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ARTICLE TYPE

Anionic phenoxy-amido rare-earth complexes as efficient catalysts for amidation of aldehydes with amines

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A series of anionic organo-rare-earth amido complexes stabilized by dianionic phenoxy-amido ligands were prepared and their catalytic behavior for amidation reactions of aldehydes with amines was elucidated. Amine elimination reaction of $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3(\mu\text{-Cl})\text{Li}(\text{THF})_3$ with an equimolar of lithium aminophenoxy $\{[\text{HNO}]^1\text{Li}(\text{THF})_2\}_2$, which was prepared by the reaction of $[\text{HNOH}]^1$ $\{[\text{HNOH}]^1 = N\text{-}p\text{-fluoro-phenyl}(2\text{-hydroxy-}3,5\text{-di-}tert\text{-butyl})\text{benzylamine}\}$ with one equivalent of $n\text{-BuLi}$ in tetrahydrofuran (THF) in situ, gave the anionic phenoxy-amido rare earth amido complexes $[\text{NO}]^1_2\text{Ln}[\text{N}(\text{SiMe}_3)_2][\text{Li}(\text{THF})_2]$ $[\text{Ln} = \text{Y} \text{ (1), Yb (2), Sm (3), Nd (4)}]$ in high isolated yields. Similar reactions of $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3(\mu\text{-Cl})\text{Li}(\text{THF})_3$ with $\{[\text{HNO}]^2\text{Li}(\text{THF})_2\}_2$, and $\{[\text{HNO}]^3\text{Li}(\text{THF})_2\}_2$ in THF gave the anionic rare-earth amides $[\text{NO}]^2_2\text{Ln}[\text{N}(\text{SiMe}_3)_2][\text{Li}(\text{THF})_2]$ $[\text{Ln} = \text{Sm (5), Nd (6)}]$ and $[\text{NO}]^3_2\text{Ln}[\text{N}(\text{SiMe}_3)_2][\text{Li}(\text{THF})_2]$ $[\text{Ln} = \text{Sm (7), Nd (8)}]$ $\{[\text{HNOH}]^2 = N\text{-}p\text{-chloro-phenyl}(2\text{-hydroxy-}3,5\text{-di-}tert\text{-butyl})\text{benzylamine}; [\text{HNOH}]^3 = N\text{-}p\text{-bromo-phenyl}(2\text{-hydroxy-}3,5\text{-di-}tert\text{-butyl})\text{benzylamine}\}$, respectively. All of these complexes were fully characterized. X-ray structural determination revealed that these complexes are isostructural, and have solvated monomeric structures. Each of the rare-earth ions is coordinated by two phenoxy-amido ligands and one $\text{N}(\text{SiMe}_3)_2$ group, and the coordination geometry can be described as a distorted trigonal bipyramid. Each of the lithium atoms is surrounded by one aryloxo group, one amido group and one THF molecule, and the coordination geometry can be described as a trigonal plane. The catalytic behavior of these rare-earth amides for the amidation reaction of aldehyde with amine was elucidated. It was found that these complexes are efficient catalysts for this transformation to produce amides in good to excellent yields under mild reaction conditions, and in some cases, diacylamide compounds can be prepared conveniently.

Introduction

The synthesis of aromatic and aliphatic acylamides has received considerable attention for a long time in organic synthesis, because the amide group is a basic functional group in many molecules, including polymers, nature products, pharmaceuticals and proteins.¹ Generally, these compounds can be prepared by the reactions of carboxylic acids or acyl halides with amines.²⁻⁴ However, the direct amidation of aldehydes with amines is one of the most desired methods to acylamides because of the atom-economic character and easy availability of the starting materials.⁵⁻⁶⁰

In recent years, an important progress achieved is that organo-rare-earth complexes can promote or catalyze the amidation reactions of aldehydes with amines with high efficiency, under mild reaction conditions, without the need for oxidants and strong bases, in comparison with the transformation of aldehydes to amides catalyzed by transition metal complexes.⁸⁻¹⁷ Wang et al. found that aromatic aldehydes can react with rare-earth amides $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3(\mu\text{-Cl})\text{Li}(\text{THF})_3$ to give acylamides via the

Cannizzaro-type disproportionation reaction.⁸ Marks et al. reported that homoleptic rare-earth complexes $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ can catalyze the transformation of aldehydes with amines to acylamides under mild reaction conditions.⁹ Further studies revealed that anionic heterobimetallic rare-earth-alkali complexes are more efficient catalysts for the above transformation with a wide range of scope for the substrates.¹⁰⁻¹¹ These results encouraged us to further elucidate the effect of the structures of heterobimetallic rare-earth/alkali metal complexes on their catalytic activity for the amidation reactions of aldehydes with amines.

Phenoxy-amido groups, as dianionic N, O chelate ligands, have several attractive features, such as possessing the dual characteristics of oxygen- and nitrogen-based ligands, being easily available, and their steric and/or electronic properties are easily tunable.¹⁸⁻²⁰ Recently, we introduced this ligand system to organo-rare-earth chemistry, and a series of neutral and anionic phenoxy-amido rare-earth complexes were prepared conveniently by the direct amine elimination reaction between rare-earth amide and aminophenols.²¹⁻²⁴ It was found that many phenoxy-amido organo-

rare-earth complexes were efficient initiators for the ring-opening polymerization of lactides and cyclic carbonate.^{21–23} To further expand the application of phenoxy-amido rare-earth complexes on homogeneous catalysis, a series of heterobimetallic rare-earth-lithium amido complexes stabilized by different aminophenoxy ligands (Chart 1) were synthesized. It was found that these rare-earth amido complexes are efficient catalysts for the amidation reaction of aldehydes with amines to produce amides in good to excellent yields under mild conditions, and in some cases, diacylamide compounds can be prepared conveniently. Here we report these results.

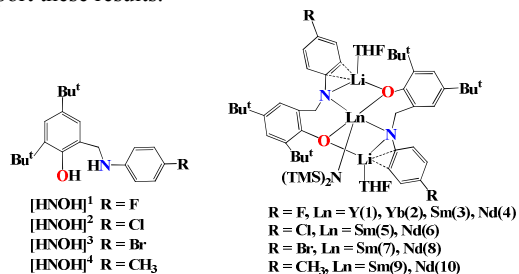


Chart 1. Aminophenoxy ligands and complexes 1-10.

Experimental Section

General Methods. All of these organo-rare-earth complexes are extremely sensitive to oxygen and moisture, thus, the manipulations were performed under a nitrogen atmosphere in glovebox. HN(SiMe₃)₂, tetrahydrofuran (THF), toluene, and hexane were dried according to the methods reported in the literature, and distilled prior to use. Aminophenol [HNOH] { [HNOH]¹ = *N*-*p*-fluoro-phenyl(2-hydroxy-3,5-di-*tert*-butyl)benzylamine, [HNOH]² = *N*-*p*-chloro-phenyl(2-hydroxy-3,5-di-*tert*-butyl)benzylamine, [HNOH]³ = *N*-*p*-bromo-phenyl(2-hydroxy-3,5-di-*tert*-butyl)benzylamine, [HNOH]⁴ = *N*-*p*-methylphenyl(2-hydroxy-3,5-di-*tert*-butyl)-benzylamine},²⁵ and the organo-rare-earth amides Ln[N(SiMe₃)₂]₃(μ-Cl)Li(THF)₃,²⁶ [NO]⁴Sm[N(SiMe₃)₂][Li(THF)]₂ (9), and [NO]⁴Nd[N(SiMe₃)₂][Li(THF)]₂ (10)²¹ were prepared according to the published procedures, respectively. Rare-earth metal analyses were performed according to the reported method.²⁷ Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. The ¹H and ¹³C NMR analyses for complex 1 were recorded in a C₆D₆ solution with a Unity Varian spectrometer. The NMR spectra for the other complexes were not determined, because of the paramagnetism of the Nd, Sm and Yb ions. The uncorrected melting points of these complexes were determined in sealed capillaries under argon.

Synthesis of [NO]¹₂Y[N(SiMe₃)₂][Li(THF)]₂ (1). A THF solution of [HNOH]¹ (30 mL, 2.00 g, 6.09 mmol) was cooled to -10 °C, and then ⁿBuLi in hexane (2.36 mL, 6.09 mmol) was added dropwise. The mixture was stirred for about 1 h at -10 °C, and then warmed to room temperature gradually. A THF solution of Y[N(SiMe₃)₂]₃(μ-Cl)Li(THF)₃ (2.52 g, 3.05 mmol) was added to this solution, and the solution was stirred overnight at 50 °C. The solvent was removed under vacuum, and toluene (30 mL) was added to extract the residue. The suspension was stirred at 50 °C for about half an hour, and the precipitate was separated by

centrifugation. The filtrate was concentrated to about 12 mL, and then 3 mL of hexane was added. Yellow crystals were obtained at room temperature in a few days (2.73 g, 83%). Mp: 237–239 °C (dec.) Anal. Calcd for C₅₆H₈₆F₂Li₂N₃O₄Si₂Y (1062.26): C, 63.32; H, 8.16; N, 3.58; Y, 8.37. Found: C, 62.83; H, 8.09; N, 3.53. Y, 8.38. ¹H NMR (300 MHz, C₆D₆, 25 °C, ppm): δ 7.52 (d, ²J(H, H) = 8.7 Hz, 4H, ArH), 7.16 (s, 8H, ArH), 4.66 (d, ²J(H, H) = 14.0 Hz, 2H, CH₂), 4.29 (d, ²J(H, H) = 14.0 Hz, 2H, CH₂), 2.79 (s, 8H, α-CH₂ THF), 1.72 (s, 18H, Bu^t), 1.45 (s, 18H, Bu^t), 0.88 (s, 8H, β-CH₂ THF), 0.14 (t, 18H, N(SiMe₃)₂). ¹³C NMR (75 MHz, C₆D₆, 25 °C, ppm): δ 159.6 (Ph), 155.2 (Ph), 138.8 (Ph), 136.6 (Ph), 129.6 (Ph), 125.2 (Ph), 123.1 (Ph), 117.9 (Ph), 117.6 (Ph), 68.3 (α-CH₂ THF), 51.1 (CH₂Ar), 35.5 (C(CH₃)₃), 34.4 (C(CH₃)₃), 32.1 (C(CH₃)₃), 31.2 (C(CH₃)₃), 25.0 (β-CH₂ THF), 4.61 (SiMe₃). IR (KBr pellet, cm⁻¹): 3390(s), 2958(s), 2866(s), 1612(s), 1510(s), 1470(s), 1438(m), 1302(s), 1215(m), 1224(s), 1130(w), 1165(w), 932(m), 833(s). Crystals suitable for an X-ray diffraction analysis were obtained by the slow cooling of a hot toluene/hexane solution.

Synthesis of [NO]¹₂Yb[N(SiMe₃)₂][Li(THF)]₂ (2). Complex 2 was prepared by the same procedure as that described for complex 1, but Yb[N(SiMe₃)₂]₃(μ-Cl)Li(THF)₃ (2.78 g, 3.05 mmol) was used instead of Y[N(SiMe₃)₂]₃(μ-Cl)Li(THF)₃. Pale-yellow microcrystals were isolated from a concentrated toluene–hexane solution at room temperature (2.93 g, 84%). Mp: 200–202 °C (dec.) Anal. Calcd for C₅₆H₈₆F₂Li₂N₃O₄Si₂Yb (1146.38): C, 58.67; H, 7.56; N, 3.67; Yb, 15.09. Found: C, 59.01; H, 7.48; N, 3.58; Yb, 15.13. IR (KBr pellet, cm⁻¹): 3450(s), 2960(s), 2866(s), 1616(s), 1510(s), 1469(s), 1416(s), 1358(m), 1306(m), 1215(m), 1215(m), 1130(w), 1049(w), 983(w), 833(m). The microcrystals were recrystallized from toluene–hexane solution to give the crystals suitable for an X-ray diffraction analysis.

Synthesis of [NO]¹₂Sm[N(SiMe₃)₂][Li(THF)]₂ (3). Complex 3 was synthesized by the same procedure as that described for complex 1, but Sm[N(SiMe₃)₂]₃(μ-Cl)Li(THF)₃ (2.71 g, 3.05 mmol) was used instead of Y[N(SiMe₃)₂]₃(μ-Cl)Li(THF)₃. Yellow crystals were obtained from a concentrated toluene–hexane solution at room temperature (2.70 g, 79%). Mp: 199–201 °C (dec.) Anal. Calcd for C₅₆H₈₆F₂Li₂N₃O₄Si₂Sm (1123.69): C, 59.86; H, 7.71; N, 3.74; Sm, 13.38. Found: C, 59.40; H, 7.68; N, 3.62; Sm, 13.37. IR (KBr pellet, cm⁻¹): 3445(s), 2957(s), 2868(s), 1616(w), 1510(s), 1477(s), 1360(w), 1227(s), 1165(s), 1049(w), 933(m), 833(s).

Synthesis of [NO]¹₂Nd[N(SiMe₃)₂][Li(THF)]₂ (4). Complex 4 was synthesized by the same procedure as that described for complex 1, but Nd[N(SiMe₃)₂]₃(μ-Cl)Li(THF)₃ (2.69 g, 3.05 mmol) was used instead of Y[N(SiMe₃)₂]₃(μ-Cl)Li(THF)₃. Pale blue crystals were obtained at room temperature in several days (2.76 g, 81%). Mp: 197–200 °C (dec.) Anal. Calcd for C₅₆H₈₆F₂Li₂N₃O₄Si₂Nd (1117.58): C, 60.18; H, 7.76; N, 3.76; Nd, 12.91. Found: C, 61.02; H, 7.53; N, 3.69; Nd, 12.86. IR (KBr pellet, cm⁻¹): 3327(s), 2959(s), 2866(s), 1616(s), 1510(s), 1469(s), 1358(m), 1231(s), 1163(m), 988(w), 931(m), 833(s).

Synthesis of [NO]²₂Sm[N(SiMe₃)₂][Li(THF)]₂ (5). Complex 5 was synthesized by the same procedure as that described for complex 3, but [HNOH]² (30 mL, 2.50 g, 7.25 mmol) was used instead of [HNOH]¹. Pale yellow crystals were obtained at room temperature in several days (3.39 g, 81%). Mp: 200–202 °C (dec.) Anal. Calcd for C₅₆H₈₆Cl₂Li₂N₃O₄Si₂Sm (1156.59): C, 58.15; H, 7.49; N, 3.63; Sm, 13.00. Found: C, 59.02; H, 7.53; N, 3.69; Sm

12.86. IR (KBr pellet, cm^{-1}): 3332(m), 2959(s), 2866(s), 1664(m), 1469(s), 1357(m), 1236(s), 1167(m), 931(m), 823(s).

Synthesis of $[\text{NO}]^2_2\text{Nd}[\text{N}(\text{SiMe}_3)_2][\text{Li}(\text{THF})_2]$ (6). Complex 6 was prepared by the same procedure as that described for complex 4, but $[\text{HNOH}]^2$ (30 mL, 2.50 g, 7.25 mmol) was used instead of $[\text{HNOH}]^1$. Pale blue microcrystals were obtained at room temperature in a few days (3.41 g, 82%). Mp: 250–252 °C (dec.) Anal. Calcd for $\text{C}_{56}\text{H}_{86}\text{Cl}_2\text{Li}_2\text{N}_3\text{O}_4\text{Si}_2\text{Nd}$ (1150.50): C, 58.46; H, 7.53; N, 3.65; Nd, 12.54. Found: C, 58.31; H, 7.48; N, 3.58; Nd, 12.39. IR (KBr pellet, cm^{-1}): 3361(s), 2955(s), 2866(s), 1604(m), 1487(s), 1359(m), 1242(s), 1049(m), 932(s), 831(s). The microcrystals were recrystallized from toluene–hexane solution to give the crystals suitable for an X-ray diffraction analysis.

Synthesis of $[\text{NO}]^3_2\text{Sm}[\text{N}(\text{SiMe}_3)_2][\text{Li}(\text{THF})_2]$ (7). Complex 7 was prepared by the same procedure as that described for complex 3, but $[\text{HNOH}]^3$ (30 mL, 2.50 g, 6.42 mmol) was used instead of $[\text{HNOH}]^1$. Pale yellow crystals were obtained at room temperature in several days (3.32 g, 82%). Mp: 172–174 °C (dec.) Anal. Calcd for $\text{C}_{56}\text{H}_{86}\text{Br}_2\text{Li}_2\text{N}_3\text{O}_4\text{Si}_2\text{Sm}$ (1245.51): C, 54.00; H, 6.96; N, 6.96; Sm, 12.07. Found: C, 53.60; H, 6.69; N, 6.92; Sm, 12.27. IR (KBr pellet, cm^{-1}): 3329(s), 2956(s), 2867(s), 1596(m), 1469(s), 1355(m), 1299(s), 1241(s), 1178(s), 1047(m), 932(w), 831(s).

Synthesis of $[\text{NO}]^3_2\text{Nd}[\text{N}(\text{SiMe}_3)_2][\text{Li}(\text{THF})_2]$ (8). Complex 8 was prepared by the same procedure as that described for complex 4, but $[\text{HNOH}]^3$ (30 mL, 2.00 g, 5.14 mmol) was used instead of $[\text{HNOH}]^1$. Pale blue microcrystals were obtained at room temperature in several days (2.61 g, 82%). Mp: 202–204 °C (dec.) Anal. Calcd for $\text{C}_{56}\text{H}_{86}\text{Br}_2\text{Li}_2\text{N}_3\text{O}_4\text{Si}_2\text{Nd}$ (1239.40): C, 54.27; H, 6.99; N, 3.39; Nd, 11.64. Found: C, 54.62; H, 6.53; N, 3.69; Nd, 11.86. IR (KBr pellet, cm^{-1}): 3329(s), 2956(s), 2866(s), 1616(m), 1469(s), 1300(m), 1240(s), 1176(s), 1051(m), 931(w), 827(s). The microcrystals were recrystallized from toluene–hexane solution to give the crystals suitable for an X-ray diffraction analysis.

Typical procedure for amidation reaction

The procedures for the reactions of aldehydes with amines catalyzed by 1 to 10 are similar, and a typical procedure is given below. A solution of catalyst (0.80 mL, 0.02 mmol) was added to a 20 mL flask by syringe, and then *N*-methyl-benzylamine was added (0.13 mL, 1 mmol). The solution was stirred for half an hour at room temperature, and then benzaldehyde was added (0.30 mL, 3.00 mmol). The mixed solution was stirred for 3h, and the reaction was terminated by adding ethyl acetate. The pure product was obtained by purification of the crude product via column chromatography using ethyl acetate/petroleum ether (1:7) as an eluent.

X-ray crystallography

Suitable single crystals of complexes 1 to 8 were sealed in a thin-walled glass capillary for determining the single-crystal structures. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo- $K\alpha$ radiation ($\lambda = 0.71070$ Å). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Tables S1 and S2.

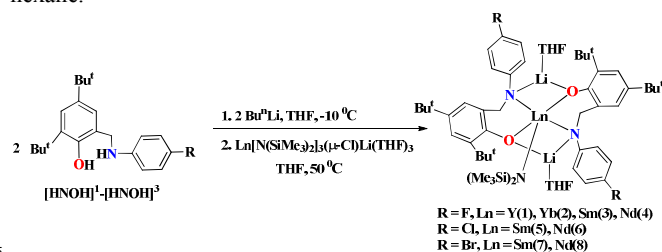
The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All the non-hydrogen atoms were refined anisotropically. All the H atoms were held stationary and included in the structure factor calculation in

the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELEXL-97 programs.

Results and discussion

Synthesis and characterization of the phenoxy-amido rare-earth metal complexes.

We previously reported that the reaction of $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3(\mu\text{-Cl})\text{Li}(\text{THF})_3$ with $\{\text{[HNO]}^1\text{Li}(\text{THF})\}_2$, which can be conveniently prepared by the reaction of aminophenol $[\text{HNOH}]$ $\{\text{[HNOH]} = N$ -*p*-methoxyphenyl(2-hydroxy-3,5-di-*tert*-butyl)benzylamine $\}$ with 1 equivalent of Bu^tLi in THF, is an efficient method for the synthesis of the anionic phenoxy-amido rare-earth metal amides $[\text{NO}]_2\text{LnN}(\text{SiMe}_3)_2[\text{Li}(\text{THF})_2]$.²¹ Thus, a series of rare-earth metal complexes stabilized by phenoxy-amido groups with different substituents were prepared by the reaction of $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3(\mu\text{-Cl})\text{Li}(\text{THF})_3$ with lithium aminophenolates $\{\text{[HNO]}^1\text{Li}(\text{THF})\}_2$ – $\{\text{[HNO]}^3\text{Li}(\text{THF})\}_2$ as shown in Scheme 1. All the anionic phenoxy-amido rare-earth metal amides 1–8 were obtained in good isolated yields, which were characterized by elemental analysis, and IR spectra. Complex 1 was further characterized by NMR spectroscopy. In the ^1H NMR spectrum of complex 1, the signals of $-\text{N}(\text{SiMe}_3)_2$ group and coordinated THF molecules were observed. Furthermore, two sets of resonances for the four *tert*-butyl substituents on the phenyl rings indicated that the chemical environments of the two phenoxy-amido groups are identical in solution. However, the resonances for the four protons of the CH_2 bridges were observed as two AB doublets at $\delta = 4.66$ and 4.29 ppm with the $^2J_{\text{HH}}$ value of 14.0 Hz, which means magnetic nonequivalence of the two protons on the bridging methylene groups. Obviously, this nonequivalence resulted from the coordination of the phenoxy-amido group to the yttrium ion, which constrained the conformation of the bridging methylene group. Similar phenomenon was also observed in the carbon-bridged bis(phenolate) titanium and aluminum complexes.²⁸ All of these complexes are extremely sensitive to air and moisture. They have good solubility in THF, and moderate solubility in toluene and hexane.



Scheme 1. Synthesis of Complexes 1–8.

The definitive molecular structures of complexes 1–8 were determined by single-crystal X-ray structure analysis. These complexes have anionic rare earth-lithium heterobimetallic structures crystallized in the tetragonal system. The overall molecular structures of these complexes are nearly the same, except one different R substituent group on the phenyl ring. Thus, only the molecular diagram of complex 1 is provided in Fig. 1. Their selected bond parameters are listed in Table 1. In these complexes, the rare-earth ion is coordinated by two oxygen atoms, two nitrogen atoms from two phenoxy-amido ligands, and one

nitrogen atom from the amido group. The coordination geometry around the rare-earth ion can be best described as a distorted trigonal bipyramid, in which O1, O1A are considered to occupy the apical positions. The lithium atom in complexes **1-8** is coordinated by one nitrogen atom and one oxygen atom from two different phenoxy-amido ligands, and one oxygen atom of the THF molecule to form a trigonal plane.

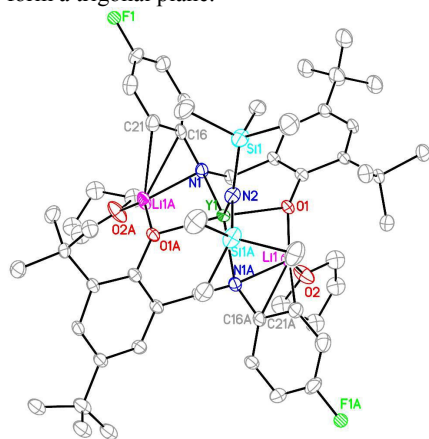


Fig. 1 Molecular structure of complex **1** showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level, and hydrogen atoms are omitted for clarity. Complex **2-8** are isomorphous with complex **1**.

The bond lengths of Ln-O(Ar) in complexes **1-8** range from 2.194(4) to 2.337(6) Å and the bond lengths of Ln-N(Ar) range from 2.206(8) to 2.454(6) Å (see Table 1), which are in agreement with the Ln-O(Ar) and Ln-N(Ar) bond lengths in anionic phenoxy-amido rare-earth metal complexes (THF)Ln[3,5-Bu^t-2-O-C₆H₂CH(NPr₂)-N-C₅H₄N]₂Li²⁰ and [NO]₂LnN(SiMe₃)₂[Li(THF)]₂,²¹ when the difference in ionic radii is considered. The Li-O(Ar) bond lengths (range from 1.83(1) to 1.87(1) Å) and the Li-N bond lengths (range from 2.05(1) to 2.08(2) Å) in complexes **1-8** (Table 1) are slightly shorter than the corresponding bond lengths in complex {[HNO]Li(THF)}₂²¹ (1.917(7) and 2.193(7) Å), but are in accordance with the corresponding bond parameters in complexes [NO]₂LnN(SiMe₃)₂[Li(THF)]₂ [Ln = Sm (**9**), Nd (**10**)].²¹ It is

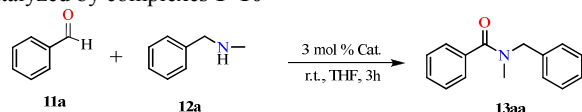
worthy to note that the π interaction between the lithium atom and the carbon atom of the phenoxy-amido ligand exists in complexes **1-8**. The distance between Li1 and C16A in complexes ranges from 2.49(1) to 2.56(2) Å, which falls in the range of π contacts between lithium ions and carbon atoms of arene rings reported in the literature (2.31–2.57 Å).²⁹⁻³¹

Catalytic activity for amidation of aldehydes with amines.

The catalytic behavior of these heterobimetallic rare-earth/alkali metal complexes for the amidation reactions of aldehydes with amines was examined. The amidation of benzaldehyde **11a** with *N*-methyl-benzylamine **12a** was first examined as a model reaction catalyzed by the heterobimetallic lanthanide complexes **1-10**, and the results are summarized in Table 2. It can be seen that all of these complexes can catalyze this transformation to yield the amide **13aa** in good to excellent yields at 25 °C with 3 mol% catalyst loading (Table 2, entries 1-10) after 3 h. The ionic radii of lanthanide metals have obvious effect on the catalytic activity, and the bimetallic samarium-lithium complexes **3** gave the highest yield under the same reaction conditions. The kinetics of the amidation of benzaldehyde with *N*-methyl-benzylamine catalyzed by complexes **1-4** have been measured in *d*₈-THF. In each case, the yields increased as the reaction time was prolonged (Fig. S1), and a first-order dependence on the concentration of *N*-methyl-benzylamine was observed in the presence of excess benzaldehyde (Fig. S2). The activity for these rare-earth complexes follows the trend Yb < Y < Nd < Sm as evidenced by respective *k*_{app} values, which may be ascribed to the fact that rare-earth metals of larger ionic radii are advantageous to the coordination of substrates. The electron effect of the aminophenoxo ligands has slight influence on the catalytic activity of these heterobimetallic complexes. The complexes with both electron-withdrawing and electron-donating groups at the *p*-position of the phenyl ring can catalyze the amidation reaction efficiently. Using the Sm complexes with different substituted group on the aminophenoxo ligand as catalysts, the isolated yields ranged from 88 to 96% (Table 2, entries 3, 5, 7 and 9).

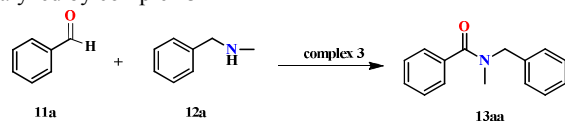
Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for Complexes **1-8**

Compound	1	2	3	4	5	6	7	8
Ln1–O1	2.229(3)	2.194(4)	2.294(4)	2.337(6)	2.289(5)	2.318(5)	2.285(4)	2.313(4)
Ln1–N1	2.344(5)	2.300(5)	2.407(5)	2.422(8)	2.406(7)	2.454(6)	2.412(5)	2.438(5)
Ln1–N2	2.244(8)	2.206(8)	2.291(8)	2.335(10)	2.295(10)	2.332(7)	2.291(9)	2.337(8)
Li1–O1	1.85(1)	1.85(1)	1.83(1)	1.85(2)	1.86(2)	1.85(2)	1.87(1)	1.85(1)
Li1–O2	1.85(1)	1.85(1)	1.86(1)	1.92(3)	1.86(2)	1.83(2)	1.80(1)	1.85(1)
Li1–N1A	2.05(1)	2.07(1)	2.06(1)	2.08(2)	2.06(2)	2.07(2)	2.07(1)	2.05(1)
Li1–C16A	2.49(1)	2.49(2)	2.52(1)	2.53(2)	2.52(2)	2.56(2)	2.53(1)	2.52(2)
O1A–Ln1–N1	79.3(1)	79.8(2)	77.7(1)	77.4(3)	77.9(2)	76.8(2)	77.4(2)	77.1(2)
O1–Ln1–N2	106.1(1)	105.2(1)	108.3(1)	109.7(2)	108.6(2)	109.8(1)	108.7(1)	109.4(1)
O1–Ln1–N1	82.4(1)	82.8(2)	80.6(1)	79.5(3)	80.2(2)	79.6(2)	80.2(2)	79.6(2)
N1–Ln1–N2	125.1(1)	125.2(2)	126.9(1)	126.7(2)	126.8(2)	127.2(2)	127.3(2)	127.4(2)
O1–Ln1–O1A	147.9(2)	149.5(3)	143.4(2)	140.7(3)	142.9(3)	140.4(2)	142.7(2)	141.2(2)
N1–Ln1–N1A	109.7(3)	109.6(3)	106.3(3)	106.7(4)	106.5(4)	105.6(3)	105.3(3)	105.3(3)

Table 2 Amidation of benzaldehyde with *N*-methyl-benzylamine catalyzed by complexes **1–10**^a

Entry	Cat.	Molar ratio 11a:12a	Yield(%) ^b
1	1	3:1	86
2	2	3:1	79
3	3	3:1	96
4	4	3:1	94
5	5	3:1	91
6	6	3:1	93
7	7	3:1	90
8	8	3:1	89
9	9	3:1	88
10	10	3:1	89

^a Amine was first added to the catalyst solution, after 30 minutes, aldehyde was added, THF as solvent, room temperature, 3h. ^b Isolated yield based on amine.

Table 3 Amidation of benzaldehyde with *N*-methyl-benzylamine catalyzed by complex **3**^a

Entry	Mol% of Cat.	Molar ratio 11a:12a	Time (h)	T (°C)	Solvent	Yield (%) ^b
1	3	1:1	3	r.t.	THF	54
2	3	2:1	3	r.t.	THF	80
3	3	3:1	3	r.t.	THF	96
4	1	3:1	3	r.t.	THF	22
5	2	3:1	3	r.t.	THF	96
6	3	3:1	2	r.t.	THF	90
7	2	3:1	1	r.t.	THF	67
8	2	3:1	2	r.t.	THF	88
9	2	3:1	3	r.t.	solvent-free	83
10	2	3:1	3	r.t.	toluene	75
11 ^c	2	3:1	3	r.t.	THF	90

^a Amine was first added to the catalyst solution, after 30 minutes, aldehyde was added. ^b Isolated yield based on amine. ^c Complex **3** was prepared *in situ*.

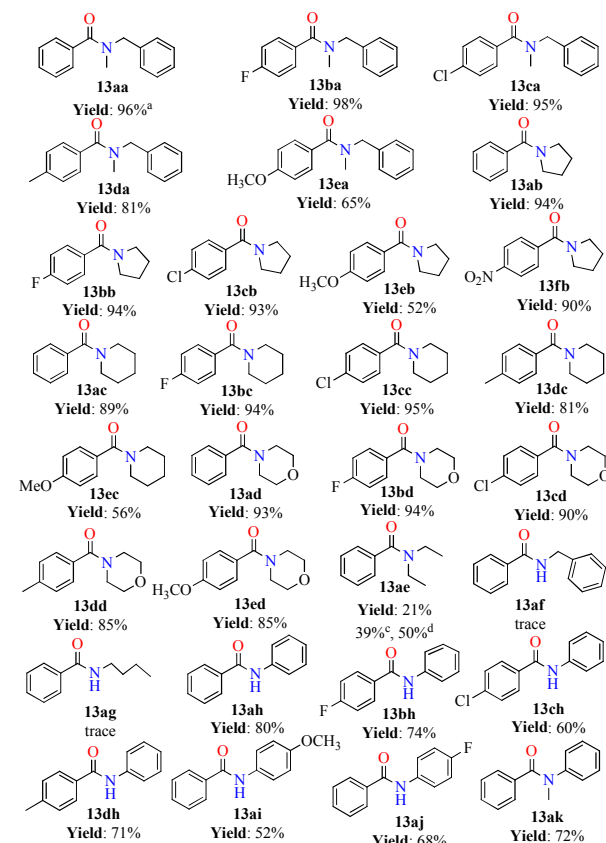
Optimization experiments were then conducted using complex **3** as the catalyst, and the results were provided in Table 3. It can

be seen that an excess of aldehyde (3 equiv) is required for reaching high yield (Table 3, entries 1-3), because aldehyde acts as not only a reactant but also an oxidant, according to the reaction mechanism suggested by Marks et al.⁹ Besides, a possibly occurred side reaction of dimerization of aldehyde, namely the Tishchenko reaction, also consumes aldehyde. In order to suppress the Tishchenko reaction, amine was added to the reaction mixture at first and the mixture was stirred for 30 min, and then aldehyde was added. Catalyst loading has obvious influence on the reaction. The yield decreases dramatically from 96% to only 22 % when the catalyst loading is decreased from 2 mol% to 1 mol% (Table 3, entries 4 and 5). The amidation reaction catalyzed by complex **3** completed after 3h. Shortening reaction time resulted in a decrease in yields (Table 3, entries 5-7). Reaction media also have somewhat influence on the reaction. It was found that THF is a better solvent than toluene (Table 3, entries 5 and 10), and the reaction was conducted in solvent-free condition to give product **13aa** in a relatively lower yield (Table 3, entries 5 and 9) in comparison with that in THF. It is worthy to note that the high yield was also obtained using complex **3** prepared *in situ* as catalyst for this transformation (Table 3, entry 11), reflecting that the anionic phenoxy-amido samarium complex can be easily prepared quantitatively.

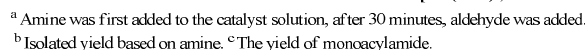
Under the optimal reaction conditions (Table 3, entry 5), the scopes of aldehydes and amines were explored, respectively, and the results were listed in Table 4. It can be seen that the amidation reaction of aromatic aldehyde proceeded smoothly to generate the expected amides in good to excellent isolated yields. Electronic effect of the aldehyde has an obvious influence on the transformation. The aromatic aldehyde with electron-withdrawing substituent at the *p*-position of the phenyl ring showed apparently higher reactivity in comparison with the aldehyde with electron-donating substituent. For example, the reaction of *p*-fluoroaldehyde with *N*-methyl-benzylamine gave the corresponding amide in 98% isolated yield, whereas the similar reaction of *p*-methoxyaldehyde with *N*-methyl-benzylamine gave the final product in 65% yield under the same reaction conditions (Table 4, **13ba** and **13ea**). This influence of the substituent on the aromatic aldehyde is consistent with that reported in the literature.⁹⁻¹¹ The bulkiness of the amine has obvious effect on the amidation reaction. The reactions of aldehydes with cyclic secondary aliphatic amines, such as pyrrolidine, piperidine and morpholine, proceeded smoothly in this system to generate the desired acylamides in excellent isolated yields (Table 4, **13ab-13ed**), whereas the reaction of diethylamine with benzaldehyde give the amide in dramatically low yield, and the yield can be improved to moderate by raising the reaction temperature or prolonging the reaction time (Table 4, **13ae**). The properties of the amines also showed significant effect on the reaction. The yields for the reactions of benzaldehyde with both linear and cyclic secondary alkyl amines range from 89 to 96%, whereas the yield is in trace amount for the reaction of benzaldehyde with primary alkyl amine, such as benzylamine (Table 4, **13af**) and butylamine (Table 4, **13ag**). This difference can be attributed to the fact that the primary alkyl amine can react easily with aldehyde to form imine and water, and the latter can decompose the catalyst. However, the reactions of aniline with aldehydes give the amide in good isolated yield (Table 4, **13ah-13dh**),

Table 4 Amidation of aldehydes and amines catalyzed by
15 complex **3**^a

15 complex **3^a**



^a Amine was first added to the catalyst solution, after 30 minutes, 3 equivolar of aldehyde was added. ^b Isolated yield based on amine. ^c Reaction temperature was 60 °C. ^d Reaction time was 24h.



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