Tetrahedron Letters 51 (2010) 5567–5570

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

$[Cd_2(tren)_2(dl\text{-alaninato})](ClO_4)_3$: an efficient water-compatible Lewis acid catalyst for chemo-, regio-, and diastereo-selective allylation of various aldehydes

Dongsheng Deng [a], Ping Liu [b], Baoming Ji [a,*], Li Wang [c,*], Weijun Fu [a]

[a] College of Chemistry and Chemical Engineering, Luoyang Normal University, Luoyang 471 022, PR China
[b] School of Chemistry & Chemical Engineering, Henan Institute of Science and Technology, Xinxiang 453 003, PR China
[c] Department of Chemistry, Central China Normal University, Wuhan 430 079, PR China

ARTICLE INFO

Article history:
Received 27 June 2010
Revised 9 August 2010
Accepted 17 August 2010
Available online 20 August 2010

Keywords:
Water-compatible Lewis acid
Aqueous media
Allylation
Dinuclear cadmium amino acid complex

ABSTRACT

The use of $[Cd_2(tren)_2(dl\text{-alaninato})](ClO_4)_3{\cdot}H_2O$ (**I**) (tren = tris(2-aminoethyl)amine) as an efficient water-compatible Lewis acid catalyst for the allylation of aldehydes in aqueous media was described. The reaction proceeded smoothly to afford the corresponding homoallyl alcohols in up to 96% yield. Additionally, cinnamyltributylstannane was selected as the allylation reagent, the regio- and diastereoselectivity of the reaction favors the formation of the γ-product and the *anti* isomers, respectively.

1. Introduction

The addition of organometallic reagents to aldehydes to yield homoallylic alcohols is an important carbon–carbon bond-forming reaction in organic chemistry and consequently has attracted extensive interest in recent years.[1–5] For this purpose, allylstannane seems to be a good allylating agent due to its stability and high reactivity.[6] In general, the allylation reactions must be generally carried out in organic solvents under strict anhydrous conditions because most Lewis acids are easily decomposed by water.[7–9] To address this issue, Kobayashi et al. have revealed a correlation between the catalytic activity of the metal cations and their hydrolysis constants (K_h) and water exchange rate constants (WERC).[10,11] The study has paved the way to identify the promising metal compounds as water-compatible Lewis acid catalysts. Therefore, in the last decade, water-tolerant Lewis acid-promoted allylation reactions in aqueous media have been extensively developed.[12–21] However, these cases involve some annoying problems: (1) use of very expensive Lewis acids, such as $Sc(OTf)_3$, $La(OTf)_3$, and $Yb(OTf)_3$; (2) catalyst activation before use; (3) requirement of an inert atmosphere; (4) substrate limitation; and (5) addition of assistant catalyst. So, a process featuring an efficient and easy-to-handle catalytic system in combination with an inexpensive catalyst would be highly desirable.

Very recently, di- or multi-nuclear complexes coordination compounds have been intensively synthesized because they have special properties such as catalysis, gas or chemical absorption, and ion-exchange [22–26]. So far, the most extensively studied Lewis acid catalysts for the allylation are various mononuclear complexes.[12–21] To the best of our knowledge, there have been no reports on the allylation of aldehydes with allylstannanes catalyzed by multi-nuclear complexes. As is known, in the context of designing the water-compatible Lewis acid catalysts, the selection of metal ion plays crucial roles.[10,11] Based on the studies by Kobayashi, Cd(II) is of low hydrolysis constants, pK_h, and soft Lewis acid character, and thus its complexes may serve as an effective catalyst in water. On the other hand, the use of amino acid complexes as catalysts remains a subject of considerable interest because of their unique catalytic properties.[27,28] Inspired by the aforementioned considerations, we aimed to couple our interest in obtaining novel amino acid complexes to catalyze the allylation reaction. Herein, we wish to report a highly efficient and convenient procedure for the allylation of various aldehydes with organometallic reagents using the dinuclear cadmium complex as a catalyst.

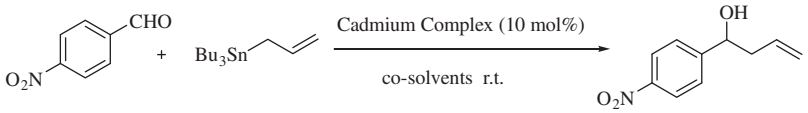
2. Results and discussion

To explore the influence of solvent on the catalytic activity of **I**-catalyzed allylation, the reaction of 4-nitrobenzaldehyde with allyltributyltin was selected as a model reaction. The results are summarized in Table 1. It was shown that the organic solvents

* Corresponding authors. Tel./fax: +86 379 65523821.
E-mail addresses: lyhxxjbm@126.com (B. Ji), wl_928@mail.ccnu.edu.cn (L. Wang).

0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.08.047

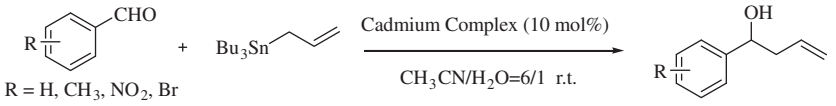
Table 1
The effect of the organic co-solvent



Entry	Co-solvent	Yield[a] (%)	Entry	Co-solvent	Yield[a] (%)
1	H_2O/CH_3CN (1:1)	80	5	H_2O/CH_3CH_2OH (1:6)	82
2	H_2O/CH_3CN (1:3)	83	6	H_2O/THF (1:6)	82
3	H_2O/CH_3CN (1:6)	96	7	H_2O/CH_3CN (1:6)	60[b]
4	H_2O/CH_3CN (1:9)	96	8	H_2O	20

[a] Catalyzed by $[Cd_2(tren)_2(dl\text{-alaninato})](ClO_4)_3\cdot H_2O$.Yields based on isolation with column chromatography. All reactions were performed in 24 h.
[b] Catalyzed by $Cd(ClO_4)_2$.

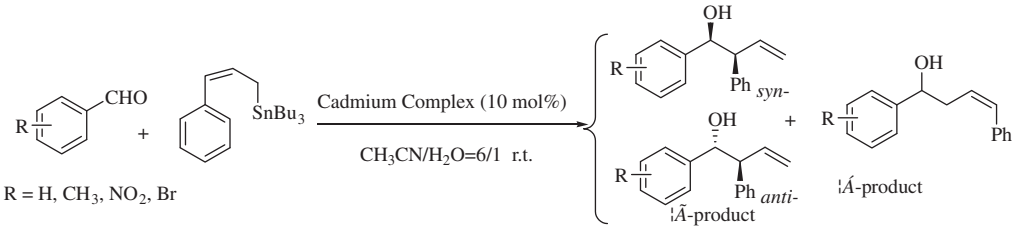
Table 2
Dinuclear cadmium complex-catalyzed allylation of aldehydes



Entry	Aldehyde	Time (h)	Yield (%)[a]
1	*p*-$NO_2C_6H_4CHO$	24	96
2	*o*-$NO_2C_6H_4CHO$	24	92
3	*m*-$NO_2C_6H_4CHO$	24	92
4	*p*-$CF_3C_6H_4CHO$	24	95
5	*p*-BrC_6H_4CHO	48	75
6	*p*-$CH_3C_6H_4CHO$	48	72
7	C_6H_5CHO	48	73
8	CH_3CH_2CHO	48	65
9	$C_6H_5COCH_3$	72	Trace
10	$(CH_2)_5CO$	72	Trace

[a] Catalyzed by $[Cd_2(tren)_2(dl\text{-alaninato})](ClO_4)_3\cdot H_2O$. Yields based on isolation with column chromatography.

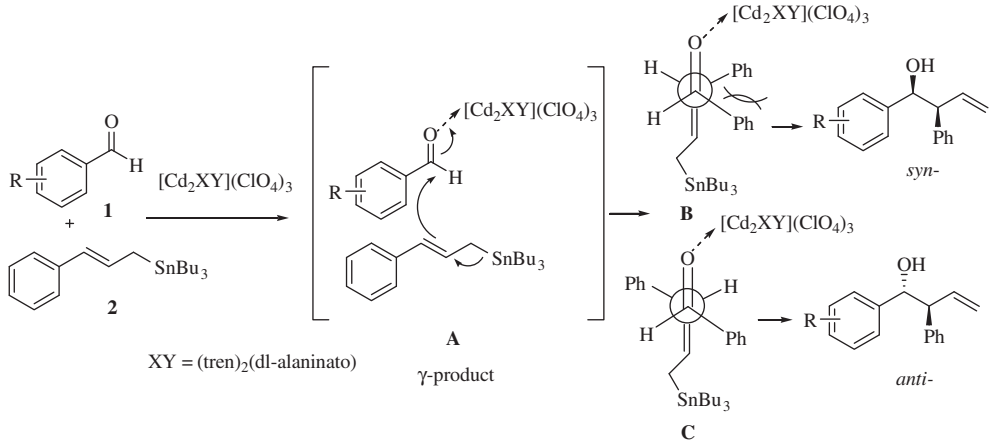
Table 3
The regio- and diastereoselectivity of the allylation reactions



Entry	Aldehyde	Time (h)	γ-Product[a] (%)
1	*p*-$NO_2C_6H_4CHO$	36	83 (7:93)
2	*o*-$NO_2C_6H_4CHO$	42	80 (10:90)
3	*m*-$NO_2C_6H_4CHO$	42	81 (12:88)
4	*p*-$CH_3C_6H_4CHO$	72	70 (10:90)
5	*p*-BrC_6H_4CHO	72	72 (10:90)
6	C_6H_5CHO	72	65 (10:90)
7	*p*-$NO_2C_6H_4CHO$	42	25 (20:80)[b]

[a] Catalyzed by $[Cd_2(tren)_2(dl\text{-alaninato})](ClO_4)_3\cdot H_2O$. Yields based on isolation with column chromatography. *Syn/anti* determined by ^1H NMR.[29]
[b] Catalyzed by $Cd(ClO_4)_2$ and $CdBr_2$.

could accelerate the reactions (Table 1, entries 1–6), and the desired allylation products were obtained in 96% yield in the presence of H_2O/CH_3CN (1:6) co-solvent (Table 1, entry 3). When performed in pure water, the reaction did not work well and



Scheme 1. A plausible mechanism for the dinuclear cadmium amino acid complex-catalyzed aldehyde allylation.

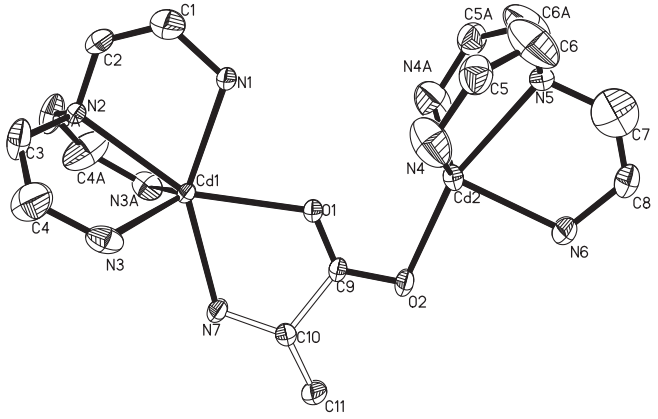


Figure 1. Crystal structure of $[Cd_2(tren)_2(dl\text{-alaninato})](ClO_4)_3{\cdot}H_2O$.

afforded the corresponding allylated adducts in 20% yield (Table 1, entry 8). While increasing the ratio of the organic solvents from 1:6 (Table 1, entry 3) to 1:9 (Table 1, entry 4), there was no significant impact on yield. When the reaction was catalyzed by $Cd(ClO_4)_2$ (Table 1, entry 7), the yield decreased obviously. Therefore, catalytic property of this dinuclear cadmium complex was much more active than that of $Cd(ClO_4)_2$. Moreover, comparing with $Y(OTf)_3$, it must be noted that this kind of catalyst need not be activated before use.[17]

By using optimal conditions with H_2O/CH_3CN (1:6) as a reaction solvent, we tried therefore a number of different aldehydes on the dinuclear cadmium complex-mediated allylation reactions and the results are shown in Table 2. It is noted that the reaction proceeded smoothly and generated good yields with substrates bearing electron-withdrawing group (Table 2, entries 1–4). As for electron-rich aromatic aldehydes (Table 2, entries 5–7) or aliphatic aldehydes (Table 2, entry 8), the reactions afforded moderate yields. On the other hand, previous reports demonstrated that some Lewis acid catalysts such as $Sc(OTf)_3$, $La(OTf)_3$, and $Yb(OTf)_3$ could promote the allylation reactions. But, in the case of aliphatic aldehydes, the allylation reactions afforded lower yields of allylation products and thus had substrate limitation.[16,17] Furthermore, by utilizing our catalytic system, ketones such as acetophenone and cyclohexanone did not react with allyltributyltin under similar reaction conditions even after a long time (Table 2, entries 9, 10). In this sense, this reaction provides a chemoselective allylation of aldehydes without affecting keto functionality.

Encouraged by the results obtained above, we then turned our attention to examine the regio- and diastereoselectivities of the reaction and the results are summarized in Table 3. When cinnamyltributylstannane was used as the allylation reagent, the reaction produced only the γ-products with main *anti* isomers (Table 3, entries 1–6). However, diastereoselectivity was decreased when $Cd(ClO_4)_2$ and $CdBr_2$ were selected to mediate the allylation reaction (Table 3, entry 7).

We are tempted to assume the mechanism for the allylation of aldehydes as follows (Scheme 1). First, we identified the crystal structure of **I** (Fig. 1). The structural analysis indicates that there are two Cd(II) atoms with different coordination environments in the asymmetric unit of **I**. The Cd1 center is six coordinated with distorted octahedral geometry, whereas the Cd2 center is five coordinated with trigonal bipyramidal geometry. It must be pointed out that the vacant sites on coordination-unsaturated Cd2 nuclei are available for reactant coordination and activation. Therefore, complex **I** may serve as a potent Lewis acid catalyst. Finally, a plausible mechanism for the exclusive formation of the γ-adduct in the reaction process can be rationalized on the basis of an initial formation of a complex between the aldehyde **1** and the Lewis acid species, which undergoes a nucleophilic attack by the C3 carbon of **2** via an S_E2 pathway. The major *anti*-addition probably occurs via an acyclic antiperiplanar transition state (C), due to big steric hindrance between the substitute phenyl group and the phenyl group in antiperiplanar transition state (B), as shown in Scheme 1.

In summary, we have presented an efficient, simple, and convenient procedure to obtain homoallyl alcohols in moderate to high yields under very mild conditions and having good substrate scopes. This dinuclear cadmium amino acid complex catalyst need not be activated before use. The reaction exhibited not only regioselectivity only giving the γ-products but also showed good diastereoselectivity favoring the *anti* isomers. Moreover, the reaction also exhibited high chemoselectivity.

3. Typical procedure of catalytic studies

Cadmium complex (0.05 mmol), aldehyde (0.5 mmol), and allyltributyltin (0.6 mmol) were added in CH_3CN/H_2O (6:1) (1 mL). The reaction was monitored by TLC and on completion was extracted by ethyl acetate (3 × 10 mL). The combined organic layers were treated by KF. The resulting solution was filtered to remove the resin and the filtrate was washed with brine, dried over anhydrous $MgSO_4$, and the solvent removed in vacuo to yield the crude product. Purification by silica gel chromatography using 100–200 mesh ZCX II eluted by hexane/ethyl acetate (3:1, v/v) gave

the allylation products. The spectroscopic characteristics of the known products were in agreement with the published data.

4. Characterization data of homoallyl alcohols

1-(4-Nitrophenyl)-2-phenyl-but-3-en-1-ol (Table 3, entry 1). Light yellow liquid, 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (*syn*/*anti* = 7:93) (*anti*) δ = 8.05 (d, J = 8.7 Hz, 2H), 7.30–7.22 (m, 5H), 7.04 (d, J = 6.4 Hz, 2H), 6.31–6.18 (m, 1H), 5.35–5.25 (m, 2H), 4.94 (d, J = 7.8 Hz, 1H), 3.51 (t, J = 8.4 Hz, 1H).

1-(2-Nitrophenyl)-2-phenyl-but-3-en-1-ol (Table 3, entry 2). Light yellow liquid, 80% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (*syn*/*anti* = 10:90) (*anti*) δ = 7.79 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.36–7.17 (m, 6H), 6.22–6.35 (m, 1H), 5.61 (d, J = 5.3 Hz, 1H), 5.16 (d, J = 11.7 Hz, 1H), 4.99 (d, J = 17.1 Hz, 1H), 3.70–3.75 (q, 1H).

1-(3-Nitrophenyl)-2-phenyl-but-3-en-1-ol (Table 3, entry 3). Light yellow liquid, 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (*syn*/*anti* = 12:88) (*anti*) δ = 8.00 (d, J = 9.1 Hz, 2H), 7.37–7.15 (m, 5H), 7.02 (d, J = 6.6, 2H), 6.16–6.28 (m, 1H), 5.22–5.32 (m, 2H), 4.91 (d, J = 7.7 Hz, 1H), 3.50 (t, J = 8.4 Hz, 1H).

1-(4-Methylphenyl)-2-phenyl-but-3-en-1-ol (Table 3, entry 4). Colorless liquid, 70% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (*syn*/*anti* = 10:90) (*anti*) δ = 7.01–7.32 (m, 7H), 6.46–6.52 (m, 1H), 6.19–6.31 (m, 2H), 5.19–5.27 (m, 2H), 4.85 (d, J = 7.5 Hz, 1H), 3.54 (t, J = 8.1 Hz, 1H), 2.36 (s, 3H).

1-(4-Bromophenyl)-2-phenyl-but-3-en-1-ol (Table 3, entry 5). Colorless liquid, 72% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (*syn*/*anti* = 10:90) (*anti*) δ = 7.33 (d, J = 8.4 Hz, 2H), 7.15–7.26 (m, 3H), 6.99–7.07 (m, 4H), 6.17–6.29 (m, 1H), 5.22–5.31 (m, 2H), 4.80 (d, J = 7.8 Hz, 1H), 3.50 (t, J = 8.4 Hz, 1H).

1,2-Diphenyl-but-3-en-1-ol (Table 3, entry 6). Colorless liquid, 65% yield. ^{1}H NMR (300 MHz, $CDCl_3$) (*syn*/*anti* = 10:90) (*anti*) δ = 7.16–7.26 (m, 8H), 7.06–7.09 (m, 2H), 6.23–6.32 (m, 1H), 5.20–5,29 (m, 2H), 4.87 (d, J = 7.8 Hz, 1H), 3.58 (t, J = 8.4 Hz, 1H).

Supplementary data

Crystallographic data for $[Cd_2(tren)_2(dl\text{-alaninato})](ClO_4)_3{\cdot}H_2O$ have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC247083. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033 or email: deposit@ccdc.cam.ac.uk).

Acknowledgments

The authors are grateful to the Natural Science Foundation of China (Nos. 20872057), the Doctor Foundation and Cultivatable Foundation (2008-PYJJ-011) of Luoyang Normal University, and the Foundation of the Education Department of Henan Province (2008A150011 and 2009B150018) for the financial support.

References and notes

1. Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207.
2. Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31.
3. Fleming, I.; Barbero, A.; Walter, D. *Chem. Rev.* **1997**, *97*, 2063.
4. Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763.
5. Solin, N.; Kjellgren, J.; Szabó, K. J. *J. Am. Chem. Soc.* **2004**, *126*, 7026.
6. Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243.
7. Nakamura, H.; Iwama, H.; Yamamoto, Y. *J. Am. Chem. Soc.* **1996**, *118*, 6641.
8. Bissett, J. S.; Greeves, N.; Levin, D. *Tetrahedron Lett.* **2002**, *43*, 319.
9. Nishiyama, Y.; Kakushou, F.; Sonoda, N. *Tetrahedron Lett.* **2005**, *46*, 787.
10. Kobayashi, S.; Nagayama, S.; Busujima, T. *J. Am. Chem. Soc.* **1998**, *120*, 8287.
11. Kobayashi, S.; Ogawa, C. *Chem. Eur. J.* **2006**, *12*, 5954.
12. Kobayashi, S.; Hachiya, I. *Tetrahedron Lett.* **1992**, *33*, 1625.
13. Hachiya, I.; Kobayashi, S. *J. Org. Chem.* **1993**, *58*, 6958.
14. Kobayashi, S. *Synlett* **1994**, 689.
15. Kobayashi, S.; Nagayama, S.; Busujima, T. *J. Org. Chem.* **1994**, *59*, 3590.
16. Aspinall, H. C.; Browning, A. F.; Greeves, N.; Ravenscroft, P. *Tetrahedron Lett.* **1994**, *35*, 4639.
17. Aspinall, H. C.; Greeves, N.; McIver, E. G. *Tetrahedron Lett.* **1998**, *39*, 9283.
18. Shibata, I.; Yoshimura, N.; Yabu, M.; Baba, A. *Eur. J. Org. Chem.* **2001**, 3207.
19. Kobayashi, S.; Aoyama, N.; Manabe, K. *Synlett* **2002**, 483.
20. Kobayashi, S.; Aoyama, N.; Manabe, K. *Chirality* **2003**, *15*, 124.
21. Loh, T.-P.; Zhou, J.-R. *Tetrahedron Lett.* **2000**, *41*, 5261.
22. Yamamoto, K.; Nakazawa, S.; Imaoka, T. *Mol. Cryst. Liq. Cryst.* **2002**, *379*, 407.
23. Yoo, S.-K.; Ryu, J. Y.; Lee, J. Y.; Kim, C.; Kim, S.-J.; Kim, Y. *J. Chem. Soc., Dalton Trans.* **2003**, 1454.
24. Liu, C. L.; Wang, M.; Zhang, T. L.; Sun, H. Z. *Coord. Chem. Rev.* **2004**, *248*, 147.
25. Cai, J.-W. *Coord. Chem. Rev.* **2004**, *248*, 251.
26. Abraham, S.; Ha, C. S.; Kim, I. *Macromol. Rapid Commun.* **2006**, *16*, 1386.
27. Darbre, T.; Machuqueiro, M. *Chem. Commun.* **2003**, 1090.
28. Fernandez-Lopez, R.; Kofoed, J.; Machuqueiro, M.; Darbre, T. *Eur. J. Org. Chem.* **2005**, 5268.
29. Tan, X.-H.; Hou, Y.-Q.; Huang, C.; Liu, L.; Guo, Q.-X. *Tetrahedron* **2004**, *60*, 6129.