Journal of Molecular Catalysis A: Chemical 314 (2009) 71–80

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Unexpected chemoselectivity of cyclic enones on introducing additional chirality in diethanolamine ligand in catalytic asymmetric Michael addition reactions using heterobimetallics

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ARTICLE INFO

Article history:
Received 2 July 2009
Received in revised form 20 August 2009
Accepted 20 August 2009
Available online 27 August 2009

Keywords:
Diethanolamine ligands
Additional chirality
Homochiral and heterochiral
heterobimetallic catalyst
Asymmetric Michael addition
Chemoselectivity
Stereochemical switch

ABSTRACT

A homochiral Al–Li heterobimetallic complex of diethanolamine was found to catalyze Michael addition reactions displaying high chemoselectivity with certain Michael acceptors and Michael donors. The heterochiral complex with stereochemical switch on the ligand displayed substrate generality. Herein we give the proposed mechanism and the effect of reversing the order of addition of substrates in causing the reversal of chemoselectivity.

1. Introduction

Although numerous enantioselective catalysts are available in literature for asymmetric Michael addition reactions, it was found that heterobimetallic catalysts are highly effective in inducing high enantioselectivity. A heterobimetallic catalyst is the one in which two different metals play different roles to enhance the reactivity of both reaction partners and position them in proximity to each other [1–5]. Heterobimetallic asymmetric catalysts promote many reactions efficiently through a synergistic cooperation between two different metals and a chiral template in a manner analogous to that seen in enzymatic processes involving metal-ion co-catalysis [6]. A key feature of enzymes is their ability not only to position substrates in proximity to each other but also to enhance their reactivity by transition state stabilization. Such stabilization is possible by the presence of functional groups present at appropriate positions in their asymmetric environment [7].

A series of efficient two-center catalysts or heterobimetallic catalysts have been reported [8]. Mechanistic studies suggested that heterobimetallic complexes promote asymmetric reactions *via* dual activation of both nucleophiles and electrophiles. One portion of the ligand engages a Lewis acid moiety that coordinates an electrophilic substrate, while another portion of the ligand coordinates to the nucleophilic substrate partner. The Al–Li–BINOL [9] and La–Na–BINOL complexes [10] developed by them were highly efficient in bringing about enantioselective Michael additions. In such complexes, the central lanthanide metal is a Lewis acid and it is proposed to coordinate the electrophile while the hemilabile BINOLate oxygens deprotonate the nucleophile [11].

The catalytic asymmetric Michael addition of enolates to α,β-unsaturated carbonyl compounds is one of the most important C–C bond forming reactions due to the ready availability of both substrates and usefulness of enantiomerically enriched Michael products [12,13]. Several studies have been carried out by different authors in our laboratory, on Al–Li heterobimetallic complex of a C_2-symmetric chiral ligand, 2-(benzyl-(2-hydroxy-2-phenylethyl)-amino)-1-phenylethanol **5** (Fig. 1). The authors observed that the heterobimetallic complex effectively catalyzed the asymmetric Michael reactions and Diels–Alder reactions of various cyclic and acyclic enones with malonates reactions affording good to excellent enantioselectivities [14–18]. Further, it has been reported that their initial efforts to examine and evaluate the effect of size of the substituents on the activity of diethanolamine ligand by intro-

Abbreviations: cp, cyclopentanone; ch, cyclohexanone.

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[1] Deceased 23.02.2007.

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doi:10.1016/j.molcata.2009.08.019

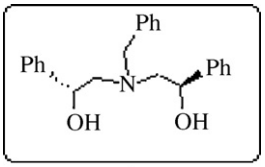

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Fig. 1. Structure of **5**.

ducing different substituents on nitrogen have demonstrated that increasing bulkiness on the ligand had a favorable effect on the enantioselectivity [19]. It is also well known from the literature precedents that the catalysts prepared from ligands that contain multiple chiral centers can lead to configurational and conformational complexities that can be transmitted as stereoselectivity in product formation [20]. High asymmetric induction has been attributed to additional chiral centers and a well-defined conformation of the catalyst as the conformational flexibility in a chiral catalyst sometimes leads to erosion of enantioselectivity [21–26].

Thus, the modular nature of ligand **5** that allows rapid synthesis of its analogues coupled with our presumption that additional chirality might lead to increased enantioselectivity prompted us to the effort of the construction of catalyst system, containing the ligand built in a similar fashion as ligand **5** but with a bulkier tether on the nitrogen in the form of additional chirality [27,28]. Herein we report the evaluation of the efficacy and the proposed mechanistic details of the chiral catalysts and the steric implications of additional chiral substituent on nitrogen. The report also focuses on the effect of stereochemical switch on the ligand in altering the chiral space in the vicinity of metal center, thus influencing the reactivity of the Michael adducts.

2. General information and experimental

For full experimental details including the spectral data, see supporting information.

Toluene and THF were distilled from sodium/benzophenone ketyl. *Racemic* styrene oxide, (*R*)-styrene oxide, and 1-phenylethylamines and $LiAlH_4$ were purchased from Aldrich and used as such without further purification.

3. Results and discussion

3.1. Our goal

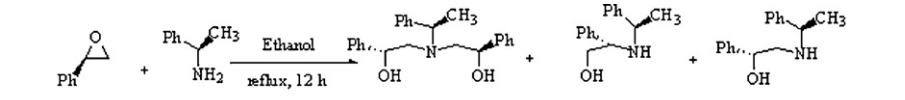
Our goal was to systematically examine the contribution of the steric and the electronic effects of the substituent on the efficiency of the Michael addition reaction. The study addresses, four components of this process: (1) the steric contribution of methyl substituent on the benzylic carbon of diethanolamine on the efficiency of the catalyst; (2) the size contribution of enones on selectivity and reactivity; (3) the contribution of substitution on malonates in modulating steric/electronic effects at oxygen and (4) the dramatic effect of the order of addition of substrates in modulating the efficiency of the catalyst.

3.2. Optimization of reaction conditions with R,R,R heterobimetallic catalyst

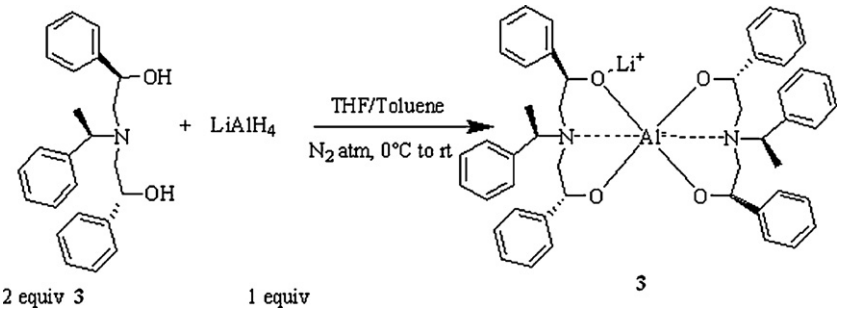
The diethanolamine (Scheme 1) readily reacted with $LiAlH_4$ (1 equiv.) in THF, under anhydrous conditions in nitrogen atmosphere. The mixture was then stirred for 30 min at 0 °C to form the Al–Li heterobimetallic complex **3** (Scheme 2). To this solution, Michael acceptors and Michael donors were added successively and stirred for 6 h at room temperature. The mixture was quenched with 1N HCl and extracted with ethylacetate. Purification by column chromatography gave Michael adducts in moderate to excellent yield. The formation of heterobimetallic complex was supported by ^{27}Al and ^{7}Li NMR spectral studies (Fig. 2).

The results compiled in Table 1 clearly demonstrate that the nature of substrates have tremendous influence on the efficiency of the reaction. Thus, it is possible to discuss the contribution of benzylic substitution on diethanolamine to the relative efficiencies in general across two substrate classes.

When the complex **3** was used in catalytic amounts the Michael addition of dialkyl malonates to cyclic and acyclic α,β-unsaturated carbonyl compounds was found to be highly chemoselective affording Michael adducts only with cyclopentenone (Scheme 3, Table 1, entries **1–7**). Although catalyst solubility was improved with increased solvent polarity, strongly polar coordinating solvent like THF was detrimental to enantioselectivity (entries **1** and **5**). It was observed that although there was a slight drop in the yield, an enantioselectivity of 25% has been observed in the product (entry **2**).



Scheme 1. Synthesis of homochiral diethanolamine **1**.



Scheme 2. Synthesis of Al–Li heterobimetallic complex **3**.

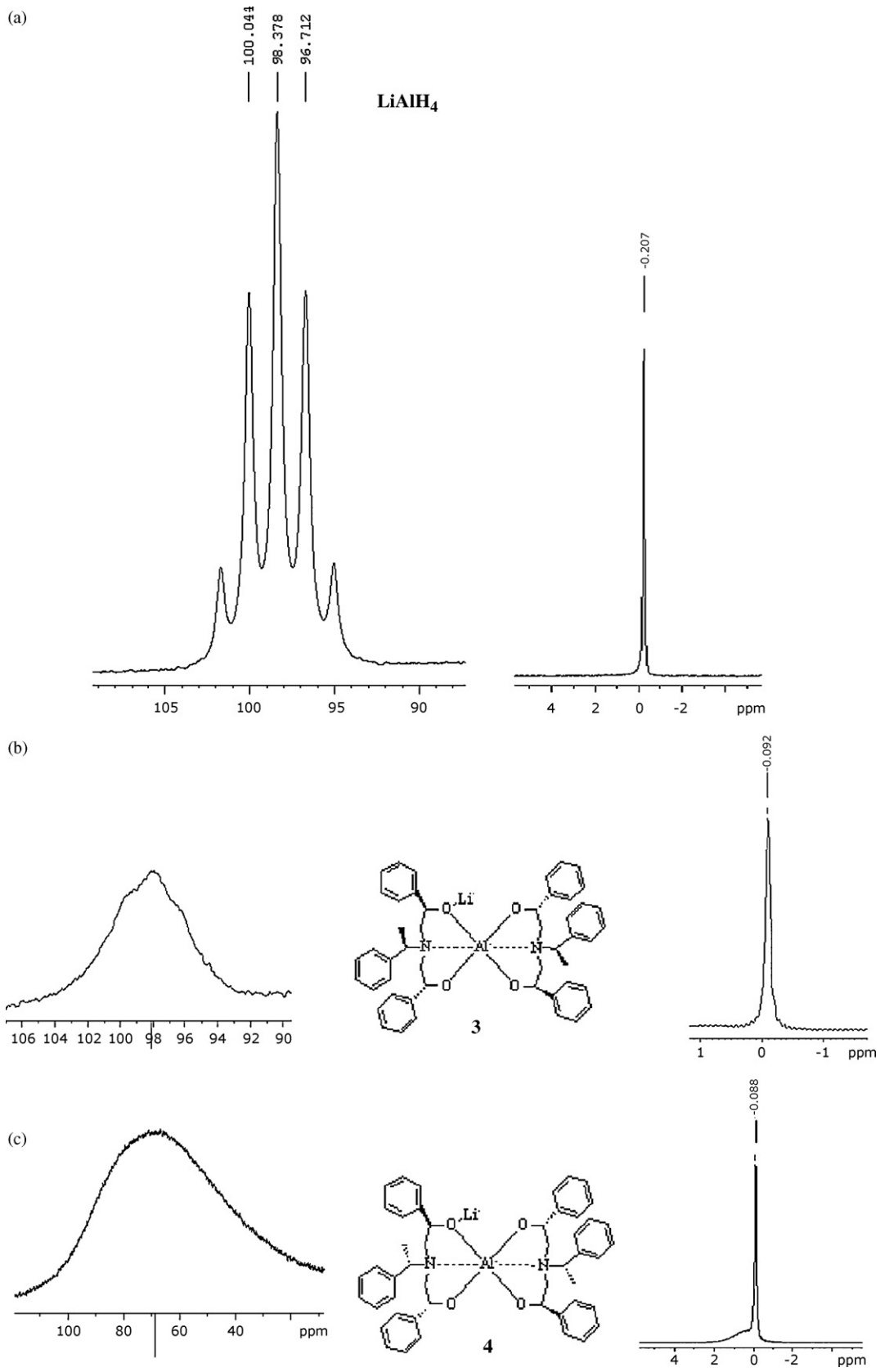


Fig. 2. ^{27}Al NMR and ^{7}Li NMR of $LiAlH_4$, **3** and **4**.

Table 1
Optimization of reaction conditions for Michael addition of malonates to cyclic enones using complex **3**.

Entry	Acceptor	Donor	Product	Solvent	Time (h)	Temp (°C)	% yield	% *ee*[a]
1	**6**	**8**	**11**	THF	0.25	rt	95	0
2	**6**	**8**	**11**	Toluene	6	rt	70	25
3	**6**	**8**	**11**	Toluene	6	0	83	50
4	**6**	**8**	**11**	Toluene	6	−20	70	22
5	**6**	**8**	**11**	Toluene	6	−40	20	10
6	**6**	**10**	**12**	THF	0.25	rt	90	0
7	**6**	**10**	**12**[b]	Toluene	6	rt	60	60
8	**6**	**10**	**12**	Hexane + toluene	6	rt	70	3
9	**6**	**9**	–	THF	48	rt	–	–
10	**7**	**8**	–	THF/toluene	6	rt	–	–
11	**7**	**9**	–	THF/toluene	6	rt	–	–
12	**7**	**10**	–	THF/toluene	6	rt	–	–

–: no reaction.
[a] Enantiomeric excesses are measured using optical rotation values by comparison with literature [14,20].
[b] The ORTEP diagram from the single crystal XRD data of **12** is given in Fig. 3.

The formation of Michael adduct in toluene, with some enantioselectivity, albeit poor, further led to examination of the effect of temperatures. Reaction temperature moderately affected the reaction yields and selectivity. In the Michael addition of diethyl malonates to cyclopentenone, decreasing of temperature to 0 °C resulted in a slight increase in the yield to 83% and enantiomeric excess was found to be doubled to 50% (entry **3**). A lowering of temperature to −20 °C resulted in a decrease in yield to 70% and enantiomeric excess was halved (entry **4**). From entry **5** it can be observed that further decrease of temperature to −40 °C led to drastic reduction of yields and enantiomeric excesses.

Comparison of entries **1–12**, reveals a strikingly strong, steric and electronic effect on the efficiency where di-*tert*-butyl malonate reacts faster than diethyl malonate and dibenzyl malonate does not react at all.

Comparison of entries **2** and **7** reveals the effect of bulkier *tert*-butyl substituent of the malonates on the efficiency of the catalyst where its Michael addition to cyclopentenone was found to be more enantioselective giving upto 60% *ee* than diethyl malonate. Solvent screening was also done with less polar solvents like toluene and hexane:toluene mixture. Toluene was found to give the best result (entries **3** and **7**). When hexane–toluene mixture was used, although the yield increased slightly a drastic reduction in the

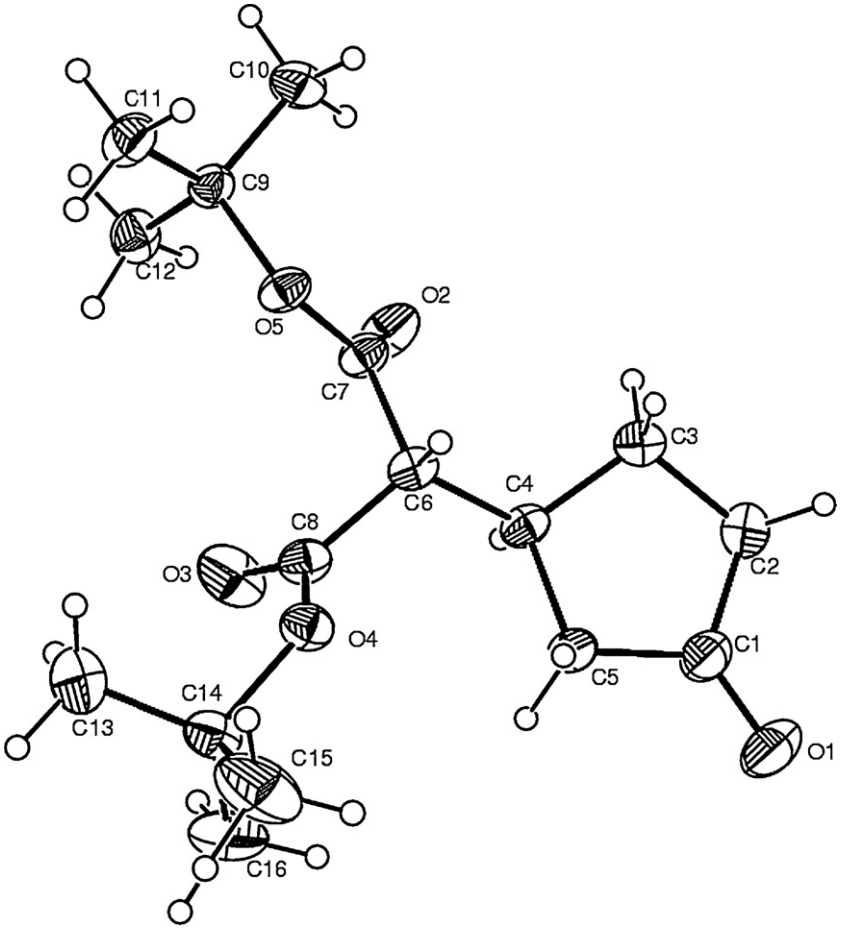
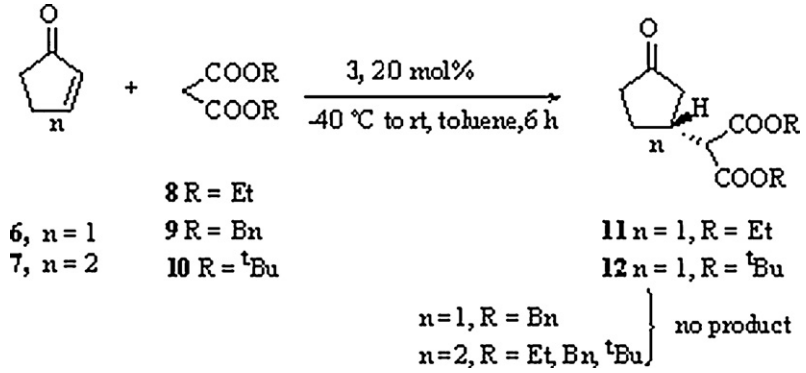
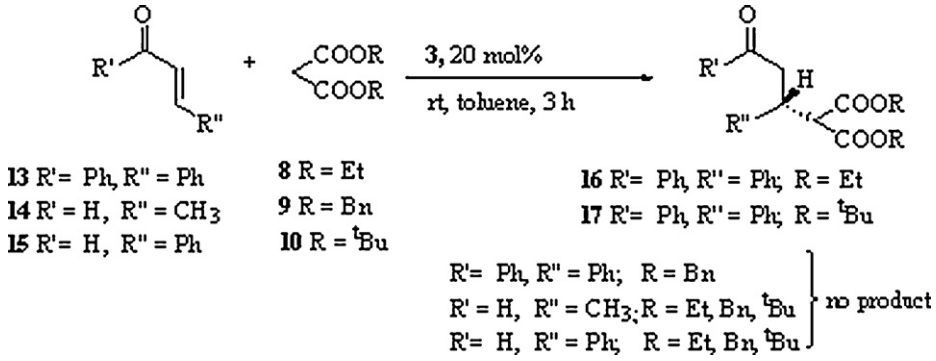


Fig. 3. The ORTEP diagram of **12**.



Scheme 3. Michael addition of malonates to cyclic enones using complex **3**.



Scheme 4. Michael addition of malonates to acyclic α,β-unsaturated carbonyl compounds with complex **3**.

enantiomeric excesses has been observed (entry **8**). The catalyst displayed chemoselectivity towards certain Michael acceptors and donors. Among malonates, it was observed that dibenzyl malonate did not react at all and hence no product was obtained from the reaction between cyclopentenone and dibenzyl malonate (entry **9**). Further, between the two cyclic enones employed, cyclohexenone was found not giving Michael products with any of the malonates (entries **10–12**).

To broaden the substrate scope to acyclic α,β-unsaturated carbonyl compounds, chalcone **13**, crotonaldehyde **14** and cinnamaldehyde **15** were chosen as Michael acceptors (Scheme 4). The Michael addition of diethyl malonate and di-*tert*-butyl malonate to chalcones resulted in almost quantitative yields but with no enantioselectivity (Table 2, entries **7** and **8**). However, the Michael addition of **9** did not occur with chalcone (entry **9**). The Michael addition of malonates to crotonaldehyde and cinnamaldehyde did not proceed (entries **1–6**) (Fig. 4).

3.3. Catalyst screening

The demonstration that complex **3** operates totally against the optimum selectivity obtained for diethanolamine **5** [14–19] was a rather surprising outcome. While the increasing bulkiness on the ligand led to increased enantioselectivity in the previous reports [19], the placement of additional bulkier chiral substituent on nitrogen was sufficient to bring down the high levels of enantiocontrol.

The adverse effects of size and rigidity of cyclic enones indicate that the complexation of the metal to the enone is important. To explain the effect of stereochemistry on nitrogen on the reactivity, we further explored the effect of switched stereochemistry on nitrogen, in the ligand to see if the change could provide a more favorable environment for asymmetric process. Therefore a heterochiral (*R*,*S*,*R*) diethanolamine, (1*R*, 5*R*)-3-aza-(1*S*-phenyl ethyl)-1,5-diphenylpenta-1,5-diol (**2**) was prepared from (*S*)-1-phenylethyl amine and (*R*)-styrene oxide by essentially the same

Table 2
Michael addition of malonates to acyclic α,β-unsaturated carbonyl compounds with complex **3**.

Entry	Acceptor	Donor	Product	Solvent	Time (h)	% yield	% *ee*[a]
1	**14**	**8**	–	THF	48	–	–
2	**14**	**9**	–	THF	48	–	–
3	**14**	**10**	–	THF	48	–	–
4	**15**	**8**	–	THF	48	–	–
5	**15**	**9**	–	THF	48	–	–
6	**15**	**10**	–	THF	48	–	–
7	**13**	**8**	**16**	Toluene + THF	3	83	0
8	**13**	**9**	**17**[b]	Toluene + THF	3	99	0
9	**13**	**10**	–	Toluene + THF	3	–	–

–: no reaction.

[a] Enantiomeric excesses were measured using optical rotation values by comparison with literature [14,20].

[b] The ORTEP diagram from the single crystal XRD data of **17** is given in Fig. 4.

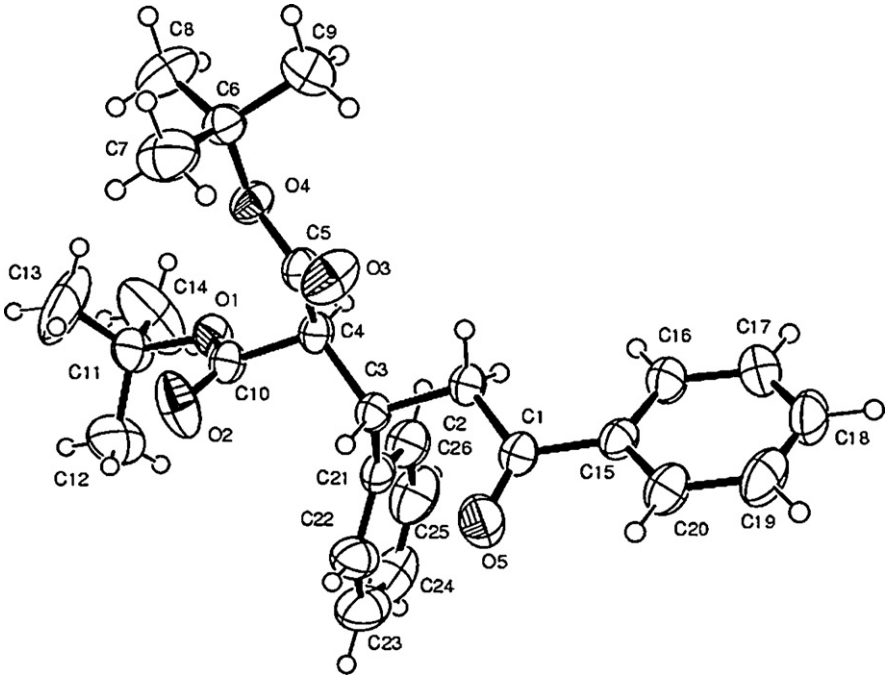
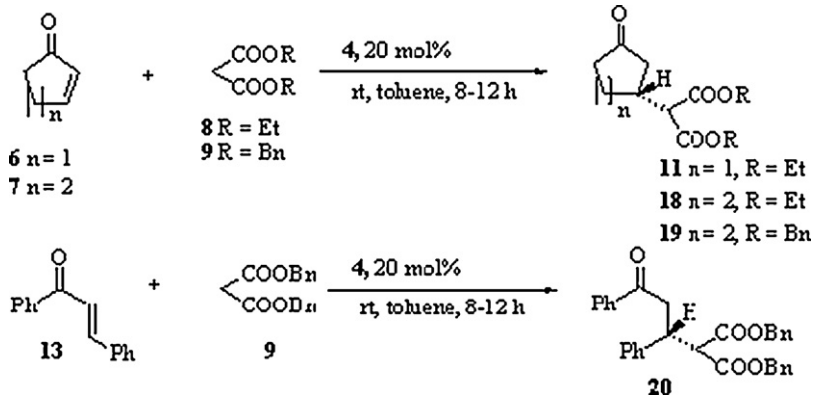


Fig. 4. The ORTEP diagram of **17**.



Scheme 5. Michael addition of malonates to cyclic and acyclic α,β-unsaturated carbonyl compounds with complex **4**.

method as given in Scheme 1. A heterobimetallic Al–Li complex **4** was prepared from **2** to be used in Michael addition reactions. We were pleased to observe that the catalyst displayed good substrate generality affording highly encouraging results in terms of reactivity but poor selectivity (Scheme 5).

The results obtained when the catalyst was used in catalytic amounts in Michael addition reactions are shown in Table 3. The following results are noteworthy. Firstly, it is clear from entries **1** and **2** that both 5- and 6-membered cyclic enones are good substrates for complex **4**. Secondly, the catalyst was found to be reactive even for dibenzyl malonate **9**. The Michael addition of **9** to **13** led to the formation of **20** in excellent yields (entry **3**). It is important to note here that, this particular reaction did not proceed at all with **3**. Also, with complex **3**, slightly increased reaction times were observed than those reported when **3** was used (entries **1–3**). In all the cases, the products were obtained in *racemic* form.

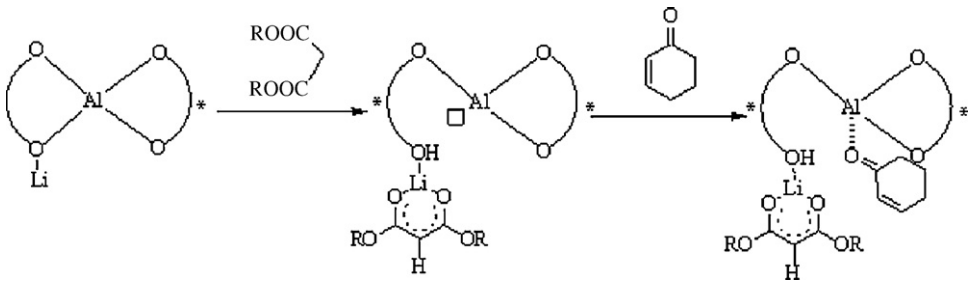
3.4. Michael addition reactions with reverse addition of substrates

We hypothesized that, if the first step in the catalytic cycle is the coordination of malonate to lithium, then it would probably cleave the oxygen–aluminum bond, leading to increased Lewis acidity and more chiral space at aluminum allowing its coordination to cyclohexenone leading to Michael attack (Scheme 6).

Table 3
Michael addition of malonates to cyclic and acyclic α,β-unsaturated carbonyl compounds using complex **4**.

Entry	Acceptor	Donor	Product	Solvent	Time (h)	% yield	% *ee*[a]
1	**6**	**8**	**11**	Toluene	8	85	0
2	**7**	**8**	**18**	Toluene + THF	8	75	0
3	**13**	**9**	**20**	Toluene	12	95	0

[a] Enantiomeric excesses were measured using optical rotation values by comparison with literature [14,20].



Scheme 6. Reaction of the substrates with the complex **3** in the reverse addition of substrates.

In order to evaluate this, we have reversed the order of addition of substrates from, addition of enone and malonate successively, to addition of malonate followed by slow addition of enone in aliquots. The strategy was found to have a remarkable effect on the substrate generality, albeit with no effect on enantioselectivity (Table 4). The Michael addition using complex **3** did not yield the products from cyclohexenone. However it was surprising to observe the formation of **18** and **19** just by reversing the order of addition of substrates but using the same catalyst (entries **2** and **3**). It was also surprising to obtain the Michael adduct of **7** and **9** (entry **3**) both of which did not react at all when the substrates enone and malonate were added successively.

It may be recalled that the successive order of adding enone and malonate afforded lesser yields for cyclopentenone. But the strategy of reversing the order of addition of substrates to malonate followed by slow addition of enone in aliquots was found to have a tremendous effect on yields (entry **1**). This reactivity of the complex **3** towards cyclohexenone on reversing the order of addition of substrates, is a clear evidence that the order of addition of substrates dictates the pathway of the reaction.

Another remarkable feature of this strategy was the decreased reaction time of 3 h as compared to 6 h for the normal course of addition of substrates (Table 1). The formation of **20** from dibenzyl malonate was another observation of significance. However, it was unfortunate to note that the strategy had no effect on the enantioselectivity on any of the Michael adducts.

3.5. Differential behaviour of cyclopentenone and cyclohexenone

It was interesting to note that with cyclohexenone, Michael addition did not occur in sharp contrast to the excellent yields obtained with cyclopentenone. The investigations reported in literature reveal marked differences between the chemistry of cyclopentenone and cyclohexenone in terms of reactivity differences owing to their geometry [29]. An aza-Michael reaction of methoxylamine to cyclic and acyclic enones and α,β-unsaturated N-acylpyrroles promoted by rare earth-alkali metal heterobimetallic complexes has been demonstrated where different enones including conformationally rigid enones and cyclohexenone were used [30]. It was observed that the enones with *s*-cis form afforded aza-Michael products in high *ee*, although the reactivity was low probably due to steric hindrance. The reaction did not proceed at all with enones with *s*-trans form.

3.6. Differential behaviour among acyclic α,β-unsaturated carbonyl compounds

The high conformational mobility of acyclic enones makes the design of effective enantioselective catalyst system a challenge. An effective way of probing the identity of catalyst transition state by simple, logical variation of enone substitution pattern in Cu-catalyzed asymmetric addition of 1,4-$ZnEt_2$ has been recently reported [31]. From a range of enones whose structures were expected to weigh the population of one of four reacting species defined by *syn* and *anti* Lewis Acid (LA) coordination, the enones were defined as poor and good substrates respectively based on their steric properties and cis/trans configuration of the ene moiety and results indicated an *anti-s*-cis arrangement in the transition state.

It was interesting to observe in the present study that the catalyst was chemoselective towards certain substrates among the acyclic α,β-unsaturated carbonyl compounds too. α,β-unsaturated aldehydes, like crotonaldehyde and cinnamaldehyde with *s-trans* configuration were ineffective in yielding Michael adducts. Whereas a high chemical yield of the expected product was obtained with *s-cis* chalcone suggesting that the *s-cis* or the *s-trans* substrate conformations of acyclic Michael acceptors, strongly determine the substrate–Lewis acid binding and reactivity. It is not clear if the binding of LA could occur *syn* (**s**) or *anti* (**a**) with respect to the ene function. But it can be understood that *s-cis* conformation places the enone in closer proximity to the Lewis acid than the *s-trans* conformation leading to Michael addition product (Fig. 5).

3.7. Proposed mechanism

It is noteworthy that the stereochemical outcome of the reaction is delicately influenced by the steric and electronic factors in the catalyst, Michael donors and acceptors and solvent used. The important step in the reaction must be formation of an intermediate where the Michael acceptor and the Michael donor are bound to the heterobimetallic complex, for the Michael addition to take place. The catalyst appears to depend highly on the structure of Michael acceptors and donors. Both the Lewis acid and Bronsted

Table 4
Michael addition of malonates to cyclic and acyclic α,β-unsaturated carbonyl compounds using complex **3** with reverse addition of substrates.

Entry	Acceptor	Donor	Product	Temp (°C)	Time (h)	% yield	% *ee*[a]
1	**6**	**8**	**11**	rt	3	95	0
2	**7**	**8**	**18**	rt	3	95	0
3	**7**	**9**	**19**	rt	3	42	3
4	**7**	**9**	**19**	−10	3	71	5
5	**13**	**9**	**20**	rt	3	99	0

[a] Enantiomeric excesses were measured using optical rotation values by comparison with literature [14,20].

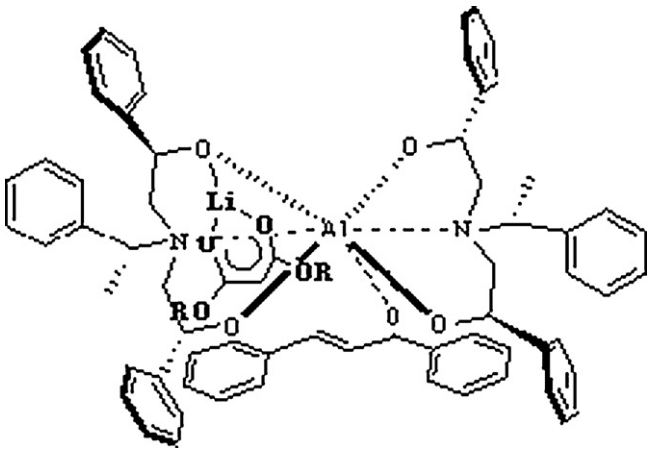
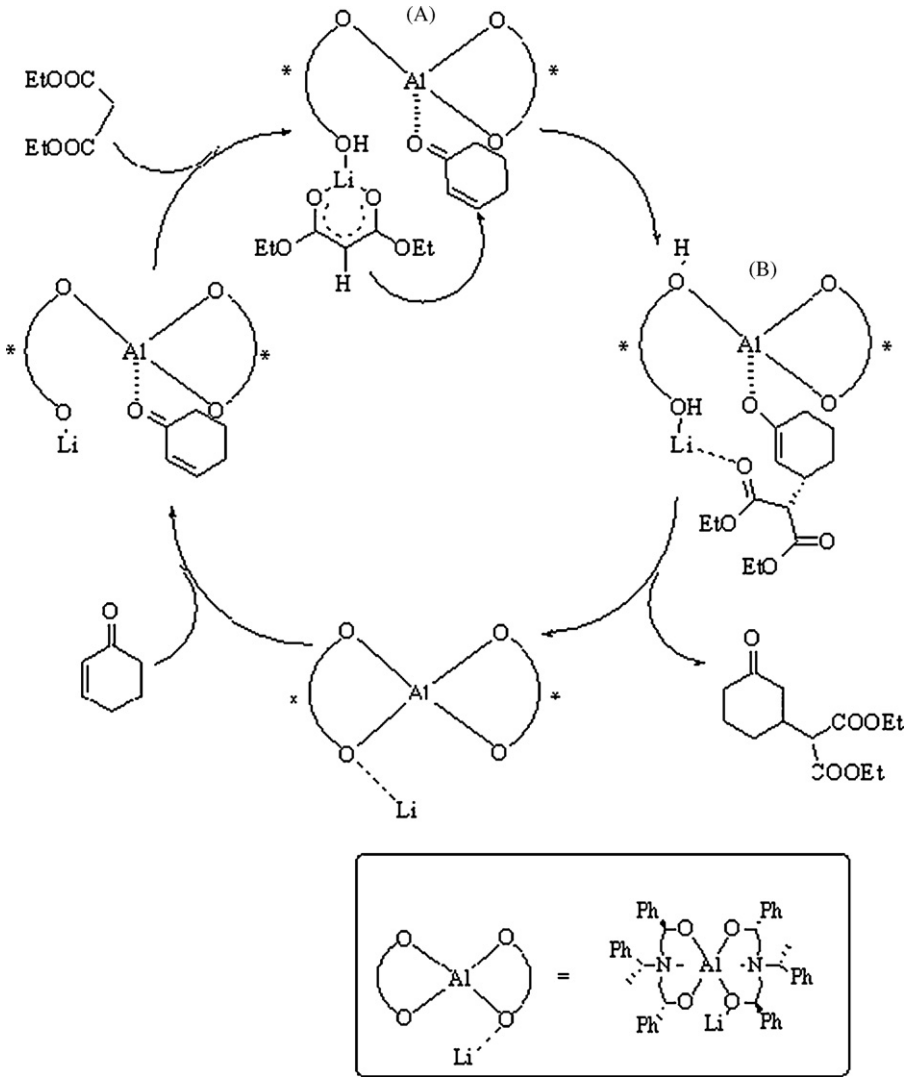


Fig. 5. Possible transition state for Michael addition using complex **3**.

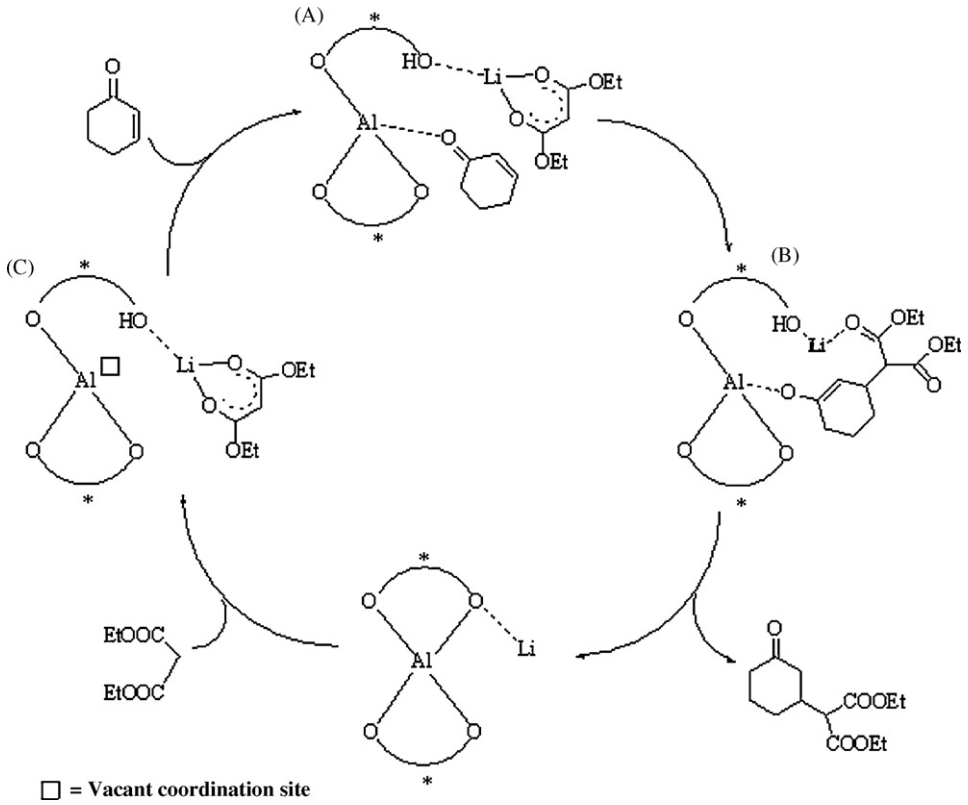
were determined to be essential for catalysis and the preceding set of experiments are all consistent with bifunctional mechanism based on the combination of Lewis acid and Bronsted base working in concert, to attain efficient molecular transformation. The possibility of other mechanisms like, Lewis acid of the complex acts alone to catalyze the addition or Bronsted base of the complex acts alone to catalyze the addition can be completely ruled out based on the information available. If the active portion of the catalyst was simply the Lewis acid, then all the malonates should give rise to Michael adducts. It is surprising to note that the largest substituent, ^{t}Bu, which might be expected to have greatest steric influence, in fact gave rise to highest enantioselectivities, while the dibenzyl malonate did not react at all, indicating that a component, Bronsted base, is needed in addition to the Lewis acid which acts in concert with the latter and the efficiency of the catalyst is significantly influenced by the structure and electronic factors of the Michael donor. The non-reactivity of cyclohexenone and reactivity of cyclopentenone is clearly attributed to the size effect and the rigidity of cyclohexenone. The catalyst might not have sufficient space at the Al to bind to the bulkier and rigid cyclohexenone, leading to its non-reactivity.

It was earlier proposed that cyclohexenone is complexed to aluminum and simultaneously, malonate is deprotonated by means of Li. Nucleophile then attacks the electrophile enantioselectively to give B, bridging Al and Li metals [14,15]. The reaction might go through this mechanism in case of normal addition of substrates (Scheme 7).

However, the non-reactivity of cyclohexenone and its reversal on reversing the order of addition of substrates is clear evidence



Scheme 7. Possible catalytic cycle for asymmetric Michael addition using complex **3** with normal addition of substrates.



Scheme 8. Possible catalytic cycle for asymmetric Michael addition using complex **3** with reverse addition of substrates.

that the order of addition of substrates dictates the pathway of the reaction. In the reverse addition of substrates, the coordination of malonate, to the lithium, cleaves the oxygen–aluminum bond, leading to increased Lewis acidity and more chiral space at aluminum allowing its coordination to cyclohexenone leading to Michael attack, reiterating that Lewis acid component is essential for the coordination of enones. A potential catalytic cycle can be envisaged for the reaction with reverse addition of substrates (Scheme 8).

Deprotonation of the malonate by the diethanoloate would yield a malonate anion forming a chelate by coordination to Li and cleaves the oxygen–aluminum bond, leading to increased Lewis acidity and more chiral space at aluminum allowing its coordination to cyclohexenone and activates the electrophile in close proximity to the nucleophile allowing Michael addition to occur. Proton transfer from the diethanolamine to the enolate intermediate would then allow product release and catalyst regeneration.

4. Conclusion

In conclusion, Al–Li heterobimetallic complexes with homochiral and heterochiral diethanolamine ligands with additional chirality on nitrogen have been synthesized and characterized. The complexes were effective in catalyzing asymmetric Michael addition reactions. The homochiral complex displayed chemoselectivity with cyclic enones where stereochemically rigid cyclohexenone failed to react at all but the heterochiral complex with switched stereochemistry on nitrogen led to reversal of chemoselectivity. The stereochemistry on nitrogen may have severe steric implications; the additional chiral moiety in the homochiral catalyst may cause severe steric strain and decreases the chiral space in the vicinity of metal center which gets released with stereochemical switch on nitrogen. The order of addition of substrates seems to determine the most likely pathway of the reaction and has electronic implications, causing chemoselectivity or its reversal by electronically tuning the Lewis acidity of the metal center in the catalyst. Thus the rational design of ligand or the choice of suitable metal that adjusts the balance of electronic and steric factors is crucially important to exploit the catalyst performance. The catalysts reported herein seem promising from a practical standpoint for their relatively high catalytic activity. The facts and problems discussed in this work may provide number of possibilities for the study of stereochemical phenomena of reactions involving catalysts with multiple stereocenters.

Acknowledgment

This study was financially supported by Department of Chemistry, IIT Chennai. The intellectual and moral support of Late Prof. G. Sundararajan and Prof. S. Sankararaman, IIT Chennai is gratefully acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.08.019.

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