Tungsten-Mediated Syntheses of Fused α-Methylenebutyrolactones from Propargyl Bromides Containing Tethered Aldehydes and Ketones

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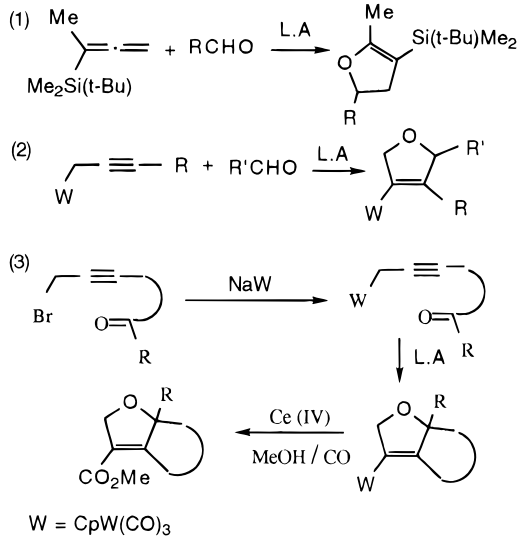
The reaction of $CpW(CO)_3Na$ with a number of propargyl bromides with tethered aldehydes and ketones afforded η^1-propargyl species that were subsequently transformed into tungsten−η^3-2-(methoxycarbonyl)allyl compounds upon treatment with *p*-TSA/CH_3OH; the overall yields exceeded 60%. Sequential treatment of these tungsten−η^3-allyl complexes with $NOBF_4$ and NaI in CH_3CN led to intramolecular allyltungsten−carbonyl cyclization, yielding fused α-methylene butyrolactones of five-, six-, and seven-membered carbocyclic rings. All the reactions proceeded with high diastereoselectivities except for 9-methylene-7-oxabicyclo[4.3.0]nonan-8-one (**22**) and 10-methylene-8-oxabicyclo[5.3.0]decan-9-one (**23**). Modification of the metal center with a chloride ligand led to significant improvement of the *trans*-stereoselection of **22**; the chloride modification did not significantly enhance stereoselection of **23**. The stereochemical course of the reaction products is rationalized on the basis of a bicyclic transition-state mechanism.

Introduction

Metal carbonyls such as $CpFe(CO)_2$, $M(CO)_5$ (M = Mn, Re), and $CpM(CO)_3$ (M = Mo, W) are important functionalities in organometallic chemistry.[1,2] These carbonyls are also useful reagents for organic syntheses[3,4] because they resemble the trimethylsilyl group as electron-donating groups.[5] The similarity of these two functional groups is best manifested by the same reaction chemistry in Lewis acid-promoted alkylation of their allyl, propargyl, and allenyl compounds[3−5] with organic carbonyls; these two types of organometallics can afford both [3 + 2] cycloaddition and S_E'-addition reaction products under suitable conditions. Scheme 1 (eqs 1 and 2) shows the examples of [3 + 2] cycloaddition of allenylsilane[6] and tungsten−propargyl compounds[4b] *via* condensation with aldehydes, yielding 2,3-dihydrofurans and 2,5-dihydrofurans, respectively.

Previously, we have examined the reactions between metal carbonyl anions with propargyl bromides containing tethered aldehydes and ketones as depicted in Scheme 1 (eq 3).[7] In this 1:1 stoichiometric reaction,

Scheme 1



$CpW(CO)_3Na$ showed kinetic differentation for the two functional groups; it reacted more rapidly with propargyl bromide to yield tungsten−propargyl species in high yields (>85%). In contrast, other metal anions such as $CpFe(CO)_2Na$ and $Re(CO)_5Na$ gave the corresponding propargyl species in low yields (0−30%).[7] One important feature of these tungsten−propargyl complexes is the lack of allenyl−propargyl equilibrium. As shown in Scheme 1 (eq 3), treatment of these tungsten−propargyl species with a suitable amount of Lewis acid delivered fused tungsten−2,5-dihydrofuryl compounds of five-, six-, and seven-membered carbocyclic rings, further providing bicyclic unsaturated ester after Ce(IV) oxidation.[7] In this study, we wish to report utilization of these functionalized propargyl complexes for the stereocontrolled syntheses of α-methylene butyrolactones fused with five-, six-, and seven-membered carbocyclic rings; the key step

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1997.

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(7) Shieh, S.-J.; Tang, T.-C.; Lee, J.-H.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Org. Chem.* **1996**, *61*, 3245.

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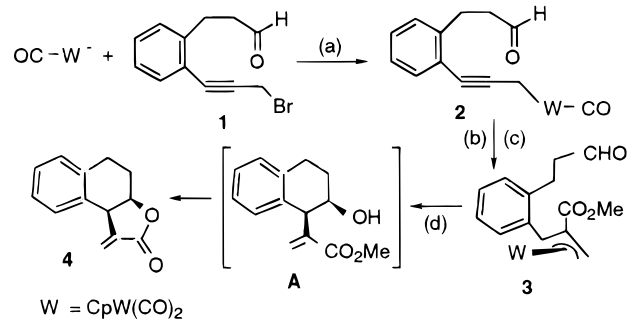
Scheme 2[a]



[a] Key: (a) 0 °C, THF, 3 h; (b) *p*-TSA (0.2 equiv)/MeOH; (c) acetone/water/*p*-TSA (0.2 equiv); (d) $NOBF_4$ (1.0 equiv)/CH_3CN; NaI (2.0 equiv).

involves intramolecular allyltungsten−carbonyl annulations (Scheme 2). Efficient synthesis of fused α-methylene butyrolactones[8−12] has attracted considerable attention in organic synthesis due to their important biological activities.[13]

Results

The η^1-propargyl compound **2** was readily prepared from the 1:1 stoichiometric reaction between $CpW(CO)_3Na$ and 3-[2-(3-bromoprop-1-ynyl)phenyl]propionaldehyde (**1**).[7] We previously reported that tungsten−η^1-propargyl species underwent alkoxycarbonylation reaction[4a] in the presence of Bronsted acid catalyst. Subsequent treatment of **2** with *p*-toluenesulfonic acid catalyst (0.20 equiv) in MeOH, followed by hydrolysis, afforded the tungsten η^3-2-(methoxycarbonyl)allyl compound **3** in 68% overall yield on the basis of the propargyl bromide **1**. To achieve the synthesis of fused α-methylene butyrolactone, compound **3** was sequentially treated with $NOBF_4$ (1.0 equiv) and NaI (2.0 equiv) in CH_3CN (23 °C) to generate a derivative of CpW(NO)I(π-allyl) that functions as an allyl anion[14] and thus induce intramolecular cyclization. After 2 h at 23 °C, workup of the solution afforded a 60% yield of **4** that has the *cis*-configuration according to proton NOE spectra and the magnitude of the coupling constant J = 8.0 Hz.[8,10] The primary product of this solution is believed to be 2-hydroxy-1,2,3,4-tetrahydronaphthalene-1-carboxylic acid methyl ester **A**, which readily undergoes lactonization under the reaction conditions.

To expand the scope of this methodology, we have synthesized organic substrates **5**−**12** listed in Table 1, which are already reported in our provious paper.[7] Experimental procedures for syntheses of tungsten−allyl compounds **13**−**15** and **17**−**20** and α-methylenebutyrolactones **21**−**27** followed exactly those of **3** and **4** (Scheme 2). The η^1-propargyl species generated from $CpW(CO)_3Na$ and **5**−**12** were directly transformed into π-allyl complexes **13**−**15** and **17**−**20** by *p*-toluenesulfonic acid/CH_3OH; the isolated yields were estimated on the basis of propargyl bromides. Generation of α-methylenebutyrolactone from the corresponding tungsten−allyl compound was performed at least twice, and the yields in Table 2 reflect an average of two runs with a distribution range within 2%. Entries 1−3 (Table 2) show the substrates **5**−**7** that were used for the syntheses of α-methylenebutyrolactones fused with five-, six-, and seven-membered rings **21**−**23**. In entry 1 (Table 2), compound **5** was used as a dioxolane form because the η^1-propargyl species generated from 7-bromo-5-heptynal underwent rapid intramolecular cyclization, yielding tungsten−η^1-2,5-dihydrofuryl species even in the absence of Lewis acid.[7] The stereochemistries of **21**−**23** were determined from proton NOE difference spectra and further confirmed with spectral data of authentic samples.[8−10] The *cis*-fused isomer of five-membered carbocyclic lactone **21**[8] was produced exclusively in 53% yield (Table 2, entry 1) whereas a mixture of *trans*/*cis* isomers were found for the formation of six- and seven-membered carbocyclic rings **22**[10]−**23**[12] (Table 2, entries 2 and 3). In the case of **21**, proton NMR spectra of the crude product showed only the signals assignable to the *cis*-isomer; no NMR signals could be found for the *trans*-isomer[8] or its *trans*-cyclopentanol precursor **A**. Separations of the two isomers of **22** and **23** were conducted on preparative SiO_2 TLC that provided the *trans*/*cis* ratios 5/2 and 1/1 for **22** and **23**, respectively. This methodology is not applicable to the reaction involving tungsten−η^3-pentadienyl species (Table 2, entry 4). In this case, compound **16** was isolated in 67% yield; this information implies that the resulting allyl compound is not stable in acidic methanol medium. The *cis*/*trans* stereoselection of α-methylenebutyrolactones depends not only on the ring sizes but also on the types of organic carbonyls. Entries 5−8 (Table 2) show the results for organic substrates **9**−**12** containing tethered ketones. Good yields were obtained for both tungsten allyl compounds **17**−**20** and α-methylenebutyrolactones **24**−**27**. Similar to **21**, *cis*-fused five-membered ring **24**[8] was formed exclusively in 70% yield (Table 2, entry 5) . In contrast with **22**, formation of six-membered carbocyclic lactone **25**[8] follows *cis*-stereoselection (Table 2, entry 6) in 65% yield. For the substrates having a fused benzene ring such as **11** and **12** (Table 2, entries 7 and 8), the resulting tricyclic lactones **26** and **27** have *cis*-configurations on their newly formed six- and seven-membered rings. The results in Table 1 suggest that our method is convenient and efficient for the construction of bicyclic α-methylene butyrolactones from bromoalkynals and -alkynones.

Stereochemical control in intramolecular addition of allyl organometallics to organic carbonyl in the formation of five-, six-, and seven-membered carbocyclic rings is an important issue in organic chemistry.[9,15−17] Previously, Faller et al. reported[14c,18] that CpMo(NO)Cl(π-crotyl) was better than CpMo(NO)I(π-crotyl) in the stereoselective synthesis of homoallylic alcohols *via* condensation with benzaldehyde. Therefore, we attempted to improve the

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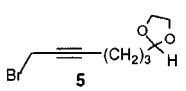
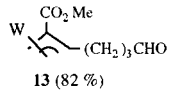
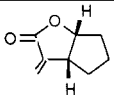
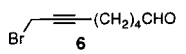
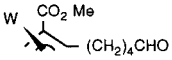
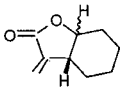
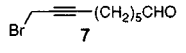
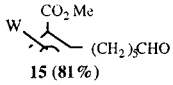
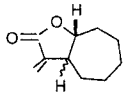
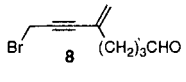
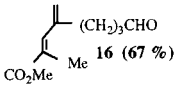
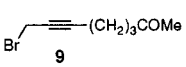
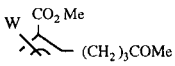
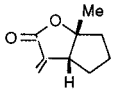
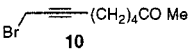
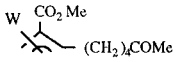
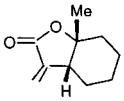
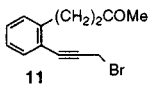
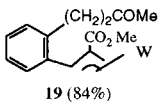
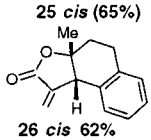
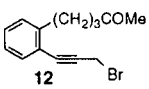
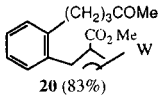
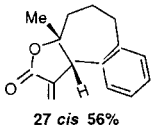
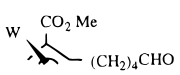
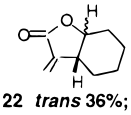
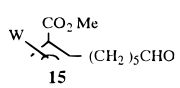
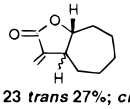
(9) (a) Semmelhack, M. F.; Wu, E. S. C. *J. Am. Chem. Soc.* **1976**, *98*, 3384. (b) Semmelhack, M. F.; Yamashita, A.; Tomesch, J. C.; Hirotsu, K. *J. Am. Chem. Soc.* **1978**, *100*, 3945.
(10) (a) Petragnani, N.; Ferraz, H. M. C. *Synthesis* **1978,** 476. (b) Grieco, P. A.; Miyashita, M. *J. Org. Chem.* **1974**, *120*, 39.
(11) Nishitani, K.; Yamakawa, K. *Tetrahedron Lett.* **1991**, *32*, 387.
(12) Kuroda, C.; Shimizu, S.; Satoh, J. Y. *J. Chem. Soc., Chem. Commun.* **1987**, 286.
(13) For review papers of the chemistry of α-methylenebutyrolactones see: (a) Hoffman, H. M. R.; Rabe, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 94. (b) Grieco, P. A. *Synthesis* **1975**, 67. (c) Sidduri, A. R.; Knochel, P. *J. Am. Chem. Soc.* **1992**, *114*, 7579 and references therein.
(14) (a) Faller, J. W.; Linebarrier, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 1937. (b) Faller, J. W.; John, J. A.; Mazzieri, M. R. *Tetrahedron Lett.* **1989**, *30*, 1769. (c) Faller, J. W.; Diverdi, M. J.; John, J. A. *Tetrahedron Lett.* **1991**, *32*, 1271.
(15) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207.
(16) (a) Keck, G. E.; Dougherty, S. M.; Savin, K. A. *J. Am. Chem. Soc.* **1995,** *117*, 6210. (b) Okuda, Y.; Nakasukasa, S.; Oshima, K.; Nozaki, H. *Chem. Lett.* **1985**, 481. (c) Drews, S. E.; Hoole, R. F. A. *Synth. Commun.* **1985**, *15*, 1067.
(17) Asao, K.; Lio, H.; Tokoroyama, T. *Tetrahedron Lett.* **1989**, *30*, 6397.

Table 1. Isolated Yields of Tungsten-η^3-2-(Methoxycarbonyl)allyl Complexes and Fused α-Methylenebutyrolactones

Entry	Substrate[a]	π-Allyl [b,c]	α-Methylene-butyrolactones[d,e]
1	 **5**	 **13** (82 %)	 **21 cis**-(53%)
2	 **6**	 **14** (82 %)	 **22** *trans* 36%; *cis* 15%
3	 **7**	 **15** (81%)	 **23** *trans* 27%; *cis* 28%
4	 **8**	 **16** (67 %)	----
5	 **9**	 **17** (88 %)	 **24** *cis* 70%
6	 **10**	 **18** (88 %)	 **25** *cis* (65%)
7	 **11**	 **19** (84%)	 **26** *cis* 62%
8	 **12**	 **20** (83%)	 **27** *cis* 56%

[a] Equimolar ratios of $CpW(CO)_3Na$ and organic substrates were used. [b] These organometallic compounds were purified on a silica column. [d] Isolated yields after chromatographic purification. [d] Isolated yields after purification by preparative silica TLC. [e] Yields were estimated based on tungsten-allyl compounds.

Table 2. Isolated Yields of Fused α-Methylenebutyrolactones over Different Metals and Halide Ligands

Entry	π-Allyl	MX	Temp	α-Methylene-but rolactones
1	 **14**	NaI	23 °C	 **22** *trans* 36%; *cis* 15%
2	**14**	LiCl	23 °C	**22** *trans* 62%
3	 **15**	NaI	23 °C	 **23** *trans* 27%; *cis* 28%
4	**15**	LiCl	23 °C	**23** *trans* 24%; *cis* 35%
5	**15**	LiCl	0 °C	**23** *trans* 42%; *cis* 21 %

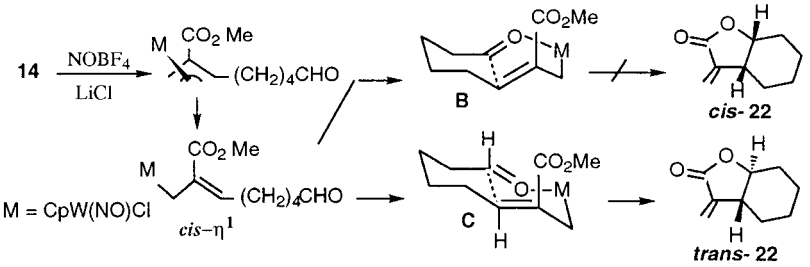
selectivities of **22** and **23** with modification of metal coordination with chloride ligand; the selectivities of compounds **22** and **23** were poor when the metal core is CpW(NO)I (Table 1, entries 2−3). A summary of the results is provided in Table 2. Fused α-methylenebutyrolactones **22** and **23** were generated from sequential treatment of the tungsten−π-allyl complex with $NOBF_4$ and MX (MX=NaI, LiCl) in CH_3CN at appropriate temperatures. The results in entries 1−4 (Table 2) reflect that chloride ligand is significantly better than iodide in the *trans*-stereoselection of **22**, consistent with Faller's results.[14c,18] Only the *trans*-fused isomer of **22** is produced in 62% yield when the metal core is CpW(NO)Cl. The chloride modification, however, did not give significant enhancement for stereoselection of the fused seven-membered carbocyclic ring **23** as shown from the results in entries 3−5 (Table 2). Notably, the reaction temperature effect is also important here; cyclization at 23 °C slightly favored the *cis*-fused isomer of **23** (entry 4, Table 2), whereas lower temperature (0 °C) preferably yielded the *trans*-fused isomer (entry 5, Table 2).

Discussion

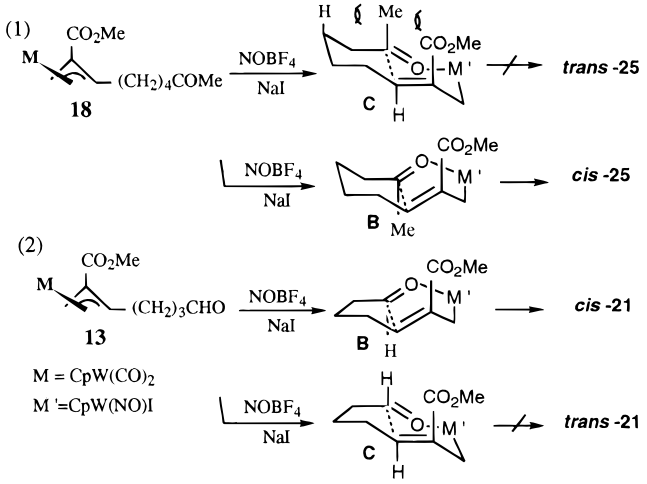
The results in Tables 1 and 2 reveals that the important factors in stereoselection of fused α-methylenebutyrolactones involve fused ring sizes and organic carbonyls. According to earlier reports by Faller, compounds

(18) Faller, J. W.; Nguyen T. N.; Mazzieri, M. *Organometallics* **1933**, *12*, 1434.

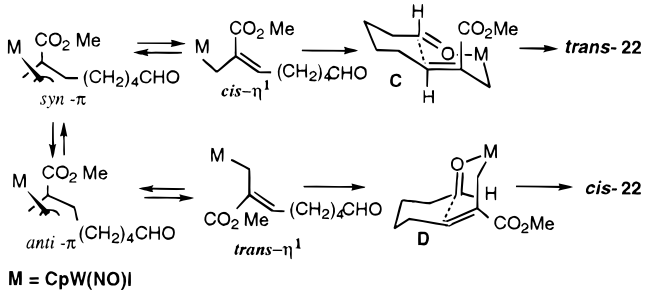
Scheme 3



Scheme 4



Scheme 5



of the type CpMo(NO)X(allyl) (X = halide)[4c,14,18] are prone to the $\eta^3 \rightarrow \eta^1$ allyl slippage to leave a coordination site for organic carbonyls, forming a chairlike transition state that controls stereoselection of homoallylic alcohols. Recently, we have utilized compounds of the type CpW(NO)I(allyl) for stereoselective syntheses of complex homoallylic alcohols; the mechanism followed a similar chairlike transition state. Here, we first rationalize preferable *trans*-stereoselection of **22** generated from π-allyl compounds **14**. Scheme 3 shows the two transition states **B** and **C** in which aldehyde coordinates to metal in a boatlike and chairlike conformation, ultimately yielding *cis* and *trans* products of **22**, respectively. In this case, we obtained excellent *trans*-stereoselection of **22** from the CpW(NO)Cl(π-allyl) derivative of **14**, indicative of a chairlike transition state **C** that is intrinsically less sterically hindered than the boat form **B**.

In the case of compound **18** in which a methyl ketone group replaces the aldehyde of **14**, the state **C** is destabilized by its axial methyl group, which suffers 1,3-diaxial interactions on both six-membered rings as shown in Scheme 4 (eq 1). Formation of the resulting product **25** thus follows *cis*-stereoselection *via* the boatolike state **B.** Such a stereochemical course also rationalizes the observed *cis*-stereoselections of bicyclic and tricyclic lactones **24**−**27** derived from several bromoalkynones in Table 1 (entries 5−8). Scheme 4 (eq 2) also shows two bicyclic transition structures to account for formation of fused lactones of five-membered carbocyclic ring **21**. Generation of *trans*-fused bicyclic carbocyclic ring **C** is more difficult to achieve due to the *trans* geometry on the newly formed five-membered ring; the predicted *cis*-stereoselection is compatible with our result.

Table 2 shows the halide effects of the CpW(NO)X core on the stereoselection of γ-lactones of six- and seven-membered carbocyclic rings **22** and **23**. Chloride ligand is better than iodo for the *trans*-stereoselection of **22**; this phenomenon is similar to the molybdenum case reported earlier by Faller.[14] The minor *cis*-product generated from CpW(NO)I may be attributed to the *cis*−*trans* isomerization of the η^1-allyl complex via *syn-anti-π*-W(NO)I(allyl) species as depicted in Scheme 5; this isomerization[19] was shown to be more kinetically facile on CpMo(NO)I but slow on CpMo(NO)Cl.[14] A similar effect may apply to our tungsten system, although attempts to prove this isomerization were unsuccessful. Further coordination of this η^1-*trans*-allyl species with aldehyde yields a chairlike transition state **D** to account for *cis*-stereoselection. The chloride modification did not improve the selectivity of seven-membered carbocyclic ring **23**. Table 2 (entries 4 and 5) shows that reaction temperature affects the *cis*/*trans* selectivity of **23**; this phenomenon reflects a very small difference in the energies of activation for *cis*/*trans* stereoselection.

Conclusion

We have demonstrated the use of $CpW(CO)_3Na$ for the syntheses of fused α-methylene butyrolactones of five to seven carbocyclic rings from propargyl bromides with tethered carbonyls. The key intermediates involve tungsten−η^1-alkynals or −η^1-alkynones that readily undergo acid-promoted alkoxycarbonylations in a MeOH solution, yielding tungsten-allyl complexes. Treatment of these allyl compounds with $NOBF_4$, and NaI induces intramolecular allyltungsten−carbonyl cyclization, yielding fused α-methylenebutyrolactones; the reaction proceeds with good diastereoselectivities in most cases except for 9-methylene-7-oxabicyclo[4.3.0]nonan-8-one (**22**) and 10-methylene-8-oxabicyclo[5.3.0]decan-9-one (**23**). Modification of the metal center with chloride ligand led to significant improvement in *trans*-stereoselection of **22**. The stereochemical courses of the intramolecular cyclization can be rationalized on the basis of a mechanism involving a bicyclic transition state.

Experimental Section

Unless otherwise noted, all reactions were carried out under nitrogen atmosphere in oven-dried glassware using a standard syringe, cannula, and septa apparatus. Benzene, diethyl ether,

(19) Faller, J. W.; Shvo, Y. *J. Am. Chem. Soc.* **1980**, *102*, 5396.

tetrahydrofuran, and hexane were dried with sodium benzophenone and distilled before use. Dichloromethane was dried over CaH_2 and distilled before use. $W(CO)_6$, *p*-toluenesulfonic acid, dicyclopentadiene, propargyl alcohol, and sodium were obtained commercially and used without purification. The syntheses of organic substrates **1** and **5**−**12** were described in our previous paper.[7] Syntheses and spectral data of compounds of the same family **14**−**20** and **22**−**27** in the repetitive operations, are listed in the Supporting Information.

Elemental analyses were performed at National Cheng Kung University, Taiwan. Mass data of molybdenum and tungsten compounds were reported according to ^{96}Mo and ^{184}W isotopes.

General Procedure for the Syntheses of Tungsten−η^3-3-(Methoxycarbonyl)allyl Compounds. Synthesis of 3. A suspension of $W(CO)_6$ (2.86 g, 8.00 mmol) and NaC_5H_5 (0.71 g, 8.0 mmol) in THF (30 mL) was heated for 84 h. To a THF solution (5.0 mL) of **1** (2.00 g, 8.00 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 **2** (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), filtered, and dried in vacuo. To the residue were added MeOH (20 mL) and *p*-toluenesulfonic acid (152 mg, 0.80 mmol) at 0 °C, and the mixture was stirred for 2 h before being dried in vacuo. The residues were redissolved in an acetone/water mixing solvent (v/v 10/1, 20 mL) containing additional *p*-TSA (150 mg, 0.80 mmol), and the mixture was heated at 80 °C for 2 h before a saturated $NaHCO_3$ solution was added. The organic layer was extracted with diethyl ether (3 × 25 mL), dried over $MgSO_4$, and concentrated. The residues were chromatographed through a silica column to yield **3** as a yellow oil (2.91 g, 5.44 mmol, 68%): IR (neat, cm^{-1}) υ(CO), 1966.3, 1898.9, 1722.1724; ^1H NMR (400 MHz, $CDCl_3$) *endo* isomer, δ 9.72 (1H, d, J = 4.0 Hz), 7.24−7.12 (m, 4H), 5.42 (5H, s), 3.48 (3H, s), 3.20 (m, 1H), 3.18 (s, 1H), 3.00 (s, 1H), 2.95 (m, 1H), 2.70 (m, 2H), 1.48 (s, 1H); *exo* isomer, δ 9.72 (1H, d, J = 4.0 Hz), 7.24−7.12 (m, 4H), 5.46 (5H, s), 3.58 (3H, s), 3.20 (m, 1H), 2.95 (m, 1H), 2.93 (s, 1H), 2.70 (m, 2H), 2.60 (s, 1H), 0.92 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) *exo* and *endo* isomers, δ 223.6, 223.7, 223.2, 219.3, 203.3, 202.9, 173.2, 170.8, 140.2, 139.9, 139.6, 137.1, 135.8, 134.7, 129.2, 128.8, 127.7, 127.4, 127.2, 126.6, 93.9, 89.2, 79.1, 70.3, 64.5, 61.0, 53.6, 52.4, 51.6, 44.5, 44.3, 27.5, 26.4, 26.1, 23.2; MS (EI, 12 eV) 536 (M^+), 508 (M^+ − CO), 480 (M^+ − 2CO). Anal. Calcd for $C_{21}H_{20}WO_5$: C, 47.04; H, 3.76. Found: C, 47.02; H, 3.77.

General Procedure for the Syntheses of Fused α-Methylenebutyrolactones. Synthesis of 1-Methylene-3a,4,5,9b-tetrahydro-1*H*-naphtho[2,1-*b*]furan-2-one (4). To a stirring CH_3CN (5 mL) solution of π-allyl compound **3** (1.00 g, 1.86 mmol) was slowly added a CH_3CN solution (1 mL) of $NOBF_4$ (218 mg, 1.86 mmol) at 0 °C; after 30 min, to the resulting solution was added NaI (550 mg, 3.72 mmol). The mixture was allowed to stir for 6 h at 23 °C before treatment with a saturated $NaHCO_3$ (2 mL) solution. The organic layer was extracted with diethyl ether (2 × 5 mL), concentrated, and eluted on a preparative TLC plate (diethyl ether/hexane = 1/1) to give **4** as an oil (R_f = 0.50, 224 mg, 1.12 mmol, 60%): IR (neat, cm^{-1}) υ(CO) 1768, 1660; ^1H NMR (400 MHz, $CDCl_3$) δ 7.24−7.12 (m, 4H), 6.25 (d, J = 2.8 Hz, 1H), 5.59 (d, J = 2.4 Hz, 1H), 5.06 (ddd, J = 8.2, 7.8, 4.2 Hz, 1H), 4.28 (dt, J = 7.8, 2.7 Hz, 1H), 2.66 (m, 2H), 2.19 (m, 1H), 1.85 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 138.8, 136.8, 134.5, 128.7, 127.2, 126.9, 123.3, 42.5, 28.3, 24.5; HRMS calcd for $C_{13}H_{12}O_2$ 200.0837, found 200.0841.

Synthesis of Tungsten−η^3-allyl Compound 13. $NaCpW(CO)_3$ (1.435 mmol), 2-(6-bromohex-4-ynyl)-1,3-dioxolane (**5**) (1.00 g, 4.31 mmol), and *p*-TSA/CH_3OH afforded **13** (1.68 g, 3.53 mmol) in 82% yield: IR (neat, cm^{-1}) υ(CO) 1958, 1886, 1708; ^1H NMR (400 MHz, $CDCl_3$, −40 °C) δ 9.73 (t, J = 2.0 Hz, 1H), 5.27 (s, 5H), 3.61 (s, 3H), 2.83 (s, 1H), 2.61 (m, 1H), 2.52 (dt, J = 7.5, 2.0 Hz, 1H), 2.20 (m, 1H), 2.05 (t, J = 7.2 Hz, 1H), 1.62 (quintet, J =7.2 Hz, 2H), 1.06 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, −40 °C) δ 224.3, 222.9, 203.4, 171.2, 88.0, 77.3, 51.1, 50.1, 43.7, 31.9, 25.1, 22.7; MS (EI, 12 eV) 474 (M^+), 446 (M^+ − CO), 418 (M^+ − 2CO). Anal. Calcd for $C_{16}H_{18}WO_5$: C, 40.53; H, 3.83. Found: C, 40.66; H, 3.88.

Synthesis of 2-Methylene-4-oxabicyclo[3.3.0]octan-3-one (21). Compound **13** (0.50 g, 1.05 mmol), $NOBF_4$ (123 mg, 1.05 mmol), and NaI (315 mg, 2.10 mmol) afforded **21** (77 mg, 53%) as a colorless oil: IR (neat, cm^{-1}) 1757.8, 1658.6; ^1H NMR (400 MHz, $CDCl_3$) δ 6.22 (d, J = 2.6 Hz, 1H), 5.67 (d, J = 2.6 Hz, 1H), 4.96 (t, J = 6.8 Hz, 1H), 3.39 (dt, J = 6.8 Hz, 2.2 Hz, 1H), 2.08 (m, 1H), 1.94 (m, 1H), 1.74−1.65 (m, 3H), 1.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 140.5, 122.7, 83.2, 42.9, 35.6, 33.6, 23.0; HRMS cacld for $C_8H_{10}O_2$ 138.0680, found 136.0680. The NMR and IR spectral data of **21** were identical to those of the authentic sample reported in literature.[8]

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

Supporting Information Available: Syntheses and spectral data of compounds of the same family **14**−**20** and **22**−**27** in the repetitive operations (6 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.

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