to cyclize these substrates chemoselectively. Selective syntheses of these alcohols can be accomplished by the intramolecular coupling of allenyl- or alkynylsilane with tethered ketones and aldehydes[8,9] even though the synthesis of these silyl substrates requires extra work.

Our previous work demonstrated that in the presence of Lewis acid $CpW(CO)_3Na$ promoted the intermolecular

[†] National Tsinghua University.
[‡] National Taiwan University.
[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) (a) Saccomano, N. A. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Schreiber, S. L., Eds.; Pergamon Press: Oxford, 1991; Vol. 1. pp 173−209. (b) Cintas, P. *Synthesis* **1992**, 248.

(2) (a) Molander, G. A. *Chem. Rev.* **1992**, 29−68. (b) Sosnowski, J. J.; Danaher, E. B.; Murray, R. K., Jr. *J. Org. Chem.* **1985**, *50*, 2759. (c) Molander, G. A.; McKie, J. A. *J. Org. Chem.* **1991**, *56*, 4112. (d) Tabuchi, T.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1986,** *27*, 1195. (e) Okuda, S.; Nakatsuhkasa, K.; Oshima, K.; Nozaki, H. *Chem. Lett.* **1985**, 481. (f) Kan, T.; Nara, S.; Ito, S.; Matsuda.; Shirahama, H. *J. Org. Chem.* **1994**, *59*, 5111.

(3) For representative natural product syntheses involving intramolecular cyclization of allyl halides with aldehydes and ketone as the key step, see: (a) Rayner, C. M.; Astles, P. C.; Paquette, L. A. *J. Am. Chem. Soc.* **1992**, *114*, 3926. (b) Still, W. C.; Mobilio, D. *J. Org. Chem.* **1983**, *48*, 4785. (c) Shibuya, H.; Ohashi, K.; Kawashima, K.; Hori, K.; Murakami, N.; Kitagawa, I. *Chem. Lett.* **1986**, 85. (d) Kato, N.; Tanaka, S.; Takeshita, H. *Chem. Lett.* **1986,** 1989. (e) Wender, P. A.; McKinney, J. A.; Mukai, C. *J. Am. Chem. Soc.* **1990**, *112*, 5369.

(4) For representative product syntheses involving intramolecular cyclization of vinyl halides with aldehydes and ketone as the key step, see: (a) Corey, E. J.; Munroe, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 6129. (b) Schreiber, S. L.; Meyers, H. V. *J. Am. Chem. Soc.* **1988**, *110*, 5198. (c) Aicher, T. D.; Buszek, K. R.; Fang, F. G.; Forsyth, C. J.; Jung, S. H.; Kishi, Y.; Matelich, M. C.; Scola, P. M.; Spero, D. M.; Yoon, S. K. *J. Am. Chem. Soc.* **1992**, *114*, 3162. (d) Rowly, M.; Kishi, Y. *Tetrahedron Lett.* **1988**, *29*, 4909. (e) Sakae, A.; Wang, T. C.; Kibayashi, C. *J. Am. Chem. Soc.* **1993**, *115*, 11393. (f) Isono, N.; Mori, M. *J. Org. Chem.* **1995**, *60*, 115.

(5) (a) Yamamoto, H. In *Comprehensive Organic Synthesis: Addition to C−X π Bonds Part II*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, Chapter 1.3, p 81. (b) Panek, J. S. In *Comprehensive Organic Synthesis: Addition to C−X π Bonds Part II*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Chapter 2.5, p 580.

(6) (a) Imai, T.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1994**, 277. (b) Place, P.; Verniere, C.; Gore, J. *Tetrahedron* **1991,** *37*, 1359. (c) Rozema, M. J.; Knochel, P. *Tetrahedron Lett.* **1991,** 1855.

(7) Aurrewechea, J. M.; Anton, R. F. S. *J. Org. Chem.* **1994**, *59*, 702.

(8) (a) Marshall, J. A.; Wang, X.-j. *J. Org. Chem.* **1992**, *57*, 3387. (b) Marshall, J. A.; Wang, X.-j. *J. Org. Chem.* **1991**, *56*, 6264.

(9) (a) Borzilleri, R. M.; Weinreb, S. M. *J. Am. Chem. Soc.* **1994**, *116*, 9789. (b) Tius, M.; Culligham, J. M. *Tetrahedron Lett.* **1898**, *30*, 3749.

S0022-3263(95)02183-9 CCC: $12.00

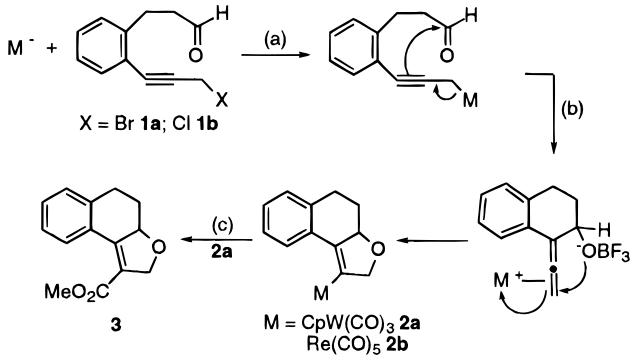
[3 + 2] cycloaddition of propargyl halides with aldehydes, yielding η^1-2,5-dihydrofuryl compounds[10,11] in excellent yields (85−90%); the intermediate was a tungsten η^1-propargyl species that could be isolated. In this case, the formation of 2,5-dihydrofuran products is unprecedented in the chemistry of metal propargyl and allenyl complexes.[5,12,13] The cycloaddition, however, fails to proceed with ketones. We now extend this methodology to an intramolecular system to yield fused 2,5-dihydrofurans of various types. Moreover, the cyclization applies to both aldehydes and ketones.

Results and Discussion

Similar to $CpW(CO)_3Na$,[14] $Re(CO)_5Na$ and $CpFe(CO)_2Na$ in conjunction with BF_3 promoted [3 + 2] cycloaddition of propargyl bromide to aldehydes to give metalated η^1-2,5-dihydrofur-3-yl compounds in ca. 80 and 50% yields, respectively. In an earlier report,[15] these three anions were found to be reactive toward aldehydes. Hence, the key feature to utilize these anions for successful intramolecular annulation relies heavily on their kinetic differentiations toward these two functionalities. The prerequisite is that the anion should react more rapidly with the propargyl halides.[9] We first examined the cyclization of the substrates **1a**,**b**[16] with these metal anions; Scheme 2 summarizes the results. To achieve the maximum effect of kinetic differentiation, a THF solution of metal anion was slowly added to **1** in THF at 0 °C. The addition was carried out in three portions with a 30-min interval. Monitoring the solution by silica TLC plate showed the formation of a tungsten−η^1-propargyl complex[17] that was extracted with diethyl ether and subsequently treated with $BF_3{\cdot}Et_2O$ (0.50 equiv) at −40 °C. After 3 h, the solution was gradually warmed to 23 °C and quenched with aqueous $NaHCO_3$ solution. After chromatography, the organometallic products **2a**,**b** (entries 1−5, Scheme 2) were shown to be bicyclic η^1-2,5-dihydro-3-furyl complexes based on spectral data and elemental analysis. Scheme 2 shows the pathway leading to **2a**,**b** through an allene cationic species. If 2 equiv of $CpW(CO)_3Na$ are used, the yields decrease drastically from 57% to 5%. Such a decrease implies that the anion reacts irreversibly with both propargyl halides and aldehydes. As expected, propargyl bromide (**1a**) is superior to its chloride analogue (**1b**) with a significant difference in the yields (entries 1 and 3, Scheme 2). In addition, $CpW(CO)_3Na$ was more effective than the other two anions (entries 4 and 5, Scheme 2); $CpFe(CO)_2Na$ failed to give the corresponding η^1-propargyl species as monitored by TLC and ^1H NMR spectroscopy even if 1 equiv of iron anion was used. An important feature of the tungsten case is the lack of allenic−propargyl equilibrium[17,18] that avoids the formation of byproducts like η^1-2,3-dihydro-4-furyl or α-alkynylcycloalkanol compounds. Oxidative demetalation of **2a** with $(NH_4)Ce(NO_3)_6$ in CH_3OH/CH_2Cl_2 under flowing CO gas afforded 3-(methoxycarbonyl)-2,5-dihydrofuran **3** in 46% yield.

To expand the scope of cyclization, we have synthesized various organic substrates listed in Table 1, some of which are known in literature.[16,19] The remaining compounds are not difficult to prepare; the synthetic schemes and spectral data are listed in the supporting information. The substrates **4**−**10** (entries 1−7, Table 1) were used for the intramolecular cyclization of propargyl halides with aldehydes, whereas **11**−**13** were employed for the cyclizations with the tethered ketones (entries 8−10, Table 1). Experimental procedures for the cyclization reactions followed exactly those of **2a** involving the use of equilmolar proportions of $CpW(CO)_3Na$ and organic substrates. In most cases, the resulting tungsten

Scheme 2



Entry	X	M	X/M (molar ratio)	products (yields)
1	Br	$CpW(CO)_3$	1.0	**2a** (57 %)
2	Br	$CpW(CO)_3$	0.5	**2a** (5 %)
3	Cl	$CpW(CO)_3$	1.0	**2a** (35 %)
4	Br	$Re(CO)_5$	1.0	**2b** (25 %)
5	Br	$CpFe(CO)_2$	1.0	–

(a) 0 °C, THF, 3 h, (b) $BF_3{\cdot}Et_2O$ (0.5 equiv), -40 °C to 0 °C, 5 h (c) $(NH_4)_2Ce(NO_3)_6$ (3.0 equiv), CO (1 atm), CH_2Cl_2/CH_3OH, -78 °C, 2 h; -78 °C to 23 °C, 5 h.

(10) (a) Wang, S.-H.; Shiu, L.-H.; Shu, H.-G.; Liao, Y.-L.; Wang, S.-L.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1994,** *116*, 5967. (b) Shu, H.-G.; Shiu, L.-H.; Wang, S.-H.; Wang, S.-L.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 530.

(11) Shiu, L.-H.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. Unpublished results.

(12) For the application of metal−allenyl and propargyl compounds in organic synthesis, see the representative review papers in ref 5 and: (a) 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. (b) Epsztein, R. In *Comprehensive Carbanion Chemistry;* Buncel, E., Durst, T., Eds.; Elsevier: Amsterdam, 1984; Part B, p 107.

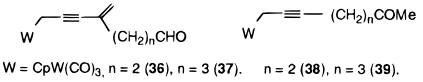
(13) For main group metal allenyl and propargyl compounds, see: (a) Seyferth, D.; Son, D. Y.; Shah S. *Organometallics* **1994**, *13*, 2105. (b) Brown, H. C. ; Khire, U. R.; Racherla, U. S. *Tetrahedron Lett.* **1993,** *34*, 15. (c) Brown, H. C.; Khire, U. R.; Narla, G.; Racherla, U. S. *J. Org. Chem.* **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.

(14) In this work, $CpW(CO)_3Na$ was prepared on heating a mixture of $W(CO)_6$ and NaC_5H_5 in THF for 72−84 h. It was also prepared by reduction of pure $Cp_2W_2(CO)_6$ with Na/Hg in THF. In this case, $Cp_2W_2(CO)_6$ should be free of the contamination with $W(CO)_6$. $Cp_2W_2(CO)_6$ is commercially available from Strem or Aldrich. Removal of $W(CO)_6$ from $Cp_2W_2(CO)_6$ is achieved in high vacuum (0.1 Pa, 50 °C, 48 h).

(15) Vargas, R. M.; Theys, R. D.; Hossain, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 777.

(16) Ciufolini, M. A.; Browne, M. E. *Tetrahedron Lett.* **1987**, *28*, 171.

(17) In this study, we have characterized several tungsten−η^1-propargyl complexes **36**−**39** (yields >80%). Here, we did not find any trace of tungsten−η^1-allenyl compounds to support a propargyl−allenyl equilibrium. Syntheses and spectral data of **36**−**39** are given in the supporting information.

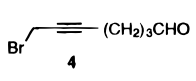
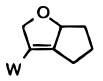
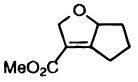
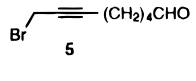
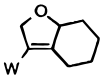
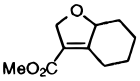
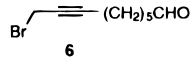
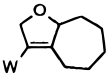
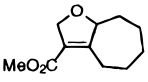
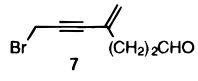
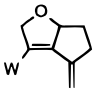
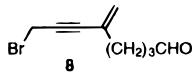
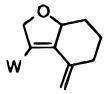
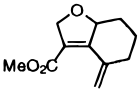
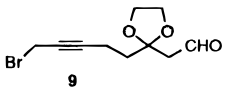
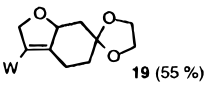
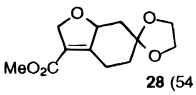
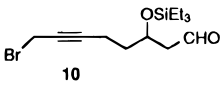
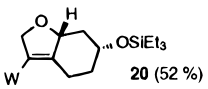
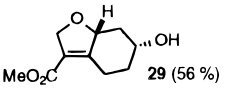
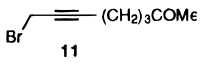
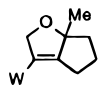
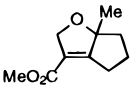
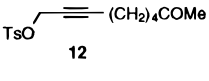
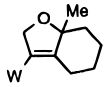
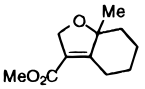
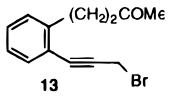
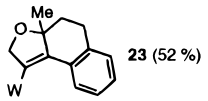
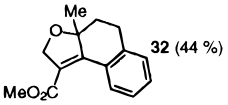


W = $CpW(CO)_3$, n = 2 (**36**), n = 3 (**37**). n = 2 (**38**), n = 3 (**39**).

(18) Bell, P. B.; Wojcicki, A. *Inorg. Chem.* **1981**, *20*, 1585.

(19) (a) Haynes, R. K.; Lambert, D. E.; Parafiniuk, K. A.; Schober, P. A.; Turner, S. G. *Aust. J. Chem.* **1987**, *40*, 273. (b) Cossy, J.; Pete, J. P. *Tetrahedron Lett.* **1986**, *27*, 573.

Table 1. Reaction Scheme and Isolated Yields of Tungsten−η^1-2,5-Dihydrofuryl Complexes and Fused 3-(Methoxycarbonyl)-2,5-dihydrofurans

Entry	Substrate[a]	L.A[b]	2,5-Dihydro-3-furyl[c,d]	Unsaturated Ester[e]
1	 **4**	--	 **14**[f] (66 %)	 **24** (56 %)
2	 **5**	$LiClO_4$	 **15** (60 %)	 **25** (58 %)
3	 **6**	$BF_3{\cdot}Et_2O$	 **16** (50 %)	 **26** (55 %)
4	 **7**	--	 **17**[f] (40 %)	----
5	 **8**	$BF_3{\cdot}Et_2O$	 **18** (52 %)	 **27** (50 %)
6	 **9**	$BF_3{\cdot}Et_2O$	 **19** (55 %)	 **28** (54 %)
7	 **10**	$BF_3{\cdot}Et_2O$	 **20** (52 %)	 **29** (56 %)
8	 **11**	$BF_3{\cdot}Et_2O$	 **21** (59 %)	 **30** (55 %)
9	 **12**	$BF_3{\cdot}Et_2O$	 **22** (68 %)	 **31** (63 %)
10	 **13**	$BF_3{\cdot}Et_2O$	 **23** (52 %)	 **32** (44 %)

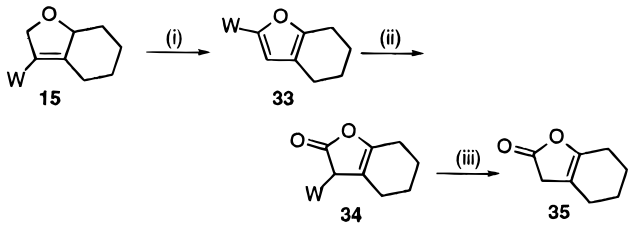
[a] Equimolar ratios of CpW(CO)3Na and organic substrates were used. [b] Lewis acid in equimolar proportions was used. [c] These organometallic compounds were purified on a silica column except **14** and **17**.[f] [d] Isolated yields after chromatographic purification. [e] Isolated yields after purification by preparative silica TLC. [f] Compounds **14** and **17** were purified on a Florisil column at 0 °C.

η^1-propargyl compounds[17] were subsequently treated with a suitable Lewis acid such as $BF_3{\cdot}Et_2O$ or $LiClO_4$. The yields of η^1-2,5-dihydro-3-furyl compounds **14**−**23** are shown in Table 1. The tungsten η^1-heterocycles were decomplexed with $(NH_4)_2Ce(NO_3)_6$[20] in CH_3OH/CH_2Cl_2 under flowing CO (1 atm) to afford the bicyclic unsaturated esters **24**−**32** in the yields shown in Table 1. No Lewis acid was required for the annulation of five-membered rings such as **14** and **17** (entries 1 and 4, Table 1) whereas $LiClO_4$ was sufficiently acidic to effect the cyclization yielding **15** (entry 2, Table 1) in 60% yield. Most of the fused η^1-2,5-hydrofur-3-yl compounds in Table 1 were purified by chromatography through a silica column. The exceptions were **14** and **17** that were chromatographed through a short Florisil column at 0 °C. Entries 1−3 are fused unfunctionalized 2,5-dihydrofurans of five- to seven-membered rings. The molecular structures of **15** and **16** have been determined by X-ray diffraction studies.[21] The cyclization was extended to functionalized substrates **7**−**10** (entries 4−9, Table 1). Entries 4−5 (Table 1) show fused dihydrofurans containing an external $=CH_2$ bond that increases the ring strain. Consequently, the five-membered ring product **17** was slightly thermally unstable at 23 °C, and the yield is low (40%). Oxidative demetalation of **17** by $(NH_4)_2Ce(NO_3)_6$ in the $CH_3OH/CH_2Cl_2/CO$ system failed to produce the corresponding 3-(methoxycarbonyl)-2,5-dihydrofuran. The annulation reactions on **9** and **10** were examined to study the effect of a bulky substituent; the yields of the resulting products **19** and **20** were 55% and 52%, respectively. Notably, only a single diastereomer was found for **20** of which the *cis*-configuration was indicated by proton NOE difference spectroscopy. In this case, irradiation of the C_9 proton signal (δ 4.80 ppm) of **20** led to an increase of the C_7 proton intensity (δ 4.18 ppm) by 4.5%. Ce(IV) oxidation of **20** in the $CH_3OH/CH_2Cl_2/CO$ system led to desilylation to give **29** in 56% yield. Although tungsten−η^1-propargyl compounds failed to react with ketones intermolecularly,[10] the intramolecular annulation of **11**−**13** proceeded smoothly yielding η^1-dihydrofuryl compounds of five- and six-membered rings such as **21**−**23** in 52−68% yields (entries 8−10, Table 1). Likewise, Ce(IV)-oxidative demetalations of **21**−**23**

(20) Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *J. Am. Chem. Soc.* **1982,** *104,* 5790.

(21) Crystal data of **15**, **16**, and **34** including ORTEP drawing, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Scheme 3[a]



[a] Key: W = $CpW(CO)_3$; (i) Ph_3CBF_4 (1.5 equiv, CH_2Cl_2, 0 °C, 1 h); (ii) $NaHCO_3$ *m*-CPBA (1.2 equiv, 0 °C, 1.5 h), NaOAc/HOAc; (iii) $Me_3NO{\cdot}H_2O$ (3.0 equiv, 23 °C, 2 h).

further provided bicyclic unsaturated ester **30**−**32** in 44−63% yields.

Our previous work[10] demonstrated that the tungsten−η^1-2,5-dihydro-3-furyl complex can be oxidized to η^1-furyl and further to Δ^3-butenolide derivatives. Extending these oxidations to fused η^1-2,5-dihydro-3-furyl compounds is of interest. Treatment of **15** with Ph_3CBF_4 (1.5 equiv) in CH_2Cl_2 (0 °C, 1.0 h) and then quenching with $NaHCO_3$(aq) delivered **33** in 83% yield (Scheme 3).[10] The conversion of **15** to **33** represents an oxidative rearrangement of a η^1-2,5-dihydro-3-furyl to η^1-2-furyl derivative, of which the mechanism has been elucidated previously.[10b] Subsequent oxidation of **33** with *m*-CPBA (2.0 equiv, 0 °C) in hexane with a NaOAc/HOAc buffer gave fused Δ^3-butenolides **34** in 73% yield. Further demetalation of **34** with $Me_3NO{\cdot}H_2O$ (3.0 equiv) produced **35** in 75% yield. The molecular structure of **34** was determined from an x-ray diffraction study.[21] Unfortunately, we could not decomplex **33** with various oxidants including Ce(IV), I_2, and *m*-CPBA to liberate one major furan. Instead, a mixture of several organic products was produced.

In conclusion, we have demonstrated the use of $CpW(CO)_3Na$ for intramolecular cyclization of propargyl bromides with tethered aldehydes and ketones. $CpW(CO)_3Na$ shows kinetic differentiation toward the two functional groups, thereby producing functionalized η^1-2,5-dihydro-3-furyl complexes of five-, six-, and seven-membered rings in moderate yields. The η^1-five-membered heterocycles are demetalated by Ce(IV) oxidation in CH_2Cl_2/CH_3OH. Although consecutive oxidations of η^1-2,5-dihydro-3-furyl compounds to η^1-2-furyl and η^1-butenolides are successful, the oxidative demetalation of η^1-2-furyl derivative is not.

Experimental Section

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere in oven-dried glassware using standard syringe, cannula, and septa apparatus. Benzene, diethyl ether, tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane was dried over CaH_2 and distilled before use. $W(CO)_6$, $Re_2(CO)_{10}$, $Cp_2Fe_2(CO)_4$, $BF_3{\cdot}Et_2O$, dicyclopentadiene, propargyl alcohol, and sodium were obtained commercially and used without purification. Organic substrates **1a**,[16] **1b**,[16] and **4**−**6**[19] were prepared according to literature reports. Syntheses and spectra data of **7-13, 15**−**23**, **25**−**32**, and **36**−**39** are listed in the supporting information.

Elemental analyses were performed at National Cheng Kung University, Taiwan. Mass data of tungsten and rhenium compounds were reported according to ^{184}W and ^{187}Re isotopes.

General Procedure for the Intramolecular Cyclization of Propargyl Halides with Aldehydes or Ketones. Annulation of 1-(3-Bromo-1-propynyl)-2-(3-oxopropyl)benzene (1a) with $CpW(CO)_3Na$. $W(CO)_6$ (3.75 g, 10.7 mmol) and NaC_5H_5 (1.03 g, 11.8 mmol) were heated in THF (150 mL) for 84 h. To a THF solution (5.00 mL) of **1a** (2.60 g, 10.7 mmol) was added dropwise the above $CpW(CO)_3Na$ solution in three portions at 30-min intervals. Monitoring the solution by silica TLC showed the formation of an η^1-propargyl species (diethyl ether/hexane = 1/1, R_f = 0.82). The solution was stirred for 2 h at the same temperature before it was evaporated to dryness in vacuo. The η^1-propargyl species was extracted with diethyl ether (2 × 20 mL) and filtered under a nitrogen atmosphere. To the ether filtrate (ca. 35 mL) was added $BF_3{\cdot}Et_2O$ (0.752 g, 5.30 mmol) at −40 °C, and the mixture was slowly warmed to 0 °C over a period of 4 h. The cyclization was monitored by silica TLC (**2a**, diethyl ether/hexane = 1/1, R_f = 0.51), and the solution was added to a saturated $NaHCO_3$ solution (10 mL). The organic layer was separated and chromatographed through a short silica column at 23 °C (diethyl ether/hexane = 1/1) to yield **2a** (3.07 g, 6.10 mmol, 57%) as a yellow solid (mp 97−99 °C dec): IR 2013, 1915 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.9 Hz, 1H), 7.21−7.08 (m, 3H), 5.62 (s, 5 H), 4.73 (m, 1H), 4.57 (dd, J = 8.5, 4.6 Hz, 1H), 4.53 (dd, J = 8.5, 4.0 Hz, 1H), 2.98−2.86 (m, 2H), 2.20 (m, 1H), 1.71 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) 227.2, 215.9, 214.5, 144.2, 137.2, 133.4, 128.6, 126.5, 126.4, 125.2, 114.9, 91.3, 89.3, 85.2, 31.4, 28.9; MS m/z 504 (M^+), 448 (M^+ − 2CO). Anal. Calcd for $C_{20}H_{16}WO_4$: C, 47.64; H, 3.20. Found: C, 47.70; H, 3.35.

Annulation of 1a with $NaRe(CO)_5$. $NaRe(CO)_5$ (2.80 g, 8.05 mmol), **1a** (2.00 g, 8.05 mmol), and $BF_3{\cdot}Et_2O$ (0.570 g, 4.02 mmol) afforded **2b** (1.01 g, 2.00 mmol, 25%) as a yellow solid (mp 67−69 °C dec): IR 2120, 2050, 2008 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 7.4 Hz, 1H), 7.10−7.25 (m, 3H), 5.38 (dd, J = 12.0, 3.1 Hz, 1H), 5.29 (dd, J = 12.0, 3.1 Hz, 1H), 3.06 (ddd, J = 12.0, 6.9, 5.2 Hz, 1H), 2.84 (ddd, J = 12.4, 7.0, 5.6 Hz), 2.14 (m, 1H), 1.95 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 212.0, 135.4, 129.3, 128.8, 127.3, 126.9, 126.3, 107.1, 81.9, 67.6, 30.7, 26.2; MS m/z 498 (M^+). Anal. Calcd for $C_{17}H_{11}ReO_6$: C, 41.04; H, 2.23. Found: C, 40.90; H, 2.48.

Annulation of 7-Bromo-5-heptynal (4) with $CpW(CO)_3Na$. $CpW(CO)_3Na$ (1.90 g, 5.30 mmol) and **4** (1.00 g, 5.29 mmol) afforded **14** (1.54 g , 3.50 mmol, 66%) as a yellow solid (mp 37−39 °C dec): IR 2018, 1908 cm^{-1}; ^1H NMR (400 MHz, C_6D_6) δ 5.10−5.13 (m, 1H m), 4.97−5.03 (dd, J = 11.0, 4.5 Hz, 1H), 4.69−4.72 (dd, J = 11.0, 3.4 Hz, 1H), 4.49 (s, 5H), 2.17−2.22 (br t, J = 9.5 Hz, 1H), 1.84−1.97 (m, 3H), 1.68−1.81 (m, 1H) , 1.41−1.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 227.2, 214.9, 214.8, 159.3, 105.1, 94.8, 90.8, 90.5, 31.3, 24.3, 24.5; MS m/z 442 (M^+), 414 (M^+ − CO), 358 (M^+ − 3CO). Anal. Calcd for $C_{15}H_{14}WO_4$: C, 40.75; H, 3.19. Found: C, 40.88; H, 3.32.

General Procedure for Demetalations of η^1-2,5-Dihydro-3-furyl Complexes. Synthesis of 3. Compound **2a** (0.20 g, 0.40 mmol) in CH_2Cl_2/CH_3OH (1/1, 3.0 mL) was cooled to −78 °C, and CO was passed through the solution. To this was added dropwise a solution of $(NH_4)_2Ce(NO_3)_6$ (0.66 g, 1.20 mmol) in 5 mL of CH_3OH at the same temperature. The solution was warmed to 0 °C over a period of 2 h. Monitoring the solution by silica TLC plate showed formation of an organic component (diethyl ether/hexane = 1/1, R_f = 0.56). The solution was concentrated and purified by preparative silica TLC to yield **3** as a colorless oil (42 mg, 0.185 mmol, 46%): IR (Nujol) 1700, 1615 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 9.01 (d, J = 7.7 Hz, 1H), 7.12 (t, J = 7.7 Hz, 1H), 7.01 (t, J = 7.7 Hz, 1H), 6.80 (d, J = 7.7 Hz, 1H), 5.07 (dd, J = 12.6, 5.1 Hz, 1H), 4.96 (dd, J = 12.6, 5.1 Hz), 3.28 (s, 3H), 2.51−2.43 (m, 2H), 2.11−2.02 (m, 1H), 1.82−1.68 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 148.0, 138.8, 128.0, 130.4, 130.2, 128.6, 125.9, 120.4, 86.5, 76.3, 51.5, 31.2, 28.5; HRMS calcd for $C_{14}H_{13}O_3$ 229.0864, found 229.0861.

Synthesis of 24. Compound **14** (0.13 g, 0.298 mmol) and $(NH_4)_2Ce(NO_3)_6$ (0.50 g, 0.90 mmol) afforded **24** as a colorless oil (28 mg, 0.167 mmol, 56%): IR (Nujol) 1700, 1615 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.18−5.13 (1H, m), 5.02−4.97 (2H, m), 3.75 (3H, s), 2.72−2.63 (1H, m), 2.39−2.32 (1H, m), 2.11−1.98 (3H, m), 1.50−1.41 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 163.6, 121.3, 92.8, 80.2, 51.3, 30.6, 25.4, 22.4; HRMS calcd for $C_9H_{12}O_3$ 168.0786, found 168.0783.

Oxidation of 15 by Ph_3CBF_4. To a CH_2Cl_2 (20 mL) solution of **15** (1.00 g, 1.22 mmol) was added Ph_3CBF_4 (0.80 g, 2.62 mmol) in CH_2Cl_2 (3 mL) at 0 °C. The solution was stirred

for 1 h before quenching with saturated $NaHCO_3$. The organic layer was separated, dried over $MgSO_4$, and evaporated to dryness under vacuum. The residue was eluted through a silica column under nitrogen (diethyl ether/hexane = 1/1, R_f = 0.87) to yield **33** (0.82 g, 1.81 mmol, 83%) as a yellow oil: IR 2018, 1924 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.26 (s, 1H), 5.52 (s, 5H), 2.56 (t, J = 6.2Hz, 2H), 2.30 (t, J = 6.2Hz, 2H), 1.71−1.77 (m, J = 6.2Hz, 2H), 1.60−1.66 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 228.5, 216.7, 158.1, 134.7, 131.4, 119.7, 92.2, 22.2, 23.6, 23.8, 21.5; MS 454 (M^+), 426 ($M^+ - CO$), 398 ($M^+ - 2CO$), 370 ($M^+ - 3CO$). Anal. Calcd for $C_{16}H_{14}WO_4$: C, 42.30; H, 3.00. Found: C, 41.98; H, 3.20.

Oxidation of 33 by *m*-CPBA. To **33** (0.84 g, 1.85 mmol) in hexane (5 mL) were added NaOAc (0.20 g, 2.4 mmol) and HOAc (0.20 mL, 3.5 mmol). To this stirred mixture was added *m*-CPBA (0.34 g, 1.95 mmol) in CH_2Cl_2 (1 mL) at 0 °C. After being stirred 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 residue was chromatographed through a silica column (diethyl ether/hexane = 1/1) to yield **34** (R_f = 0.29, 0.64 g, 1.35 mmol, 73%) as an orange solid (mp 65−68 °C dec): IR 2021, 1923, 1734 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.45 (s, 5H), 3.74 (s, 1H) 2.23 (t, J = 7.2 Hz, 2H), 2.03 (t, J = 7.2 Hz, 2H), 1.76 (m, 2H), 1.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 227.5, 217.8, 216.6, 188.2, 140.9, 122.8, 92.9, 24.4, 22.7, 22.6, 22.2, 6.8; MS 470 (M^+), 442 ($M^+ - CO$), 414 ($M^+ - 2CO$), 386 ($M^+ - 3CO$). Anal. Calcd for $C_{16}H_{14}WO_5$: C, 40.86; H, 2.97. Found: C, 40.88; H, 3.15.

Demetalation of 34 by Me_3NO. To a solution of **34** (0.20 g, 0.43 mmol) in CH_2Cl_2 (5 mL) were added anhydrous Me_3NO (64 mg, 0.86 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), and the organic layer was extracted with diethyl ether, dried in vacuo, and eluted through a silica column (diethyl ether/hexane = 1/1) to produce **35** (R_f = 0.63, 45 mg, 0.32 mmol, 75%) as a colorless oil: IR 2057, 1964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.10 (m, J = 3.7 Hz, 2 H), 2.17 (td, J = 6.0, 3.7 Hz, 2 H), 2.00 (m, J = 7.9 Hz, 2H), 1.72 (m, J = 6.6, 6.0 Hz, 2H), 1.63 (m, J = 7.9, 6.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 150.5, 110.5, 36.0, 22.5, 22.3, 22.1; HRMS calcd for $C_8H_{10}O_2$ 138.0680, found 138.0677.

Acknowledgment. The authors thank the National Science Council, ROC, for financial support of this work.

Supporting Information Available: Listing of sample preparation, spectral data, and elemental analyses of organic and organometallic compounds including **7**−**13**, **15**−**23, 25**−**32**, and **36**−**39**[17] (60 pages). This material is contained in 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.

JO952183R