Stereo- and Regio-controlled Carbon–Carbon Bond Formation Mediated by Tungsten in the s-trans-η3-Diene Cationic Intermediates


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

The tungsten-η2-2-substituted pentadienyl complexes WC6H5(CO)2(syn-η3-2-R-C5H6) (R = COOMe; CMe=CH2) undergo BF3-catalysed stereoselective carbon–carbon bond formation with aldehydes to afford isolable s-trans-diene cations which after hydrolysis produces tungsten-η3-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 allylsilanes1 or boranes2 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 reported3 that the metal η3-pentadienyl complexes MC6H5(CO)2(syn-η3-3-C5H6) (M = Mo, W) undergo BF3-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 H2O, MeOH and NaBH3CN add equally to the a and b carbons of the diene moieties. Such features severely limit its synthetic applications. To circumvent this problem we now report the stereoochemical course of a novel tungsten-mediated Prins-like4 reaction as described in Scheme 1. An unusual feature of this reaction is the stereoselective synthesis of W-η3-allyl-1,3-diols in a one-pot reaction.

Treatment of 15 with the aldehydes RCHO (R = PhCH2, Ph, Me2CH, Me; 2.0 equiv.) in the presence of BF3·Et2O (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 1905(vs) and 2005(vs) cm−1, characteristic of an η3-diene cation.6 Clarification of the s-trans-diene conformation was deduced from structural analysis7 of the W-η3-allyl 1,3-diols 2–5, produced from its subsequent hydrolysis by H2O–MeCN. The syn configuration is indicated by the chemical shift of the H(3) proton (δ 3.0) being more upfield than that (δ 3.4) of the syn-proton, H(2).

Reagents and conditions: i, BF3·Et2O, −40°C; ii, H2O-MeCN. −78°C

Scheme 1 Reagents and conditions: i, BF3·Et2O, −40°C; ii, H2O-MeCN, −78°C

† The nucleophilic attack on the η3-s-cis-diene cation is expected to give anti-η1-allyl complexes, see ref. 6.

† Complex 7 crystallizes in the monoclinic space group C2/c, a = 23.876(7), b = 13.635(3), c = 16.617(3) Å, α = 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, 2357 were considered observed having I > 3σ(I) which gave final R = 0.0278 and R semana = 0.0245 [w−1 = σ2(F)+0.0001F2].

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.
CeIV-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 2-substituted allyl systems. Outlined in Scheme 3, complex CeIV-oxidation, yields a new class of α-methylene-γ-butyrolactone and furanone skeletons. Further studies of this reaction mechanism are in progress.

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, Me2CH) in the presence of BF3·Et2O 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 = Me2CH 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 Ph2CuLi (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 useful 1,3-diols, α-methylene-γ-butyrolactone and furanone skeletons. Further studies of this reaction mechanism are in progress.

Received, 6th August 1991; Com. 1104119C

References

§ Complex 21 crystals in the triclinic space group P̅1, 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 = 0.057, R = 0.066 for 4359 reflections > 2σ(I) out of 6721 unique reflections.