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Heterobimetallic Dinuclear Lanthanide Alkoxide Complexes as Acid–Base Difunctional Catalysts for Transesterification

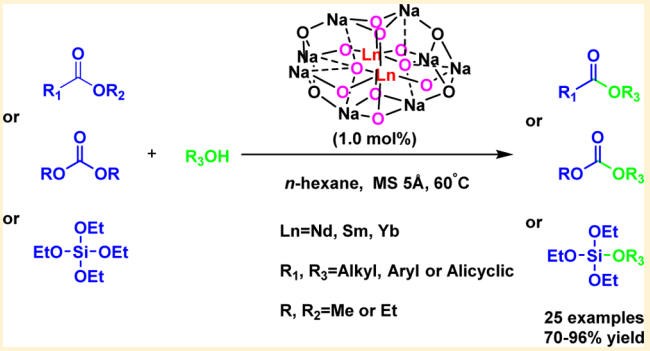
Ruijie Zeng,[†] Hongting Sheng,*[,†] Yongcang Zhang,[†] Yan Feng,*[,†] Zhi Chen,[†] Junfeng Wang,[†] Man Chen,[†] Manzhou Zhu,[†] and Qingxiang Guo[‡]

[†]School of Chemistry and Chemical Engineering & Key Laboratory of Environment-friendly Polymer Materials of Anhui Province, Anhui University, Hefei 230039, China

[‡]Department of Chemistry, University of Science and Technology of China, Hefei, 230026, China

Supporting Information

ABSTRACT: A practical lanthanide(III)-catalyzed transesterification of carboxylic esters, weakly reactive carbonates, and much less-reactive ethyl silicate with primary and secondary alcohols was developed. Heterobimetallic dinuclear lanthanide alkoxide complexes $[Ln_2Na_8\{(OCH_2CH_2NMe_2)\}_{12}(OH)_2]$ (Ln = Nd (**I**), Sm (**II**), and Yb (**III**)) were used as highly active catalysts for this reaction. The mild reaction conditions enabled the transesterification of various substrates to proceed in good to high yield. Efficient activation of transesterification may be endowed by the above complexes as cooperative acid–base difunctional catalysts, which is proposed to be responsible for the higher reactivity in comparison with simple acid/base catalysts.



INTRODUCTION

Esters play an essential role in synthetic organic chemistry both as protecting groups of several natural products[1,2] and as key intermediates in functional group transformations.[3,4] Transesterification is regarded as a more efficient method for synthesis of esters than dehydrative condensation of carboxylic acids with alcohols.[3,5] Substrates used in transesterification have better solubility in common organic solvents, while the latter sometimes requires large excess amounts of either carboxylic acids or alcohols to smooth conversion. Also, some types of esters such as carbonates (R′O-COOR) and silicates $[(R'O)_3SiOOR)]$ cannot be synthesized by direct dehydrative condensation due to the less stable nature of carbonic acid monoesters (R′O-COOH) and silicic acid esters $[(R'O)_3SiOOH]$.[6] Therefore, transesterifications have wide applications in both academic and industrial research, especially in the process for obtaining biodiesel, in which triglycerides react with low molecular weight alcohols such as methanol and ethanol.[7−10] However, high conversions are difficult to achieve because the transesterification process is an equilibrium reaction. Recently, several new procedures have been developed for transesterification, of which not only protic and Lewis acids but also organic and inorganic bases under homogeneous and heterogeneous conditions can be used as catalysts for this reaction.[11−20] Therefore, in principle, acid–base bifunctional catalytic activation of both esters and alcohols should be effective in the transesterification process.[21−23]

In comparison with conventional metal catalysts, Ln(III) complexes can be regarded as the powerful tools to achieve high efficiency and selectivity in catalytic organic reactions.[24−33] Taking transesterification as an example, Okano reported for the first time that transesterification of carboxylic esters (0.1 mmol scale) was efficiently catalyzed by La(O*i*-Pr)$_3$ (2 mol %) under heating conditions in excess molar amounts of primary and secondary alcohols.[34,35] Subsequently, the La(OMe)(OTf)$_2$-catalyzed methanolysis of aryl and alkyl esters was reported by Brown.[36,37] They proposed that a methoxy-bridged La(III) dimer might efficiently catalyze methanolysis based on Lewis acid–Lewis base dual activation. Recently, La(III) isopropoxide-catalyzed transesterification of carboxylic esters was reported by Ishihara.[38] The catalyst was prepared in situ, and the generation of a dinuclear La(III) complex was confirmed by ESI-MS analysis during the investigation of a possible reaction mechanism. Therefore, they suggested that a dinuclear La(III) salt might be used as an efficient Lewis acid–Lewis base difunctional catalyst for transesterification. However, to date no dinuclear Ln(III) alkoxide complex with a clear crystal structure is being used in the transesterification process. In our previous report, heterobimetallic dinuclear lanthanide/sodium alkoxide complexes $[Ln_2Na_8(OCH_2CH_2NMe_2)_{12}(OH)_2]$ were found to be more active catalysts for ring-opening polymerization of ε-caprolactone and trimethylene carbonate.[39] The molecular weights of the resulting polymers are lower than those expected from the monomer-to-cluster ratio, suggesting that transesterification as a side reaction may take place in the polymerization process.

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Encouraged by the results, we report an efficient method of transesterification under mild conditions in this work.

RESULTS AND DISCUSSION

Heterobimetallic dinuclear lanthanide/sodium alkoxide complexes were used as highly active catalysts to promote the transesterification reaction of carboxylic esters, weakly reactive carbonates, and much less-reactive ethyl silicate with primary and secondary alcohols. The complexes $[Ln_2Na_8\{(OCH_2CH_2NMe_2)\}_{12}(OH)_2]$ (Ln = Nd (**I**), Sm (**II**), and Yb (**III**)) and the corresponding monometallic lanthanide complex $[Nd(OR)_3]$ (OR = $OCH_2CH_2NMe_2$) (**IV**) were synthesized according to the reported literature method.[39,40] X-ray crystal structures of $[Ln_2Na_8\{(OCH_2CH_2NMe_2)\}_{12}(OH)_2]$ (Ln = Nd (**I**), Sm (**II**)) are shown in Figure 1.[39] With the well-defined

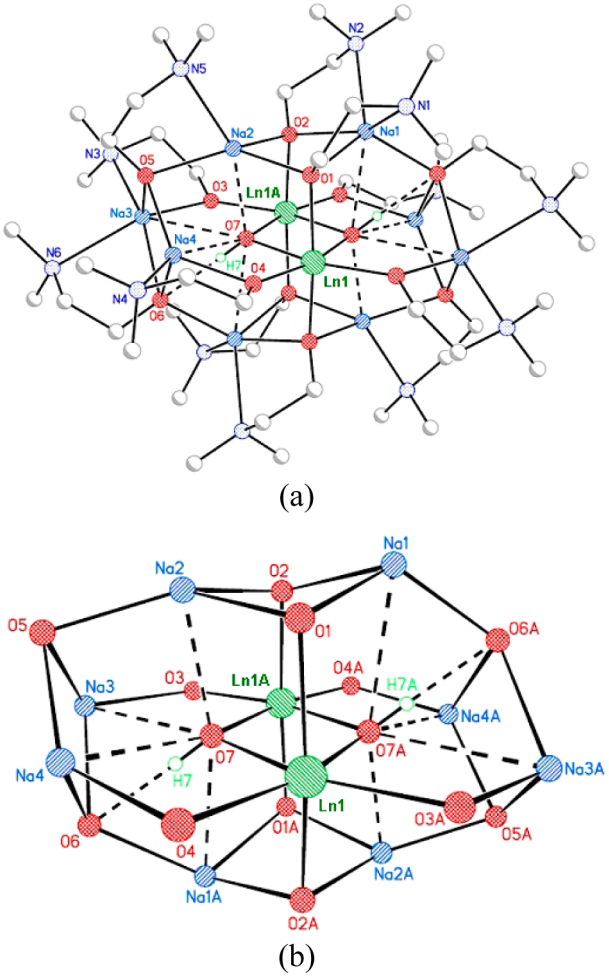
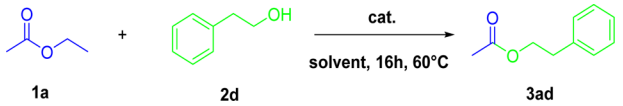


Figure 1. (a) Molecular structure of $[Ln_2Na_8\{(OCH_2CH_2NMe_2)\}_{12}(OH)_2]$, in which Ln1 and Ln1A are formed by (**I**) Ln1 = Ln1A = Nd; (**II**) Ln1 = Ln1A = Sm.[39] (b) Ball-and-stick figure of $[Ln_2Na_8\{(OCH_2CH_2NMe_2)\}_{12}(OH)_2]$ with all of the $CH_2CH_2NMe_2$ groups omitted for clarity (atomic displacement parameters set at the 30% level).

heterobimetallic dinuclear lanthanide alkoxide complexes in hand, ethyl acetate (**1a**) and phenethyl alcohol (**2d**) were used as model substrates to investigate the optimal reaction conditions, including various catalysts, different catalyst loadings, and diverse solvents for the reaction process. The results are summarized in Table 1.

Table 1. Optimization of Conditions for the Reaction of 1a with 2d[a]



entry	catalyst	mol % of catalyst	solvent	yield (%)[b]
1	**I**	1.0	*n*-hexane	91
2	**II**	1.0	*n*-hexane	80
3	**III**	1.0	*n*-hexane	65
4	**IV**	1.0	*n*-hexane	8
5	NaOR[c]	1.0	*n*-hexane	20
6	**I**	0.1	*n*-hexane	66
7	**I**	0.2	*n*-hexane	70
8	**I**	0.5	*n*-hexane	86
9	**I**	1.0	THF	86
10	**I**	1.0	toluene	88
11	**I**	1.0	DME	86
12	**I**	1.0	ethyl acetate	80
13	**I**	1.0	DMSO	76
14	**I**	1.0	solvent free	80
15[d]	**I**	1.0	*n*-hexane	95

[a]Reaction conditions: **1a** (1.6 mmol), **2d** (1.6 mmol), and catalyst in solvent (500 μL) at 60 °C under an argon atmosphere for 16 h. [b]GC yield. [c]OR = $OCH_2CH_2NMe_2$. [d]5 Å molecular sieves were used.

As expected, all heterobimetallic dinuclear lanthanide complexes (**I**, **II**, **III**) could be used as catalysts for transesterification. Ester (**3ad**) was efficiently achieved with a yield range from 65% to 91% at 60 °C for 16 h with 1.0 mol % catalyst loading (Table 1, entries 1−3). In contrast, the monometallic lanthanide complex (**IV**) and the sodium alkoxide complex NaOR (OR = $OCH_2CH_2NMe_2$) showed much lower activity, and the corresponding **3ad** was obtained with only 8% and 20% yields under the same conditions (Table 1, entries 4 and 5). In general, the monometallic lanthanide complex can be treated as a soft Lewis acid catalyst, and the sodium alkoxide complex may be used as a hard Brønsted base catalyst. The experimental results showed that heterobimetallic complexes have reactivity obviously higher than that of a simple acid/base catalyst. The dinuclear lanthanide metal ions acted as Lewis acids to activate oxygen atoms of esters, while sodium metal alkoxides functioned as a Brønsted base to bring the alcohol into close proximity (Scheme 1). The intramolecular cooperativity that is possessed by heterobimetallic dinuclear lanthanide complexes may lead to higher activity in comparison with the monometallic lanthanide complex and sodium alkoxide complex, respectively. The above acid−base bifunctional catalysis mechanism was also mentioned for other reactions.[21,34−38,41] Moreover, it is found that the reactivity depends profoundly on the lanthanide metal of the complex. The activity sequence (Yb < Sm < Nd) observed here (Table 1, entries 1−3) is consistent with the increase in ionic radius. The increase in catalyst loading from 0.1% to 1.0% led to greater yield, from 66% to 91% (Table 1, entries 1 and 6−8). The evaluation of solvents in the model transesterification reaction catalyzed by **I** was also undertaken at 60 °C with 1.0 mol % catalyst loading (Table 1, entries 1 and 9−14). The nonpolar solvent *n*-hexane was optimal among six different solvents examined. Polar solvents, such as ethyl acetate and DMSO, inhibited the reaction to some degree probably due to coordination of solvent to the lanthanide center, which diminished the Lewis acidity of the lanthanide catalyst. Because

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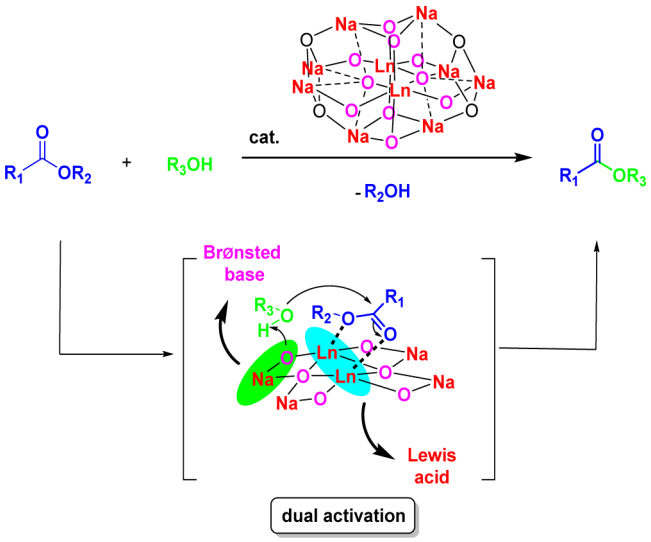
Scheme 1. Transesterification with the Heterobimetallic Dinuclear Lanthanide Complex as an Acid–Base Difunctional Catalyst

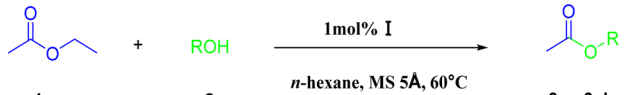


the transesterification is an equilibrium process, conversion of the reaction is influenced by the treatment method for the liberated alcohol.[42] In this work, 5 Å molecular sieves were used to absorb the liberated ethanol. The result shows that the yield can be improved to 95% when the reaction is performed in the presence of molecular sieves 5 Å (Table 1, entry 15).

Transesterification with ethyl acetate is usually difficult due to its low electrophilicity and low boiling point. With the optimized reaction conditions (Table 1, entry 15), we then examined the acylation of various alcohols with ethyl acetate (Table 2). From Table 2, it is evident that various primary alcohols and secondary alcohols are applicable for acylation with ethyl acetate to achieve the corresponding esters. Compared with primary alcohols, secondary alcohols proceeded less smoothly and afforded lower yields under the same conditions. For example, primary alcohols **2a**, **2b**, **2c**, and **2d** worked well with ethyl acetate. The reaction conversions can reach 96% for **3aa**, 95% for **3ab**, 91% for **3ac**, and 95% for **3ad**, respectively. However, for secondary alcohols **2g**, **2h**, and **2i**, the yield can only reach 70% for **3ag**, 85% for **3ah**, and 83% for **3ai**. Transesterification with tertiary alcohols, however, did not proceed due to steric hindrance. According to the data in Table 2, the aliphatic alcohols having reactivity higher than that of aromatic alcohols were also observed (Table 2, entries 1–9). The electronic nature and steric factor effects observed here may be explained by the nucleophilic addition of an alcohol oxygen atom to a C=O double bond, similar to that observed in other transesterification systems.[43−45] In addition, acidic alcohols such as phenol did not participate in the transesterification reaction because phenol is inherently unreactive due to its weak nucleophilicity (Table 2, entry 10). Moreover, the double acetylations of diols (**2k** and **2l**) with excess ethyl acetate also proceeded smoothly to provide the desired products in high yields (Table 2, entries 11 and 12). In general, primary alcohols are more active than secondary alcohols, and aliphatic alcohols have higher reactivity than aromatic alcohols in most cases.

Further studies were carried out to generalize the scope of substrates and flexibility of the proposed methodology. Table 3 summarizes the results for the reactions of carboxylic esters **1b–e** with primary alcohol **2d** and secondary alcohol **2i**. All carboxylic esters were converted to the corresponding esters in good or

Table 2. Transesterification of Ethyl Acetate (1a) with Various Alcohols by Catalyst I[a]



entry	alcohol	product	yield (%)[b]
1	**2a**	**3aa**	96
2	**2b**	**3ab**	95
3	**2c**	**3ac**	91
4	**2d**	**3ad**	95
5	**2e**	**3ae**	86
6	**2f**	**3af**	84
7	**2g**	**3ag**	70
8	**2h**	**3ah**	85
9	**2i**	**3ai**	83
10	**2j**	**3aj**	0
11[c]	**2k**	**3ak**	92
12[c]	**2l**	**3al**	90

[a]Reaction conditions: **1a** (1.6 mmol), **2** (1.6 mmol), 5 Å MS, and **I** (0.016 mmol) in 500 μL of *n*-hexane at 60 °C under an argon atmosphere for 16 h. [b]Isolated yield. [c]**1a** (4 mmol), **2** (1.6 mmol).

excellent yield. Esters having base-sensitive groups such as ethyl 2-chloroacetate (**1b**) reacted smoothly with phenethyl alcohol (**2d**) in 85% yield with no side reaction (Table 3, entry 1). Similarly, methyl acrylate (**1c**) reacted with phenethyl alcohol (**2d**) to offer the transesterification product in 87% yield, and 1,4-adducts as byproducts were not generated in the reaction (Table 3, entry 2). When methyl dodecanoate (**1d**) was used as a substrate, the reactions with **2d** and **2i** also proceeded smoothly. The yields of desired esters can reach 89% for **3dd** and 84% for **3di** (Table 3, entries 3 and 4). In addition to aliphatic esters, methyl benzoate (**1e**) also underwent transesterification. Corresponding phenethyl benzoate **3ed** and *l*-menthyl benzoate **3ei** were obtained in 90% and 82% yield, respectively (Table 3, entries 5 and 6).

Carbonates (R′O-COOR) and silicates [$(R'O)_3$-SiOOR)] cannot be synthesized by direct dehydrative condensation due to the lower stability of carbonic acid monoesters (R′O-COOH)

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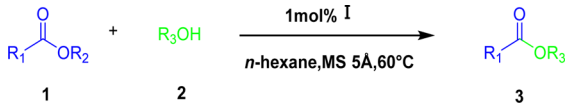
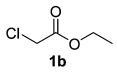
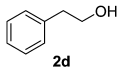
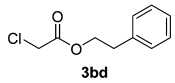
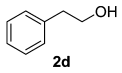
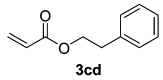
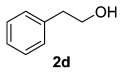
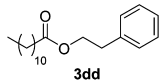
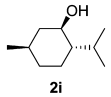
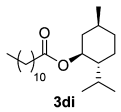
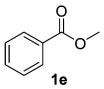
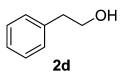
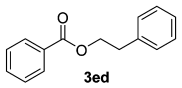
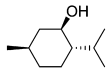
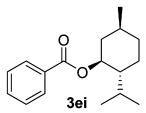
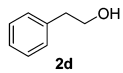
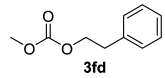
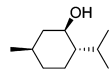
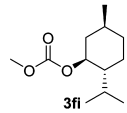
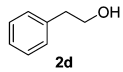
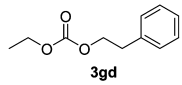
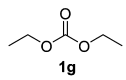
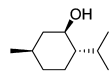
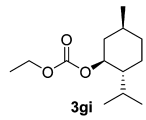
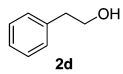
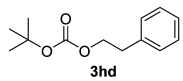
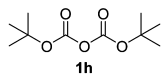
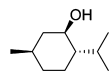
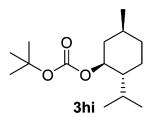
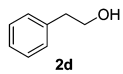
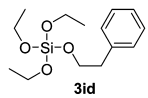
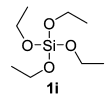
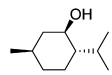
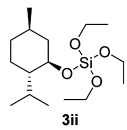
Table 3. Transesterification of Carboxylic Esters with Alcohols by Catalyst I[a]



entry	ester	alcohol	product	yield (%)[b]
1	 1b	 2d	 3bd	85
2	 1c	 2d	 3cd	87
3	 1d	 2d	 3dd	89
4		 2i	 3di	84
5	 1e	 2d	 3ed	90
6		 2i	 3ei	82

[a]Reaction conditions: **1** (2.0 mmol), **2** (2.0 mmol), 5 Å MS, and **I** (0.020 mmol) in 500 μL of *n*-hexane at 60 °C under an argon atmosphere for 16 h. [b]Isolated yield.

Table 4. Transesterification of Carbonates and Ethyl Silicate with Alcohols by Catalyst I[a]

entry	ester	alcohol	product	yield (%)[b]
1		 2d	 3fd	92
2	 1f	 2i	 3fi	90
3		 2d	 3gd	86
4	 1g	 2i	 3gi	84
5		 2d	 3hd	79
6	 1h	 2i	 3hi	72
7[c]		 2d	 3id	84
8[c]	 1i	 2i	 3ii	76

[a]Reaction conditions: **1** (2.0 mmol), **2** (2.0 mmol), 5 Å MS, and **I** (0.020 mmol) in 500 μL of *n*-hexane at 60 °C under an argon atmosphere for 16 h. [b]Isolated yield. [c]**1** (2.4 mmol), **2** (2.0 mmol).

and silicic acid esters [$(R'O)_3$-SiOOH]. Therefore, transesterification may be a better choice for the synthesis of carbonates and silicate esters. However, a key problem is that reactivity of carbonates and silicate esters in the transesterification process is much lower than that of carboxylic esters. For example, the less reactive dimethyl carbonate was scarcely used in transesterification, although it is much safer and easier to handle under open-air conditions than highly toxic phosgene and harmful methyl chloroformate.[6] Therefore, a more efficient and generally applicable transesterification procedure is still strongly desired. As shown in Table 4, the heterobimetallic complexes can be used as highly reactive catalysts for the transesterification of carbonates (**1f**–**h**) and silicate ester (**1i**) with primary alcohol **2d** and secondary alcohol **2i**. Compared to dimethyl carbonate, the yields were slightly lower although diethyl carbonate reacted smoothly with corresponding alcohols (Table 4, entries 1–4). Di-*tert*-butyl dicarbonate ($(Boc)_2O$), which is recognized as an important and popular protective group for amines,[46−50] was also acceptable for the synthesis of **3id** and **3ii** in yields of 84% and 74%, respectively (Table 4, entries 5 and 6). Similarly, ethyl silicate is uncommonly used in transesterification reactions. Thus, the reaction of ethyl silicate with **2d** and **2i** was also investigated. As predicted, with 1.2 equiv of ethyl silicate, the corresponding esters **3id** and **3ii** were obtained in good yields (Table 4, entries 7 and 8).

Selective protection of primary over secondary alcohols is of importance in organic synthesis. It can be achieved by using catalytic systems such as distannoxane/enol ester,[51] $Sc(OTf)_3$/Ac_2O,[52] Et_2Zn/vinyl acetate,[53] and NHCs/vinyl acetate.[54] By taking advantage of different activities of transesterification between primary and secondary alcohols, selective acylation was examined. Phenethyl alcohol (**2d**) and benzhydrol (**2g**) in the present of excess ethyl acetate were employed by using complex **I** as the catalyst under the optimized conditions. The conversion for each alcohol was determined by GC and ^{1}H NMR, and the result indicated that the primary alcohol **2d** was preferentially acylated in this system (Scheme 2).

A La(III) isopropoxide complex developed by Ishihara is an effective catalyst for practical transesterification, and they suggested that a possible dinuclear La(III) salt might efficiently catalyze transesterification based on Lewis acid−Lewis base dual activation. However, the supposed dinuclear La(III) complex was only confirmed by ESI-MS analysis.[38] Considering these results and other mechanism studies of acid−base bifunctional catalysis and metal alkoxide-catalyzed transesterifications in the literature,[21−23,34−37,43] we think transesterification catalyzed by the heterobimetallic dinuclear lanthanide alkoxide complex with clear X-ray crystal structure[39] may be regarded as a further sufficient evidence to test the reaction mechanism, and a preliminary hypothesis for the above mechanism is proposed in

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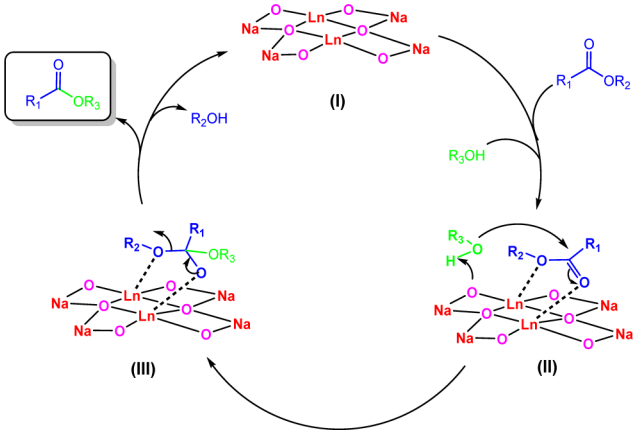
Scheme 2. Selective Acylation of Primary Alcohol 2d

Scheme 3. Heterobimetallic dinuclear lanthanide alkoxide complex **I**, which serves as an acid–base bifunctional catalyst,

Scheme 3. Proposed Catalytic Cycle for Transesterification Catalyzed by Heterobimetallic Dinuclear Lanthanide Alkoxide Complex



activates both the ester and alcohol to generate the adduct **II**. That is, dinuclear lanthanide metal ions act as double Lewis acid centers to activate simultaneously the carbonyl and alkoxy oxygen atoms of the ester. The sodium alkoxide moiety functions as a Brønsted base to bring the alcohol into close proximity. The nucleophilic attack of the activated alcohol on the electrophilic carbon center of the carbonyl moiety leads to an sp^3-hybridized tetrahedral intermediate (**III**). The sterically congested **III** then collapses to regenerate the sp^2-hybridized carbonyl unit and the active species **I**, resurrected along with the release of transesterified product and alcohol.

CONCLUSIONS

In summary, heterobimetallic dinuclear lanthanide alkoxide complexes were used as a new class of acid–base bifunctional catalysts for transesterification of ethyl acetate, methyl/ethyl carboxylate, weakly reactive carbonates, and much less-reactive ethyl silicate with primary and secondary alcohols. The new catalysts showed high catalytic activity and a wide scope of substrates for transesterification with good to excellent yields under mild reaction conditions. Selectivity experiments revealed that primary alcohols can be acylated more efficiently than secondary alcohols in the presence of the catalyst. The efficient activation of transesterification was endowed by the cooperative catalyst comprising soft Lewis acid and hard Brønsted base. The fact that transesterification can be catalyzed efficiently by a dinuclear lanthanide complex with clear X-ray crystal structure may be regarded as a further evidence for the proposed mechanism.

EXPERIMENTAL SECTION

General Methods. All manipulations and reactions were performed under an atmosphere of argon with standard Schlenk techniques. The esters and alcohols were obtained commercially. Heterobimetallic dinuclear lanthanide alkoxide complexes $[Ln_2Na_8\{(OCH_2CH_2NMe_2)\}_{12}(OH)_2]$ (Ln = Nd (**I**), Sm (**II**), and Yb (**III**)) and the corresponding monometallic complex $[Nd(OR)_3]$ (OR = $OCH_2CH_2NMe_2$) (**IV**) were prepared according to the literature.[39,40] ^1H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as the internal standard. The GC and GC-MS analyses were carried out using N_2 and He as the carrier gas, respectively. High-resolution mass spectra (HRMS) were carried out using a TOF-MS instrument with an EI or ESI source. Column chromatography was performed using silica gel (200–300 mesh). Petroleum ether (PE) used was the fraction boiling in the range 60–90 °C.

*Typical Procedure for Transesterification of Esters with Alcohols. (**3ad** as an example).* A mixture of $Nd_2Na_8\{(OCH_2CH_2NMe_2)\}_{12}(OH)_2$ (**I**) (25 mg, 0.016 mmol), ethyl acetate (155 μL, 1.6 mmol), 2-phenylethanol (190 μL, 1.6 mmol), 5 Å molecular sieves (500 mg), and *n*-hexane (500 μL) was stirred at 60 °C for 16 h under argon. The resulting mixture was then filtered through a small plug of silica gel to remove the catalyst. The crude product was purified by silica gel column chromatography (EtOAc/PE = 1:20) to provide the title compound **3ad** (248 mg, 95%) as a colorless oil.

*Octyl acetate (**3aa**).*[55] colorless oil (264 mg, 96% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 3.98 (t, *J* = 6.8 Hz, 2H), 1.97 (s, 3H), 1.61 (m, 2H), 1.30–1.20 (m, 10H), 0.81 (t, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 64.7, 31.8, 29.3, 29.2, 28.6, 26.0, 22.7, 21.0, 14.1 ppm; GC-MS *m*/*e* 172.140.

*Dodecyl acetate (**3ab**).*[56] colorless oil (347 mg, 95% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 3.98 (t, *J* = 6.8 Hz, 2H), 1.97 (s, 3H), 1.54–1.48 (m, 2H), 1.30–1.11 (m, 18H), 0.81 (t, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 64.6, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.6, 25.9, 22.7, 21.0, 14.1 ppm; GC-MS *m*/*e* 228.200.

*2-(2-(2-Methoxyethoxy)ethoxy)ethyl acetate (**3ac**).* colorless oil (300 mg, 91% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 4.25–4.19 (m, 2H), 3.75–3.68 (m, 2H), 3.67–3.63 (m, 6H), 3.59–3.53 (m, 2H), 3.39 (s, 3H), 2.08 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 71.8, 70.4, 70.3, 69.0, 63.5, 58.9, 20.8 ppm; GC-MS *m*/*e* 206.120; HRMS (EI) Found: 206.1155. Calcd for $C_9H_{18}O_5$: 206.1154.

*Phenethyl acetate (**3ad**).*[57] colorless oil (248 mg, 95% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.20–7.14 (m, 2H), 7.09 (t, *J* = 6.8 Hz, 3H), 4.15 (t, *J* = 7.1 Hz, 2H), 2.80 (t, *J* = 7.1 Hz, 2H), 1.88 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 137.8, 128.9, 128.5, 126.6, 65.0, 35.1, 21.0 ppm; GC-MS *m*/*e* 164.100.

*2-Pyridylmethyl acetate (**3ae**).*[58] colorless oil (208 mg, 86% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (m, 1H), 7.69 (m, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.23–7.22 (m, 1H), 5.22 (s, 2H), 2.16 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 155.7, 149.4, 136.8, 122.9, 121.8, 66.8, 20.9 ppm; GC-MS *m*/*e* 151.050.

*Furfuryl acetate (**3af**).*[59] colorless oil (188 mg, 84% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 1H), 6.25 (d, *J* = 2.9 Hz, 1H), 6.21 (m, 1H), 4.90 (s, 2H), 1.92 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 149.4, 143.3, 110.6, 110.5, 58.0, 20.8 ppm; GC-MS *m*/*e* 140.050.

*Benzhydryl acetate (**3ag**).*[60] colorless oil (253 mg, 70% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.12 (m, 10H), 6.79 (s, 1H), 2.04 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 140.3, 128.6, 128.0, 127.2, 77.0, 21.3 ppm; GC-MS *m*/*e* 226.100.

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*Cyclohexyl acetate (**3ah**).*[56] colorless oil (193 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 (td, J = 8.5, 3.9 Hz, 1H), 1.95 (s, 3H), 1.78−1.76 (m, 2H), 1.69−1.61 (m, 2H), 1.53−1.43 (m, 1H), 1.39−1.15 (m, 5H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 71.7, 30.6, 24.4, 22.8, 20.4 ppm; GC-MS m/e 142.150.

*Menthyl (1R,2S,5R)-(−)-acetate (**3ai**).*[55] colorless oil (263 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.60 (td, J = 10.9, 4.4 Hz, 1H), 1.96 (s, 3H), 1.92 (m, 1H), 1.85 (m, 1H), 1.65−1.56 (m, 2H), 1.48 (m, 1H), 1.34 (m, 1H), 1.05 (m, 1H), 0.96(m, 1H), 0.83 (d, J = 6.8, 3H), 0.82 (d, J = 6.2, 3H), 0.80−0.74 (m, 1H), 0.70 (d, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 74.1, 47.0, 40.9, 34.2, 31.4, 26.3, 23.5, 22.0, 21.3, 20.7, 16.4 ppm; GC-MS m/e 198.200.

*Butane-1,4-diol diacetate (**3ak**).*[61] colorless oil (256 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (t, J = 5.1 Hz, 4H), 2.00 (s, 6H), 1.64 (t, J = 12.6 Hz, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 63.8, 25.2, 20.8 ppm; GC-MS m/e 174.100.

*Diethylene glycol diacetate (**3al**).*[62] colorless oil (274 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30−4.17 (m, 4H), 3.79−3.65 (m, 4H), 2.09 (s, 6H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 68.0, 62.4, 19.9 ppm; GC-MS m/e 190.100.

*Phenethyl 2-chloroacetate (**3bd**).*[63] colorless oil (337 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 7.4 Hz, 2H), 7.27−7.19 (m, 3H), 4.40 (t, J = 7.0 Hz, 2H), 4.04 (s, 2H), 2.98 (t, J = 7.0 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 137.2, 129.0, 128.62, 126.8, 66.6, 40.9, 34.9 ppm; GC-MS m/e 198.050.

*2-Phenylethyl acrylate (**3cd**).*[64] colorless oil (306 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.27 (m, 2H), 7.26−7.18 (m, 3H), 6.38 (d, J = 17.3 Hz, 1H), 6.10 (dd, J = 17.3, 10.4 Hz, 1H), 5.80 (d, J = 10.4 Hz, 1H), 4.37 (t, J = 7.1 Hz, 2H), 2.98 (t, J = 7.1 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 137.8, 130.8, 129.0, 128.6, 128.5, 126.6, 65.0, 35.1 ppm; GC-MS m/e 176.120.

*Phenethyl dodecanoate (**3dd**).* colorless oil (541 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33−7.26 (m, 2H), 7.25 (d, J = 6.6 Hz, 1H), 7.21 (d, J = 7.3 Hz, 2H), 4.29 (t, J = 7.0 Hz, 2H), 2.93 (t, J = 7.0 Hz, 2H), 2.27 (t, J = 7.5 Hz, 2H), 1.58−1.57 (m, 2H), 1.28−1.25 (m, 16H), 0.88 (t, J = 6.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 137.9, 128.9, 128.5, 126.5, 64.7, 35.2, 34.4, 31.9, 29.6, 29.5, 29.4, 29.3, 29.1, 25.0, 22.7, 14.1 ppm; GC-MS m/e 304.250; HRMS (EI) Found: 304.2403. Calcd for $C_{20}H_{32}O_2$: 304.2402.

*Lauric acid (1R,2S,5R)-menthyl ester (**3di**).* colorless oil (568 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.75−4.60 (m, 1H), 2.27 (t, J = 7.4 Hz, 2H), 1.98 (m, 1H), 1.91 (m, 1H), 1.76−1.55 (m, 4H), 1.39−1.22 (m, 18H), 1.14−0.93 (m, 2H), 0.88 (m, 10H), 0.75 (d, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 73.8, 47.0, 41.0, 34.8, 34.3, 31.9, 31.4, 29.6, 29.5, 29.3, 29.2, 29.1, 26.2, 25.2, 23.4, 22.7, 22.0, 20.8, 16.3, 14.1 ppm; GC-MS m/e 338.320; HRMS (EI) Found: 338.3187. Calcd for $C_{22}H_{42}O_2$: 338.3185

*Phenethyl benzoate (**3ed**).*[65] colorless oil (407 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.0 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.35−7.26 (m, 3H), 7.25−7.15 (m, 2H), 4.51 (t, J = 7.0 Hz, 2H), 3.05 (t, J = 7.0 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 138.0, 133.0, 130.4, 129.6, 129.1, 128.6, 128.4, 126.7, 65.6, 35.3 ppm; GC-MS m/e 226.100.

*Benzoic acid (1R,2S,5R)-menthyl ester (**3ei**).*[38] colorless oil (426 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 4.94 (td, J = 10.7, 3.6 Hz, 1H), 2.13 (m, 1H), 1.97 (m, 1H), 1.73−1.71 (m, 2H), 1.57−1.53 (m, 2H), 1.21−1.03 (m, 2H), 0.97−0.87 (m, 7H), 0.79 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 131.7, 129.8, 128.5, 127.3, 73.8, 46.2, 39.9, 33.3, 30.4, 25.5, 22.6, 21.0, 19.8, 15.5 ppm; GC-MS m/e 260.200.

*Methyl phenethyl carbonate (**3fd**).*[66] colorless oil (331 mg, 92% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 7.2 Hz, 2H), 7.22 (d, J = 6.7 Hz, 3H), 4.33 (q, J = 7.4 Hz, 2H), 3.75 (s, 3H), 2.97 (t, J = 6.8 Hz, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 137.3, 129.0, 128.6, 126.7, 68.4, 54.7, 35.2 ppm; GC-MS m/e 180.130.

*Methyl l-menthyl carbonate (**3fi**).* colorless oil (385 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (td, J = 10.9, 4.4 Hz, 1H), 3.77 (s, 3H), 2.13−2.04 (m, 1H), 2.02−1.91 (m, 1H), 1.74−1.63 (m, 2H), 1.56−1.35 (m, 2H), 1.14−0.99 (m, 2H), 0.91 (d, J = 6.9 Hz, 6H), 0.85 (m, 1H), 0.79 (d, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 78.4, 54.5, 47.0, 40.7, 34.1, 31.4, 26.0, 23.3, 22.0, 20.7, 16.3 ppm; GC-MS m/e 214.160; HRMS (EI) Found: 214.1571. Calcd for $C_{12}H_{22}O_3$: 214.1569.

*Ethyl phenethyl carbonate (**3gd**).*[67] colorless oil (334 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.26 (m, 2H), 7.25−7.18 (m, 3H), 4.37−4.28 (t, J = 7.2 Hz, 2H), 4.21−4.12 (t, J = 7.0 Hz, 2H), 2.96 (q, J = 6.8 Hz, 2H), 1.29 (t, 7.1 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 137.3, 129.0, 128.6, 126.7, 68.2, 63.9, 35.2, 14.3 ppm; GC-MS m/e 194.100.

*Ethyl l-menthyl carbonate (**3gi**).* colorless oil (383 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (td, J = 10.9, 4.2 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.08 (m, 1H), 1.96 (m, 1H), 1.68 (m, 2H), 1.53−1.36 (m, 2H), 1.34−1.25 (m, 3H), 1.06 (m, 2H), 0.91 (d, J = 6.9 Hz, 6H), 0.84 (m, 1H), 0.79 (d, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 77.1, 62.6, 46.0, 39.8, 33.1, 30.4, 25.0, 22.2, 21.0, 19.7, 15.2, 13.3 ppm; GC-MS m/e 228.180; HRMS (EI) Found: 228.1727. Calcd for $C_{13}H_{24}O_3$: 228.1725.

*tert-Butyl phenethyl carbonate (**3hd**).*[63] colorless oil (351 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.29 (m, 2H), 7.24−7.22 (m, 3H), 4.27 (t, J = 7.3 Hz, 2H), 2.97 (t, J = 7.3 Hz, 2H), 1.47 (s, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 137.4, 128.9, 128.5, 126.6, 82.0, 67.4, 35.2, 27.8 ppm; GC-MS m/e 222.120.

*tert-Butyl l-menthyl carbonate (**3hi**).* colorless oil (369 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47 (td, J = 10.7, 4.0 Hz, 1H), 2.04 (m, 1H), 2.00−1.89 (m, 1H), 1.67 (m, 2H), 1.48−1.46 (m, 11H), 1.04 (m, 2H), 0.90−0.88 (m, 7H), 0.79 (d, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.7, 81.5, 77.8, 47.0, 40.8, 34.1, 31.4, 27.8, 26.1, 23.3, 22.0, 20.7, 16.2 ppm; GC-MS m/e 256.210; HRMS (EI) Found: 256.2039. Calcd for $C_{15}H_{28}O_3$: 256.2038.

*Triethyl phenethyl orthosilicate (**3id**).* colorless oil (477 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24−7.17 (m, 2H), 7.17−7.08 (m, 3H), 3.94−3.65 (m, 8H), 2.81 (t, J = 7.2 Hz, 2H), 1.22−1.07 (m, 9H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 129.1, 128.3, 126.2, 64.5, 59.2, 39.0, 18.1 ppm; GC-MS m/e 284.150; HRMS (EI) Found: 284.1446. Calcd for $C_{14}H_{24}O_4Si$: 284.1444.

*Triethyl l-menthyl orthosilicate (**3ii**).* colorless oil (483 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88−3.81 (m, 6H), 3.67 (td, J = 10.6, 4.2 Hz, 1H), 2.35−2.17 (m, 1H), 2.15−1.98 (m, 1H), 1.67−1.56 (m, 2H), 1.50−1.32 (m, 1H), 1.28−1.20 (m, 10H), 1.10−0.92 (m, 2H), 0.89 (d, J = 7.0 Hz, 6H), 0.86−0.80 (m, 1H), 0.77 (d, J = 6.9 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 73.2, 59.1, 49.7, 44.6, 34.5, 31.7, 25.3, 25.3, 22.8, 22.3, 21.2, 18.1, 15.7 ppm; GC-MS m/e 318.230; HRMS (EI) Found: 318.2229. Calcd for $C_{16}H_{34}O_4Si$: 318.2226.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra for the products. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: sht_anda@126.com.
*E-mail: fy70@163.com.

Notes

The authors declare no competing financial interest.

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