Stereo- and Regio-controlled Carbon–Carbon Bond Formation Mediated by Tungsten in the s-*trans*-η^4-Diene Cationic Intermediates

Ming-Huei Cheng,[a] Yuung-Hsing Ho,[a] Sue-Lein Wang,[a] Chih-Yi Cheng,[a] Shie-Ming Peng,[b] Gene-Hsian Lee[b] and Rai-Shung Liu*[a]

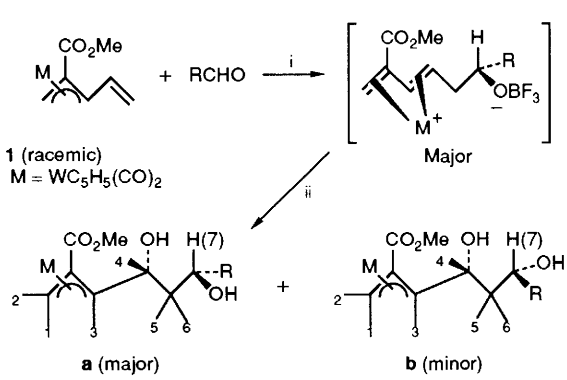
[a] *Department of Chemistry, National Tsinghua University, Hsinchu 30043, Republic of China*
[b] *Department of Chemistry, National Taiwan University, Taipei 10764, Republic of China*

The tungsten-η^3-2-substituted pentadienyl complexes $WC_5H_5(CO)_2(syn\text{-}\eta^3\text{-}2\text{-}R\text{-}C_5H_6)$ (R = COOMe; $CMe{=}CH_2$) undergo BF_3-catalysed stereoselective carbon–carbon bond formation with aldehydes to afford isolable s-*trans*-diene cations which after hydrolysis produces tungsten-η^3-allyl-1,3-diols; utilization of the diols for stereoselective synthesis of α-methylene-γ-butyrolactones, furanone skeletons, have been reported in good yields (> 80%).

Lewis acid-catalysed stereocontrolled condensation of allylsilanes[1] or boranes[2] with aldehydes has been recognized as an important carbon–carbon bond forming process in synthetic organic chemistry. In connection to this chemistry, we have recently reported[3] that the metal η^3-pentadienyl complexes $MC_5H_5(CO)_2(syn\text{-}\eta^3\text{-}C_5H_7)$ (M = Mo, W) undergo BF_3-catalysed condensation with aldehydes to generate an interesting s-*trans*-diene cationic intermediate. Nevertheless, the carbon–carbon bond formation in this case is non-stereoselective, and nucleophiles H_2O, MeOH and $NaBH_3CN$ add equally to the α and δ carbons of the diene moieties. Such features severely limit its synthetic applications. To circumvent this problem we now report the stereochemical course of a novel tungsten-mediated Prins-like[4] reaction as described in Scheme 1. An unusual feature of this reaction is the stereoselective synthesis of W-η^3-allyl-1,3-diol in a one-pot reaction.

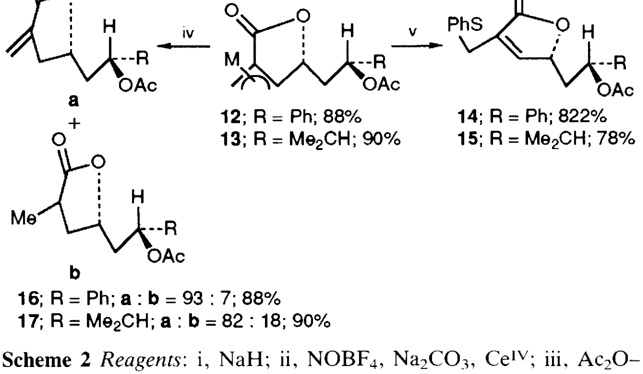
Treatment of **1**[5] with the aldehydes RCHO (R = $PhCH_2$, Ph, Me_2CH, Me; 2.0 equiv.) in the presence of $BF_3{\cdot}Et_2O$ (1.0 equiv.) in cold toluene (−40 °C) slowly deposited a dark-orange precipitate, very sensitive to air. Its IR spectrum (Nujol mull) exhibited terminal ν(W–CO) stretching at 2050(vs) and 2005(vs) cm^{-1}, characteristic of an η^4-diene cation.[6] Clarification of the s-*trans*-diene conformation was deduced from structural analysis† of the W-*syn*-η^3-allyl 1,3-diols **2**–**5**, produced from its subsequent hydrolysis by H_2O–MeCN. The *syn* configuration is indicated by the chemical shift of the H(3) proton (δ 2.0) being more upfield than that (δ 3.0) of the *syn*-proton, H(2). Only one single diastereoisomer is isolable for **2** (91%) although the molecule contains three chiral centres. The two diastereoisomers **a** and **b** of **3**–**5** were readily separable on a silica column and the ratios **a** : **b** were 88 : 12, 91 : 9, 75 : 25 for R = Ph, Me_2CH and Me, respectively. All the 1,3-diols above have the same magnitude of the coupling parameters J_{34} 9.3–9.5 Hz, indicating that the isomers **a** and **b** have different stereoconfigurations in the chiral CH(OH)R carbon. The absolute configuration of the major isomer **a** was determined from X-ray structural analysis of the W-butyrolactone **7**,‡ produced from a NaH-promoted lactonization of **3a** given in Scheme 2. For the given *R*-form of **1** as the reference (Scheme 1), the vinyl carbon adds preferentially to the *Re*-face at the aldehydes, generating unusual s-*trans*-diene cationic intermediates; H_2O subsequently adds regio- and stereo-selectively at the δ-diene carbon *trans* to the $WC_5H_5(CO)_2$ fragment.

The BF_3-catalysed reactions above are synthetically useful because they simultaneously create two asymmetric secondary hydroxylic carbons in a one-pot synthesis. To demonstrate this synthetic utility, we have treated the lactones **6**–**8**, with $NOBF_4$, generating an electrophilic allyl cation, which after a period of stirring with Na_2CO_3 (1.5 h, MeCN, 23 °C) and then



R	a : b	Yields(%)
2; CH_2Ph	**a** only	91
3; Ph	89 : 11	88
4; $CHMe_2$	91 : 9	88
5; Me	75 : 25	87

Scheme 1 *Reagents and conditions*: i, $BF_3{\cdot}Et_2O$, −40 °C; ii, H_2O–MeCN, −78 °C



Scheme 2 *Reagents*: i, NaH; ii, $NOBF_4$, Na_2CO_3, Ce^{IV}; iii, Ac_2O–Et_3N; iv, $NOBF_4$, $NaBH_3CN$, Ce^{IV}; v, $NOBF_4$, PhSNa, Ce^{IV}

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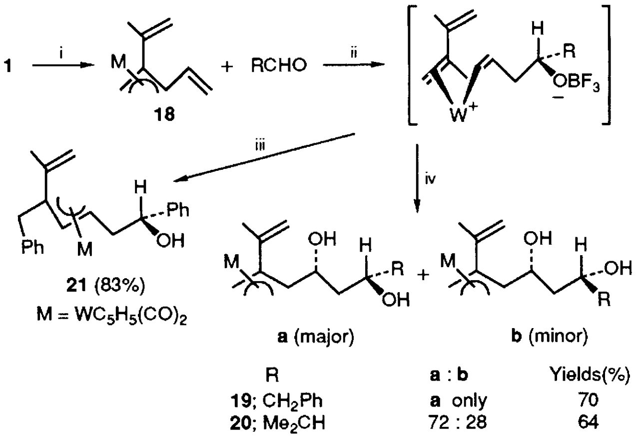
† The nucleophilic attack on the η^4-s-*cis*-diene cation is expected to give *anti*-η^3-allyl complexes, see ref. 6.

‡ Complex **7** crystallizes in the monoclinic space group *C2/c*, *a* = 23.876(7), *b* = 13.635(3), *c* = 11.617(3) Å, β = 97.43(2)°, *Z* = 8. Data were collected on a Nicolet R 3m/V diffractometer using Mo-Kα radiation. A total of 5099 reflections were collected. Of the 3326 unique reflections, 2123 were considered observed having $I > 3\sigma(I)$ which gave final *R* = 0.0278 and R_w = 0.0245 [$w^{-1} = \sigma^2(F) + 0.0001F^2$].

For structures **7** and **21**, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, p. 5.



R	a : b	Yields(%)
19; CH_2Ph	**a** only	70
20; Me_2CH	72 : 28	64

Scheme 3 *Reagents and conditions*: i, MeLi (2 equiv.), CF_3SO_3H (1 equiv.), $LiN(SiMe_3)_2$; ii, $BF_3{\cdot}Et_2O$, −40 °C; iii, Ph_2CuLi, −78 °C, R = Ph; iv, H_2O–MeCN, −40 °C

Ce^{IV}-oxidation, produces the bicyclic molecules **9–11** (yields > 85%) as a single stereoisomer. Compounds **9–11** belong to the class of α-methylene-γ-butyrolactone which has been a subject of synthetic interest.[7] The stereochemistries of **9–11** have been determined by a NOE experiment. In the case of **11**, irradiation of the H(7) signal at δ 3.68 exerts an Overhauser enhancement on the H(3) (δ 4.82) and H(4) (δ 5.00) signals. The mechanisms of formation of **9–10** seems to involve an intramolecular attack of the $CHRO^-$ terminus on the γ-carbon opposite to the $WC_5H_5(CO)_2$ fragment. Further treatment of the NO-cation of the acetyl derivatives **12**, **13** with PhSNa followed by Ce^{IV}-oxidation delivered the furanones **14** and **15** in a single diastereoisomer (yields > 75%). Treatment of the acetyl-NO cation with $NaBH_3CN$ and then Ce^{IV}-oxidation, yields a new class of α-methylene-γ-butyrolactones **16** and **17**, exclusively (**a** : **b** > 4.5, yields > 80%). In contrast with **14** and **15**, the H^- here adds preferentially to the more substituted terminus of the allyl moiety.

To test the generality of this reaction, we have studied other 2-substituted allyl systems. Outlined in Scheme 3, complex **18** was conveniently synthesized from **1** in a sequence of reactions with an overall yield of 54%. The reaction of **18** with RCHO (R = Ph, Me_2CH) in the presence of $BF_3{\cdot}Et_2O$ in cold toluene (−40 °C) likewise generated a precipitate which after hydrolysis produced 1,3-diols **19** and **20** in good yields. The diastereoselectivity is excellent for R = Ph **19**, and modest for R = Me_2CH **20** with an isomeric ratio of **a** : **b** = 72 : 28. Structural elucidation of **19–20** relies on an X-ray study of **21**,§ which was produced as a single diastereoisomer from addition of Ph_2CuLi (THF, −78 °C) to the s-*trans*-diene (85% yield). From the ORTEP drawing of **21**, the C–C bond forming stereochemistry herein is essentially identical to that in Scheme 1.

Acid-catalysed stereocontrolled condensation of alkenes with aldehydes, inter- or intra-molecularly, has been well-established in organic chemistry and give β-hydroxy alkenes a distinct 'ene' reaction pathway.[8] The new tungsten-mediated Prins-like reaction offers a convenient and practical method for construction of synthetically usefully 1,3-diols, α-methylene-γ-butyrolactone and furanone skeletons. Further studies of this reaction mechanism are in progress.

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§ Complex **21** crystallizes in the triclinic space group $P\bar{1}$, a = 10.638(1), b = 15.574(4), c = 17.542(3) Å, α = 110.27(2), β = 102.45(2), γ = 98.66(2)°, Z = 4. Each asymmetric unit contains two independent molecules. Data were collected on an Enraf-Nonius CAD-4 diffractometer, using Mo-Kα radiation. Final R = 0.065, R_w = 0.066 for 4359 reflections > $2\sigma(I)$ out of 6721 unique reflections.