5. **N-(R)- α -Methylbenzyl-1-Benzyl 5-Tetrazole Imine (6):** ^{1}H NMR δ=7.67 (1H, b-d, *J* =7.2 Hz imine H), 7.45-7.26 (10H, m, aromatic), 5.94 (2H, dd, *J* =14.0, 14.0 Hz, benzyl), 5.24 (1H, quin, *J* =7.2 Hz, chiral benzyl H), 1.59 (2H, d, *J* =7.2 Hz, chiral benzyl CH_3). ^{13}C NMR δ=154.08, 146.44, 141.68, 133.83, 128.92, 128.79, 127.90, 126.09, 52.58, 49.61, 21.74, 17.77. IR (cm^{-1})=1659, 1563, 716. M/S(M^+): 292
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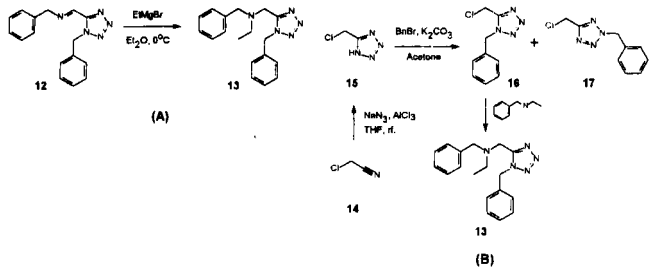
11. **Spectroscopic data for 9a (R^1=Et):** ^{1}H NMR δ=7.32-7.23 (8H, m, aromatic), 6.96-6.92 (2H, m, aromatic), 5.45 (2H, dd, *J* =15.2, 15.2 Hz, benzyl), 3.88 (1H, q, *J* = 6.8 Hz, chiral benzyl H), 3.78 (2H, dd, *J* =14.2, 14.2 Hz, α -tetrazole), 2.65 (1H, hex, *J* =6.6 Hz, N-ethyl CH_2), 2.39 (1H, hexe, *J* =6.6 Hz, N-ethyl CH_2), 1.35 (3H, d, *J* =6.7 Hz, N-ethyl CH_3), 0.96 (3H, t, *J* =6.8 Hz, chiral benzyl CH_3). ^{13}C NMR δ=152.98, 142.23, 133.66, 128.85, 128.43, 127.79, 127.41, 127.39, 58.53, 50.39, 43.95, 42.51, 15.14, 11.69). IR (cm^{-1})=1459, 731.

The N-addition product **13** obtained under the same reaction condition from **12** was found to be identical to the compound prepared by a different synthetic method (route B) in ^{1}H, ^{13}C NMR and M/S.



Controlling Factors Governing Catalytic Process : Asymmetric Allylation Reaction Promoted by BINOL-Zr(IV) Catalyst with Synergetic Reagent

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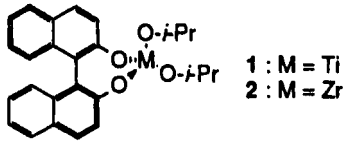
As one of fundamental asymmetric bond forming reactions, allyl transfer reactions from chiral reagents to the carbonyl functionality in forming enantiomerically rich homoallylic alcohols attract considerable attention from the synthetic community because the resulting products serve as chiral building block for multistep synthesis.[1] The exceptional power of the allyllation reaction has been enhanced by newly developed enantioselective versions, especially chiral Lewis acid catalysed allyl transfer reactions.[2] The development of synthetic methods for achieving absolute stereoselection by the utilization of chiral catalysts increasingly requires precise control of the reaction pathway based on mechanistic behavior.[3] Recently, we demonstrated that the utilization of molecular accelerator for the catalytic asymmetric allylation reaction promoted by BINOL-Ti(IV) complex **1** resulted in not only significantly increasing reaction rate but also reducing dosage of chiral catalyst.[4] Described herein is an extension of the conception concerning molecular accelerating strategy to find new catalytic systems and to realize useful and practical asymmetric synthesis, There have been quite limited reports which appeared with chiral Zr species for the catalytic asymmetric synthesis, especially allylic transfer reaction.[5] In the present research, two major progress have been made in this field for the enantioselective synthesis of homoallylic alcohols: (1) the system employing BINOL-Zr(IV) catalyst with an accelerator exhibited dramatical increasing of catalytic capability (up to 5 mol %); (2) reduced side reaction significantly.



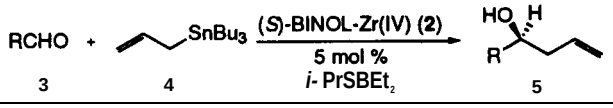
(S)-BINOL-Zr(IV) complex **2** was prepared from the reaction of (S)-BINOL with Zr(O- *i*- Pr)$_4$ in the presence of activated 4 A molecular sieves. Treatment of **3** (R=CH_2CH_2Ph) with **4** in the presence of chiral catalyst **2** (5 mol %) in CH_2Cl_2 at – 20 °C for 24 h afforded product **5** (R=CH_2CH_2 Ph) in 41% yield with 87% ee. We have subsequently observed that synergetic reagents can also be employed for this purpose. After surveying a series of alkylthioboranes and alkylthiosilanes for the allylation promoted by chiral catalyst **2,** several key findings emerged: (1) *i* -PrSBEt$_2$[6] was generally superior to other reagents including *i* -PrSSiMe$_3$; (2) a 1 : 1 mixture of BINOL/Zr(O- *i*- Pr)$_4$ complex was proved to be most effective; (3) the new system exhibited sig-

nificantly increasing catalytic ability in comparison to that of non-accelerator system; (4) none or trace amounts of primary alcohols via Meerwein-Pondorf-Valley reduction were produced during the process[7]; (5) optimal chemical yields and enantioselectivities were observed with the use of CH_2Cl_2 as the solvent compared to others such as toluene, diethyl ether, or propionitrile. Upon optimal condition, the catalytic allyl transfer reaction was conducted by dropwise addition of *i*-$PrSBEt_2$ (1.2 eq) in CH_2Cl_2 at -20 °C to the mixture of **3** (R=CH_2CH_2Ph, 1.0 eq) and **4** (1.3 eq) in the presence of chiral catalyst **2** (5 mol %). After 5 h at -20 °C, the resulting reaction mixture was treated with an aqueous $NaHCO_3$ solution. After usual work up, final purification of homoallyl alcohol **5** (R=CH_2CH_2Ph) can be effected by silica gel chromatography (82% isolated yield with 95% ee). Additional experiments with various aldehydes were performed and representative results are summarized in Table 1. The reactions are generally complete after 5 h at -20 °C.

The role of *i*-$PrSBEt_2$ to accelerate allyl transfer reaction must be a reinforcement of regeneration of chiral catalyst as a consequence of the dissociation of product from the reaction complex by virture of strong bond affinities between B-O and Sn-S and relatively weaker B-S bond. However, the exact mechanistic behavior has not been rigorously elucidated whether concerted involvement in the transition state or stepwise participation.

After developing new system for catalytic asymmetric allylation by the use of molecular accelerators, we decided to explore the utilization of more easily accessible chiral catalyst such as oxazaborolidine **6.**[8] When **4** was added to the solution of benzaldehyde in the presence of catalyst **6** (R^1=Pb, R^2=H, 20 mol %) in CH_2Cl_2, only a detectable amount of product **7** was produced (0 °C, 40 h). Indeed, we were delighted to find again that the synergetic reagent, *i*-$PrSBEt_2$, enhenced catalytic process significantly; reaction underwent even at -78 °C. The allylated product **7** was isolated in 71% chromatographed yield with 77% ee from the reaction at -78 °C for 8 h. Although the range of asymmetric induction has not reached useful level yet, modification of chiral catalyst **6** by changing substituents R^1 and R^2 should promise to come up to an optimum.

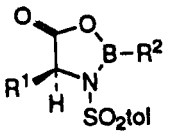
Table 1. Enantioselective allylation accelerated by *i*-$PrSBEt_2$[a,b]



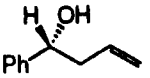
3 4 5

entry	RCHO (3)	yield, %[c]	ee, %[d]
1	$PhCH_2CH_2$	82	95
2	*n*-C_6H_{13}	79	93
3	*c*-C_6H_{11}	63	83
4	PhCH=CH	75	76
5	Ph	71	88

[a] All reactions were run at -20 °C in CH_2Cl_2. [b] Absolute configurations were determined by direct comparison values of specific rotations with known alcohols. [d] Chromatographed yields. [c] Enantiomeric excess was determined by ^1H NMR analysis using chiral shift reagent, $Eu(hfc)_3$ as well as ^1H NMR analysis of (+)-MTPA ester derivative.



6



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In summary, an efficient method for the catalytic enantioselective addition of allyltributylstannane to aldehydes is described which employs synergetic reagent, *i*-$PrSBEt_2$, and chiral catalysts **2** and **6,** furnishing homoallylic alcohols in good yields with useful levels of enantioselectivity. Studies are in progress to extend this method to more complicate tin reagents including allenyl- and propargyl-stannanes to obtain enantiomerically rich allenyl and propargyl carbinols.

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A Novel Clay-Like Layered Host Clathrate with the Guest Molecule Accommodated in the Intralayer Cavity: The Structure of $[\{Cd(imH)_2\}\{Cd(H_2O)\}_2\{Cd(CN)_3\}_2\{Cd(CN)_3(imH)\}_2\{Cd(CN)_3\}_2] \cdot 2C_6H_5C_2H_5$ (imH=imidazole)

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Cadmium cyanide and polycyanopolycadmates $[Cd_x(CN)_y]^{2x-y}$ give a great variety of clathrate inclusion structures, as has been reported by our group and others.[1~5] Except for the $Cd(CN)_2$ host that involves tetrahedral Cd only,[1] their multi-dimensional hosts, even for those of apparent composition $Cd(CN)_2$, are constructed of the CN linkages among tetrahedral Cd(t) and octahedral Cd(o) atoms; in some cases trigonal-bipyramidal five-coordinate Cd(p) atoms are involved. The presence or absence of secondary ligand L is one of the important factors for the host to provide cavities appropriate in size and shape for guest molecules. This paper reports on the results that we have obtained clathrate of the composition $9Cd(CN)_2 \cdot 4C_3H_4N_2 \cdot 2H_2O \cdot 2C_6H_5C_2H_5$ using imidazole (imH), a five-membered aromatic amine, as the secondary ligand. This polycyanopolycadmate inclusion structure is the first example of the clay-like layered neutral host accommodating ethylbenzene neutral guest in the intralayer cavity.

The title clathrate was prepared as single crystals by the following procedure. Into 100 mL of water, 10 mmol of $CdCl_2 \cdot 2.5H_2O$, 10 mmol of $K_2[Cd(CN)_4]$, and 10 mmol of imH were dissolved successively under stirring. The solution was covered with a layer of neat phase of the ethylbenzene guest species and kept standing at ambient temperature for a few days. Colorless crystals were obtained at the interface between the organic and the aqueous phases and the bottom of the latter. The composition of clathrate and the accommodation of guest molecule were confirmed by elemental analyses, IR and GC techniques. Anal. Found for clathrate: C, 27.2; H, 2.05; N, 18.1; Cd, 50.2. Calcd. for $C_{46}H_{40}N_{26}O_2Cd_9$: C, 27.6; H, 2.02; N, 18.2; Cd, 50.6%. The clathrate liberates the ethylbenzene guest molecule gradually under ambient atmosphere.

Single crystals coated with epoxy resin were subjected to the collection of the intensity data on a Rigaku AFC-5S four-circle automated diffractometer using graphite-monochromated Mo- Kα radiation (λ=0.71069 Å); no decay was observed through monitoring three representative reflections by every 100 interval. The crystal structure was solved using the SHELX 76[6] and UNICS III[7] programs. The crystal data are: $C_{46}H_{40}N_{26}O_2Cd_9$, M=2000.70, monoclinic, $P2_1/c$, a= 17.221(2), b =8.499(3), c =23.537(2) Å, β=105.90(1)°, U= 3313(1) Å^3, Z=2, D_x=2.01, D_m=2.00(6) gcm^{-3}, 10520 reflections observed, 6879 used, 376 parameters to R=0.045 and R_w=0.059.

Crystallographic diagrams were obtained using the ORTEP program.[8] The solved crystal structure is shown in Figure 1. There are crystallographically independent two octahedral Cd atoms and three tetrahedral Cd atoms in the layer host structure. The projection of the layer along the *b* axis has the shape of the belt extending along the c axis with pentagonal meshes cornered by the Cd atoms. There are two set of the linear but bent linkages connected by single and coordination bonds across the belt: N(imH)-Cd(t2)-(CN)-Cd(t1)-CN-Cd(o1)-NC-Cd(t1)-(CN)-Cd(t2)-N(imH) and O(H_2O)-Cd(o2)-NC-Cd(t3)-CN-Cd(o1)-NC-Cd(t3)-CN-Cd(o2)-O(H_2O). Both linear arrays intercross at bis-imH-ligated Cd(o1) on the inversion center of the unit cell and interconnected between the respective pairs of Cd(t2) and Cd (o2) on the surface of the layer. The coupled linear arrays are further interconnected to one another up and down

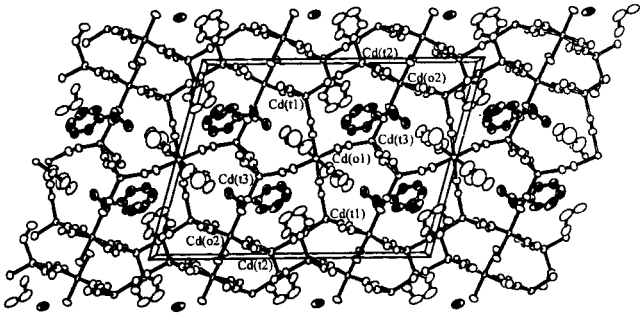

Figure 1. View of the unit cell structure of $[\{Cd(imH)_2\}\{Cd(H_2O)\}_2\{Cd(CN)_3\}_2\{Cd(CN)_3(imH)\}_2\{Cd(CN)_3\}_2] \cdot 2C_6H_5C_2H_5$ along the *b* -axis.