Tungsten(II)−Carbene Complex Functions as a Dicationic Synthon: Efficient Constructions of Furan and Pyran Frameworks from Readily Available α,δ- and α,ϵ-Alkynols

Kwei-Wen Liang,[†] Wen-Tai Li,[†] Shie-Ming Peng,[‡] Sue-Lein Wang,[†] and Rai-Shung Liu*,[†]

Contribution from the Department of Chemistry, National Tsing-Hua University, Hsinchu, 30043, Taiwan, R.O.C., and Department of Chemistry, National Taiwan University, Taipei, 10764, Taiwan, R.O.C.

Received January 2, 1997[⊗]

Abstract: Treatment of tungsten−η^1-α,δ- and −η^1-α,ϵ-alkynols **4**−**6** with RCHO/$BF_3 \cdot Et_2O$ (R = alkyl, aryl) in cold diethyl ether effected cycloalkenation reaction, yielding tungsten−η^1-furylidene and −η^1-pyrylidene salts in excellent yields (>95%). The structures of these oxacarbeniums were elucidated through X-ray diffraction studies of the representative compounds **7** and **8** in addition to standard NMR and IR spectral data. In contrast with conventional metal carbeniums, these tungsten oxacarbeniums reacted with two molecules of nucleophiles such as H_2O, $NaBH_3CN$, and Grignard reagents, resulting in α,α-double addition reactions to afford furan and pyran derivatives in good yields. In the hydride case, unsymmetric α,α-double addition of η^1-furylidenium salts was achieved via treatment with $NaBH_4$/MeOH. Organocuprates also effected double alkylations of these salts but in a distinct 1,3-addition pathway. The reactions of these oxacarbeniums with CH_2N_2 were examined; the outcome depends on their vinyl substituents. When the substituent is an aliphatic group, the carbenium species undergo highly diastereoselective cyclopropanation with CH_2N_2. For an aryl substituent, the reaction with CH_2N_2 yielded a new tungsten oxacarbenium with a significantly altered structure; in this case ^{13}C- and ^2H-labeling experiments were performed to elucidate the reaction mechanism.

Introduction

Although a vast number of low-valent transition metal carbene cations[1−3] have been prepared in the form of $CpMLn({=}CRR')^+$ (M = Fe, Ru, Os; Mo, W, Re; L = CO, R_3P, NO^+), compounds of this type are less useful than neutral Fisher chromium carbenes.[4,5] Even though cations of the type $CpFe(CO)_2({=}C_\alpha\text{-}RR')^+$ undergo stereoselective cyclopropanation with alkenes stoichiometrically,[6,7] the scope of this reaction is somewhat limited by the types both of olefins and of R and R′ substituents on the carbene C_α carbon. One common organometallic reaction of these carbeniums is the reaction with one nucleophile;[1−3] the resulting products have little synthetic value. Although several $CpML_2[{=}C(OR)R']^+$ (M = Fe, Ru, L = CO, R_3P) cations react with two nucleophiles, the reaction proceeded with cleavage of the C−O bond.[8,9]

We previously reported that propargyl tungsten compounds[10] are useful for synthesis of complex oxygen heterocycles, and the reaction pathway is significantly different from those of conventional propargyl silanes, stannanes, and boranes.[11] Alkynyl organometallics of main group[12] metals is less useful than their allyl and propargyl species. As a continuing effort to explore synthetic potential of unsaturated tungsten hydrocarbyl species,[10] we report here the utilization of tungsten−alkynols for the synthesis of new tungsten η^1-furylideniums or pyrylidiniums. A remarkable feature of these cations is their reactions with two molecules of nucleophiles to yield various oxygen heterocycles; details of this method are reported herein.

[†] National Tsing-Hua University.

[‡] National Taiwan University.

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

(1) (a) Hegedus, L. S. *Transition Metals in the Synthesis of Complex Organic Molecules*; University Science Books: Mill Valley, 1994; Chapter 6, p 151. (b) Casey, C. P.; Miles, W. M. *J. Organomet. Chem.* **1976**, *117*, 189. (c) Cutler, A.; Hanna, P. K.; Vites, J. E. *Chem Rev.* **1988**, 1363.

(2) (a) Schubert, U. *Advances in Metal Carbene Chemistry*; Kluwer Academic Publishers: Berlin, 1988. (b) Dotz, K. H.; Fischer, H.; Hofmann, P.; Kriessel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Diiefield Beach, FL, 1983.

(3) Representative examples, see: (a) Kiel, W. A.; Lin, G.-Y.; Bodner, G. S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 4958. (b) Brookhart, M.; Liu, Y.; Buck, R. C. *J. Am. Chem. Soc.* **1988**, *110*, 2337. (c) Casey, C. P.; Tukada, H.; Miles, W. H. *Organometallics* **1982**, *1*, 1083. (d) Baird, G. L.; Davies, S. G.; Makerly, T. R. *Organometallics* **1984**, *3*, 1764.

(4) (a) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: London, England, 1989; Vol. 1, p 209. (b) Dotz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(5) Hegedus, L. S. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press: New York, 1995; Vol. 12, Chapter 5, p 387.

(6) (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (b) Helquist, P. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: London, England, 1991; Vol. 2, p 209.

(7) (a) Brookhart, M.; Liu, Y.; Goldman, E. W.; Tommers, D. A.; Williams, G. D. *J. Am. Chem. Soc.* **1991**, *113*, 927. (b) Brookhart, M.; Liu, Y. *J. Am. Chem. Soc.* **1991**, *113*, 939.

(8) (a) Bodnar, T.; Coman, G.; Lacroce, C.; Lambert, C.; Menard, K.; Cutler, A. R. *J. Am. Chem. Soc.* **1981**, *103*, 2471. (b) Davison, A.; Martinez, N. *J. Organometal. Chem.* **1974**, *74*, C12.

(9) Consiglio, G.; Morandini, F.; Ciani, G. F.; Sironi, A. *Organometallics* **1986**, *5*, 1976.

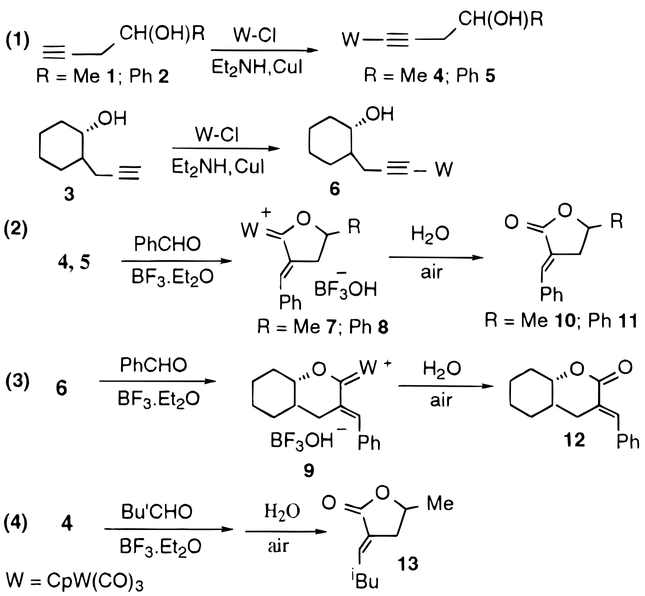
(10) (a) Wang, S.-H.; Shiu, L.-H.; Shu, H.-G.; Liao, Y.-L.; Wang, S.-L.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1994,** *116*, 5967. (b) Chen, C.-C.; Fan, J.-S.; Lee, G.-H.; Peng, S.-M.; Wang, S.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **1995**, *117*, 2933. (c) Shu, H.-G.; Shiu, L.-H.; Wang, S.-H.; Wang, S.-L.; Lee, G.-H.; Peng, S.-M.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 530. (d) Chen, C.-C.; Fan J.-S.; Shieh, S.-J.; Lee, G.-H.; Peng, S.-M.; Wang, S.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **1996**, *118*, 9279.

(11) Representative examples: (a) Herndon, J. W.; Wu, C. *Synlett* **1990**, *1*, 411. (b) Danheiser, R. L.; Takahashi, T.; Bertok, R.; Dixon, B. R. *Tetrahedron Lett.* **1993**, *34*, 3845. (c) Danheiser, R. L.; Ksasigroch, C. A.; Tsai, Y. M. *J. Am. Chem. Soc.* **1985**, *107*, 7233. (d) Panek, J. S.; Yang, M. *J. Am. Chem. Soc.* **1991**, *113*, 9868.

(12) Representative examples, see: (a) Lozar, L. D.; Clark, R. D.; Heathcock, C. H. *J. Org. Chem.* **1977**, *42*, 1386. (b) Johnson, W. S.; Yarnell, T. M.; Myers, R. F.; Morton, D. R. *Tetrahedron Lett.* **1978**, *26*, 3201. (c) Johnson, W. S.; Yarnell, T. M.; Myers, R. F.; Morton, D. R.; Boots, D. R. *J. Org. Chem.* **1980**, *45*, 1254

S0002-7863(97)00020-6 CCC: $14.00

Scheme 1



Results

Cycloalkenation of Tungsten–Alkynol Complexes. The starting tungsten–η^1-alkynyl compounds **4**–**6** were readily prepared in 75–78% yields from α,δ- or α,ϵ-alkynols **1**–**3** and $CpW(CO)_3Cl$ in Et_2NH in the presence of CuI catalyst (3 mol %);[13] the reaction route is outlined in Scheme 1. Treatment of **4**–**6** with PhCHO (2.0 equiv) and $BF_3{\cdot}Et_2O$ (1.0 equiv) in cold Et_2O (−40 °C) immediately deposited **7**–**9** as orange precipitates in quantitative yields (>95%). With careful handling, we isolated and characterized these highly air-sensitive salts with appropriate physical methods. Diagnostic for the structures of **7**–**9** are ^1H and ^{13}C NMR spectra that show the presence of a W═C carbene carbon signal in the δ 275–290 ppm region in addition to NMR signals due to a vinyl ═CHPh group. The OCH proton NMR signals of **7**–**9** were shifted downfield by ca. 1.2–2.5 ppm relative to those of η^1-alkynols **4**–**6**. These spectral data indicate that electrophilic alkylations of η^1-alkynols **4**–**6** with aldehydes effect cycloalkenylations to form η^1-furylidenium and η^1-pyrylideniums such as **7**–**9**. Confirmation of the structures of **6**–**8** relies ultimately on the X-ray diffraction measurements on **8** and **9**,[14] of which the ORTEP drawings are provided in Figures 1 and 2. Treatment of a CH_2Cl_2 solution of **7**–**9** with water under air (23 °C, 12 h) delivered unsaturated γ- and δ-lactones **10**–**12** in 80–90% yields (eqs 2 and 3, Scheme 1). Equation 4 shows a convenient one-pot synthesis of unsaturated γ-lactone **13** via sequential treatment of a dichloromethane solution of **4** with $^iBuCHO/BF_3{\cdot}Et_2O$ and water/air; the yield of **13** was 83%.

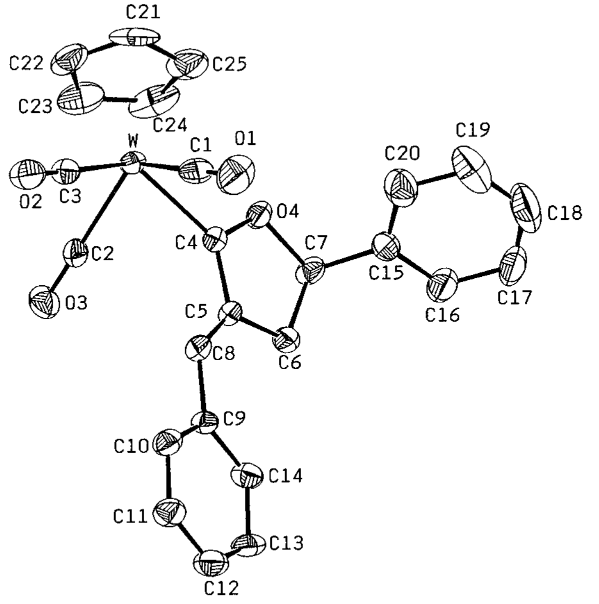


Figure 1. ORTEP drawing of tungsten–η^1-furylidenium **8** with selected bond distances: W–C(4) = 2.177(8) Å, C(4)–O(4) = 1.298(15) Å, C(7)–O(4) = 1.483(10) Å, C(4)–C(5) = 1.440(10) Å, C(5)–C(8) = 1.336(12) Å.

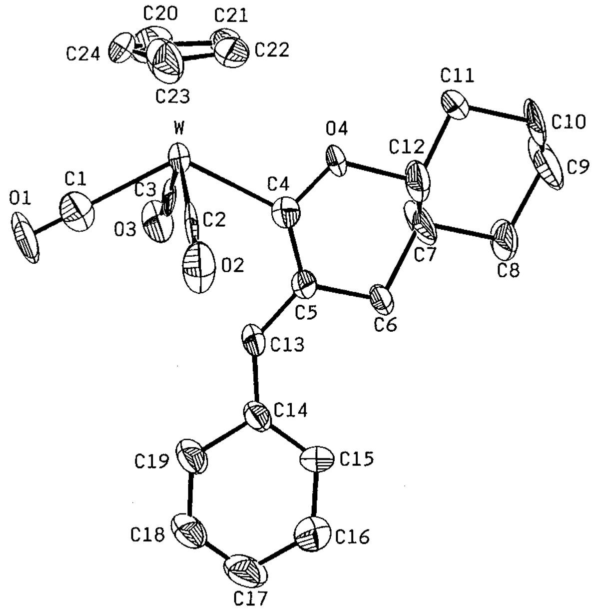
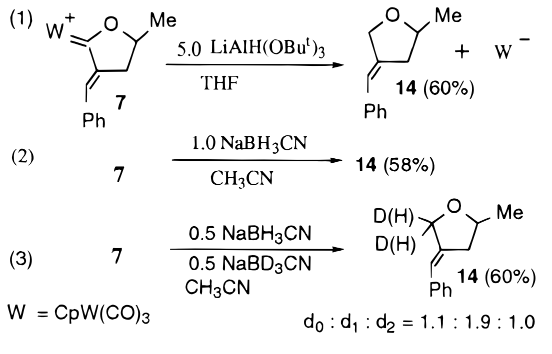


Figure 2. ORTEP drawing of tungsten–η^1-pyrylidenium **9** with selected bond distances: W–C(4) = 2.234(25) Å, C(4)–O(4) = 1.33(3) Å, C(12)–O(4) = 1.54(3) Å, C(4)–C(5) = 1.38(3) Å, C(5)–C(6) = 1.53(3) Å, C(5)–C(13) = 1.38(3) Å.

Scheme 2



Symmetric and Unsymmetric 1,1-Hydride Addition Reactions. A notable feature of these oxacarbeniums is their function as a dication equivalent;[15] these salts undergo demetalation with two hydrides as shown in Scheme 2. Treatment of η^1-furylidenium **7** with $LiAlH(OBu^t)_3$ (5.0 equiv) in cold THF (−40 °C) resulted in a color change of the solution, from the original red to light yellow. Monitoring of the reaction by solution IR

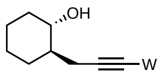
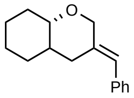
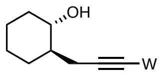
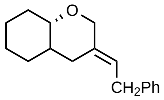
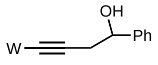
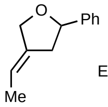
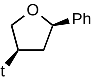
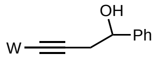
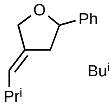
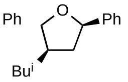
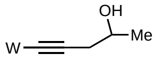
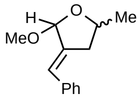
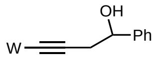
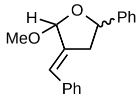
---

[13] Bruce, M. I.; Humphrey, M. G.; Mattisons, J. G.; Roy, S. K.; Swincer, A. G. *Aust. J. Chem.* **1984**, 1041.

[14] (a) Crystal data for **8**: monoclinic, space group $P21/n$, $a = 12.248(3)$ Å, $b = 10.0913(18)$ Å, $c = 19.8041(19)$ Å, $\beta = 95.132(20)°$, $V = 2437.9(8)$ Å^3; final $R = 0.037$ and $R_w = 0.036$. The X-ray data of **8** is provided in Supporting Information. (b) Crystal data for **9**: triclinic, space group $P1$, $a = 9.949(3)$ Å, $b = 10.8459(20)$ Å, $c = 14.153(3)$ Å, $\alpha = 76.548(20)°$, $\beta = 69.417(23)°$, $\gamma = 84.624(19)°$, $V = 1390.4(6)$ Å^3; final $R = 0.081$ and $R_w = 0.098$. The X-ray data of **8** is provided in Supporting Information.

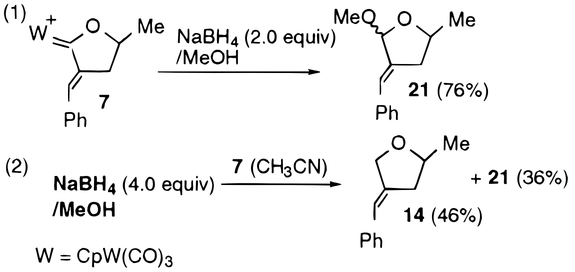
[15] For organic dicationic equivalence, see the representative papers: (a) Luh, T.-Y. *Pure Appl. Chem.* **1996**, *68*, 105. (b) Naso, F. *Pure Appl. Chem.* **1988**, *60*, 79. (c) Marsi, M.; Rosenblum, M. *J. Am. Chem. Soc.* **1984**, *56*, 129.

Table 1. Isolated Yields for Demetalations with Boron Hydrides

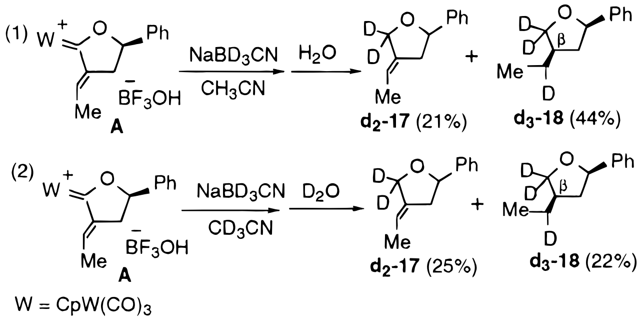
entry	η^1-alkynols[a]	$BF_3 \cdot Et_2O$/RCHO[b]	hydrides[c]	products isolated yield (%)[d,e]
1	 **6**	PhCHO	$NaBH_3CN$ (1.0 equiv)	 **15** (81%)
2	 **6**	$PhCH_2CHO$	$NaBH_3CN$ (1.0 equiv) (6.0 equiv)[f]	 **16** (83%) (81%)[f]
3	 **5**	MeCHO	$NaBH_3CN$ (1.0 equiv) (6.0 equiv)[f]	  **17** (50%) **18** (15%) (14%)[f] (50%)
4	 **5**	Pr^iCHO	$NaBH_3CN$ (6.0 equiv)	  **19** (18%) **20** (51%)
5	 **4**	PhCHO	$NaBH_4$ (2.0 equiv)[g]/MeOH	 **21** (*trans*/*cis* = 3/1, 76%)
6	 **5**	PhCHO	$NaBH_4$ (2.0 equiv)[g]/MeOH	 **22** (*trans*/*cis* = 2/1, 88%)

[a] W = $CpW(CO)_3$. [b] The amount of $BF_3 \cdot Et_2O$ and aldehyde were 1.0−1.1 and 2.0−5.0 equimolar proportions, respectively. [c] Solvent: CH_2Cl_2/CH_3CN (1/1 volume ratio) for $NaBH_3CN$, −40 °C, 2 h. [d] Isolated yields were estimated based on tungsten−η^1-alkynol compounds. [e] Compounds **16**−**22** were separated on a preparative silica TLC. [f] These yields refer to the reaction involving six equimolar of $NaBH_3CN$. [g] This mixture was prepared by stirring of $NaBH_4$ (2.0 equiv) with CH_3OH (1 mL) for 5.0 min before slow addition to a cold CH_2Cl_2 solution of carbenes.

Scheme 3



Scheme 4



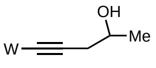
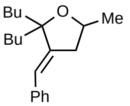
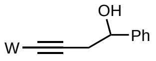
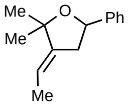
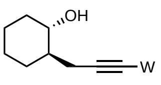
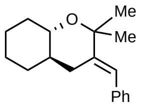
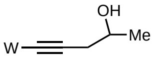
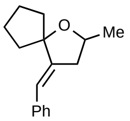
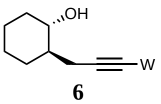
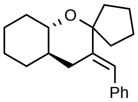
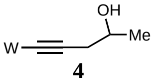
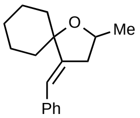
spectra revealed that $CpW(CO)_3^-$ anion was the predominant species (υ(CO) 1896, 1792 cm^{-1}).[16] Subsequent treatment of this solution with H_2O delivered α,α-addition product **14** in 60% yield. Demetalation of oxacarbenium **7** was also achieved by $NaBH_3CN$ to afford **14** in 58%; each $NaBH_3CN$ molecule must provide two hydrides because only 1 equiv suffices for demetalation. Equation 3 showed the reduction of **7** with equal amount (0.5 equiv) of $NaBH_3CN$ and $NaBD_3CN$; the resulting product **14** has the following deuterium ratios d_0:d_1:d_2 = 1.1:1.9:1.0 that were estimated according to ^1H,^2H NMR and mass spectral data. Apparently, the two $C_\alpha H_2$ methylene protons of **14** are not necessary from the same $NaBH_3CN$ molecule. Table 1 shows a one-pot operation for synthesis of five- and six-membered oxygen heterocycles **14** via direct annulation of three components including tungsten−alkynol, aldehyde, and metal hydrides.

Following the replacement of diethyl ether liquor with dichloromethane, the red oxacarbenium salts generated *in situ* were subsequently treated with appropriate metal hydrides at −40 °C (2−3 h) and then quenched with excess water to liberate organic products **15**−**22** listed in Table 1. In entries 1 and 2, $NaBH_3CN$ (1.0 equiv) reduction of tungsten pyrylidiniums generated *in situ* led to α,α-double addition, producing **15** and **16** in 81 and 83% yields, respectively. In the case of **16** (entry 2), use of excess $NaBH_3CN$ (6.0 equiv) did not cause further reduction. For the η^1-furylideniums generated from **5** and RCHO (R = Me, Pr^i) in entries 3 and 4, excess $NaBH_3CN$ (6.0 equiv) effected further reduction to yield mainly *cis*-2,4-disubstituted tetrahydrofurans **18** and **20** in 50 and 51% yields, respectively. The *cis* configurations of **18** and **20** were determined by ^1H NOE difference spectra. When 1 equiv of $NaBH_3CN$ was used (entry 3), β-alkylidene furan derivative **17**

---

[16] Darensbourg, M. Y.; Jimenez, P.; Sackett, J. P.; Hancket, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521.

Table 2. Isolated Yields for Demetalations with Grignard Reagents

entry	η^1-alkynyl complexes[a]	BF_3·Et_2O/RCHO[b]	nucleophiles[c]	products isolated yield (%)[d]
1	 **4**	PhCHO	Bu^nMgBr (2.0 equiv)	 **23** (65%)
2	 **5**	MeCHO	MeMgBr (2.0 equiv)	 **24** (74%)
3	 **6**	PhCHO	MeMgBr (2.0 equiv)	 **25** (82%)
4	 **4**	PhCHO	$MgBr(CH_2)_4MgBr$ (3.0 equiv)	 **26** (58%)
5	 **6**	PhCHO	$MgBr(CH_2)_4MgBr$ (3.0 equiv)	 **27** (64%)
6	 **4**	PhCHO	$MgBr(CH_2)_5MgBr$ (3.0 equiv)	 **28** (58%)

[a] W = $CpW(CO)_3$. [b] The amount of BF_3·Et_2O and aldehyde were 1.0 and 2.0−5.0 equimolar proportions, respectively. [c] Reaction conditions: CH_2Cl_2, −40 °C, 2 h. [d] Isolated yields were estimated based on tungsten−η^1-alkynyl compounds.

was formed in 50% yield. These oxacarbeniums are also susceptible to α,α-unsymmetric hydride additions in the presence of suitable boron hydrides. As depicted in entries 5 and 6, sequential treatment of **4** and **5** with PhCHO/BF_3·Et_2O, and $NaBH_4$/MeOH afforded **21** and **22** in good yields (>76%); in these cases, the C_α carbon of **21** and **22** has a hydrogen and MeO substituent, respectively. The solution species in the $NaBH_4$/MeOH mixture is presumbly $NaBH(OMe)_3$.[17] The major diastereomers of **21** and **22** have a *trans* configuration according to the proton NOE effect.

Scheme 3 illustrates the results for unsymmetric reduction of oxacarbenium **7** under different reaction conditions; kinetic course seems to be very important. Slow addition of a $NaBH_4$/MeOH mixture to **7** in cold CH_3CN (−40 °C) afforded **21** in 76% without formation of **14** (eq 1, Scheme 2). A reverse and slow addition of a CH_3CN solution of **7** to the same $NaBH_4$/MeOH mixture at −78 °C gave **14** and **21** in 46 and 36% yields, respectively.

Formation of 2,4-disubstituted tetrahydrofurans **18** and **20** via excess $NaBH_3CN$ reduction of tungsten−η^1-furylideniums is an interesting issue. To assist understanding this mechanism, we examined the reduction of carbenium salt **A** with $NaBD_3CN$ (98 atom %, 6.0 equiv) in CH_3CN as depicted in Scheme 4. Prior to hydrolysis, the mainly organometallic species in the solution is still the $CpW(CO)_3^-$ anion according to solution IR study. After treatment with H_2O, the resulting deuterated product **18**-d_3 contained three deuterium atoms in each molecule; the deuterium atoms are located at the C_α and Me*C*HD carbons, respectively, according to ^1H and ^{13}C NMR and mass spectral data. To trace the $C_\beta H$ hydrogen source of **18**-d_3, we have performed a reaction involving the use of $NaBD_3CN$, CD_3CN (99.8 atom %), and D_2O; the resulting product **18**-d_3 still has the hydrogen form in the $C_\beta H$ position (eq 2); the yield of **18**-d_3 is lower (22%).

Reactions with Grignard Reagents and Organocuprates. Shown in Table 2 are the results for Grignard reagent RMgBr that can also effect α,α-dialkylation of η^1-oxacarbeniums. Entries 1−3 show formation of 3-alkylidene tetrahydrofurans and -pyrans **23**−**25** with yields exceeding 65%. This reaction is applicable to both furan and pyran systems containing vinyl substituents of aryl and aliphatic groups (R = Ph, Me). In entry 2, the resulting oxacarbenium intermediate lost no proton in the presence of MeMgBr. To expand the application, we employed 1,4-di-Grignard reagent $MgBr(CH_2)_4MgBr$[18] to achieve a remarkable [4+1] cycloaddition reaction, yielding spirofuran and spiropyran derivatives **26** and **27** in 58 and 64%, respectively. With utilization of $MgBr(CH_2)_5MgBr$,[18] we also realized a [5+1] cycloaddition reaction on a tungsten−furylidenium (entry 6), affording **28** in 60% yield.

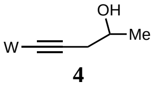
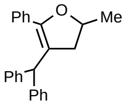
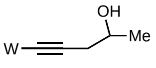
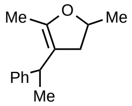
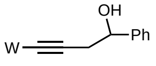
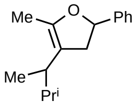
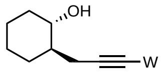
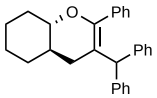
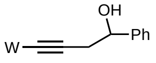
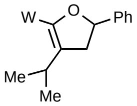
Table 3 provides results for organocopper reagent R_2CuLi that effects a distinct 1,3-dialkylation of tungsten oxacarbeniums. The action of R_2CuLi (R = Ph, Me) on tungsten−η^1-furylidenium generated in entries 1 and 2 afforded 1,3-addition products **29** and **30** with yields exceeding 76%. Similar 1,3-addition

---

(17) Evans, D. A.; Chapman, K. T.; Carreira, E. M. *J. Am. Chem. Soc.* **1988**, *110*, 3560.

(18) Holtkamp, H. C.; Shat, G.; Blomberg, C.; Bickelhaupt, F. *J. Organomet. Chem.* **1982**, *240*, 1.

Table 3. Isolated Yields for Demetalations with Organocuprates

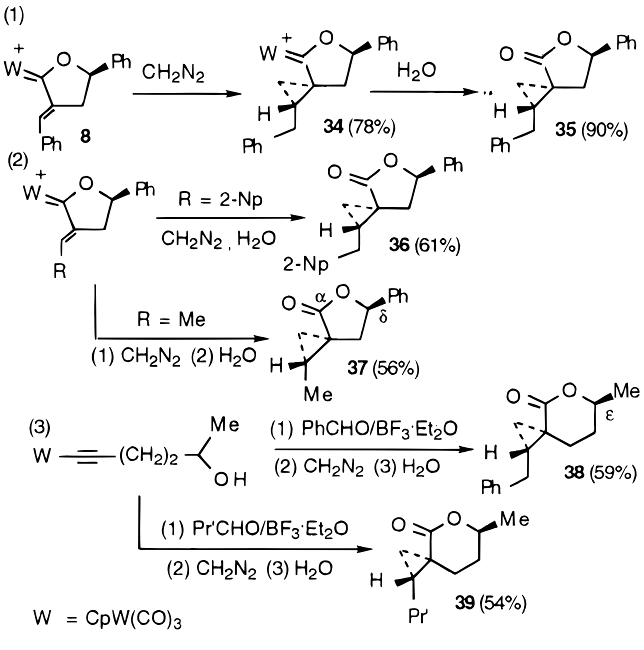
entry	η^1-alkynyl complexes[a]	BF_3•Et_2O/RCHO[b]	nucleophiles[c]	products isolated yield (%)[d]
1	 **4**	PhCHO	Ph_2CuLi (2.0 equiv)	 **29** (85%)
2	 **4**	PhCHO	Me_2CuLi (2.0 equiv)	 **30** (76%)[e]
3	 **5**	Pr^iCHO	Me_2CuLi (2.0 equiv)	 **31** (40%)[f]
4	 **6**	PhCHO	Ph_2CuLi (2.0 equiv)	 **32** (68%)
5	 **5**	MeCHO	Me_2CuLi (2.0 equiv)	 **33** (72%)

[a] W = $CpW(CO)_3$. [b] The amount of BF_3•Et_2O and aldehyde were 1.0 and 2.0−5.0 equimolar proportions, respectively. [c] Reaction conditions: CH_2Cl_2, −40 °C, 2 h. [d] Isolated yields were estimated based on tungsten−η^1-alkynyl compounds. [e] Diastereomeric ratio =1.8/1. [f] Diastereomeric ratio = 1.4/1.

reactions apply to the furylidenium having aliphatic isopropyl group (entry 3), and to the pyran system (entry 4), furnishing **31** (40%) and **32** (68%), respectively. Compounds **30** and **31** were obtained in 1.8/1.0 and 1.4/1.0 diastereomeric mixtures, respectively, separation of the two diastereomers was unsuccessful. The vinyl substituent size of tungsten oxacarbenium is important for 1,3-dialkylation. For a small methyl group as shown in entry 5, the reaction with Me_2CuLi delivered tungsten−η^1-furyl species **33** (72% yield) via a single alkylation at the =*C*HMe carbon. Attempts to achieve a second addition on **33** with excess organometallics (4−5 equiv) such as $NaBH_3CN$, MeMgBr, or Ph_2CuLi were unsuccessful, in each case compound **33** was recovered exclusively.

Cyclopropanation of Tungsten Carbeniums with Diazomethane. The preceding tungsten oxacarbeniums undergo facile cyclopropanation reaction with CH_2N_2 in cold CH_2Cl_2 (0 °C). As shown in Scheme 5, treatment of tungsten−η^1-furylidenium **8** with dry CH_2N_2, followed by addition of excess diethyl ether produced a new furylidenium **34** in 78% yield; the salt was fully characterized by NMR and IR spectroscopies. The W=C_α carbon NMR signal of **34** was observed at δ 296.4 ppm. Hydrolysis of **34** with H_2O instantly produced γ-lactone **35** (υ(CO) = 1778 cm^{-1}). Although NMR spectra of **34** and **35** revealed that only one species was exclusively formed, elucidation of the structure was difficult because two CH_2 units of diazomethane were uptaken in the reaction accompanied with a considerably altered structure. A proton NMR decoupling experiment indicated that a methine CH carbon occurs between the two new CH_2 fragments. We succeeded in obtaining single crystals of 2-naphthyl γ-lactone derivative **36** of which the proton NMR pattern resembled those of **35**. The ORTEP drawing[19] of **36** in Figure 3 reveals a 1,2-migration of the naphthyl group away from the parent furan ring. A new cyclopropane ring was formed opposite the C_δ-phenyl substituent, and was linked to the naphthyl group via a CH_2 bridge. In the case of a tungsten oxacarbenium containing a methyl substituent, the reaction only uptakes one molecule of CH_2N_2 to form a cyclopropane ring; this case is manifested by compound **37** that was formed in 56% yield. Shown in eq 3 is the direct synthesis of δ-lactones **38** and **39** from the corresponding tungsten−η^1-α,ϵ-alkynol; this operation represents an unusual case for annulation of four functional components. The

Scheme 5



---

[19] Crystal data for **36**: orthorombic, space group *Pbca*, *a* = 8.4640(2) Å, *b* = 18.8677(2) Å, *c* = 21.4270(5) Å, *Z* = 8, *V* = 3421.83(14) $Å^3$; final *R* = 0.062 and R_w = 0.054. The X-ray data of **36** is provided in Supporting Information.

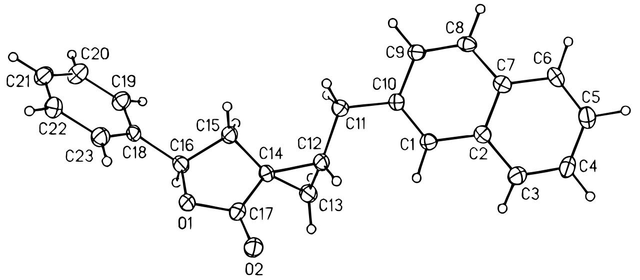
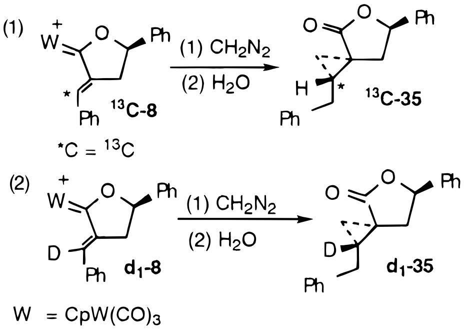


Figure 3. ORTEP drawing of compound **36**: C(17)−O(1) = 1.350(6) Å, C(16)−O(1) = 1.456(6) Å, C(17)−O(2) = 1.204(7) Å, C(17)−C(14) = 1.487(7) Å, C(14)−C(15) = 1.505(7) Å, C(15)−C(16) = 1.531(7) Å, C(12)−C(14) = 1.504(7) Å, C(13)−C(14) = 1.520(7) Å, C(12)−C(13) = 1.486(7) Å, C(11)−C(12) = 1.512(6) Å.

Scheme 6



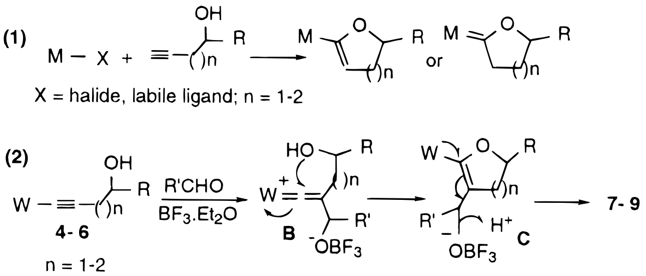
effect of the vinyl substituent is also pronounced here; the resulting δ-lactone **38** has two new CH_2 units in addition to the 1,2-phenyl migration. The isopropyl group of **39** generates only a simple cyclopropanation reaction. The yields of **38** and **39** were 59 and 54%, respectively. The stereochemistries of compounds **34**, **35**, and **37**−**39** were inferred from the X-ray structure of **36** (Figure 3); the cyclopropane rings of these compounds were formed opposite the C_δ-phenyl or C_ϵ-methyl substituents.

The substantial structural transformation for aryl products **34**−**36** and **38** requires an isotopic labeling experiment to clarify its reaction mechanism. We prepared a ^{13}C-labeled η^1-furylidenium ^{13}C-**8** prepared from Ph^{13}CHO (ca. 5 atm %) and η^1-alkynol **5**; after cyclopropanation, the resulting γ-lactone ^{13}C-**35** has ^{13}C enrichment exclusively at the cyclopropyl methine carbon according to ^{13}C NMR spectra (eq 1, Scheme 6). ^{13}C NMR signals of **35** were assigned on the basis of ^{1}H−^{13}C correlation NMR spectra. In a separate experiment, we prepared a deuterated sample **8**-d_1 derived from PhCDO (deuterium content > 98%). After the reaction with CH_2N_2, the resulting γ-lactone **35**-d_1 has deuterium content exclusively (deuterium content > 98%) at the same methine carbon (eq 2), consistent with the ^{13}C-labeling experiment. On the basis of these labeling results, we conclude that the η^1-furylidene cation **8** underwent 1,2-phenyl migration with cleavage of the single C−Ph σ bond during cyclopropanation.

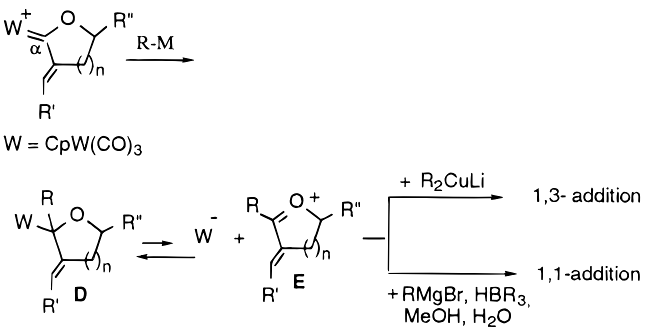
Discussion

Cycloalkenylation Reactions of Tungsten−η^1-Alkynols. Scheme 7 (eq 1) shows a typical pattern for the alkylations of low-valent metal species M−L or M−X (L = labile ligand, X = halide) with α,δ- and α,ϵ-alkynols; these reactions lead exclusively to intramolecular cyclizations to yield metal−η^1-oxacarbenes or cyclic η^1-vinyl ethers depending on the reaction condition.[20−22] Such a general pattern limits the applications of transition metal alkynyls to organic syntheses. Our synthetic approach starts with a modestly electron-rich CpW(CO)$_3$ fragment that affords desirable tungsten−η^1-alkynols **4**−**6**. Electrophilic alkylation of these η^1-alkynols with RCHO/BF$_3$·Et$_2$O induced cycloalkenation into tungsten carbeniums **7**−**9**. This process involves sequential bond-making and bond-breaking processes comprising two key intermediates **B** and **C**. Intramolecular cyclization of **B** via attack of the tethered alcohol at the central W=C$_\alpha$=C carbon releases a proton that assists cleavage of the C−O bond to yield **C**. The roles of tungsten in this cyclization are 2-fold: (1) to activate addition of the alkynyl C_β-carbon[23] toward RCHO/BF$_3$ complex and (2) to stabilize carbenium species such as intermediate **B** and **7**−**9**.

Scheme 7



Scheme 8



Dication Synthons of Tungsten−Oxycarbeniums. Tables 1−3 show our new method to transform η^1-alkynols directly into various furan and pyran derivatives; this method allows multiple bonds to form or to break simultaneously in a one-pot operation. The success of this chemical transformation relies primarily on the versatile dicationic equivalence of tungsten oxacarbeniums such as **7**−**9**. Conventional transition metal carbenes including related Cp(CO)LFe[=C(OMe)Et]$^+$ reacted only with one molecule of nucleophiles including LiAlH$_4$ and MeMgBr.[3c,24] Scheme 8 shows one plausible mechanisms to account for the 1,1- and 1,3-double additions of these salts with various organometallic reagents. The fact that tungsten−η^1-2,3-dihydrofuryl species **33** (Table 3, entry 5) fails to react further with Grignard reagent or NaBH$_3$CN implies that the double addition must proceed via addition of nucleophiles at the carbenium W=C_α carbon to generate species **D**. One important piece of information revealed by Scheme 3 is that the rate for second addition of nucleophile on tungsten oxacarbenium is much faster than that of the first hydride addition; this kinetic phenomenon supports formation of a highly reactive

---

(20) (a) Chisholm, H. C.; Clark, H. C. *J. Am. Chem. Soc.* **1972,** *94,* 1532. (b) Chisholm, H. C.; Clark, H. C. *J. Am. Chem. Soc.* **1973**, *6*, 241.

(21) (a) Hinkle, R. J.; Stang, P.; Arif, A. M. *Organometallics* **1993**, *12*, 3510. (b) Bruce, M. I.; Swincer, A. G.; Thompson, B. J.; Wallis, R. C. *Aust. J. Chem.* **1980**, *33*, 2605. (c) Le Bozec, H.; Ouzzine, K.; Dixneuf, P. H. *Organometallics* **1991**, *10*, 2768. (d) O'Connor, J. M.; Pu, L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1990**, 112, 6232.

(22) (a) McDonald, F. E.; Bowman, J. L. *Tetrahedron Lett.* **1996**, 4675. (b) McDonald, F. E.; Schultz, C. C. *J. Am. Chem. Soc.* **1994**, *116*, 9363. (c) Quayle, P.; Rahman, S.; Herbert, J. *Tetrahedron Lett.* **1995**, *36*, 8078.

(23) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 257.

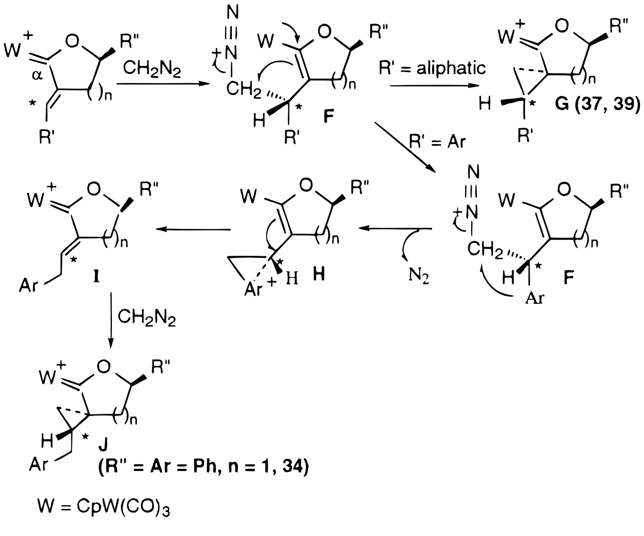
(24) Curtis, P. J.; Davies, S. J. *J. Chem. Soc., Chem. Commun.* **1984**, 747.

intermediate that reacts instantly with any second nucleophile present in the solution. Accordingly, we propose a small degree of self-ionization of **D** (Scheme 8) to generate $CpW(CO)_3^-$ and a reactive oxonium[25,26] species **E**. In this case, the $CpW(CO)_3$ group of **D** serves as an excellent leaving group, due partly to its sterically demanding size and partly to the oxygen lone-pair repulsion. Furyl and pyryl oxoniums are known to be stable species in solution and are useful intermediates in organic syntheses.[26] Nucleophilic regioselectivity of **E** thus follows that of organic enone chemistry,[27] which is compatible with our observation. In this case, only organocuprates undergo 1,3-addition reaction. In the case of unsymmetric hydride addtion, addition of the second nucleophile MeOH to this oxonium will give a mixture of *trans* and *cis* products[25] as observed for **21** and **22**; the preference for the *trans* product (*trans*/*cis* = 2−3, Table 1, entries 6 and 7) is compitable with those (2/1 = 3/1) reported for nucleophic addition on furyl oxonium.[26] We are aware that one equimolar of $NaBH_3CN$ suffices for the reaction. The second addition likely proceeds via attack of BH_2CN at the enonium **D** to deliver the hydride;[28] transfer of this hydride is accelerated by the presence of anion species such as $CpW(CO)_3^-$ and BF_3OH^- via coordination to BH_2CN.

Remaining unclear is the mechanism for overreduction of tungsten−η^1-furylidenium with excess $NaBH_3CN$ shown in Scheme 4; this reaction proceeded with high *cis* stereoselection. Although the reduction may be caused by the presence of water to induce formation of reactive $CpW(CO)_3H$,[29] this possibility is questioned by the absence of $[CpW(CO)_3]_2$ in the system.[30] The isotopic results shown in Scheme 4 may suggest a radical mechanism; but the present information is insufficient for full characterization of the mechanism.

Cyclopropanation of Tungsten Oxacarbeniums with CH_2N_2. The reaction pathways between CH_2N_2 and tungsten−η^1-oxacarbeniums depend on their vinyl substituents. If the substituent is an aryl group, the reaction proceeds with considerable structural rearrangement as depicted in Scheme 9 (eq 1); such transformation is an interesting issue in organometallic chemistry. The most important information from ^{13}C- and ^2H-labeling results indicate that the formation of carbenium **34** involves 1,2-aryl shift with cleavage of the =C−Ph single bond. A plausible mechanism is proposed in Scheme 9, in which CH_2N_2 initiates the reaction via attack at the =CHR′ bond preferably opposite to the R″ group, yielding the diazo salt **F**. A counterattack of the tungsten−vinyl bond at the $-CH_2N_2^+$ carbon leads to formation of a cyclopropane ring as represented by **G**. This process rationalizes formation of compounds **37** and **39** in which the R′ substituent is an aliphatic group. If R′ is an aryl group, it may exert the effect of neighboring participation to accelerate ionization, generating a bridging phenonium ion **H**.[31] An intramolecular attack of the tungsten−vinyl bond of this intermediate at its bridging phenonium forms a new cation **I** that is susceptible to a second cyclopropanation, eventually yielding a new η^1-furylidene **J** as represented by compound **34** (R′ = Ph, *n* = 1). This reaction scheme also rationalizes the observed stereochemistry of the cyclopropanation products.

Scheme 9



Conclusions

Alkylations of $CpW(CO)_3Cl$ with α,δ- and α,ϵ-alkynols in the presence of CuI/Et_2NH afforded desirable tungsten−η^1-α,δ- and −η^1-α,ϵ-alkynols in good yields. Treatment of these tungsten−η^1-alkynols with $RCHO/BF_3{\cdot}Et_2O$ leads to cycloalkenation to generate tungsten oxacarbeniums containing furan and pyran framework. These η^1-oxacarbeniums are chemically atypical relative to common metal carbenes because they are susceptible to attack of two nucleophiles to liberate various furan and pyran derivatives; the intermediate likely involves furyl and pyryl oxoniums. This reaction is applicable to diverse nucleophiles, including water, boron hydrides, Grignard reagents, and organocuprates. Organocuprates follow a 1,3-addition pathway in contrast to 1,1-addition observed for boron hydrides and Grignard reagents. Unsymmetric double additions of tungsten furylideniums are successful with the use of a $NaBH_4/CH_3OH$ mixture. The atypical behavior of these oxacarbeniums is also demonstrated by the CH_2N_2 reaction; the outcome depends on the types of their vinyl substituents. A significant structural change is observed for the aryl substituent for which isotopic labeling experiments were performed to elucidate a mechanism that involves a bridging phenonium intermediate. To show the potential value of this work, we demonstrate a number of examples for direct transformation of tungsten−η^1-alkynols into various furan and pyran derivatives including spiro-typed heterocycles; the yields were generally good.

We are now expanding this new methodology to the syntheses of more useful oxygen-, nitrogen-, and sulfur-containing heterocycles from suitable functionalized terminal alkynes and organometallic reagents.

---

[25] Weinberg, N. L.; Weinberg, H. R. *Chem. Rev.* **1968**, *68*, 449.

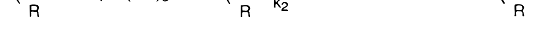
[26] Rychnovsky, S. D.; Dahanukar, V. H. *J. Org. Chem.* **1996**, *61*, 7648.

[27] Duval, D.; Geribaldi In *The Chemistry of Enones*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1989; p 355.

[28] $HSiEt_3$, $CpW(CO)_3H$, and related metal hydrides can transfer one hydride to carbocation species; see: Bullock, R. M.; Song, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 8602.

[29] Organic olefins can be hydrogenated by $CpW(CO)_3H$, $CpFe(CO)_2H$, and related metal hydride via a radical mechanism; see the representative examples: (a) Bullock, R. M.; Song, J.-S. *J. Am. Chem. Soc.* **1990**, *112*, 6886. (b) Sweany, R. L.; Halpern, *J. Am. Chem. Soc.* **1977**, *99*, 8335.

[30] We are aware that the presence of water may produce $CpW(CO)_3H$ that can reduce olefin via a radical mechanism as shown below (eqs 1 and 2). In eq 1, the second step is known to be faster,[29] i.e. $k_2 > k_1$; in this case $[CpW(CO)_3]_2$ should be formed exclusively.



[31] (a) Lawton, R. G. *J. Am. Chem. Soc.* **1961**, *83*, 2399. (b) Diaz A.; Lazdins, I.; Winstein, S. *J. Am. Chem. Soc.* **1968**, *90*, 6546.

[32] (a) Richey, H. G. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, Chapter 25. (b) Childs, R. F.; Faggiani, R.; Lock, C. J.; Mahendran, M.; Zweep, S. D. *J. Am. Chem. Soc.* **1986**, *108*, 1692.

[33] Saunders, M.; Siehl, H.-U. *J. Am. Chem. Soc.* **1980**, *102*, 6869.

[34] Pocker, Y. In *Molecular Rearrangement*; de Mayo, P., Ed.; Wiley-Interscience: New York, 1963.

[35] Coxon, J. N.; Hartshorn, M. P.; Rae, W. J. *Tetrahedron* **1970**, *26*, 1091.

Experimental Section

Unless otherwise noted, all reactions were carried out under a 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. $W(CO)_6$, $BF_3{\cdot}Et_2O$, dicyclopentadiene, propargyl alcohol, and sodium were obtained commercially and used without purification. Alkynols **1**−**3** were prepared according to procedures described in the literatures. Elemental analyses were performed at National Cheng Kung University, Taiwan. Mass data of tungsten compounds were reported against ^{184}W.

General Procedure for Synthesis of Tungsten−η^1-Alkynols. Synthesis of 4. To an Et_2NH solution (40 mL) of $CpW(CO)_3Cl$ (3.69 g, 10.0 mmol) and CuI (51.1 mg, 0.3 mmol) was added 4-pentyn-2-ol (1.26 g, 15.0 mmol) at 23 °C in the absence of light, the mixture was stirred for 30 min before it was concentrated to ca. 2 mL. The residue was chromatographed through a silica column (diethyl ether/hexane = 1/1) to yield a yellow band that afforded **4** ($R_f = 0.15$) as a dark orange solid (3.12 g, 7.50 mmol, 75%): IR (Nujol, cm^{-1}) υ(OH) 3410 (br s), υ(C≡C) 2115 (w), υ(CO) 2034 (s), 1935 (s); ^1H NMR (300 MHz, $CDCl_3$) δ 5.54 (5H, s, Cp), 3.77 (1H, m, C*H*Me), 2.70 (1H, dd, *J* = 16.4, 4.9 Hz, CH*H*′), 2.55 (1H, dd, *J* = 16.4, 6.8 Hz, C*H*H′), 2.25 (1H, s, OH), 1.32 (3H, d, *J* = 6.8 Hz, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 229.3, 212.0, 124.3, 91.4, 67.0, 32.9, 22.0; MS (75 eV, *m/e*) 416 (M^+). Anal. Calcd for $C_{13}H_{12}WO_4$: C, 37.53; H, 2.91. Found: C, 37.39; H, 2.92.

General Procedure for the Synthesis of Tungsten−Oxacarbeniums. Synthesis of 7. To a diethyl ether solution (15 mL) of **4** (210 mg, 0.505 mmol) was added PhCHO (107.1 mg, 1.01 mmol) and $BF_3{\cdot}Et_2O$ (0.07 mL, 0.569 mmol) at −40 °C; a dark orange precipitate was immediately deposited. The mother diethyl ether liquor was cannulated out; the remaining precipitate was washed with diether ether (2 × 10 mL) and dried in vacuo to yield **7** as an orange precipitate (286.0 mg, 0.485 mmol, 96%): IR (Nujol, cm^{-1}) υ(CO) 2054 (s), 1947 (s), υ(C=C) 1642 (w); ^1H NMR (400 MHz, CD_2Cl_2) δ 7.76 (1H, t, *J* = 2.6 Hz, =CH), 7.52−7.66 (5H, m, Ph), 5.99 (5H, s, Cp), 5.66 (1H, m, C*H*-O), 2.66 (1H, ddd, *J* = 16.6, 8.3, 2.6 Hz, C*H*H′), 2.33 (1H, ddd, *J* = 16.6, 5.6, 2.6 Hz, CH*H*′), 1.60 (3H, d, *J* = 6.4 Hz, Me); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 279.6, 216.2, 215.3, 214.8, 157.7, 151.5, 134.5, 133.9, 132.8, 130.3, 99.5, 96.5, 34.5, 22.2. Anal. Calcd for $C_{20}H_{17}WO_5BF_3$: C, 40.18; H, 2.91. Found: C, 40.78; H, 2.88.

General Procedure for Oxidative Demetalation of Tungsten−Oxacarbeniums. Synthesis of 10. To a CH_2Cl_2 (5 mL) solution of **7** (245.0 mg, 0.415 mmol) was added water (2 mL) at 23 °C under air atomsphere, and the solution was stirred for 24 h. The organic layer was extracted with diethyl ether (5 mL), concentrated, and eluted on a preparative silica TLC to yield **10** as a colorless solid (62.4 mg, 0.332 mmol, 80%): IR (Nujol, cm^{-1}) υ(C=O) 1758 (s), υ(C=C) 1660 (w); ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (1H, dd, *J* = 3.2, 2.4 Hz, =CH), 7.36−7.48 (5H, m, Ph), 4.75 (1H, m, C*H*-O), 3.36 (1H, ddd, *J* = 16.6, 7.8, 2.4 Hz, C*H*H′), 2.77 (1H, ddd, *J* = 16.6, 5.3, 3.2 Hz, CH*H*′), 1.46 (3H, d, *J* = 6.2 Hz, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 136.3, 134.6, 129.8, 29.4, 128.4, 124.7, 73.9, 35.1, 22.2; HRMS calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0837.

Oxidative Demetalation of 8. Demetalation of **8** (297.1 mg, 0.450 mmol) with water under air atomsphere gave **11** as a colorless solid (93.4 mg, 0.374 mmol, 83%): IR (Nujol, cm^{-1}) υ(C=O) 1756 (s), υ(C=C) 1656 (w); ^1H NMR (300 MHz, $CDCl_3$) δ 7.62 (1H, dd, *J* = 3.1, 2.8 Hz, =CH), 7.32−7.48 (10H, m, 2 Ph), 5.59 (1H, dd, *J* = 8.6, 6.1 Hz, C*H*), 3.69 (1H, ddd, *J* = 17.6, 8.6, 2.8 Hz, C*H*H′), 3.15 (1H, ddd, *J* = 17.6, 6.1, 3.1 Hz, CH*H*′); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 140.3, 137.0 134.6, 130.0, 129.9, 128.9, 128.5, 125.4, 124.1, 78.1, 36.5; HRMS calcd for $C_{17}H_{14}O_2$ 250.0994, found 250.0992.

Oxidative Demetalation of 9. Demetalation of **9** (314.3 mg, 0.482 mmol) with water under air atomsphere gave **12** as a colorless solid (105.1 mg, 0.434 mmol, 90%): IR (Nujol, cm^{-1}) υ(C=O) 1738 (s), υ(C=C) 1664 (w); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (1H, dd, *J* = 3.0, 1.5 Hz, =CH), 7.30−7.41 (5H, m, Ph), 3.95 (1H, ddd, *J* = 12.6, 10.6, 4.5 Hz, C*H*), 2.88 (1H, ddd, *J* = 16.6, 4.6, 1.5 Hz), 2.15 (1H, br d, *J* = 10.0 Hz), 2.14 (1H, ddd, *J* = 16.6, 12.3, 3.0 Hz), 1.87 (2H, m), 1.72 (1H, br d, *J* = 10.0 Hz), 1.60 (m, 1H), 1.46 (m, 1H), 1.25 (m, 2H), 1.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 141.2, 135.1, 130.2, 129.1, 128.5, 125.9, 81.7, 38.4, 33.1, 32.1, 31.1, 24.9, 23.9; HRMS calcd for $C_{16}H_{18}O_2$ 242.1307, found 242.1312.

One-Pot Synthesis of 5-Methyl-3-(3-methylbutylidene)dihydrofuran-2-one) (13) from Tungsten−η^1-Alkynol 4. To a diethyl ether solution (5 mL) of **4** (170.6 mg, 0.410 mmol) was added Bu^iCHO (70.7 mg, 0.821 mmol) and $BF_3{\cdot}Et_2O$ (0.06 mL, 0.471 mmol) at −40 °C, immediately depositing an orange precipitate. To the solution was added water (2 mL) with stirring under air. The organic layer was extracted with diethyl ether (5 mL), concentrated, and eluted on a preparative silica TLC to yield **13** as a coloress oil (57.2 mg, 0.340 mmol, 83%): IR (Nujol, cm^{-1}) υ(C=O) 1757 (s), υ(C=C) 1657 (w); ^1H NMR (300 MHz, $CDCl_3$) δ 6.73 (1H, m, =CH), 4.64 (1H, m, C*H*O), 2.94 (1H, ddd, *J* = 16.8, 9.2, 2.8 Hz,C*H*H′), 2.33 (1H, ddd, *J* = 16.8, 5.9, 4.0 Hz, CH*H*′), 2.05 (2H, dd, *J* = 8.3, 4.4 Hz, =CHC*H*$_2$), 1.76 (1H, m, CH), 1.38 (3H, d, *J* = 6.2 Hz, Me), 0.91 (6H, d, *J* = 6.2 Hz, 2 Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 139.7, 127.2, 73.9, 39.3, 33.1, 28.1, 22.4, 22.3; HRMS calcd for $C_{10}H_{16}O_2$ 168.1150, found 168.1156.

Synthesis of 4-Benzylidene-2-methyltetrahydrofuran (14). To a THF solution (10 mL) of **7** (301 mg, 0.530 mmol) was slowly added $LiAlH(OBu^t)_3$ (0.67 g, 2.65 mmol) in THF (5.0 mL) at −40 °C; the mixture was stirred for 2 h, added with water (0.3 mL), finally concentrated to yield **14** as a colorless oil (55.4 mg, 0.318 mmol, 60%): IR (Nujol, cm^{-1}) υ(C=C) 1660 (w); ^1H NMR (400 MHz, $CDCl_3$) δ 7.21−7.37 (5H, m, Ph), 6.31 (1H, t, *J* = 2.2 Hz, =CH), 4.45 (2H, AB q, *J* = 13.1 C*HH*′O), 4.12 (1H, m, CH-O), 2.93 (1H, ddd, *J* = 16.2, 4.0, 2.2 Hz,C*H*H′), 2.37 (1H, ddd, *J* = 16.2, 8.5, 2.2 Hz, CH*H*′), 1.43 (3H, d, *J* = 6.0 Hz, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 137.6, 128.3, 127.9, 126.4, 119.4, 76.4, 72.6, 38.8, 20.5; HRMS calcd for $C_{12}H_{12}O$ 174.1045, found 174.1039.

Direct Synthesis of 3-Benzylideneoctahydrochromene (15) from Tungsten−η^1-Alkynol 6. To a diethyl ether solution of tungsten−η^1-alkynol **6** (268.2 mg, 0.561 mmol) was added PhCHO (118.9 mg, 1.122 mmol) and $BF_3{\cdot}Et_2O$ (0.07 mL, 0.569 mmol) at −40 °C, immediately yielding an orange precipitate. The mother ether liquor was cannulated away; the residue was redissolved in CH_2Cl_2 (2 mL). To this solution was slowly added a CH_3CN solution (2 mL) of $NaBH_3CN$ (35.3 mg, 0.561 mmol) at −40 °C; the mixture was stirred for 2 h, added with water (0.3 mL), finally concentrated to yield **15** as a colorless oil (102.4 mg, 0.449 mmol, 81%): IR (Nujol, cm^{-1}) υ(C=C) 1664 (w); ^1H NMR (400 MHz, $CDCl_3$) δ 7.20−7.36 (5H, m, Ph), 6.37 (1H, s, =CH), 4.23 (2H, AB q, *J* = 12.4 Hz, CH*H*′-O), 3.12 (1H, ddd, *J* = 16.4, 9.6, 4.1 Hz), 2.88 (1H, ddd, *J* = 16.4, 3.8, 2.2 Hz), 1.98 (1H, m), 1.88 (1H, t, *J* = 10.8 Hz), 1.80 (1H, m), 1.62 (2H, br t, *J* = 10.8 Hz), 1.30 (3H, m), 1.20 (1H, m), 1.10 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.9, 128.9, 128.1, 126.4, 124.0, 81.8, 74.1, 43.0, 33.7, 32.3, 31.9, 25.4, 24.8; HRMS calcd for $C_{16}H_{20}O$ 228.1514, found 228.1511.

Synthesis of 3-Benzylidene-2-methoxytetrahydrofuran (21). $NaBH_4$ (38.2 mg, 1.01 mmol) was dissolved in CH_3OH (1.0 mL) at 23 °C, and the mixture was stirred for 5 min at which no gas was evolved. The carbenium **7** was prepared from η^1-alkynol **4** (210 mg, 0.505 mmol), PhCHO (107 mg, 1.01 mmol), and $BF_3{\cdot}Et_2O$ (0.070 mg, 0.569 mmol). To a CH_2Cl_2 (10 mL) solution of **7** was added dropwise the above $NaBH_4/CH_3OH$ solution at −40 °C in a period of 1 h; the mixture was stirred for 2 h before it was added a saturated NH_4Cl solution. The solution was brought to dryness and eluted on preparative silica TLC to yield **21** as a colorless oil (*trans*/*cis* = 3/1, 78.3 mg; 0.384 mmol, 76%): IR (neat, cm^{-1}) υ(C=C) 1659 (w); ^1H NMR (400 MHz, $CDCl_3$) *trans* isomer, δ 7.24−7.41 (5H, m, Ph), 6.74 (1H, s, =CH), 5.51 (1H, s, C*H*OMe), 4.46 (1H, m, C*H*Me), 3.53 (3H, s, OMe), 2.82 (1H, ddd, *J* = 16.4, 7.3, 3.3 Hz, C*H*H′), 2.23 (1H, ddd, *J* = 16.4, 10.0, 2.1 Hz, CH*H*′), 1.36 (3H, d, *J* = 6.3 Hz, Me); *cis* isomer, δ 7.24−7.41 (5H, m, Ph), 6.74 (1H, s, =CH), 5.51 (1H, s, C*H*OMe), 4.28 (1H, m, C*H*Me), 3.53 (3H, s, OMe), 2.77 (1H, ddd, *J* = 16.2, 7.1, 3.2 Hz, C*H*H′), 2.45 (1H, ddd, *J* = 16.2, 10.0, 2.1 Hz, CH*H*′), 1.36 (3H, d, *J* = 6.2 Hz, Me); ^{13}C NMR (100 MHz, $CDCl_3$) *trans* isomer, δ 142.5, 138.7, 129.6, 129.4, 128.0, 125.7, 107.7, 75.2, 55.1, 38.6, 21.6; *cis* isomer, δ 142.2, 138.5, 129.7, 129.1, 128.0, 125.8, 107.9, 76.4, 54.7, 37.6, 23.6; HRMS calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1153.

Synthesis of 3-Benzylidene-2,2-dibutyl-5-methyltetrahydrofuran (23). η^1-Alkynol **4** (208.8 mg, 0.502 mmol), PhCHO (110.2 mg, 1.04 mmol), $BF_3{\cdot}Et_2O$ (0.07 mL, 0.569 mmol), and Bu^nMgCl (1.04 mmol) in cold CH_2Cl_2 afforded **23** (93.6 mg, 0.326 mmol, 65%) as a colorless oil: IR (Nujol, cm^{-1}) υ(C═C) 1654 (w); ^1H NMR (300 MHz, $CDCl_3$) δ 7.21−7.37 (5H, m, Ph), 6.09 (1H, t, J = 2.6 Hz, ═CH), 4.10 (1H, m, *CH*-O), 2.97 (1H, ddd, J = 16.2, 5.9, 2.6 Hz, C*H*H′), 2.37 (1H, ddd, J = 16.2, 9.6, 2.6 Hz, CH*H*′), 1.74−1.22 (6H, m), 1.32 (3H, d, J = 6.0 Hz, Me), 0.89 (6H, t, J = 6.9 Hz, 2 Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 138.0, 128.3, 128.1, 126.3, 119.5, 88.3, 72.9, 40.7, 40.6, 40.3, 26.3, 25.9, 23.3, 23.1, 21.2, 14.1; HRMS calcd for $C_{20}H_{30}O$ 286.2297, found 286.2296.

Synthesis of 4-Benzylidene-2-methyl-1-oxaspiro[4.4]nonane (26). η^1-Alkynol **4** (174.7 mg, 0.42 mmol), PhCHO (90.1 mg, 0.85 mmol), $BF_3{\cdot}Et_2O$ (0.06 mL, 0.472 mmol), and $MgBr(CH_2)_4MgBr$ (1.26 mmol) afforded **26** (55.5 mg, 0.244 mmol, 58%) as a colorless oil: IR (Nujol, cm^{-1}) υ(C═C) 1657 (w); ^1H NMR (400 MHz, $CDCl_3$) δ 7.20−7.32 (5H, m, Ph), 6.20 (1H, dd, J = 3.0, 2.0 Hz, ═CH), 3.99 (1H, m, *CH*-O), 2.94 (1H, ddd, J = 16.2, 5.6, 3.0 Hz, C*H*H′), 2.45 (1H, ddd, J = 16.2, 9.4, 2.0 Hz, CH*H*′), 1.59−1.98 (8H, m), 1.33 (3H, d, J = 6.0 Hz, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 137.9, 128.3, 128.0, 126.3, 118.9, 93.8, 72.2, 41.1, 40.4, 40.1, 25.0, 24.8, 20.8; HRMS calcd for $C_{16}H_{20}O$ 228.1514, found 228.1519.

Synthesis of 4-Diphenylmethyl-2-methyl-5-phenyl-2,3-dihydrofuran (29). η^1-Alkynol **4** (180.2 mg, 0.433 mmol), PhCHO (91.8 mg, 0.866 mmol), $BF_3{\cdot}Et_2O$ (0.06 mL, 0.472 mmol), and Ph_2CuLi (194.6 mg, 0.866 mmol) afforded **29** (140.2 mg, 0.368 mmol, 85%) as a colorless oil: IR (Nujol, cm^{-1}) υ(C═C) 1660 (w); ^1H NMR (400 MHz, $CDCl_3$) δ 7.16−7.63 (15H, m, Ph), 5.33 (1H, s, C*H*(Ph)$_2$), 4.78 (1H, m, C*H*-O), 2.79 (1H, dd, J = 15.2, 9.6 Hz,C*H*H′), 2.29 (1H, dd, J = 15.2, 7.6 Hz, CH*H*′), 1.40 (3H, d, J = 6.4 Hz, Me); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 143.3, 143.2, 141.2, 131.7, 128.9, 128.8, 128.7, 128.3, 128.2, 127.4, 127.2, 127.1, 126.3, 126.2, 110.0, 76.0, 48.2, 39.9, 22.0; HRMS calcd for $C_{24}H_{22}O$ 326.1671, found 326.1570.

Cyclopropanation of Oxacarbenium 8. To a CH_2Cl_2 solution (20 mL) of tungsten oxacarbenium **8** (200 mg, 0.307 mmol) was added a diethyl ether solution of CH_2N_2 (77.4 mg, 1.842 mmol) at −20 °C; the mixture was stirred for 4 h before it was reduced to ca. 3 mL in vacuo at 23 °C. To this concentrated solution was added excess diethyl ether (20 mL) to yield an orange precipitate of **34**. Recrystallization of **34** from a saturated CH_2Cl_2/diethyl ether solution afforded red crystalline solid (163 mg, 0.239 mmol) in 78% yield: IR (neat, cm^{-1}) υ(CO) 1953 (s) 2035 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.15−7.43 (10H, m, Ph), 6.50 (1H, dd, J = 10.6, 7.6 Hz, C*H*-O), 5.92 (5H, s, Cp), 2.83 (1H, dd, J = 14.6, 7.6 Hz, CH*H*), 2.65 (1H, dd, J = 14.6, 10.6 Hz, CH*H*), 2.48 (1H, dd, J = 12.6, 7.6 Hz, C*H*H), 2.40 (1H, m, CH), 2.32 (1H, dd, J = 12.6, 8.0 Hz, CH*H*), 1.70 (1H, dd, J = 5.5, 7.6 Hz, CH*H*), 0.85 (1H, dd, J = 6.9, 5.5 C*H*H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 296.4, 216.0, 214.8, 214.6, 138.4, 135.8, 129.8, 129.1, 129.0, 128.7, 128.5, 126.4, 100.7, 95.8, 93.3, 61.8, 34.6, 33.4, 31.0. Anal. Calcd for $C_{27}H_{23}WO_5BF_3$: C, 47.65; H, 3.41. Found: C, 46.56; H, 3.67.

Synthesis of 1-Benzyl-6-phenyl-5-oxaspiro[2,4]heptan-4-one (35). To a CH_2Cl_2 solution (20 mL) of oxacarbenium **34** (162.6 mg, 0.239 mmol) was added water at 23 °C; the mixture was stirred for 2 h before it was brought dryness in vacuo. The residue was chromatographed on a preparative silica TLC to yield **35** as a colorless solid (59.8 mg, 0.215 mmol, 90%): IR (neat, cm^{-1}) υ(CO) 1778 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.15−7.35 (5H, m, Ph), 5.62 (1H, t, J = 7.8 Hz, C*H*-O), 2.65 (1H, dd, J = 15.2, 6.4 Hz, CH*H*), 2.53 (1H, dd, J = 12.9, 7.8 Hz, CH*H*), 2.51 (1H, dd, J = 15.2, 7.9 Hz, CH*H*), 2.38 (1H, dd, J = 12.9, 7.8 Hz, C*H*H), 1.95 (1H, m, CH), 1.56 (1H, dd, J = 4.4, 8.9 Hz, CH*H*), 0.91 (1H, dd, J = 4.4, 6.7 Hz, C*H*H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.3, 140.0 139.4, 128.7, 128.5, 128.3, 128.0, 126.3, 125.3, 78.6, 35.3, 34.9, 25.3, 25.2, 21.9; HRMS calcd for $C_{19}H_{18}O_2$ 278.1306, found 278.1302.

One-Pot Synthesis of 1-Benzyl-6-methyl-5-oxaspiro[2,5]octan-4-one (38) from Tungsten−Alkynol and CH_2N_2. To $CpW(CO)_3(\eta^1$-6-hydroxyheptyn-1-yl) (262 mg, 0.61 mmol) in cold diethyl ether (15 mL, 0 °C) was added PhCHO (77.2 mg, 0.728 mmol) and $BF_3{\cdot}Et_2O$ (103.3 mg; 0.728 mmol) to yield a red oil of carbenium salt. The diethyl mother liquor was decanted away; the carbenium salt was washed twice with diethyl ether before it was dissolved in CH_2Cl_2. To this CH_2Cl_2 solution was added CH_2N_2 (153.6 mg, 3.654 mmol) at −20 °C, and the mixture was stirred for 2 h before treatment of water (1.0 mL). The mixture was concentrated and eluted on a preparative silica TLC to yield **38** as a colorless solid (82.7 mg, 0.359 mmol; 59%): IR (neat, cm^{-1}) υ(CO) 1710 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 7.14−7.41 (5H, m, Ph), 4.49−4.56 (1H, m, CH-O), 2.78 (1H, dd, J = 15.3, 7.5 Hz, CH*H*), 2.65 (1H, dd, J = 15.3, 7.5 Hz, CH*H*), 1.78−1.99 (3H, m), 1.69 (1H, dd, J = 4.6, 4.0 Hz, CH*H*), 1.33−1.41 (2H, m), 1.31 (3H, d, J = 6.4 Hz, CH_3), 0.60 (1H, dd, J = 6.9, 4.0 Hz, C*H*H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 140.2, 128.1, 127.0, 126.2, 76.5, 34.4, 30.0, 29.8, 23.5, 23.3, 22.9, 19.9; HRMS calcd for $C_{15}H_{18}O_2$ 230.1306, found 230.1311.

One-Pot Synthesis of 1-Isobutyl-6-methyl-5-oxaspiro[2,5]octan-4-one (39) from Tungsten−Alkynol and CH_2N_2. This compound was prepared from a procedure similar to that of **37** except Pr^iCHO was used; the yield of **39** is 54%: IR (neat, cm^{-1}) υ(CO) 1775 (s); ^1H NMR (400 MHz, $CDCl_3$) δ 4.51 (1H, m, CH-O), 1.94 (1H, m), 1.54−1.79 (4H, m), 1.51 (1H, dd, J = 16.2, 3.7 Hz, C*H*H), 1.37 (3H, d, J = 6.2 Hz, CH_3), 1.02 (3H, d, J = 6.2 Hz, CH_3), 0.97 (3H, d, J = 6.4 CH_3), 0.88 (1H, m, C*H*) 0.41 (1H, dd, J = 3.7, 6.9 Hz, CH*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.5, 76.7, 38.7, 30.7, 28.6, 23.7, 23.3, 22.9, 22.4, 22.3, 21.3; HRMS calcd for $C_{11}H_{18}O_2$ 1182.1306, found 182.1311.

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

Supporting Information Available: Syntheses and spectral data of compounds **5**, **6**, **8**, **9**, **16−20**, **22**, **24**, **25**, **27**, **28**, **30−33**, **36**, and **37**; tables of crystal data, atomic coordinates, bond distances and angles of **8**, **9**, and **36** (34 pages). See any current masthead page for ordering and Internet access instructions.

JA970020+