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Practical approach for catalytic asymmetric allylation of aldehydes with a chiral bidentate titanium(IV) complex

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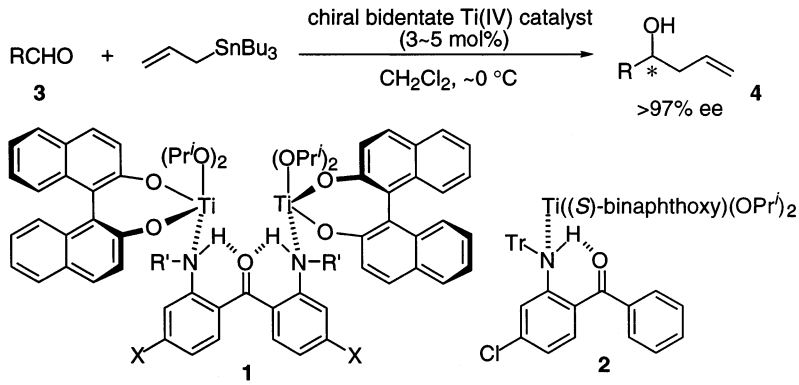
Abstract—A new, chiral bidentate Ti(IV) complex of type **1** was successfully designed and can be utilized for simultaneous coordination to aldehyde carbonyls, thereby allowing the precise enantioface discrimination of such carbonyls for a new catalytic, practical enantioselective allylation of aldehydes with allyltributyltin.

As one of the fundamental yet powerful C–C bond-forming reactions, enantioselective allylation of aldehydes attracts considerable attention in asymmetric synthesis.[1] Given the versatile chemistry of the resulting homoallylic alcohols,[2] this asymmetric transformation constitutes a valuable process. Despite considerable recent progress in this area using a stoichiometric amount of chiral Lewis acids,[3] only a few types of reagents have been reported for catalytic versions, and continuing improvements in the efficiency of these Lewis acids have been made within the field of asymmetric catalysis.[4–7] In this respect, a most practical catalytic allylation should utilize an inexpensive and readily available chiral ligand, and provide uniformly high and predictable enantioselectivity across a wide range of aldehyde substrates. For instance, in the case of cinnamaldehyde, previously reported catalytic processes generally exhibited less satisfactory enantioselectivity (~90% ee).[4–7] This is mainly because previous strategies utilize a single coordination complex **A** between an aldehyde and chiral monodentate Lewis acids which inevitably causes free rotation at the M–O bond, and the *anti*-coordination **A** of a Lewis acid (ML*) toward an aldehyde would also decrease the enantioselection compared to the unfavorable *syn*-coordination **B**. In order to overcome these intrinsic problems by the approaches currently known, we are interested in the possiblity of forming double coordination complex **C** with chiral bidentate Lewis acids, thereby allowing more precise enantioface discrimination of aldehyde carbonyl. Here we wish to disclose a new catalytic, practical enantioselective



Scheme 1.

Keywords: allylation; binaphthol; asymmetric reactions; titanium and compounds.
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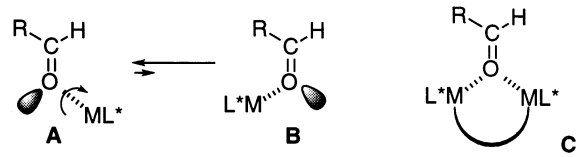
allylation of aldehydes with allyltributyltin using a newly designed, chiral bidentate Ti(IV) complex of type **1**, as shown in Scheme 1.

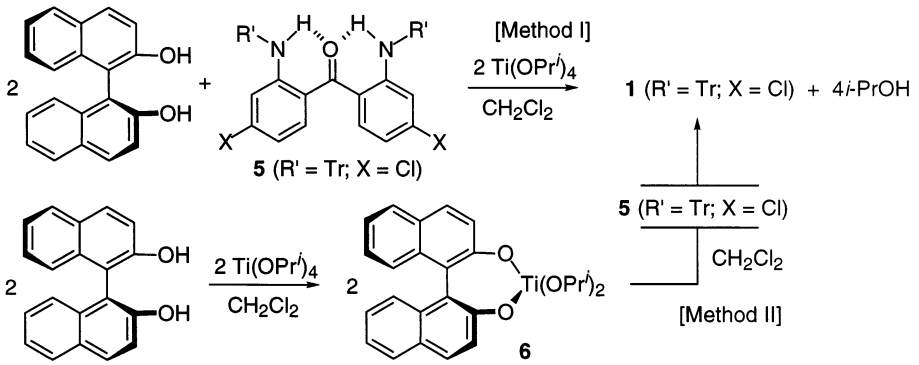


The design of chiral bidentate Ti(IV) catalysts originates from our recently developed bidentate Lewis acid chemistry,[8,9] and one of the most characteristic features in this study is the rational control of the desired two-Ti distance for carbonyl trapping by dative interactions rather than ionic interactions as utilized previously.[8] Accordingly, the requisite chiral bidentate catalyst **1** (R′=Tr; X=Cl) is prepared by mixing of 2,2′-bis(tritylamino)-4,4′-dichlorobenzophenone **5** (5 mol%; R′=Tr; X=Cl) with $Ti(OPr^i)_4$ (10 mol%) in CH_2Cl_2 at room temperature for 1 h and subsequent treatment with (*S*)-binaphthol (10 mol%) at room temperature for 15 h [Method I in Scheme 2]. Reaction of benzaldehyde with allyltributyltin (1 equiv.) under the influence of in situ generated chiral bidentate catalyst **1** (5 mol%; R=Tr; X=Cl) in CH_2Cl_2 at 0°C for 2 h gave rise to 1-phenyl-3-buten-1-ol **4** (R=Ph) in 95% yield with 99% ee.[10–12] The absolute configuration of the homoallylic alcohol was determined to be *S* by correlation to the authentic sample.[5b] The amount of catalyst **1** can be reduced to 3 mol% with similar chemical yield and enantioselectivity (96% yield, 98% ee) except for the need of longer reaction time, as shown in Table 1 (entry 1).

The chiral bidentate catalyst **1** (R=Tr; X=Cl) can be also prepared from Ti((*S*)-binaphthoxy)$(OPr^i)_2$ (**6**)[13] and **5** (R=Tr; X=Cl) in CH_2Cl_2 [Method II in Scheme 2]. This *i*-PrOH-free catalyst **1** (R=Tr; X=Cl) is more reactive than the in situ generated chiral catalyst **1**, and the asymmetric allylation with the *i*-PrOH-free catalyst **1** (5 mol%; R=Tr; X=Cl) proceeded at −20°C for 2 h to furnish homoallylic alcohol **4** (R=Ph) in 85% yield with 98–99% ee (entry 4).[14] It should be noted that both the reaction rate and the enantioselectivity of the allylation are much lower (e.g. 9 and 90% ee for benzaldehyde) under similar reaction conditions with a chiral monodentate Ti(IV) complex **2** derived from $Ti(OPr^i)_4$, (*S*)-binaphthol, and 4-chloro-2-(tritylamino)benzophenone as monodentate ligand (each 5 mol%). In addition, a chiral, in situ generated Ti((*S*)-binaphthoxy)$(OPr^i)_2$ (**6**) (5 or 10 mol%) from $Ti(OPr^i)_4$ and (*S*)-binaphthol retarded the allylation to a great extent, giving homoallylic alcohol **4** (R=Ph) in only 3% yield (71% ee) or 5% yield (72% ee).

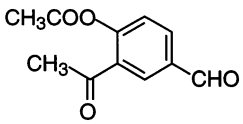
Other selected examples are listed in Table 1. Several characteristic features of the present allylation follow: (1) The chiral bidentate Ti(IV) catalyst **1** (R′=Tr; X=Cl) exhibits uniformly high asymmetric induction as well as high chemical yield. As a general tendency, the *i*-PrOH-free catalyst **1** (R=Tr; X=Cl) is more reactive than the in situ generated **1**, and the asymmetric allylation with the *i*-PrOH-free catalyst **1** (3–5 mol%; R=Tr; X=Cl) proceeds at lower or similar reaction temperature with shorter reaction time. In the case of low enantioselectivity observed in entries 17 and 23, the *i*-PrOH-free catalyst **1** (3 mol%; R=Tr; X=Cl) was pretreated with 4 equiv. of *i*-PrOH (12 mol%) to furnish the catalyst **C**, which should be similar to the in situ generated **1**, and indeed exhibited similar reactivity and enantioselectivity (entries 18 and 24). (2) The simultaneous coordination and double activation ability of the bidentate Ti(IV) catalyst **1** (R′=Tr; X=Cl) toward aldehyde carbonyls strongly accelerated the rate of allylation compared to previously reported BINOL–$Ti(OPr^i)_4$ complexes.[5] (3) The enantioselectivity of the present allylation is largely insensitive to the reaction temperature (i.e. 98–99% ee at −15–20°C in the case of benzaldehyde). (4) This asymmetric procedure is operationally quite simple. Thus, commercially available $Ti(OPr^i)_4$ and chiral binaphthol are sequentially added to 2,2′-bis(tritylamino)-4,4′-dichlorobenzophenone (**5**) (R′=Tr; X=Cl) in CH_2Cl_2 at room temperature to generate the requisite catalyst **1** (R′=Tr; X=Cl), which is then treated with aldehyde **3** and allyltributyltin at 0°C for several hours. (5) The present asymmetric allylation is highly chemoselective in the presence of other carbonyl moieties such as ketone and ester functionalities, leaving these groups intact (entry 25).

Among several possible reaction pathways, the high reactivity and selectivity of the bidentate Ti(IV) complex **1** (R′=Tr; X=Cl) is ascribed to the simultaneous coordination of two Ti to a carbonyl oxygen, thereby



Scheme 2.

Table 1. Asymmetric allylation of aldehydes with allyltributyltin catalyzed by chiral bidentate Ti(IV) complex **1** (R′ = Tr; X = Cl)[a]

Entry	Aldehyde	Catalyst[b] (mol%)	Condition (°C, h)	% Yield[c]	% Ee[d] (config)[e]
1	PhCHO	[**A**] (3)	0, 5	96	98 (*S*)
2		[**A**] (5)	0, 2	95	99 (*S*)
3		[**B**] (3)	−15, 15	74	97 (*S*)
4		[**B**] (5)	−20, 2	85	98 (*S*)
5	$CH_3(CH_2)_6CHO$	[**A**] (5)	0, 12	82	97 (*R*)[f]
6		[**B**] (3)	0, 2	75	98 (*R*)[f]
7		[**B**] (5)	0, 0.5	88	99 (*R*)[f]
8	$(CH_3)_2CHCHO$	[**A**] (5)	0, 24	54	98 (*R*)[g]
9		[**B**] (5)	0, 1	77	>99 (*R*)[g]
10	$PhCH_2CH_2CHO$	[**A**] (3)	0, 4	89	97 (*S*)[h]
11		[**A**] (5)	0, 2	83	98 (*S*)[h]
12		[**B**] (3)	−10, 12	71	98 (*S*)[h]
13	PhCH=CHCHO	[**A**] (10)	0, 10	79	97 (*S*)
14		[**B**] (5)	0, 5	88	97 (*S*)
15	*p*-Bromobenzaldehyde	[**A**] (3)	0, 12	87	97 (*S*)[i]
16		[**A**] (5)	0, 12	97	98 (*S*)[i]
17		[**B**] (3)	0, 3	98	94 (*S*)[i]
18		[**C**] (3)	0, 12	90	97 (*S*)[i]
19	2-Naphthaldehyde	[**A**] (5)	0, 10	92	98
20		[**B**] (3)	0, 6	99	97
21	Furfural	[**A**] (3)	0, 5	85	97
22		[**A**] (5)	0, 6	82	98
23		[**B**] (3)	0, 2	88	95
24		[**C**] (3)	0, 4	84	97
25		[**A**] (10)	0, 20	96	97

[a] Unless otherwise noted, the reaction of aldehyde and $Bu_3SnCH_2CH{=}CH_2$ (1 equiv.) was carried out in the presence of chiral bidentate Ti(IV) catalyst **1** (3–5 mol%; R′ = Tr; X = Cl) in CH_2Cl_2 under the given reaction conditions.

[b] Catalyst [**A**] refers to the in situ generated **1** (R′ = Tr; X = Cl) by Method I. Catalyst [**B**]: *i*-PrOH-free catalyst **1** by Method II. Catalyst [**C**]: *i*-PrOH-free catalyst **1**+4*i*-PrOH.

[c] Isolated yield.

[d] Determined by HPLC analysis using Chiralcel OD and OJ.

[e] Determined by comparison of the sign of optical rotation with reported values. See Refs. 3o and 5b.

[f] Determined by GC analysis using a chiral column (GL SCIENCE CP-CHIRASIL-DEX CB).

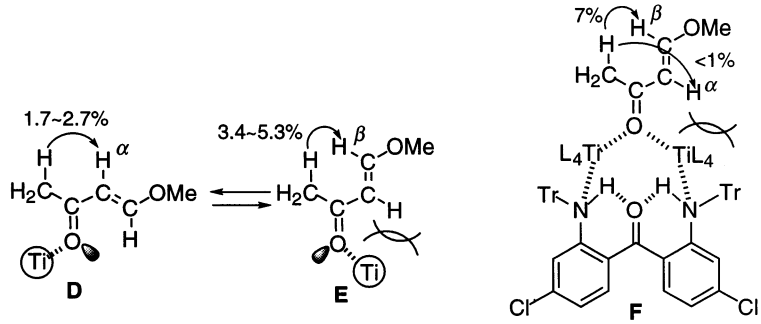
[g] Determined by GC analysis (chiral GL SCIENCE CP-CHIRASIL-DEX CB column) after conversion to its benzoate.

[h] Correlated to (*S*)-**4** (R = CH=CHPh) (entry 13) by the catalytic hydrogenation of **4** ($R = CH_2CH_2Ph$) with Pd/C and H_2 to 1-phenyl-3-hexanol.

[i] Correlated to (*S*)-**4** (R = Ph) (entry 1) by debromination of **4** (R = *p*-bromophenyl) with BuLi in ether.

allowing the double activation of the aldehyde carbonyls. Such activation is also observed by ^{13}C NMR and IR spectroscopy using 2,6-dimethyl-γ-pyrone as the carbonyl substrate: ^{13}C NMR (CD_2Cl_2 at 20°C) δ 165.32 (free pyrone β carbons); δ 166.26 (pyrone β carbons of the 1:1 2,6-dimethyl-γ-pyrone/monodentate **2** complex); δ 167.75 (pyrone β carbons of the 1:1 2,6-dimethyl-γ-pyrone/bidentate **1** (R′ = Tr; X = Cl) chelation complex); δ 166.40 (pyrone β carbons of the 2:1 2,6-dimethyl-γ-pyrone/bidentate **1** (R′ = Tr; X = Cl) chelation complex); IR (CH_2Cl_2) 1669 cm^{-1} (free pyrone C=O); 1656 cm^{-1} (pyrone C=O of the 1:1 2,6-dimethyl-γ-pyrone/monodentate **2** complex); 1652 cm^{-1} (pyrone C=O of the 1:1 2,6-dimethyl-γ-pyrone/bidentate **1** (R′ = Tr; X = Cl) chelation complex).

The double coordination phenomenon of **1** (R′ = Tr; X = Cl) is supported by the difference NOE measurement with *trans*-4-methoxy-3-buten-2-one at low temperature (−20°C), where the enone conformation around the single bond can be determined. The free *trans*-4-methoxy-3-buten-2-one exists in both *s-cis* and *s-trans* conformations, since irradiation of $CH_3C{=}O$ protons resulted in moderate NOE to both α and β methoxyvinyl protons (3.1 and 5.6%, respectively). On complexation with monodentate Ti(IV) Lewis acid **2**, irradiation of $CH_3C{=}O$ protons again resulted in similar NOE to both α and β methoxyvinyl protons (1.7 and 3.4%, respectively). This result implies that both *s-cis* and *s-trans* conformers, (**D**) and (**E**), exist in a similar ratio to the free enone in solution. A similar tendency is also observed with a complex derived from *trans*-4-methoxy-3-buten-2-one and Keck's reagent[5c] (2.7 and 5.3% for the α and β protons, respectively). In marked contrast, however, in the bidentate **1** (R′ = Tr; X = Cl)/enone complex, irradiation of the methyl proton of enone resulted in moderate NOE to the only β proton of the *trans*-methoxyvinyl group, implying the existence of the *s-trans* conformer (**F**) predominantly because of the double coordination.



Acknowledgements

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10. Our initial attempt to use chiral bidentate Ti(IV) catalysts of type **1** (5 mol%) from the parent 2,2′-diaminobenzophenone **5** (R′=X=H) as a spacer by combining $Ti(OPr^i)_4$ and chiral (*S*)-binaphthol turned out to be less satisfactory (11% yield and 91% ee at 0°C for 6 h) in the asymmetric allylation of benzaldehyde with allyltributyltin. Introduction of alkyl or silyl moieties on the amino groups in **5** in order to make two Ti closely aligned by their steric repulsion resulted in enhancement of reactivity of the asymmetric allylation. Indeed, bidentate Ti(IV) catalyst **1** (5 mol%; R′=Pr and $SiBu^tPh_2$; X=H) derived from **5** (R′=Pr and $SiBu^tPh_2$; X=H), $Ti(OPr^i)_4$, and (*S*)-binaphthol afforded **4** (R=Ph) in 30% (91% ee) and 34% yields (92% ee), respectively (at 0°C for 6 h). Among various spacers examined for designing of bidentate Ti catalysts, 2,2′-bis(tritylamino)-4,4′-dichlorobenzophenone **5** (R′=Tr; X=Cl) was found to be the most effective.
11. Introduction of chloro substituents (X=Cl) in ligand **5** is crucially important to stabilize the tritylamino moiety in the catalyst **1** (R′=Tr; X=Cl). Asymmetric allylation of benzaldehyde with catalyst **1** (R′=Tr; X=H) under similar conditions (i.e. in CH_2Cl_2 at 0°C for 2 h) gave rise to homoallylic alcohol **4** (R=Ph) in 85% yield (99% ee) accompanied by some cleavage of the tritylamino moiety in ligand **5** (R′=Tr; X=H).
12. Attempted addition of 2 more equiv. of (*S*)-binaphthol to the bidentate catalyst **1** (R′=Tr; X=Cl) resulted in decreasing both the enantioselectivity (97% ee) and chemical yield (87%) in the asymmetric allylation of benzaldehyde with allyltributyltin under similar conditions.
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