Stereocontrolled Synthesis of Acyclic 1,3-Diols via Condensation of Tungsten−*syn*-π-Pentadienyl Complexes with Aldehydes. A New Prins Reaction via *s*-*trans*-Diene Cationic Intermediates

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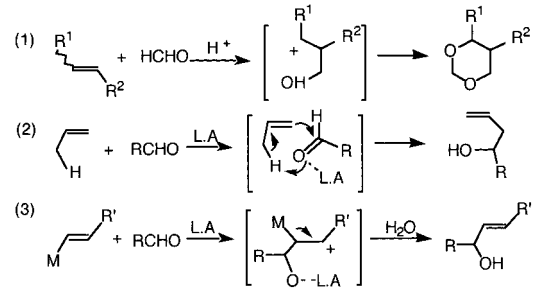
In the presence of $BF_3{\cdot}Et_2O$, condensation of $CpW(CO)_2$(*syn*-π-2-methoxycarbonylpentadienyl) with aldehydes generated tungsten−η^4-*trans*-diene cation in cold toluene, and hydrolysis of this salt afforded tungsten−π-allyl-*anti*-1,3-diols in good yields. This new synthesis of *anti*-1,3-diols represents an atypical Prins reaction that is applicable to normal aldehydes. The anti/syn ratios of 1,3-diols increased with an increase in the size of the aldehydes. These *anti*-1,3-diols were transformed into various complex oxygen heterocycles based on two demetalations: (1) conversion to an allyl cation followed by nucleophilic attack and (2) condensation with aldehydes via its CpW(NO)Cl derivative, to give functionalized α-methylene butyrolactones. A semi-emperical calculation was performed to deduce the transition-state structure to rationalize the anti-stereoselectivity.

Introduction

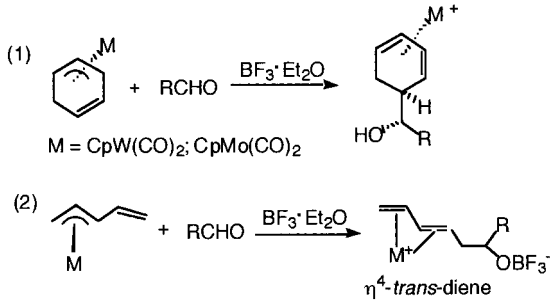
The condensation of olefins with formaldehyde in the presence of acid is called the Prins reaction, which can produce 1,3-diol derivatives efficiently via a carbocation intermediate (Scheme 1, eq 1).[1] Unfortunately, this condensation is not applicable to common aliphatic and aromatic aldehydes which in the presence of Lewis acid give homoallylic alcohols following an "ene" reaction pathway (Scheme 1, eq 2).[2] In the presence of Lewis acid catalysts, alkenyl complexes of boranes, silanes, and stannanes have been proposed to form carbocationic intermediates in condensation with aldehydes.[3,4] However, the carbocation intermediates cannot be trapped by water to yield the desired 1,3-diols (Scheme 1, eq 3) and instead give homoallylic alcohols exclusively. A similar phenomenon is observed for their allyl and propargyl analogues.[3,4] 1,3-Diols are versatile building blocks for complex natural molecules.[5] The synthesis of 1,3-diols from an olefin and common aldehydes is a challenging issue in synthetic chemistry.

Recently, we reported that molybdenum− and tungsten−η^4-cyclohexadienyl complexes form stable η^4-cyclohexadiene cations upon condensation with BF_3/RCHO (Scheme 2, eq 1).[6,7] However, the cation is too stable to react with water over a prolonged period. 1,3-Diols may be obtained if the intermediate involves reactive metal−η^4-*trans*-diene species. Along these lines, we report here a detailed stereocontrolled synthesis of 1,3-diols via acid-promoted condensation of metal−π-pentadienyl complexes with aldehydes; this process involves a η^4-*trans*-diene cationic intermediate (Scheme 2, eq 2).

Scheme 1



Scheme 2



* To whom correspondence should be addressed. Phone: (886)-3-5721424. Fax: (886)-3-5711082.

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(2) For the ene reaction, see selected review papers: (a) Mikami, K.; Shimizu, M. *Chem, Rev*. **1992**, *92*, 1021. (b) Snider, B. B. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: London, 1991; Vols. 2 and 5. (c) Hoffmann, R. W. *Angew. Chem*. **1987**, *26*, 489.

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(7) Cheng, M.-F.; Ho, Y.-H.; Lee G.-H.; Peng, S.-M.; Liu R.-S. *J. Chem. Soc., Chem. Commun*. **1991**, 697.

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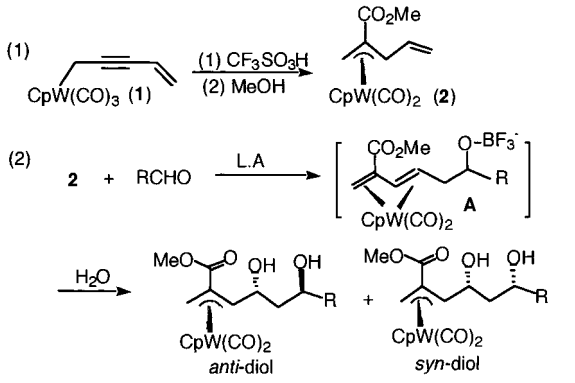
Scheme 3



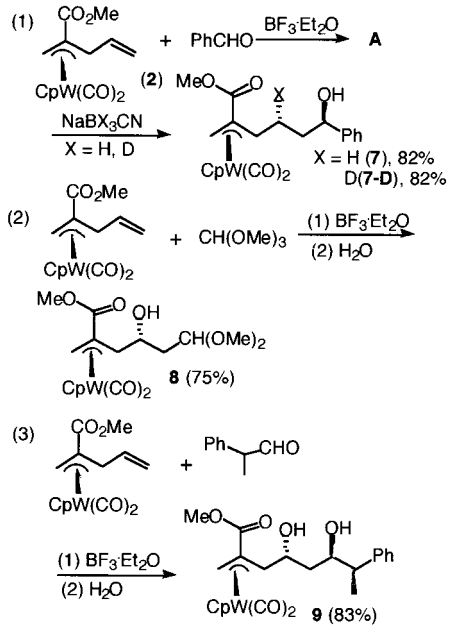
entry	aldehydes	L.A	isolated yields
1	R = Me	$BF_3{\cdot}Et_2O$	**3**-***anti*** (58%); **3**-***syn*** (24%)
2	R = Et	$BF_3{\cdot}Et_2O$	**4**-***anti*** (65%); **4**-***syn*** (14%)
3	R = Ph	$BF_3{\cdot}Et_2O$	**5**-***anti*** (70%); **5**-***syn*** (10%)
4	R = ^{i}Pr	$BF_3{\cdot}Et_2O$	**6**-***anti*** (79%); **6**-***syn*** (8%)
5	R = ^{i}Pr	$TiCl_4$	**6**-***anti*** (49%); **6**-***syn*** (12%)
6	R = ^{i}Pr	$SnCl_4$	**6**-***anti*** (51%); **6**-***syn*** (13%)
7	R = ^{i}Pr	$AlCl_3$	**6**-***anti*** (31%); **6**-***syn*** (12%)

Results

Our synthetic protocol requires the synthesis of metal−*syn*-π-pentadienyl complexes to realize the Prins reaction. Scheme 3 shows the synthesis of tungsten−*syn*-2-methoxycarbonylpentadienyl complex **2** via alkoxycarbonylation of tungsten−η^1-vinylpropargyl complex **1**.[8] Compound **2** is speculated to lead to complex oxygen heterocycles if it can effect the Prins reaction. Condensation of compound **2** with aldehydes was performed in cold toluene (−40 °C), and yellow precipitates slowly deposited when 1 equiv of Lewis acid was added to the solution. Treatment of this yellow slurry with a mixture of $NaHCO_3$(aq)/CH_3CN at −40 °C afforded tungsten−*syn*-π-allylic diols **3**−**6** as a mixture of *anti*- and *syn*-diols. These two diastereomers were separable on a silica column, and the isolated yields are shown in eq 2 (Scheme 3). The major *anti*-diols **3**(*anti*)−**6**(*anti*) were formed preferably (yields >55%) if $BF_3{\cdot}Et_2O$ was used (entries 1−4). The anti/syn ratios increased with an increase in the size of the aldehydes. The stereochemistry of the major diastereomers was determined by X-ray diffraction studies of the lactonyl derivatives of compound **5**-*anti* (vide infra). Compounds **3**−**6** have a *syn*-π-allyl configuration; i.e., the diol fragment lies on the same side as the methoxycarbonyl group. This implies that η^4-*trans*-diene cation is the observed precipitate that yields diols upon hydrolysis. The water attacks regioselectively at the diene C_δ carbon opposite the tungsten fragment. $BF_3{\cdot}Et_2O$ is superior to other Lewis acids including $TiCl_4$, $SnCl_4$, and $AlCl_3$; these acids gave compound **6**-*anti* in lower yields (entries 5−7).

According to our previous study[8] on $CpW(CO)_2$(η^4-*trans*-2-methoxycarbonylpentadiene) cation, the C_δ-carbon of η^4-*trans*-diene cation **A** (Scheme 4) can be attacked selectively by amines, alcohols, thiols, and hydride. RMgBr and R_2CuLi can attack at the C_α-carbon. Attempts to obtain 1,3-amino alcohols and related 1,3-functionalized alcohols were unsuccessful via the addition of NH_3(aq), NaSH(aq), and NaI(aq) to the *trans*-diene cation **A** generated from **2** and benzaldehyde. Compound **2** was recovered exclusively, indicating that these nucleophiles attack at the OBF_3^- end of species **A** to give the reverse reaction. Reduction of the cation **A** by $NaBH_3CN$ and $NaBD_3CN$ proceeded smoothly to yield the allyl alcohol **7** and **7D** in 82% yield. Although this Prins-type condensation does not work for ketones, imines, and epoxides, it is applicable to trimethoxymethane.[10] 1,3-Difunctionalized compound **8** was obtained from trimethoxymethane in 75% yield following the same reaction sequence. Scheme 4 (eq 3) shows a remarkable diastereoselectivity in the condensation of **2** with 2-phenylpropionaldehyde (2.0 equiv) with $BF_3{\cdot}Et_2O$ (1.0 equiv), and hydrolysis of the resulting η^4-*trans*-diene cation gave only a single diastereomer **9** in 83% isolated yield. Compound **9** is assigned an erythro-configuration by comparison of its proton NMR spectral data and proton NOE effect to those of related homoallylic alcohol analogues.[11] This configuration is consistent with the Felkin−Ahn model.

Scheme 4



We also prepared tungsten−π-pentadienyl complex **10** in three steps from **2** following a convenient operation (Scheme 5). Compound **10** shows a preference for *anti*-diols in analogous reactions; the isolated yields are given in eq 1 (Scheme 5). The condensation proceeded with less efficiency compared to compound **2**. Structural characterization of the *anti*-diols relies on the X-ray characterization[12] of compound **14** obtained from the addition of Ph_2CuLi to the η^4-*trans*-diene cationic intermediate (eq 2). Notably, tungsten−π-2-vinylallyl compound **11** can potentially undergo BF_3-promoted addition with alde-

(8) Cheng, M.-H.; Ho, Y.-H.; Lee, G.-H.; Peng, S.-M.; Chu, S.-Y.; Liu, R.-S. *Organometallics* **1994**, *13*, 4082.

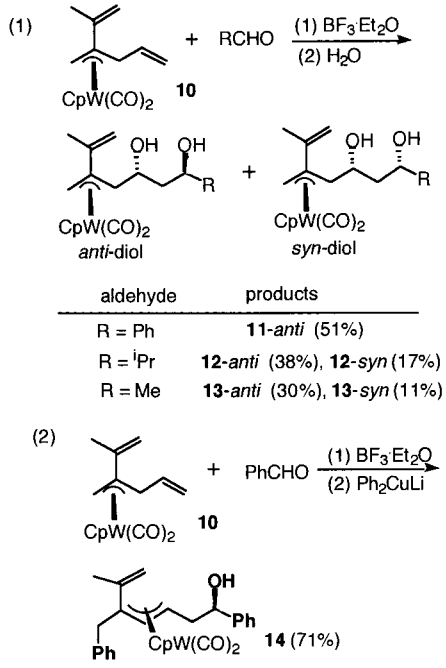
(9) The crystal data for **15b**: monoclinic, *C*2/*c*, a = 23.876 (7) Å, b = 13.635(3) Å, c = 11.617(3) Å, β = 97.43 (2)°, Z = 8, V = 3750.0(15) Å^3, R = 0.0278, and R_w = 0.0245 for 3326 independent reflections with 2123 > 3σ(I).

(10) Li, Y.-L.; Liu, R.-S. Unpublished results.

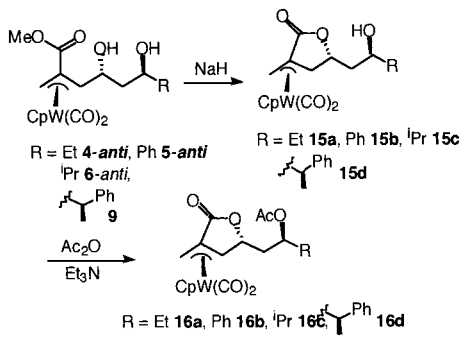
(11) Heathcock, C. H.; Kiyooka, S. K.; Blumenkopf, T. A. *J. Org. Chem.* **1984**, *49*, 4214.

(12) Crystal data for compound **14**: triclinic, space group *P*-1, a = 10.6375(19) Å, b = 15.574(4) Å, c = 17.542(3) Å, α = 110.266(18)°, β = 102.446(15)°, γ = 98.656(19)°, z = 2580.5(9) A^3.

Scheme 5



Scheme 6

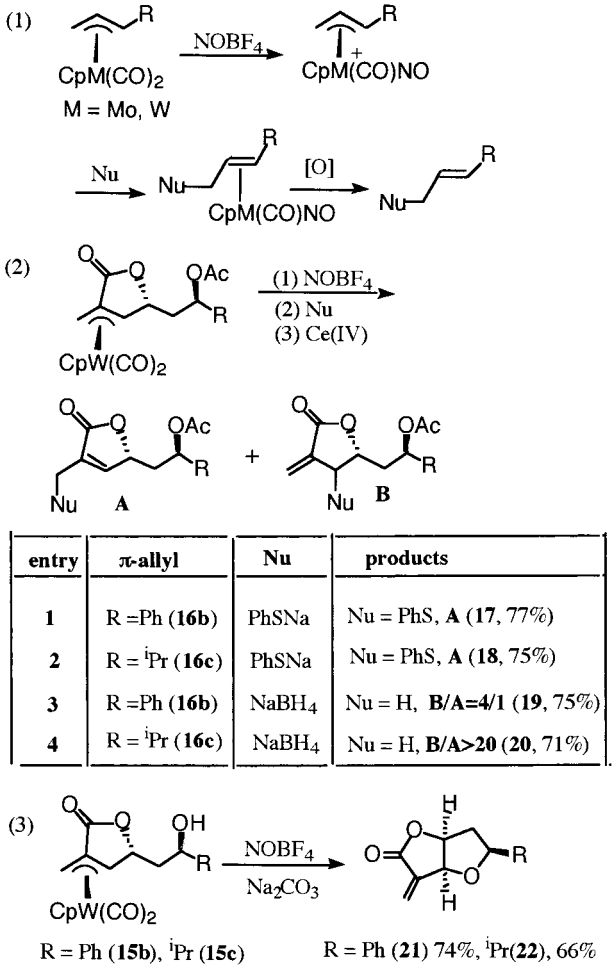


hydes at its 2-vinyl group, and η^4-trimethylenemethane cation is the intermediate that can be trapped by nucleophiles.[13] However, no such products were found for compound **10** in which the 3-vinyl group is more reactive and forms the *trans*-η^4-diene cationic intermediate.

Highly functionalized tungsten−π-allylic diols are useful intermediates for the synthesis of complex butyrolactones. As shown in Scheme 6, treatment of the diols **4**(*anti*)−**6**(*anti*) and **9** with NaH afforded the π-lactonyl complexes **15a**−**d** in good yields (>82%). Compounds **15a**−**d** were protected with an acetyl group to yield **16a**−**d** with yields exceeding 80%. The molecular structure of **15b** was determined by an X-ray diffraction study[9] to clarify its stereochemistry.

Two efficient methods have been developed for demetalation of molybdenum and tungsten-π-allyl complexes (Scheme 7), and both can be performed in a one-pot operation. The carbonyl group of $CpM(CO)_2$(π-allyl) (M = Mo, W) is easily replaced by $NOBF_4$ to yield an allyl cation that reacts with nucleophiles to give functionalized olefins after oxidation.[14,15] Entries 1 and 2 (Scheme 7)

Scheme 7



show two instances for the synthesis of furanones **17**−**18** via the addition of PhSNa to allyl cations derived from **16b**,**c**. Reduction of the same cations with $NaBH_4$ (entries 3−4) gave α-methylene butyrolactones **19B** and **20B** exclusively, and the regiochemistry is distinct from those in entries 1−2. Only a small amount of γ-lactone **20A** was found for **16C** (entry 4). Isomerization probably occurred when tungsten−olefin species were formed.[16] Equation 3 shows an intramolecular cyclization for the allyl cation generated from **16b**,**c**. The bicyclic lactones **21** and **22** were obtained in 65−74% yield. The stereochemistries of **21** and **22** were determined by proton NOE-difference spectra. These two lactones were produced from attack of the hydroxy group of the cations at their allyl Cγ-carbons opposite the tungsten fragment.

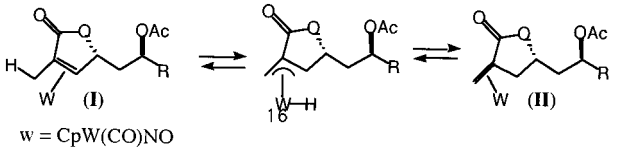
Scheme 8 shows an alternative demetalation of tungsten−π-allyl complex; this involves condensation of their CpW(NO)Cl derivatives with aldehydes to yield homoallylic alcohols.[17] A chairlike transition state is proposed

(13) Yang, G.-M.; Yang, G.-M.; Liu, R.-S. *Organometallics* **1992**, *11*, 3444.

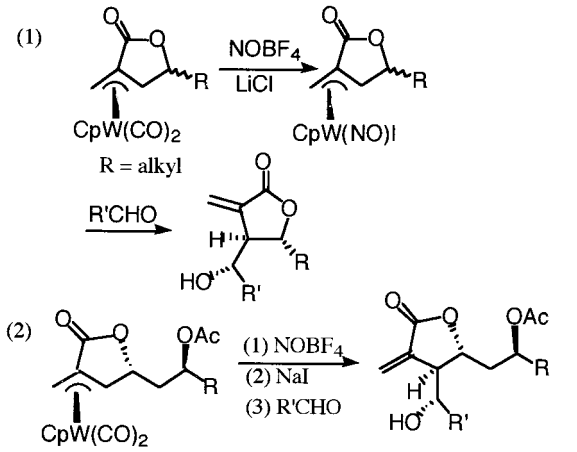
(14) (a) Faller, J. W.; Rosan, A. M., *J. Am. Chem. Soc.* **1976**, *98*, 3388. (b) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858.

(15) Adams, R. D.; Chodosh, D. F. Faller, J. W.; Rosan, A. M. *J. Am Chem. Soc.* **1979**, *101*, 2570.

(16) In eq 2 (Scheme 7), formation mechanism of α-methylene butyrolactones **19** and **20** is proposed in the following mechanism. In this isomerization, the tungsten−olefin species **(I)** are the kinetically favorably products that undergo isomerization to the more stable species **(II)** via a tungsten−allyl hydride species.



Scheme 8



entry	π-allyl	aldehyde	products
1	R = Et (**17a**)	R' = Ph	**23a** (57%)
2	R = Ph (**17b**)	R' = Ph	**23b** (65%)
3	R = Ph (**17b**)	R' = ^{i}Pr	**23c** (51%)
4	R = ^{i}Pr (**17c**)	R' = Ph	**23d** (58%)
5	R = (**17d**) 	R' = Ph	**23e** (61%)

to control the product stereochemistry. We previously reported[18] that the syn- and anti-isomers of tungsten−π-lactonyl complexes gave the same *trans*-α-methylene lactones bearing an anti-homoallylic alcohol (Scheme 8, eq 1). We used such functionalized lactones for the synthesis of natural lactones such as (+)-dihydrocanadensolide,[19] racemic avenociolide,[20] and (+)-methylenelactocin.[21] Equation 2 (Scheme 8) shows applications of tungsten−π-allyl complexes **16a**−**d** to the synthesis of highly functionalized *trans*-α-methylene lactones following this approach. The whole reaction was carried out in a one-pot operation. The π-allyl complexes **16a**−**d** were sequentially treated with $NOBF_4$, NaI in CH_3CN, and finally aldehydes, and the resulting α-methylene butyrolactones **23a**−**e** were obtained in respective yields of 51−65%. The ^{1}H NMR spectral data of **23a**−**e** match those of isostructural *trans*-α-methylene butyrolactones,[18] as represented by eq 1 (Scheme 8).

Discussions

Condensations of tungsten−π-pentadienyl complexes with aldehydes proceeds in open transition states.[22] We have performed semi-emperical calculation with the pm3 using the program suit SPARTAN 5.0.[23] Table 1 shows the relative energies of the two most likely transition states in condensation of compound **2** with various aldehydes. The structures of representative transition states are shown in Figure 1. In the case of benzaldehyde, the two structures **2-Ph(A)** and **2-Ph(B)** adopt synclinal conformation with OBF_4^- fragment approaching tungsten fragment to maximize electrostatic attraction. The tungsten fragment becomes a cationic center as η^4-*trans*-diene cation is forming as a reaction intermediate. This orientation stabilizes these two states to control reaction stereoselectivities. State **2-Ph(A)** is lower in energy than **2-Ph(B)** by −3.86 cal/mol because the latter adopts an unfavorable *s-cis*-conformation for the BF_3−PhCHO complex. The corresponding *s-trans*-conformation is destabilized by stereic hindrance between OBF_4^- and allyl fragment. This model accounts for the observed anti-stereoselection. A similar pattern is found for the reaction of compound **2** with RCHO·BF_3 (R = Et, Me) as shown in entries 2 and 3. The energy differences between these two states become smaller for less bulky aldehydes (R = Et, ΔE = 2.58 kcal/mol; R = Me, ΔE = 0.89 kcal/mol), consistent with the observed anti/syn ratios. For isobutyraldehyde, a different structure **2-^{i}Pr(C)** is found to be the second favorable state that has ca. 5.37 kcal/mol

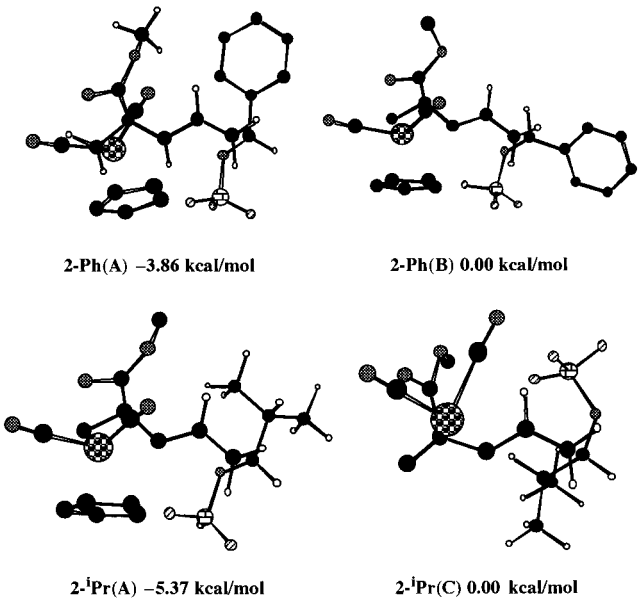


Figure 1. Two most likely structures of transition states in the condensation of compound **2** with RCHO·BF_3·Et_2O. Part of the methoxycarbonyl group of 2-^{i}Pr(C) was omitted for clarity.

Table 1. Relative Energies of Transition States for Condensation of Compound 2 with Aldehydes

entry	reactants	T.S. (kcal/mol)	selectivities	anti/syn
1	$PhCHO^+$	**2-Ph(A), −3.86**	*anti*-diol	70/10
	BF_3·Et_2O	**2-Ph(B), 0.00**	*syn*-diol	
2	$EtCHO^+$	**2-Et(A), −2.58**	*anti*-diol	65/14
	BF_3·Et_2O	**2-Et(B), 0.00**	*syn*-diol	
3	$MeCHO^+$	**2-Me(A), −0.89**	*anti*-diol	58/24
	BF_3·Et_2O	**2-Me(B), 0.00**	*syn*-diol	
4	$^{i}PrCHO^+$	**2-^{i}Pr(A), −5.37**	*anti*-diol	79/8
	BF_3·Et_2O	**2-^{i}Pr(B), 0.00**	*syn*-diol	

(17) (a) Faller, J. W.; Linebarrier, D. L. *J. Am. Chem. Soc.* **1989**, *111*, 1937 (b) Faller, J. W.; Diverdi, M. J.; John, J. A. *Tetrahedron Lett.* **1991**, *32*, 1271. (c) Faller, J. W.; Nguyen, J. T.; Ellis, W.; Mazzieri, M. R. *Organometallics* **1993**, *12*, 1434.

(18) 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.

(19) .Chen M.-J.; Narkulan, K.; Liu, R.-S. *J. Org. Chem.* **1999**, 64. 8311.

(20) Narkunan, K.; Liu, R.-S. *J. Chem. Soc., Chem. Commun.* **1998**, 1521.

(21) Chandrasekharam, M.; Liu, R.-S. *J. Org. Chem.* **1998**, 63, 9122..

(22) (a) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207. (b) Roush W. R. In *Comprehensive Organic Chemistry: Addition to C−X π-bond. Part II*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Chapter 1.1, p 1.

(23) (a) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209. (b) Stewart, J. J. P. *J. Comput. Chem.* **1991**, *12*, 320. (c) SPARTAN 5.1.1, Wavefunction Inc., Irvine, CA.

higher in energy than state **2-^{i}Pr(A)**, in favor of anti-stereoselection

In summary, we have reported a new tungsten-mediated Prins reaction via condensation of tungsten−*syn*-π-pentadienyl complexes with aldehydes/$BF_3{\cdot}Et_2O$ in cold toluene. This reaction generates tungsten−η^4-*trans*-diene cationic intermediates that react with water to yield tungsten−π-allyl-*anti*-1,3-diols. These *anti*-1,3-diols were transformed into various complex oxygen heterocycles based on two demetalations yielding functionalized α-methylene butyrolactones: (1) conversion to an allyl cation followed by nucleophilic attack and (2) condensation with aldehydes via its CpW(NO)Cl derivative.

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. Mass data of tungsten compounds were reported according to ^{184}W. Allyltungsten compounds **2** were prepared according to procedures described in the literature. Spectral data of compounds **4**−**6**, **9**−**13**, **18**, **15b**,**c**, **16b**−**d**, **18**, **20**, **22**, and **23b**−**e** in repetitive experiments are provided in the Supporting Information.

Synthesis of Tungsten−*syn*-π-Allyl-1,3-diol 3. To a toluene solution (10 mL) of compound **2** (200 mg, 0.46 mmol) were added acetaldehyde (0.04 mL, 0.71 mmol) and $BF_3{\cdot}Et_2O$ (0.07 mL, 0.56 mmol) at −40 °C, and the mixtures were stirred for 2 h to complete the generation of orange precipitates. To this suspension was added a CH_3CN/H_2O mixture at −40 °C to yield a clear yellow solution. The organic layer was separated, dried in vacuo, and chromatographed through a silica column (diethyl ether/hexane = 2/1) to yield the *anti*-diol (0.13 g, 0.27 mmol, 58%, $R_f = 0.18$) and *syn*-diol (50 mg, 0.11 mmol, 24%).

Spectral data for compound **3-*anti***: IR (Nujol) υ(CO) 1966 (vs), 1895 (vs), 1690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (3H, d, $J = 7.0$ Hz), 1.32 (1H, s), 1.66 (1H, m), 2.10 (1H, d, $J = 9.5$ Hz), 2.90 (1H, s), 3.71 (3H, s), 4.09 (1H, m), 5.27 (5H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.0, 24.5, 43.7, 51.8, 52.6, 65.5, 71.7, 77.5, 88.4, 173.4, 221.0, 222.4; MS (12 eV, EI) 492 (M^+). Anal. Calcd for $C_{16}H_{20}WO_6$: C, 39.05; H, 4.10. Found: C 39.24; H, 4.22.

Spectral data for compound **3-*syn***: IR (Nujol) υ(CO) 1966 (vs), 1895 (vs), 1690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (3H, d, $J = 6.1$ Hz), 1.33 (1H, s), 1.55 (1H, m), 2.03 (1H, d, $J = 9.3$ Hz), 2.90 (1H, s), 3.72 (3H, s), 4.08 (1H, m), 5.28 (5H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.1, 24.5, 43.6, 51.9, 52.5, 65.6, 71.8, 77.6, 88.5, 173.5, 221.0, 222.4; MS (12 eV, EI) 492 (M^+). Anal. Calcd for $C_{16}H_{20}WO_6$: C, 39.05; H, 4.10. Found: C, 38.78; H, 4.30.

Synthesis of Tungsten−*syn*-π-Allylic Alcohol 7. To a cold toluene (−40 °C) solution (5.0 mL) of compound **2** (0.20 g, 0.46 mmol) were added $BF_3{\cdot}Et_2O$ (0.070 mL, 0.56 mL) and benzaldehyde (0.070 mL, 0.69 mmol), and the mixtures were stirred for 2 h for complete generation of *s-trans*-diene precipitates. To this suspension was added a CH_3CN solution (2.0 mL) of $NaBH_3CN$ (150 mg, 2.39 mmol), and the solution was warmed to 23 °C before addition of a saturated NH_4Cl solution. The organic layer was separated, concentrated, and eluted through a silica column (diethyl ether/hexane = 2/1) to give compound **7** as a yellow solid (0.20 g, 0.38 mmol, 82%): IR (Nujol) υ(CO) 1960 (vs), 1889 (vs), 1694 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.05 (1H, s), 1.84 (2 H, m), 2.07 (1H, br t, $J = 6.63$ Hz), 2.34 (1H, m), 2.83 (1H, m), 2.91 (1H, s), 3.65 (1H, s), 4.77 (1H, t, $J = 7.5$ Hz), 5.27 (5H, s), 7.30 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.8, 29.0, 42.8, 50.6, 51.0, 73.1, 77.9, 88.3, 126.0, 127.4, 128.5, 145.1, 172.2, 223.3, 224.1; MS (12v eV, EI) 538 (M^+). Anal. Calcd for $C_{21}H_{22}WO_5$: C, 46.86; H, 4.12. Found: C, 46.71; H, 4.33.

Synthesis of Tungsten−*syn*-π-Allylic Alcohol 8. To a cold toluene (−40 °C) solution (25.0 mL) of compound **2** (1.00 g, 2.33 mmol) were added $BF_3{\cdot}Et_2O$ (0.35 mL, 2.79 mL) and trimethoxymethane (0.51 mL, 4.65 mmol), the mixtures were stirred for 2 h before addition of water, and the solution was warmed to 23 °C. The organic layer was separated, concentrated, and eluted through a silica column (diethyl ether/hexane = 2/1) to give compound **8** as a yellow solid (0.94 g, 1.75 mmol, 75%): IR (Nujol) υ(CO) 1960 (vs), 1891 (vs), 1691 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.11 (1H. s), 2.06 (1H, m), 2.50 (1H, m), 3.36 (1H, s), 3.51 (3H, s), 3.62 (3H, s), 3.73 (3H, s), 3.88 (3H, s), 4.68 (5H, s), 5.22 (1H, dd, $J = 8.0$, 3.2 Hz), 5.32 (1H, dt, $J = 9.8$, 3.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 221.9, 221.8, 170.8, 102.7, 88.6, 77.7, 77.2, 56.2, 54.4, 52.2, 51.5, 51.1, 41.5, 24.4; MS (12v eV, EI) 536 (M^+). Anal. Calcd for $C_{18}H_{24}WO_7$: C, 40.29; H, 4.51. Found: C, 40.00; H, 4.33.

Synthesis of Tungsten−π-Allyl Complex 14. To a cold toluene (−40 °C) solution (5.0 mL) of compound **10** (0.20 g, 0.49 mmol) were added $BF_3{\cdot}Et_2O$ (0.12 mL 0.49 mmol) and benzaldehyde (0.060 mL, 0.60 mmol), and the mixtures were stirred for 2 h before addition of a THF solution of Ph_2CuLi (0.62 mmol). The solution was stirred for 2 h before it was brought to 23 °C, and to this mixture was added a saturated NH_4Cl solution. The organic layer was separated and chromatographed through a silica column to give compound **14** (diethyl ether/hexane =1/1) as a yellow solid (0.24 g, 0.37 mmol, 82%): IR (Nujol) υ(CO) 1921 (vs), 1839 (vs), υ(OH) 3350 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (s, 3H), 1.85 (1H, m, $J = 11.2$ Hz), 2.58 (1H, m), 2.60 (1H, d, $J = 16.0$ Hz), 2.80 (1H, m), 2.84 (1H, d, $J = 16.0$ Hz), 3.53 (1H, d, $J = 10.0$ Hz), 4.41 (1H, s), 4.43 (1H, s), 4.86 (1H, dd, $J = 6.6$, 5.1 Hz), 5.38 (5H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 47.2, 48.7, 49.3, 70.0, 73.3, 77.2, 91.8, 113.3, 125.7, 126.4, 127.4, 127.8, 127.9, 128.7, 140.5, 143.4, 145.9, 226.8, 226.9; MS (12 eV, EI) 596 (M^+). Anal. Calcd for $C_{28}H_{28}WO_3$: C, 56.39; H, 4.73. Found: C, 56.64; H, 4.85.

Synthesis of Tungsten−π-Lactonyl Complex 15a. To a THF solution (15 mL) of compound **4-*anti*** (260 mg, 0.55 mmol) was added NaH (22 mg, 0.55 mmol) at 0 °C, and the mixtures were stirred for 2 h. To this mixture was added a saturated NH_4Cl solution, and the organic layer was extracted with diethyl ether, concentrated, and eluted through a silica column (diethyl ether/hexane = 1/1) to give complex **15a** (232 mg, 0.49 mmol, 89%): IR (Nujol) υ(CO) 1933 (vs), 1876 (vs), 1758 (s), υ(OH) 3350 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.34 (5H, s), 4.87 (1H, dd. $J = 9.6$, 3.8 Hz), 3.83−3.92 (1H, m), 3.47 (1H, s), 3.11 (1H, d, $J = 3.6$ Hz), 1.77−1.99 (2H, m), 1.46−1.56 (2H, m), 1.40 (1H, d, $J = 3.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 225.3, 219.4, 176.1, 93.9, 81.3, 77.2, 69.9, 67.1, 45.8, 31.0, 21.4; MS (75 eV, *m*/*e*) 446 (M − CO). Anal. Calcd for $C_{16}H_{18}WO_5$: C, 40.50; H, 3.83. Found: C, 40.44; H, 3.69.

Synthesis of Tungsten−π-Lactonyl Complex 16a. To a Et_3N (10 mL) solution of **15a** (260 mg, 0.55 mmol) was added acetic anhydride (1.0 mL) and CH_2Cl_2 (5.0 mL), and the mixture was refluxed for 3 h. To this mixture was added H_2O (10 mL), and the organic layer was extracted with diethyl ether. The extract was concentrated and eluted through a silica column (diethyl ether/hexane = 1/1) to yield compound **16a** as a yellow solid (223 mg, 0.43 mmol, 80%): IR (Nujol) υ(CO) 1950 (vs), 1870 (vs), 1725 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.89 (3H, t, $J = 7.4$ Hz), 1.48 (1H, d, $J = 3.8$ Hz), 1.64 (2H, m), 1.92−2.01 (1H, m), 2.07−2.17 (1H, m), 2.06 (3H, s), 3.10 (1H, d, $J = 3.8$ Hz), 3.40 (1H, s), 4.61 (1H, dd, $J = 8.1$, 4.7 Hz), 5.02−5.10 (1H, m), 5.32 (5H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 225.4, 219.1, 176.1, 170.7, 93.9, 81.1, 77.2, 72.4, 66.2, 42.5, 27.5, 21.5, 21.2, 9.2; MS (75 eV, *m*/*e*) 516 (M^+). Anal. Calcd for $C_{18}H_{20}WO_6$: C, 41.85; H, 3.91. Found: C, 41.77; H, 3.77.

Synthesis of Furanone 17. To a CH_3CN solution (5.0 mL) of compound **16b** (0.18 g, 0.32 mmol) was added $NOBF_4$ (0.040 g, 0.34 mmol), and the mixture was stirred for 20 min before addition of NaSPh (0.40 mmol). The resulting red suspension was stirred for 3 h, $(NH_4)_2Ce(NO_3)_6$ (0.35 g, 0.64 mmol) was added, and the solution was evaporated to dryness. The

residue was extracted with diethyl ether and eluted through a preparative TLC plate (diethyl ether/hexane = 1/1) to yield furanone **17** (90 mg, 0.24 mmol, 77%) as a colorless oil: IR (neat) υ(CO) 1760 (vs), 1732 (vs); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (1H, m), 2.00 (3H, s), 2.14 (1H, m), 3.64 (s, 2H), 4.90 (1H, dt, J = 6.3, 2.3 Hz), 5.82 (1H, J = 9.7, 3.5 Hz), 6.67 (1H, d, J = 2.3 Hz), 7.17−7.27 (m, 10H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) 20.9, 28.1, 40.1, 72.4, 78.0, 126.3, 126.7, 127.2, 128.9, 129.3, 130.5, 131.1, 139.8, 150.0, 168.1, 170.1; MS (12 eV, *m*/*e*) 368 (M^+); HRMS calcd for $C_{21}H_{20}SO_4$ 368.1083, found 368.1092.

Synthesis of α-Methylene Butyrolactone 19A,B. To a CH_3CN solution of compound **16b** (0.18 g, 0.32 mmol) was added $NOBF_4$ (50 mg, 0.40 mmol) at 0 °C, and the mixture was stirred for 1.0 h before addition of solid $NaBH_3CN$ (0.10 g, 1.56 mmol). The mixtures were stirred for 1 h before addition of $(NH_4)_2Ce(NO_3)_6$ (0.35 g, 0.64 mmol). The solution was concentrated and eluted through a preparative TLC plate (diethyl ether/hexane = 1/1) to give compound **19A**,**B** as a colorless oil (**19B**/**19A** = 4.2, 62 mg, 0.24 mmol, 75%): IR (neat) υ(CO) 1761 (vs), 1731 (vs), υ(C=C) 1655 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) **19B** δ 2.00 (3 H, s), 2.05 (1H, m), 2.17 (1H, m), 2.55 (1H, m), 3.02 (1H, m), 4.55 (1H, m), 5.57 (1H, d. J = 2.3 Hz), 5.85 (1H, dd, J = 9.4, 4.0 Hz), 6.16 (1H, t, J = 2,8 Hz), 7.20−7.30 (m, 5H), **19A** selected peaks 6.91 (1H, s), 5.88 (1H, dd, J = 9.0, 4.2 Hz), 4.96 (1H, m), 2.32 (1H, m), 1.89 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 33.4, 43.0, 72.3, 73.8, 122.5, 126.1, 128.2, 128.7, 134.0, 140.0, 170.0, 170.4; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 33.4, 43.0, 72.3, 73.8, 122.5, 126.1, 128.2, 128.7, 134.0, 140.0. 170.0, 170.4; MS (12 eV, *m*/*e*) 260 (M^+); HRMS calcd for $C_{15}H_{16}O_4$ 260.1049, found 260.1055.

Synthesis of α-Methylene Butyrolactone 21. To a CH_3CN solution (7.0 mL) of compound **15b** (0.20 g, 0.38 mmol) was added $NOBF_4$ (50 mg, 0.43 mmol) at 0 °C, and the mixture was stirred for 0.50 h before addition of a saturated Na_2CO_3 (500 mg) solution. The mixture was stirred for 12 h in air at 23 °, and concentrated in vacuo. Elution of this residue on a preparative TLC plate (diethyl ether/hexane = 1/1) gave compound **21** as a colorless oil (60 mg, 0.28 mmol, 74%): IR (neat) υ(CO) 1763 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (1H, m), 2.74 (1H, m), 4.92 (1H, d, J = 5.3 Hz), 4.96 (1H, m), 5.04 (1H, m), 6.01 (1H, s), 6.39 (1H, s), 7.30 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.9, 78.5, 81.9, 126.1, 128.3, 128.4, 129.7, 135.7, 139.9, 169.2; HRMS calcd for $C_{13}H_{12}O_3$ 216.0785, found 216.0766.

Synthesis of Functionalized α-Methylene Butyrolactone 23a. To a CH_3CN solution (5.0 mL) of compound **17a** (200 mg, 0.40 mmol) was added $NOBF_4$ (52 mg, 0.44 mmol) at 0 °C, and the mixtures were stirred for 20 min before addition of NaI (124 mg, 0.84 mmol). The resulting red solution was stirred for an additional 20 min before benzaldehyde (220 mg, 2.04 mmol) was added. The mixtures were stirred for 8 h, concentrated, and eluted through a preparative silica TLC plate (diethyl ether/hexane = 1/1) to give the lactone **23a** (72 mg, 0.24 mmol, 57%) as a colorless oil: IR (neat) υ(CO) 1748 (vs), υ(OH) 3458 (vs) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, t, J = 7.6 Hz), 1.25−1.44 (2H, m), 1.59−1.66 (2H, m), 2.11 (3H, s), 3.03 (1H, m), 4.26 (1H, m), 4.67 (1H, dd, J = 7.7, 3.4 Hz), 4.99−5.02 (1H, m), 5.80 (1H, d, J = 2.3 Hz), 6.37 (1H, d, J = 2.3 Hz), 7.26−7.40 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.2, 21.1, 27.5, 37.4, 52.7, 72.1, 76.3, 79.4, 126.1, 126.6, 128.1, 128.6, 135.1, 140.5, 169.6, 169.8; MS (75 eV, *m*/*e*) 318 (M^+); HRMS calcd for $C_{18}H_{22}O_5$ 318.1467, found 318.1467.

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Supporting Information Available: Syntheses and spectral data of compounds **4**−**6**, **9**−**13**, **18**, **15b**,**c**, **16b**−**d**, **18**, **20**, **22**, and **23b**−**e** in repetitive synthesis; crystal data, ORTEP drawing, atomic coordinates, thermal parameters, full bond lengths and angles of compound **15b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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