Enantioselective syntheses of α-methylene butyrolactones *via* asymmetric aminocarbonylation of tungsten–prop-2-ynyl compounds

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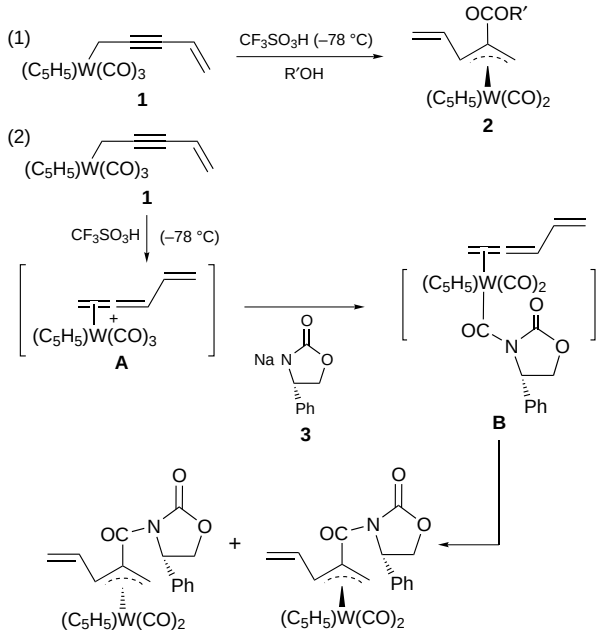
A tungsten–η¹-vinylprop-2-ynyl compound undergoes enantioselective aminocarbonylation to afford an optically pure tungsten–π-γ-lactone; this π-allyl complex is useful for the efficient synthesis of optically pure α-methylene butyrolactone.

In the last twenty years, utilization of stoichiometric transition-metal reagents in organic syntheses has undergone considerable progress.[1–3] The unique electronic properties of transition metals can direct and facilitate carbon–carbon bond formation of unusual types, providing easy access to useful organic substructures.[1–3] Nevertheless, most of these reactions[1–3] are carried out with racemic organometallic reagents although naturally occurring compounds often exist in optically pure forms. [M(η⁵-C_5H_5)(CO)$_2$(π-allyl)] (M = Mo, W) complexes have proved to be very useful in organic synthesis.[4,5] In this laboratory, we recently reported the use of complexes of this type for stereoselective syntheses of various oxygen heterocycles, 1,3-diols and 1,3,5-triols.[6] To further enhance the synthetic applications of these π-allyl complexes, we report herein an enantioselective aminocarbonylation of tungsten–vinylprop-2-ynyl complexes to afford an optically pure tungsten–π-γ-lactone that can be elaborated for asymmetric synthesis of α-methylene butyrolactones.

Although tungsten–prop-2-ynyl complexes are prone to alkoxycarbonylation[6b,c] to yield π-2-alkoxycarbonylallyl complexes **2** [Scheme 1, eqn. (1)], attempts to use chiral secondary alcohols such as (+)-menthol and (+)-neomenthol to induce enantioselective alkoxycarbonylation of **1** were unsuccessful.



Scheme 1

The resulting products **2** consisted of 1:1 diastereomeric mixtures that were inseparable by fractional crystallization and column chromatography. We found that (*S*)-4-phenyl-2,5-oxazolidinone[7] **3** was an effective chiral auxiliary for enantioselective aminocarbonylation of **1**. In a typical operation, CF_3SO_3H acidification of **1** (*ca.* 1.50 g) in cold diethyl ether yielded a dark orange precipitate **A**, presumbly being containing η²-vinylallene cations.[8] After replacement of diethyl ether with THF, precipitate **A** was treated with the sodium oxazolidinonate **3** (1.2 equiv.) at −40 °C and 15-crown-5 (1.2 equiv.), followed by slowly warming the solution to 0 °C (*ca.* 12 h), yielding a mixture of **4a** {$[\alpha]_D$ −53.4 (*c* 0.5, C_6H_6)} and **4b** {$[\alpha]_D$ 282.1 (*c* 0.5, C_6H_6)} in 81% yield (**4a**/**4b** = 3.8). Further separation of these two diastereomers on a silica column gave **4a** and **4b** in 51 and 16% yields, respectively. In this aminocarbonylation, **3** initially attacks the coordinated carbonyl of **A** to yield tungsten–η¹-aminocarbonyl species **B** which subsequently undergoes insertion of the aminocarbonyl group into its central allene carbon, yielding the two isomers **4a**,**b**. The crystal structure of **4a** has been determined by an X-ray diffraction study† to clarify its absolute configuration; the ORTEP drawing is shown in Fig. 1.

As shown in Scheme 2, further treatment of **4a** with CF_3SO_3H (1.1 equiv.) in cold ether (−40 °C) produced an orange precipitate **C**; subsequent hydrolysis of this salt with a saturated Na_2CO_3 solution yielded an optically active π-ε-lactonylallyl complex **5** {$[\alpha]_D$ 157.8 (*c* 0.5, C_6H_6)} in 80% yield. Fig. 2 shows the the crystal structure† of this optically active complex **5** which has an *anti*-configuration, *i.e.* the methyl group lies away from W(η⁵-C_5H_5)(CO)$_2$ fragment. The configuration of the tungsten–π-allyl fragment of **5** is retained relative to that of **2a**. To rationalize the stereochemical transformation of **4a** into **5**, we propose that η⁴-*s-trans*-diene **C** was first formed in the acidification of **4a** with CF_3SO_3H; subsequent attack of water at the η⁴-diene intermediate **C** occurs

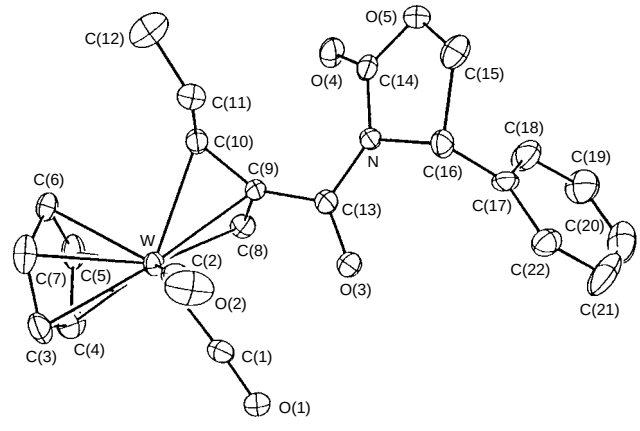
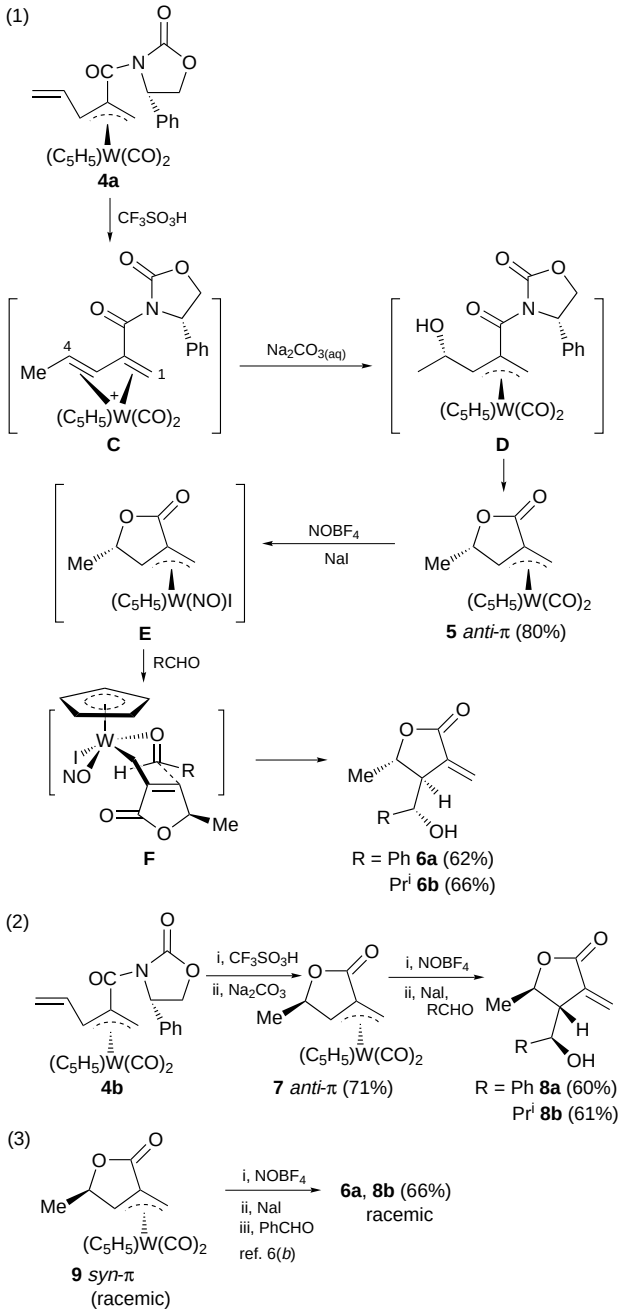


Fig. 1 ORTEP drawing of the optically active tungsten–π-allyl complex **4a**. Pertinent bond lengths (Å): W–C(8) 2.252(7), W–C(9) 2.251(6), W–C(10) 2.321(6), C(8)–C(9) 1.427(9), C(9)–C(10) 1.411(8), C(10)–C(11) 1.459(9), C(11)–C(12) 1.320(10).



Scheme 2

regioselectively at the C(4)-carbon opposite W(η^5-C_5H_5)$(CO)_2$ to yield an α-hydroxyallyl complex **D.** In aqueous Na_2CO_3 species **D** is prone to undergo base-catalyzed intramolecular lactonization, yielding the π-*anti*-allyl stereoisomer **5**.

To realize the synthetic utility of this asymmetric aminocarbonylation, compound **5** was sequentially treated with $NOBF_4$ (1.0 equiv.) and NaI (1.0 equiv.) in MeCN to generate the W(η^5-C_5H_5)(NO)I derivative **E** that functions as an allyl anion;[9] this anion reacted *in situ* with RCHO (R = Ph, Pr^i) to afford optically active α-methylene butyrolactones **6a** {$[\alpha]_D$ −71.1 (*c* 0.5, C_6H_6)} and **6b** {$[\alpha]_D$ −90.2 (*c* = 0.5, C_6H_6)} in 62 and 66% yields, respectively. The ee values of **6a** and **6b** were 93 and 94% according to HPLC analysis (column: Chirasphere). Following the same procedure, the chiral π-allyl complex **4b** was converted to π-allyl–γ-lactone **7** {$[\alpha]_D$ −157.2 (*c* 0.5, C_6H_6)} in 71% yield. Sequential treatment of **7** with $NOBF_4$ and NaI, and then RCHO afforded α-methylene butyrolactones **8a** {$[\alpha]_D$ 70.3 (*c* = 0.5, C_6H_6)} and **8b** {$[\alpha]_D$ 90.4 (*c* 0.5, C_6H_6)} in 60 and 61% yields, respectively. HPLC analyses of **8a** and **8b** gave the ee values of 92 and 94%, respectively. Herein, a chair-like-transition state **F** is likely involved to control the stereochemistry of the products. We previously reported[6b] that the racemic form of **6a** (or **8a**) could also be produced from the π-*syn*-γ-lactone **9** following the same operation; the reaction mechanism was similarly elucidated to involve the transition state **F**.[6b] An interesting observation of this study is that two π-*anti* and -*syn*-stereoisomers **5** and **9** have the same transition states **F** for generation of α-methylene-γ-lactone **6a** (or **8a**).

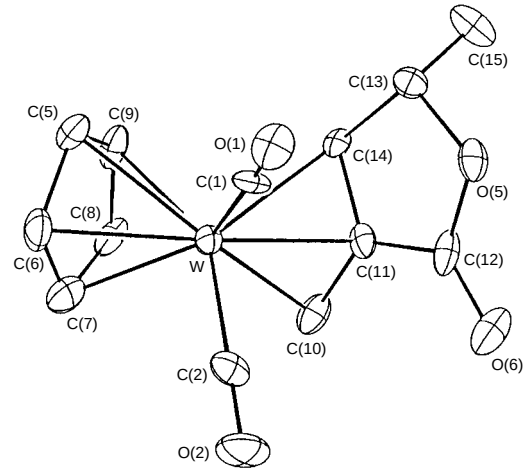


Fig. 2 ORTEP drawing of the optically active tungsten–π-γ-lactone **5**. Pertinent band lengths (Å): W–C(10) 2.292(15), W–C(11) 2.241(14), W–C(14) 2.330(16), C(10)–C(11) 1.392(15), C(11)–C(14) 1.407(24), C(12)–O(6) 1.201(22).

Footnotes and References

† *Crystal data*: **4a**: monoclinic, space group $P2_1$, a = 8.9928(2), b = 9.4679(2), c = 12.0133(2) Å, β = 93.881(3)°; U = 1020.5(4) Å^3, Z = 2. Final R = 0.0170, R_w = 0.0187 for 2381 reflections with $I > 3.0\sigma(I)$ out of 2531 unique reflections.

5: monoclinic, space group $P2_1$, a = 8.8390(2), b = 10.8836(3), c = 13.6346(4) Å, β = 101.23(2)°, U = 1286.53(8) Å^3, Z = 8. Each assymmetric unit contains two independent molecules. Final R = 0.0360, R_w = 0.0374 for 3191 reflections with $I > 3.0\sigma(I)$ out of 3902 unique reflections. CCDC 182/604.

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