

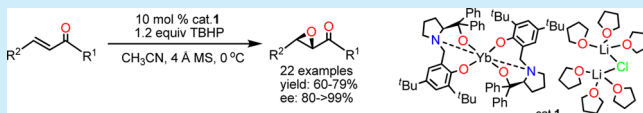
Asymmetric Epoxidation of Unsaturated Ketones Catalyzed by Heterobimetallic Rare Earth–Lithium Complexes Bearing Phenoxy-Functionalized Chiral Diphenylprolinolate Ligand

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S Supporting Information

ABSTRACT: Four novel heterobimetallic complexes [RE₂]-{(THF)₃Li}₂(μ-Cl)} stabilized by chiral phenoxy-functionalized prolinolate (RE = Yb (1), Y (2), Sm (3), Nd (4), H₂L = (S)-2,4-di-*tert*-butyl-6-[[2-(hydroxydiphenylmethyl)pyrrolidin-1-yl]methyl]phenol have been synthesized and characterized.

These readily available complexes are highly active in catalyzing the epoxidation of α,β -unsaturated ketones, while the enantioselectivity varies according to the ionic radii of the rare earth center. A series of chalcone derivatives were converted to chiral epoxides in 80 → 99% ee at 0 °C using TBHP as the oxidant in the presence of 10 mol % of 1.



Enantioselective epoxidation of olefins is of great importance in organic synthesis because the resulting products, chiral epoxides, are the most versatile building blocks for optically pure natural products and pharmaceuticals with biological activities.¹ In the 1980s, Sharpless developed an elegant method to prepare enantiomers of epoxides from allylic alcohols using substoichiometric amounts of titanium and tartrate.² This pioneering work plays a particularly important role in asymmetric epoxidation.³ Ever since then, a range of catalysts, which can be mainly divided into organocatalysts and metal-based catalysts, have been developed for the asymmetric epoxidation of alkenes, especially for that of electron-deficient C=C bonds in α,β -unsaturated ketones. Organocatalysts capable of catalyzing asymmetric epoxidation mainly include cinchona alkaloids,⁴ polyamino acids,⁵ and chiral amine-based molecules.⁶ In addition, the work by Lattanzi et al. deserves special comment, which represents the first successful example of asymmetric epoxidation of α,β -unsaturated ketones catalyzed by commercially available α,α -diphenyl-L-prolinol.⁷ In a subsequent study, the chiral prolinol skeleton and its analogues proved to be ideal organocatalysts for enantioselective epoxidation of α,β -unsaturated ketones.⁸ However, this approach suffers from relatively large catalyst loading (usually 20–30 mol %), long reaction time, required additive, and an unsatisfying ee value. To circumvent these problems, metal-based catalysts have been intensively studied. Various metal–ligand combinations, e.g., ZnEt₂/didentate [N,O] or [N,N] ligands,⁹ *n*-BuLi and Bu₂Mg/diethyl tartrate,¹⁰ Sc(OTf)₃/N,N'-dioxide,¹¹ Fe/Mn complexes bearing proline-derived multidentate N ligands,¹² and Fe(OTf)₂/phenanthroline ligands,¹³ have been reported to catalyze the enantioselective epoxidation. Moreover, lanthanide–binol and its derivatives have also been investigated, which gave rise to high enantioselectivities in many cases and show the great potential of lanthanides in catalyzing such a transformation.¹⁴

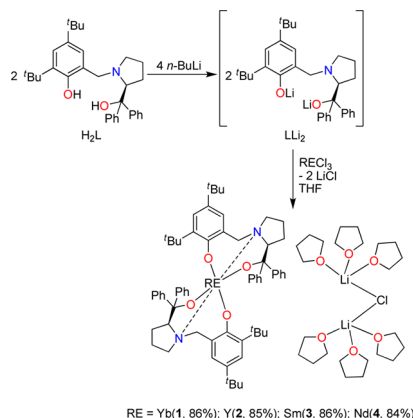
Heterobimetallic complexes incorporating both rare earth (RE) and alkali metals are reported to display outstanding activities in organic synthesis and polymer chemistry owing to the cooperative effect between two metal centers and are gaining an increasing amount of interest.¹⁵ Since the early 1990s, Shibasaki has conducted the synthesis of chiral heterobimetallic lanthanide/alkali metal complexes and discovered their versatile applications in a wide range of asymmetric reactions.¹⁶ Meanwhile, several groups also reported successful cases using heterobimetallic lanthanide/alkali metal complexes as catalysts in catalyzing reactions such as the reduction reaction, Strecker reaction, and Michael reaction.¹⁷ To the best of our knowledge, the application of RE–alkali metal complexes bearing chiral ligands in asymmetric epoxidation of α,β -unsaturated ketones have not yet been reported.

Our group has a long-standing interest in lanthanide complex synthesis and their catalytic activities in organic synthesis and polymer chemistry.¹⁸ Recently, we reported that heterobimetallic lanthanide–alkali metal complexes showed higher activities in organic synthesis and ring-opening polymerization of cyclic esters than monometallic analogues.¹⁹ These findings motivated us to further explore the synthesis and catalytic behavior of heterobimetallic RE–alkali metal complexes, especially their behavior in catalyzing asymmetric reactions. Four new heterobimetallic RE–lithium complexes stabilized by a chiral phenoxy-functionalized prolinolate ligand were synthesized and characterized. Furthermore, their applications in the asymmetric epoxidations of α,β -unsaturated ketones were also investigated, which gave rise to a series of epoxides in good yields and up to 99% ee.

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The in situ prepared dilithium salt LLi_2 from n -BuLi and the proligand H_2L ((S)-2,4-di-*tert*-butyl-6-[[2-(hydroxydiphenylmethyl)pyrrolidin-1-yl]methyl]phenol)²⁰ in a 2:1 ratio were treated with a slurry of anhydrous $RECl_3$ in THF, which gave rise to heterobimetallic RE–lithium complexes $[RELi_2] \cdot [(THF)_3Li]_2(\mu-Cl)$ (RE = Yb (1), Y (2), Sm (3), Nd (4)) in high isolated yields (Scheme 1). The identities of complexes 1–4 were confirmed by X-ray diffraction analysis, elemental analysis, IR spectra, as well as NMR spectroscopy in the case of complex 2.

Scheme 1. Synthesis of Complexes 1–4



The molecular structures of complexes 1–4 are isomorphism, which comprise a rare discrete $[(THF)_3Li]_2(\mu-Cl)^+$ cation and a $[L_2Ln]^-$ anion.²¹ The solid-state structure of complex 1 is depicted in Figure 1 as a representative.²²

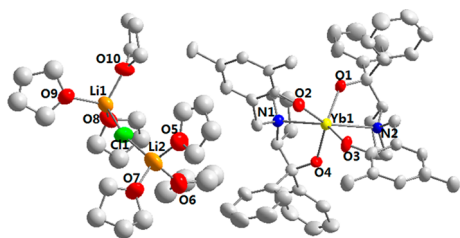


Figure 1. Solid-state structure of complex 1.

To explore the catalytic behavior of ionic heterobimetallic RE–lithium complexes 1–4, the asymmetric epoxidation of α,β -unsaturated ketones was investigated. Using commercially available chalcone as the starting material, asymmetric epoxidation reaction was catalyzed by complexes 1–4 in the presence of oxidant TBHP (*tert*-butyl hydroperoxide) or CMHP (cumene hydroperoxide). The results of this model reaction are summarized in Table 1.

To our delight, all heterobimetallic complexes 1–4 catalyzed this transformation to yield the targeted epoxide in 93–95% yields with 10 mol % catalyst loading, while the enantioselectivities are far apart (Table 1, entries 1–4). The central metal significantly influences the enantiomeric excess of the product with the decreasing tendency of Yb(1) $\sim$ Y(2) > Sm(3) > Nd(4), which is opposite to the trend of the ionic radii. Presumably, the congestion around the RE, the Lewis acidity of the RE, and the nucleophilicity of the RE peroxide species are in a good compromise for complexes 1 and 2, which is

Table 1. Epoxidations of Chalcone Catalyzed by Complexes 1–4^a

entry	cat.	temp (°C)	time (h)	solvent	yield ^b (%)	ee ^c (%)
1	1	25	4	THF	94	51
2	2	25	4	THF	93	50
3	3	25	4	THF	95	15
4	4	25	4	THF	93	<1
5 ^d	1	25	4	THF	94	39
6 ^e	1	25	4	THF	95	38
7 ^f	1	25	4	THF	88	9
8	1	25	4	CH ₃ CN	88	73
9	1	0	12	CH ₃ CN	74	89
10	1	−10	12	CH ₃ CN	66	85
11 ^g	1	0	12	CH ₃ CN	70	85
12 ^h	1	0	12	CH ₃ CN	50	95
13 ^h	1	0	20	CH ₃ CN	70	94
14 ⁱ		0	20	CH ₃ CN	trace	nd

^aReactions were performed with chalcone (0.5 mmol), TBHP (0.6 mmol), and MS 4 Å (100 mg) in 3.3 mL of solvent. ^bHPLC yields. ^cDetermined by chiral HPLC. ^d1.5 equiv of oxidant. ^e2.0 equiv of oxidant. ^fThe oxidant is CMHP. ^gAddition of 30 mol % of Ph₃PO as the additive. ^hThe amount of MS 4 Å is 15 mg (30 mg/mmol). ⁱThe control reaction without any metal, just using 20 mol % of ligand. nd = not detected.

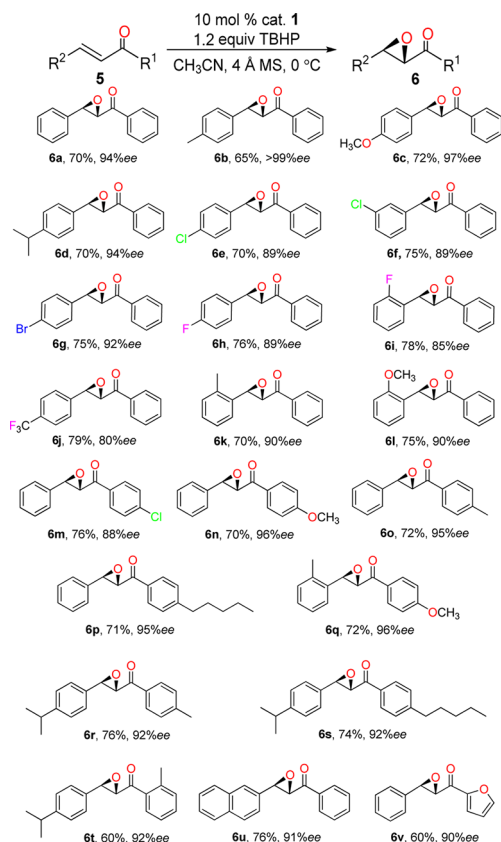
considered critical in catalyzing the transformation and controlling the enantioselectivity.^{14e,16k,23}

Using ytterbium–lithium complex 1 as the catalyst, the reaction conditions, including the amount of oxidant and molecular sieves, temperature, reaction time, and solvent, were screened (Table 1). Use of 1.2 equiv of oxidant TBHP proved to be efficient (Table 1, entries 1, 5, and 6), while CMHP led to negligible enantioselectivity (Table 1, entry 7). The reaction is sensitive to solvent, and acetonitrile proved to be the optimal choice (Table 1, entries 1 and 8; Table S10, Supporting Information). When the reaction temperature dropped to 0 °C, the ee value was improved to 89%, although the yield was sacrificed (Table 1, entries 8 and 9). Further decreasing the temperature to −10 °C resulted in similar ee values and even lower yield (Table 1, entry 10). Moreover, the addition of Ph₃PO failed to improve the ee value of the product as expected (Table 1, entry 11). In view of both yield and ee value of the product, the optimal conditions of 20 h reaction time in CH₃CN at 0 °C with the MS 4 Å loading of 30 mg/mmol was selected, which yielded the epoxidation product in moderate yield and excellent enantioselectivity (Table 1, entry 13).

To gain a deep insight into the substrate scope of the asymmetric epoxidation reaction catalyzed by the RE–lithium complex, a series of reactions with readily accessible chalcone derivatives were carried out. To our delight, a number of substrates underwent the asymmetric reactions smoothly to produce the corresponding epoxides in good to excellent enantiomeric excess of greater than 99% and moderate yields of 60–79%. The results are listed in Scheme 2.

The electronic effect of the substituents on the phenyl ring significantly affects the reaction outcomes. Substrates bearing electron-donating groups at the *para* position of either phenyl ring gave rise to corresponding epoxides in excellent ee values of 94–99% and 65–72% yields (Scheme 2, **6b–d** and **6n–p**). When the electron-donating groups are located at the *ortho*

Scheme 2. Epoxidation of α,β -Unsaturated Ketones Catalyzed by Complex 1^a



^aReactions were performed with chalcone and its derivatives (0.5 mmol), TBHP (0.6 mmol), and MS 4 Å 15 mg in 3.3 mL of solvent at 0 °C for 20 h in the presence of 10 mol % of complex 1. HPLC yields. The ee values were determined by chiral HPLC.

positions of the phenyl rings adjacent to carbonyl groups, the steric hindrance of the substituents has apparent effect on the ee value (drop to 90%), comparing with the *para* substituted ones (Scheme 2, entries 6k and 6l versus 6b and 6c). When the phenyl rings are substituted with electron-withdrawing groups, the yields increase to 70–79%, while ee values decrease to 80–92%. (Scheme 2, entries 6e–j and 6m). *p*-CH₃ substituted substrate gave the highest enantiomeric excess (6b in >99% ee), whereas the *p*-CF₃-substituted substrate led to the lowest one (6j in 80% yield) under identical conditions, which strongly suggests that the electronic properties of substrates play a crucial role on enantioselectivities of the asymmetric epoxidation. Encouraged by these findings, additional chalcone derivatives with two electron-donating groups on both phenyl rings were tested in the asymmetric epoxidation, and the ee values of the desired epoxides are excellent (Scheme 2, 6q–t). An epoxide with good ee value was also obtained with α,β -unsaturated ketones bearing aromatic heterocycles, such as (*E*)-1-furan-2-yl-3-phenylpropenone (Scheme 2, 6v). However, the catalyst system is inert to aliphatic substrates, and no products were observed under the same conditions as used for aromatic substrates.

In summary, four novel heterobimetallic rare earth–lithium complexes stabilized by a chiral phenoxy-functionalized prolinolate ligand have been synthesized and characterized. All complexes showed similarly high catalytic activities in the

asymmetric epoxidation of α,β -unsaturated ketones but substantially different enantioselectivity. Yb–Li complex 1 proved to be the optimal catalyst in terms of both efficiency and selectivity, and a wide range of chalcones of different electronic and steric properties were expediently converted to various epoxides in good to excellent enantiomeric excess and moderate yields at 0 °C in the presence of 10 mol % of catalyst.

■ ASSOCIATED CONTENT

Supporting Information

General procedures for preparation of complexes and substrates and catalysis, characterization data, ¹H and ¹³C NMR spectra, HPLC chromatograms, crystallographic data for complexes 1–4 [CCDC: 980573 (1), 980574 (2), 980575 (3), 980576 (4)] and figures depicting solid-state structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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