

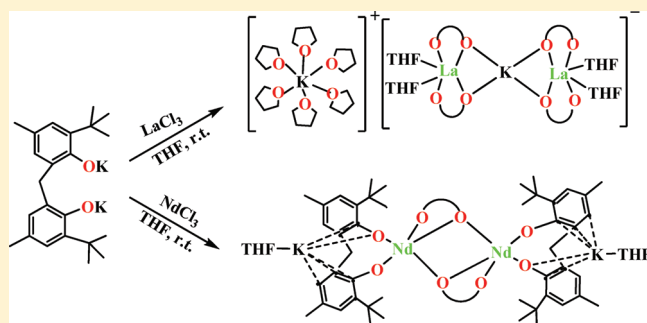
# Synthesis and Structural Diversity of Heterobimetallic Lanthanide–Potassium Complexes and Catalytic Activity for Amidation of Aldehydes with Amines

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Supporting Information

**ABSTRACT:** Four heterobimetallic lanthanide–potassium complexes stabilized by the carbon-bridged bis(phenolate) ligand MBMP<sup>2−</sup> (MBMP = 2,2′-methylene bis(6-*tert*-butyl-4-methylphenolate)), [ $\{(\text{MBMP})_2\text{La}(\text{THF})_2\}_2\text{K}\}[\text{K}(\text{THF})_6]$  (1), [ $(\text{MBMP})\text{Nd}(\mu\text{-MBMP})\text{K}(\text{THF})_2$ ] (2), [ $(\text{THF})_2\text{Sm}(\text{MBMP})_2\text{K}(\text{THF})_2$ ] (3), and [ $(\text{THF})_2\text{Yb}(\text{MBMP})_2\text{K}(\text{THF})_3$ ] (4), were synthesized, and their structural features were provided. It was found that the ionic radii of lanthanide metals have a profound effect on the structures of the heterobimetallic complexes. Complexes 1 to 4 are efficient catalysts for amidation reactions of aldehydes with amines to produce amides in good to excellent yields under mild conditions.



## INTRODUCTION

The synthesis and characterization of bimetallic complexes have received considerable attention, because these kinds of complexes offer the possibility of unique and more selective catalytic transformations in homogeneous catalysis owing to the potential cooperative effect between two metal centers.<sup>1</sup> Heterobimetallic complexes of a lanthanide metal and an alkali metal have been well known for a long time, but their catalytic behavior has not been explored intensively, because most of these complexes were reported as unexpected ligand redistributed products during the syntheses of organolanthanide complexes.<sup>2</sup> However, it has been found that some heterobimetallic lanthanide–alkali metal complexes showed interesting activity in catalytic transformations. For example, the heterobimetallic lanthanide–alkali metal complexes based on BINOL were versatile catalysts in a wide range of asymmetric reactions, which have never been possible using monometallic lanthanide catalysts.<sup>3</sup> Our recent results revealed also that heterobimetallic lanthanide–alkali metal complexes are more efficient catalysts in organic synthesis and ring-opening polymerization of cyclic esters than the monometallic ones.<sup>4</sup> These successful examples prompted us to further study the synthesis and catalytic behavior of heterobimetallic lanthanide–alkali metal complexes. Furthermore, although a variety of heterobimetallic lanthanide–lithium and lanthanide–sodium complexes have been reported,<sup>2,3</sup> the study of the synthesis and characterization of heterobimetallic lanthanide–potassium complexes is relatively limited.<sup>5</sup>

On the other hand, bridged bis(phenolate) ligands have attracted recent attention in organolanthanide chemistry, because

they are easily available, tunable, and even potentially recyclable.<sup>6</sup> To date, numerous organolanthanide complexes stabilized by a number of bridged bis(phenolate) ligands have been prepared, but the application of these complexes focused on the ring-opening polymerization of cyclic esters. To expand the scope of the application of bridged bis(phenolate) lanthanide complexes, four new heterobimetallic lanthanide–potassium complexes stabilized by carbon-bridged bis(phenolate) groups were prepared. It was found that these heterobimetallic complexes are efficient catalysts for amidation reactions of aldehydes with amines. Here we report these results.

## EXPERIMENTAL SECTION

All reagents are reagent grade, commercially available, and used as received unless otherwise noted. All manipulations were performed under argon, using the standard Schlenk techniques. THF, toluene, and hexane were distilled from sodium benzophenone ketyl before use. Lanthanide metal analysis was performed by EDTA titration with a xylenol orange indicator and a hexamine buffer.<sup>7</sup> Carbon and hydrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. IR spectra were recorded with a Nicolet-550 FT-IR spectrometer as KBr pellets. <sup>1</sup>H NMR spectra were obtained on an INOVA-400 MHz apparatus. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges.

**Synthesis of [ $\{(\text{MBMP})_2\text{La}(\text{THF})_2\}_2\text{K}\}[\text{K}(\text{THF})_6]$  (1).** To a slurry of anhydrous LaCl<sub>3</sub> (1.97 g, 8.03 mmol) in THF (60 mL) was

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Table 1. Crystallographic Data for Complexes 1 to 4

	1	2·4C <sub>7</sub> H <sub>8</sub>	3·0.5(C <sub>4</sub> H <sub>8</sub> O+ C <sub>7</sub> H <sub>8</sub> )	4
formula	C <sub>132</sub> H <sub>200</sub> K <sub>2</sub> La <sub>2</sub> O <sub>18</sub>	C <sub>128</sub> H <sub>168</sub> K <sub>2</sub> Nd <sub>2</sub> O <sub>10</sub>	C <sub>67.5</sub> H <sub>100</sub> KO <sub>8.5</sub> Sm	C <sub>66</sub> H <sub>100</sub> KO <sub>9</sub> Yb
fw	2430.94	2233.30	1236.92	1249.60
T (K)	193(2)	193(2)	193(2)	193(2)
cryst syst	orthorhombic	triclinic	triclinic	monoclinic
space group	C <sub>2</sub> 21	P $\bar{1}$	P $\bar{1}$	P <sub>2</sub> <sub>1</sub> /c
a (Å)	23.823(2)	13.7855(7)	13.071(2)	15.085(1)
b (Å)	24.848(2)	15.4725(11)	16.239(3)	17.347(2)
c (Å)	24.213(2)	15.9167(9)	18.208(3)	28.382(3)
α (deg)		75.615(5)	111.279(4)	
β (deg)		68.163(5)	92.015(2)	94.639(2)
γ (deg)		77.512(6)	107.289(4)	
V (Å <sup>3</sup> )	14333(2)	3023.5(3)	3394.0(10)	7402.8(11)
Z	4	1	2	4
D <sub>calcd</sub> (g cm <sup>-3</sup> )	1.127	1.227	1.210	1.121
μ (mm <sup>-1</sup> )	0.701	0.972	0.976	1.365
F(000)	5152	1174	1308	2628
cryst size (mm)	0.53 × 0.40 × 0.14	0.79 × 0.70 × 0.20	0.50 × 0.30 × 0.20	0.50 × 0.38 × 0.30
θ <sub>max</sub> (deg)	25.35	25.35	25.35	25.35
collected reflns	70 550	29 550	33 076	70 885
unique reflns	13 113	11 000	12 344	13 509
obsd reflns [I > 2.0σ(I)]	11 359	10 350	9757	10 501
no. of variables	650	635	693	689
GOF	1.169	1.129	1.154	1.166
R	0.0870	0.0391	0.0828	0.0824
R <sub>w</sub>	0.2233	0.1009	0.1775	0.2040

added a THF solution of K<sub>2</sub>MBMP (36.2 mL, 16.1 mmol). The mixture was stirred at room temperature for about 48 h, and a gel-like precipitate formed gradually. The precipitate was removed from the reaction mixture by centrifugation, and a pale green solution was obtained. The solution was concentrated to about 25 mL under vacuum, and colorless microcrystals were obtained from the solution at room temperature in one day (4.86 g, 50% based on lanthanum). Mp: 212–214 °C. Anal. Calcd for C<sub>132</sub>H<sub>200</sub>K<sub>2</sub>La<sub>2</sub>O<sub>18</sub>: C, 65.22; H, 8.29; La, 11.43. Found: C, 65.47; H, 8.44; La, 11.02. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz, 25 °C): δ 1.35 (br, 40H, THF), 1.49 (s, 72H, C(CH<sub>3</sub>)<sub>3</sub>), 2.27 (s, 24H, ArCH<sub>3</sub>), 3.38 (br, 40H, THF), 3.55 (d, J = 14.0 Hz, 2H, CH<sub>2</sub>), 3.92 (d, J = 15.0 Hz, 2H, CH<sub>2</sub>), 4.10 (d, J = 15.0 Hz, 2H, CH<sub>2</sub>), 4.89 (d, J = 14.0 Hz, 2H, CH<sub>2</sub>), 6.82–7.02 (m, 16H, Ar). <sup>1</sup>H NMR (300 MHz, d<sub>8</sub>-THF, 25 °C): δ 7.00 (s, 4H, Ph), 6.71 (s, 4H, Ph), 6.70 (s, 4H, Ph), 6.64 (s, 4H, Ph), 4.78 (d, J = 12.4 Hz, 4H, CH<sub>2</sub>), 3.13 (d, J = 13.6 Hz, 4H, CH<sub>2</sub>), 2.14 (s, 12H, CH<sub>3</sub>), 2.10 (s, 12H, CH<sub>3</sub>), 1.38 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>), 1.36 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, d<sub>8</sub>-THF, 25 °C): δ 164.27 (Ph), 161.32 (Ph), 159.32 (Ph), 137.02 (Ph), 136.26 (Ph), 134.33 (Ph), 132.27 (Ph), 129.36 (Ph), 128.46 (Ph), 125.03 (Ph), 124.59 (Ph), 121.21 (Ph), 119.65 (Ph), 68.18 (CH<sub>2</sub>), 35.40 (C(CH<sub>3</sub>)<sub>3</sub>), 35.22 (C(CH<sub>3</sub>)<sub>3</sub>), 30.52 (C(CH<sub>3</sub>)<sub>3</sub>), 30.19 (C(CH<sub>3</sub>)<sub>3</sub>), 26.18 (CH<sub>2</sub>), 21.21 (CH<sub>3</sub>), 21.02 (CH<sub>3</sub>). IR (KBr, cm<sup>-1</sup>): 2956(s), 2917(s), 2869(m), 1605(m), 1526(m), 1434(s), 1240(s), 1156(s), 1050(m), 862(m). Crystals suitable for structure determination were obtained by slow cooling of a hot THF solution.

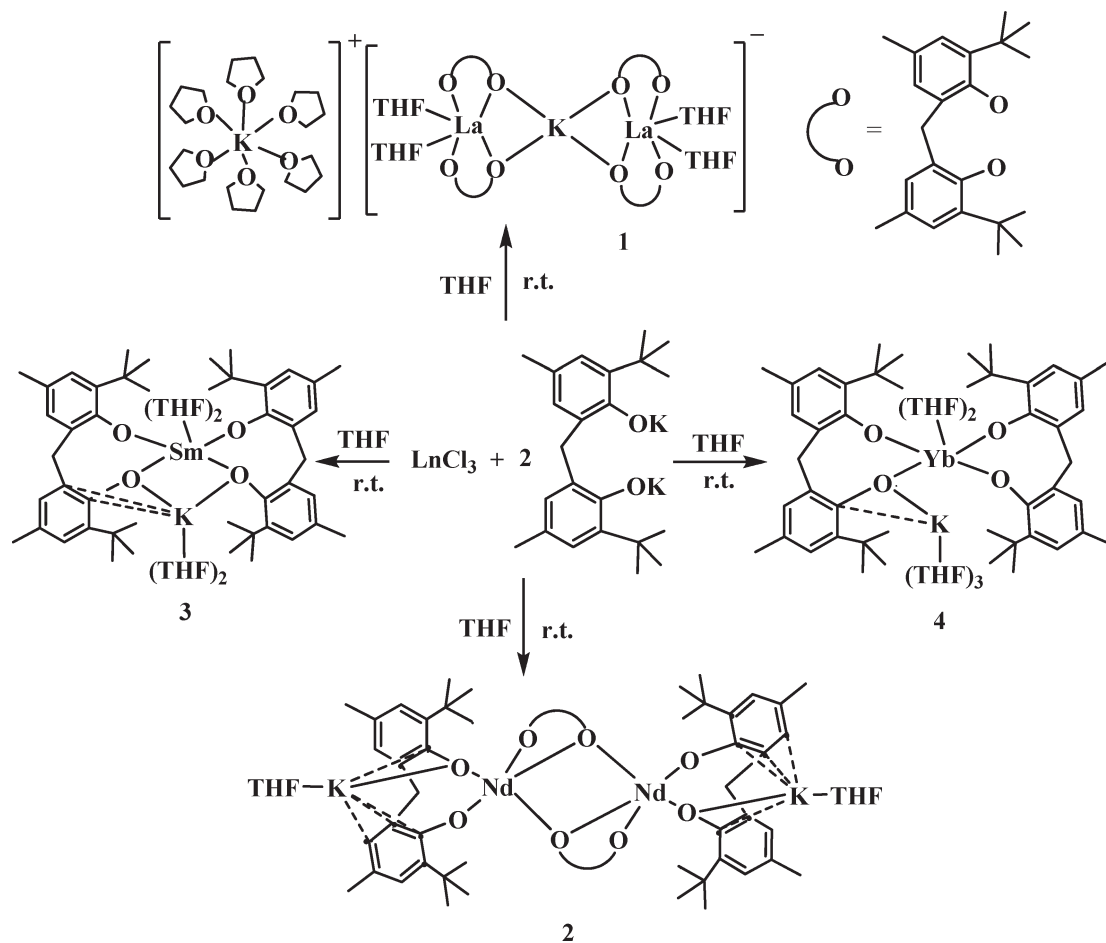
**Synthesis of [(MBMP)Nd(μ-MBMP)K(THF)]<sub>2</sub> (2).** The synthesis of complex 2 was carried out in the same way as that described for complex 1, but NdCl<sub>3</sub> (1.58 g, 6.31 mmol) was used in place of LaCl<sub>3</sub>. After workup, a pale blue solution was obtained. The solution was concentrated to about 20 mL, and a colorless, crystal-like solid formed in 2 days (3.73 g, 63% based on neodymium). Mp: 196–198 °C. Anal.

Calcd for C<sub>100</sub>H<sub>136</sub>K<sub>2</sub>Nd<sub>2</sub>O<sub>10</sub>: C, 64.41; H, 7.35; Nd, 15.47. Found: C, 64.75; H, 7.53; Nd, 15.04. IR (KBr, cm<sup>-1</sup>): 2954(s), 2909(s), 2871(m), 1606(m), 1526(m), 1442(s), 1240(s), 1156(s), 1050(m), 862(m). Crystals suitable for an X-ray structure analysis were obtained by slow cooling of a hot THF solution.

**Synthesis of [(THF)<sub>2</sub>Sm(MBMP)<sub>2</sub>K(THF)<sub>2</sub>] (3).** To a slurry of anhydrous SmCl<sub>3</sub> (0.88 g, 3.43 mmol) in THF (30 mL) was added a THF solution of K<sub>2</sub>MBMP (15.4 mL, 6.86 mmol). The mixture was stirred at room temperature for about 36 h, and a gel-like precipitate formed gradually. The precipitate was removed from the reaction mixture by centrifugation, and a pale yellow solution was obtained. The solvent was completely evaporated under vacuum, and hot toluene (30 mL) was added. Pale yellow microcrystals of complex 3 were obtained in 4 days in 62% yield (1.00 g). Mp: 167–169 °C. Anal. Calcd for C<sub>62</sub>H<sub>92</sub>KO<sub>8</sub>Sm: C, 64.48; H, 8.03; Sm, 13.02. Found: C, 64.72; H, 8.22; Sm, 12.75. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 6.86–7.01 (d, 8H, Ph), 5.96 (s, 4H, CH<sub>2</sub>), 3.55 (s, 16H, THF), 2.11 (s, 12H, CH<sub>3</sub>), 1.40 (br, 36H, C(CH<sub>3</sub>)<sub>3</sub>) 1.23 (s, 16H, THF). IR (KBr, cm<sup>-1</sup>): 2951(s), 2912(s), 1608(w), 1466(s), 1435(s), 1385(m), 1084(s), 860(m). Crystals suitable for an X-ray structure analysis were obtained by slow cooling of a hot THF–toluene solution.

**Synthesis of [(THF)<sub>2</sub>Yb(MBMP)<sub>2</sub>K(THF)<sub>3</sub>] (4).** The synthesis of complex 4 was carried out in the same way as that described for complex 3, but YbCl<sub>3</sub> (0.92 g, 3.29 mmol) was used in place of SmCl<sub>3</sub>. After workup, a yellow solution was obtained, which was concentrated to about 25 mL, and a colorless crystal-like solid formed in 2 days (2.37 g, 58% based on ytterbium). Mp: 141–143 °C. Anal. Calcd for C<sub>66</sub>H<sub>100</sub>KO<sub>9</sub>Yb: C, 63.44; H, 8.07; Yb, 13.85. Found: C, 63.88; H, 8.38; Yb, 13.44. <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 6.87–7.03 (d, 8H, Ph), 5.91 (s, 4H, CH<sub>2</sub>), 3.71 (s, 8H, THF), 2.10 (s, 12H, CH<sub>3</sub>), 1.43 (s, 36H, C(CH<sub>3</sub>)<sub>3</sub>); 1.22 (s, 8H, THF). IR (KBr, cm<sup>-1</sup>): 2954(s), 2909(s),

Scheme 1



2869(m), 1604(w), 1466(s), 1526(m), 1240(s), 1156(s), 1050(m), 862(m). Crystals suitable for an X-ray structure analysis were obtained by slow cooling of a hot toluene solution.

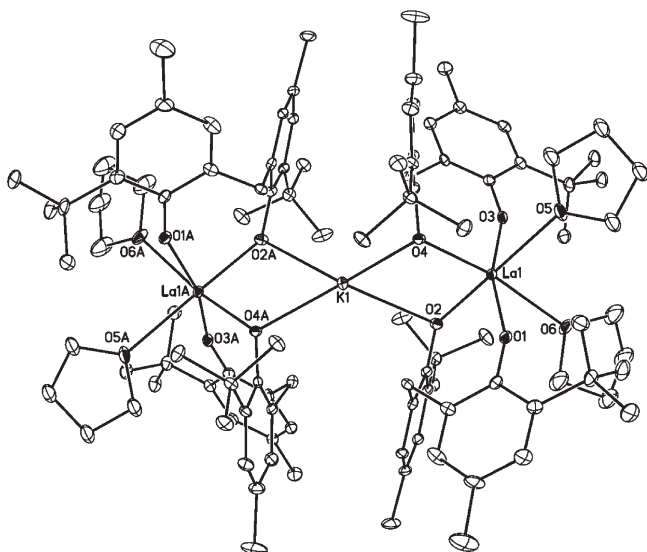
**Typical Procedure for Amidation Reaction.** The procedures for amidation reactions of aldehydes and amines catalyzed by complexes 1 to 4 are similar, and a typical reaction procedure is given below. A 20 mL Schlenk flask was charged with a solution of catalyst (2.00 mL, 0.05 mmol), and aniline was added (0.09 mL, 1 mmol). The mixture was stirred for 0.5 h, and then benzaldehyde was added (0.30 mL, 3.00 mmol). The reaction mixture was stirred at 25 °C for 22 h and then filtered through a small plug of silica gel to remove the catalyst. The crude product was purified by column chromatography (ethyl acetate–petroleum ether, 1:15) to obtain the final product.

**X-ray Crystallography.** Suitable single crystals of complexes 1 to 4 were sealed in a thin-walled glass capillary for determining the single-crystal structure. Intensity data were collected with a Rigaku Mercury CCD area detector in  $\omega$  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 Table 1.

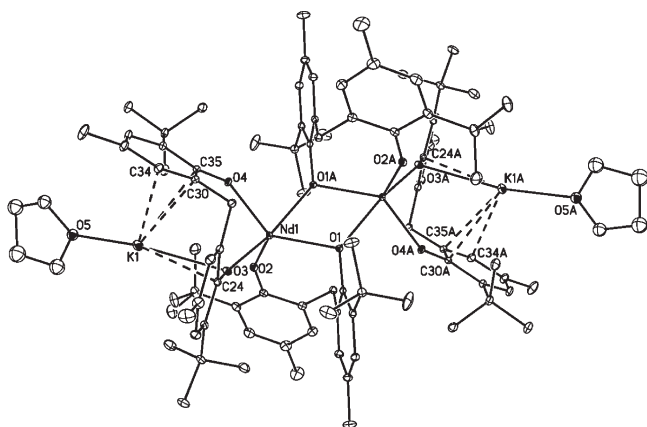
The structures were solved by direct methods and refined by full-matrix least-squares procedures based on  $|F|^2$ . All the non-hydrogen atoms were refined anisotropically. All the H atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELXL-97 programs.

## RESULTS AND DISCUSSION

**Synthesis and Characterization of Heterobimetallic Complexes.** The metathesis reactions of anhydrous  $\text{LnCl}_3$  (Ln = La, Nd, Sm, Yb) with 2 equiv of  $\text{K}_2\text{MBMP}$  in THF at room temperature, after workup, gave the heterobimetallic lanthanide–potassium complexes  $[(\text{MBMP})_2\text{La}(\text{THF})_2]_2\text{K}[\text{K}(\text{THF})_6]$  (1),  $[(\text{MBMP})\text{Nd}(\mu\text{-MBMP})\text{K}(\text{THF})_2]$  (2),  $[(\text{THF})_2\text{Sm}(\text{MBMP})_2\text{K}(\text{THF})_2]$  (3), and  $[(\text{THF})_2\text{Yb}(\text{MBMP})_2\text{K}(\text{THF})_3]$  (4) in relatively high isolated yields, as shown in Scheme 1. These complexes gave satisfactory elemental analyses, and their infrared spectra showed absorptions characteristic of the bis(phenolate) ligands. For the diamagnetic lanthanum complex 1, the  $^1\text{H}$  NMR spectrum was obtained in  $\text{C}_6\text{D}_6$ . The  $^1\text{H}$  NMR spectrum shows one set of resonances of the methyl and *tert*-butyl substituents on the arene rings at  $\delta$  2.27 and 1.49 ppm, respectively. Similarly, one set of two broad resonances of THF molecules was observed at  $\delta$  3.38 and 1.35 ppm. However, the methylene protons of the bridges give rise to four doublets at  $\delta$  3.55, 3.92, 4.10, and 4.89 ppm with  $J_{\text{HH}} = 14.0$  and 15.0 Hz, respectively. Nonequivalence for the two hydrogen atoms in the bridging methylene is also observed in other carbon-bridged bis(phenolate) metal complexes, and the  $J_{\text{HH}}$  values in complex 1 are in accordance with those reported in the literatures.<sup>8</sup> The more complicated splitting of the methylene protons indicated a loss of symmetry of the anion (see below), which indicated that the trinuclear structure remained in solution. The definitive molecular

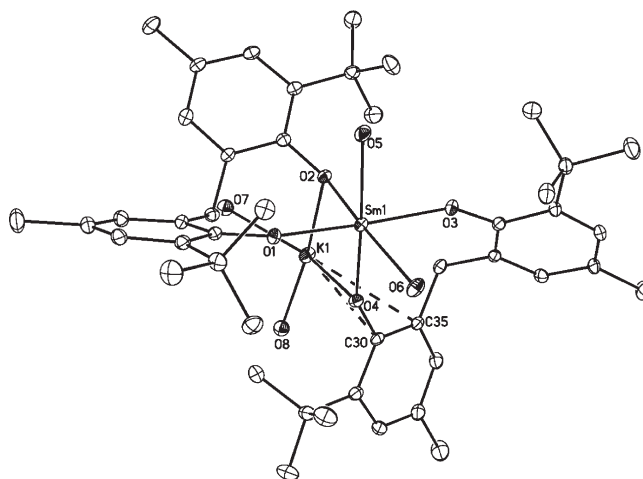


**Figure 1.** ORTEP diagram of the anion of complex 1 showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms and the cation  $[K(THF)_6]$  are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): La(1)–O(1) 2.316(6), La(1)–O(2) 2.291(6), La(1)–O(3) 2.338(6), La(1)–O(4) 2.334(6), La(1)–O(5) 2.631(8), La(1)–O(6) 2.635(7), K(1)–O(2) 2.854(6), K(1)–O(4) 2.694(6); O(1)–La(1)–O(4) 94.8(2), O(4)–La(1)–O(3) 99.2(2), O(3)–La(1)–O(6) 89.0(2), O(1)–La(1)–O(6) 77.7(2), O(2)–La(1)–O(5) 176.2(2), O(2)–La(1)–O(1) 92.3(2), O(2)–La(1)–O(4) 85.1(2), O(4)–K(1)–O(2) 68.60(18), O(2)–K(1)–O(2A) 138.4(3), O(4A)–K(1)–O(4) 135.2(3).

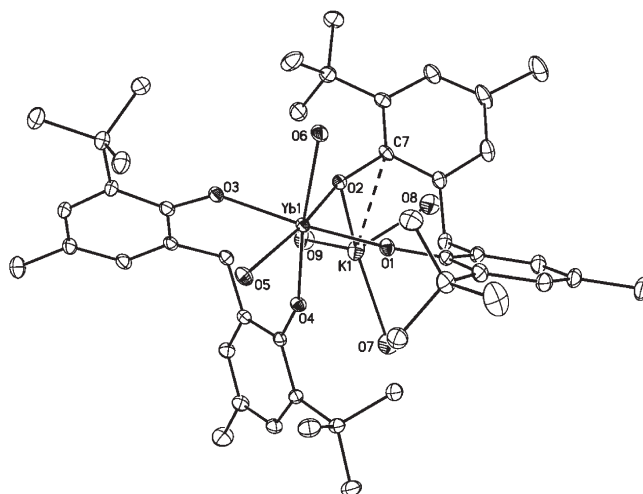


**Figure 2.** ORTEP diagram of complex 2 showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Nd(1)–O(1) 2.378(2), Nd(1)–O(1A) 2.423(2), Nd(1)–O(2) 2.188(2), Nd(1)–O(3) 2.277(2), Nd(1)–O(4) 2.248(2), Nd(1)–C(1) 3.041(3), K(1)–O(3) 2.946(3), K(1)–O(5) 2.731(8), K(1)–C(24) 3.078(3), K(1)–C(30) 3.058(3), K(1)–C(34) 3.230(4), K(1)–C(35) 3.032(3); O(2)–Nd(1)–O(1) 110.78(8), O(2)–Nd(1)–O(4) 114.58(9), O(4)–Nd(1)–O(1) 130.59(8), O(3)–Nd(1)–O(1A) 161.61(8), O(4)–Nd(1)–O(3) 83.68(8), O(1)–Nd(1)–O(1A) 69.56(8), Nd(1)–O(1)–Nd(1A) 110.44(8).

structures of complexes 1 to 4 were confirmed by X-ray structure determination. Complexes 1 and 2 are slightly soluble in THF and in toluene, whereas complexes 3 and 4 are well soluble in THF and toluene.



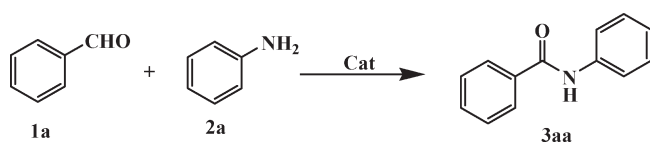
**Figure 3.** ORTEP diagram of complex 3 showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms and carbon atoms of THF molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sm(1)–O(1) 2.240(5), Sm(1)–O(2) 2.246(5), Sm(1)–O(3) 2.238(5), Sm(1)–O(4) 2.209(5), Sm(1)–O(5) 2.508(5), Sm(1)–O(6) 2.525(5), K(1)–O(2) 2.768(5), K(1)–O(4) 2.884(5), K(1)–C(30) 3.107(7), K(1)–C(35) 3.296(7); O(1)–Sm(1)–O(2) 94.40(17), O(3)–Sm(1)–O(2) 94.33(18), O(3)–Sm(1)–O(6) 80.28(18), O(1)–Sm(1)–O(6) 91.62(17), O(4)–Sm(1)–O(5) 177.31(17), O(4)–Sm(1)–O(3) 92.51(17).



**Figure 4.** ORTEP diagram of complex 4 showing the atom-numbering scheme. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms and carbon atoms of THF molecules are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Yb(1)–O(1) 2.148(6), Yb(1)–O(2) 2.155(6), Yb(1)–O(3) 2.162(6), Yb(1)–O(4) 2.098(5), Yb(1)–O(5) 2.429(6), Yb(1)–O(6) 2.448(6), K(1)–O(2) 2.867(6), K(1)–C(7) 3.152(8); O(1)–Yb(1)–O(4) 93.5(2), O(3)–Yb(1)–O(4) 96.9(2), O(3)–Yb(1)–O(6) 90.3(2), O(1)–Yb(1)–O(6) 79.1(2), O(2)–Yb(1)–O(5) 172.0(2), O(1)–Yb(1)–O(2) 96.4(2).

The molecular structures of complexes 1 to 4 are shown in Figures 1 to 4, with their selected bond lengths and bond angles. The molecular structure of complex 1 is comprised of a discrete  $[K(THF)_6]^+$  cation and a  $[(MBMP)_2La(THF)_2)_2K]^-$  anion.



**Table 2.** Amidation of **1a** with **2a** Catalyzed by Complexes **1–4**<sup>a</sup>

entry	molar ratio ( <b>1a</b> : <b>2a</b> )	catalyst	mol % of catalyst <sup>b</sup>	time (h)	<i>T</i> (°C)	yield (%) <sup>c</sup>
1	3:1	<b>1</b>	10	22	25	73
2	3:1	<b>2</b>	10	22	25	36
3	3:1	<b>3</b>	10	22	25	53
4	3:1	<b>4</b>	10	22	25	30
5	3:1	<b>5</b>	10	22	25	trace
6	3:1	<b>5</b>	30	22	25	11
7	3:1	<b>1</b>	5	22	25	68
8	3:1	<b>1</b>	15	22	25	77
9	3:1	<b>1</b>	10	22	65	78

<sup>a</sup> Amine was first added to the catalyst solution, and after 30 min, aldehyde was added; THF as solvent. <sup>b</sup> Based on lanthanide metal. <sup>c</sup> Isolated yield based on amine.

Although there are a lot of examples of lanthanide–alkali metal complexes with discrete ion pair structures,<sup>9</sup> to the best of our knowledge, there is no example of a lanthanide–potassium complex with such structure. The anion has a centrosymmetric trinuclear structure, in which two anionic [(MBMP)<sub>2</sub>La(THF)<sub>2</sub>]<sup>−</sup> moieties are connected with one potassium atom. Each lanthanum atom is six-coordinated by four oxygen atoms from two bis(phenolate) ligands and two oxygen atoms from two THF molecules to form a distorted octahedral geometry. The potassium atom is coordinated with four oxygen atoms from four different bis(phenolate) ligands.

In complex **1**, the average terminal La–O(Ar) bond length of 2.327(6) Å is slightly longer than the terminal La–O(Ar) bond length in (MBMP)La(THF)(μ-MBMP)<sub>2</sub>La(THF)<sub>2</sub> (2.286(4) Å)<sup>10</sup> and (THF)La(O-2,6-Pr<sup>*i*</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>(μ-O-2,6-Pr<sup>*i*</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub>M(THF)<sub>2</sub> (M = Li, Na; 2.208(3)–2.227(6) Å).<sup>11</sup> To our surprise, the average bridging La–O(Ar) bond length of 2.312(6) Å is nearly the same as the terminal La–O(Ar) bond length, whereas the bridging La–O(Ar) bond length is apparently longer than the terminal one in (MBMP)La(THF)(μ-MBMP)<sub>2</sub>La(THF)<sub>2</sub>.<sup>10</sup> The K–O(Ar) bond distances are 2.854(6) and 2.694(6) Å, respectively, giving an average bond distance of 2.774(6) Å, which is comparable with those values observed in the potassium aryloxo compounds reported in the literature.<sup>12</sup>

Complex **2** is composed of four dianionic MBMP ligands, two neodymium atoms, two potassium atoms, and two THF molecules to form a centrosymmetric tetranuclear molecule. In complex **2**, two neodymium atoms are connected with two MBMP groups, and each of the neodymium atoms is coordinated by two oxygen atoms from one terminal MBMP group and three oxygen atoms from two bridged MBMP groups. The coordination geometry about the neodymium atom can be best described as a distorted trigonal bipyramid. Different from that observed in complex **1**, the coordination sphere of K1 is completed by four carbon atoms from two arene rings of the bis(phenolate) ligand, one oxygen atom from the bis(phenolate) ligand, and one oxygen atom from one THF molecule. The coordination

geometry can be described as a distorted tetrahedron if three carbon atoms from one arene ring were considered to occupy one coordination site.

In complex **2**, the terminal Nd–O(Ar) bond lengths range from 2.188(2) to 2.277(2) Å, giving an average of 2.238(2) Å, which is well comparable with that in [(MBMP)Nd(μ-OPr<sup>*i*</sup>)(THF)<sub>2</sub>]<sub>2</sub> (2.215(6) Å).<sup>13</sup> As expected, the average bridged Nd–O(Ar) bond length of 2.400(2) Å is apparently longer than the terminal one, which is quite different from that observed in complex **1**. It is worth noting that there is a remote π interaction between one carbon atom of one arene ring and the neodymium atom. The Nd–C(1) bond length of 3.041(3) Å is in accordance with that observed in [(MBMP)Nd(μ-OPr<sup>*i*</sup>)(THF)<sub>2</sub>]<sub>2</sub> (3.080(4) Å).<sup>13</sup> The K–O(Ar) bond length of 2.946(3) Å is considerably longer than those in complex **1**, which indicates that the coordination of the potassium atom with O3 is weak. There are relatively strong π interactions between K1 and C24, C30, C34, and C35. The bond lengths, ranging from 3.032(3) to 3.230(4) Å, fall in the range of π interactions of potassium ions to the arene rings in {[Bu<sup>*t*</sup>-OPO]K<sub>2</sub>(THF)<sub>2</sub>]<sub>2</sub> ([Bu<sup>*t*</sup>-OPO]H<sub>2</sub> = bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-*tert*-butylphosphine), ranging from 3.007(5) to 3.275(5) Å.<sup>12b</sup>

Complex **3** has a dinuclear structure. The overall molecular geometry comprises a six-coordinated samarium metal center, which is coordinated by the four oxygen atoms of the two MBMP<sup>2−</sup> groups, and two THF ligands in a distorted octahedron as well as a four-coordinate potassium cation, which is coordinated by the two oxygen atoms from the MBMP<sup>2−</sup> groups and two THF ligands in a distorted tetrahedron. In addition, there are remote π interactions of K1 with C30 and C35. The overall coordination geometry around the samarium atom is similar to that of the neodymium atom in (THF)<sub>2</sub>Nd(MBMP)<sub>2</sub>Na(THF)<sub>2</sub>.<sup>9d</sup> The average terminal Sm–O(Ar) bond lengths are 2.239(5) Å, which compares well with the terminal Nd–O(Ar) bond length in (THF)<sub>2</sub>Nd(MBMP)<sub>2</sub>Na(THF)<sub>2</sub> (2.278(2) Å)<sup>9d</sup> when the difference in ionic radii is considered. The average bridging Sm–O(Ar) bond length of 2.227(5) Å is comparable with the terminal Sm–O(Ar) bond length, which is similar to that observed in complex **1**.

Complex **4** is composed of two MBMP ligands, one ytterbium atom, one potassium atom, and five THF molecules to form a dinuclear molecule. The ytterbium center is six-coordinated by the four oxygen atoms from the two MBMP groups and two oxygen atoms from the two THF molecules to form a distorted octahedron. The overall coordination geometry is similar to that of the samarium atom in complex **3**, but is different from that of the ytterbium atom in (THF)Yb(MBMP)<sub>2</sub>Na(THF)<sub>2</sub>,<sup>9d</sup> in which only one THF molecule is coordinated to the ytterbium atom. The average terminal Yb–O(Ar) bond length of 2.155(6) Å is comparable with the corresponding Sm–O(Ar) bond length in complex **3** when the difference in ionic radii is considered. The bridging Yb–O(Ar) bond length of 2.126(6) Å is also slightly shorter than the terminal one. There is also a remote π interaction between K1 and C7. The distance between K1 and C7 of 3.152(8) Å is comparable with those observed in complexes **2** and **3**.

**Catalytic Activity for Amidation of Aldehydes with Amines.** The synthesis of aromatic and aliphatic acylamides is of significant importance in organic synthesis, because the amide group is an essential motif in polymers, nature products, and pharmaceuticals. The direct amidation of aldehydes with amines is

Table 3. Amidation of Aldehydes with Amines Catalyzed by Complex 1<sup>a,b</sup>

$$\text{R}-\text{CHO} + \text{R}_1\text{NHR}_2 \xrightarrow{\text{complex 1}} \text{R}-\text{C}(=\text{O})\text{N}(\text{R}_1)\text{R}_2$$

1                      2                                      3

Entry	aldehyde	amine	amide	yield (%) <sup>b</sup>
1				73
2				79
3				78
4				54
5				91
6				95
7				94
8				69
9				96
10				94
11				95
12				82
13				93
14				97
15				96
16				77

<sup>a</sup> Amine was first added to the catalyst solution, and after 30 min, aldehyde was added. <sup>b</sup> Isolated yield based on amine.

the most desired approach to acylamides because of atom economy and easy availability of starting materials. In recent years, the

amidation reactions of aldehydes with amines mediated/catalyzed by lanthanide complexes have received considerable attention

because of their high efficiency and mild reaction conditions. Wang et al. found that aromatic aldehydes reacted with lanthanide amides  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3(\mu\text{-Cl})\text{Li}(\text{THF})_3$  to give amides via the Cannizzaro-type disproportionation reaction.<sup>14</sup> Marks et al. reported that homoleptic lanthanide amides  $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$  can catalyze efficiently the amidation reaction of aldehydes with amines under mild conditions without the use of peroxide.<sup>15</sup> Subsequently, we found that some anionic lanthanide–alkali metal complexes are more efficient catalysts for this reaction, and they have a wider range of scope for the amines.<sup>4c,d</sup> To further explore the application of bridged bis(phenolate) lanthanide complexes, the catalytic behavior of these heterobimetallic lanthanide–potassium complexes on the amidation reaction of aldehydes with amines was tested.

The amidation of benzaldehyde **1a** with aniline **2a** was first examined as a model reaction catalyzed by the lanthanide heterobimetallic complexes **1–4**, and the results are summarized in Table 2. It can be seen that all of these heterobimetallic lanthanide–potassium complexes can catalyze this transformation to yield the amide **3aa** in moderate to excellent yields at 25 °C with 10 mol % catalyst loading (Table 2, entries 1–4). The lanthanum–potassium complex **1** gave the highest yield under the same reaction conditions, and the yield for these complexes follows the trend  $\text{Yb} < \text{Nd} < \text{La}$ , which is consistent with the trend of their ionic radii. For comparison, the catalytic behavior of the neutral ytterbium complex  $(\text{MBMP})\text{Yb}(\text{MBMPH})(\text{THF})_2$  (**5**) for this reaction was also tested.<sup>16</sup> It was found that the yield is only 11% using complex **5** as the catalyst even when the loading of the catalyst is increased to 30% (Table 2, entry 6). These results revealed that the heterobimetallic structure plays a key role in this reaction system. Using complex **1** as the catalyst, the yield increases with an increase in catalyst loading (Table 2, entries 1, 7, and 8), and the reaction with 10 mol % of complex **1** can afford a good yield (Table 2, entry 1). The reaction proceeds smoothly at room temperature (25 °C) to give **3aa** in good isolated yield, and the yield increases slightly when the reaction temperature increases to 65 °C (Table 2, entries 1 and 9).

The generality and scope of the amidation reaction catalyzed by complex **1** were also investigated, and the results are listed in Table 3. It can be seen that all of the reactions proceeded smoothly to produce the corresponding amides in good to excellent isolated yields. Electronic effects of the aromatic aldehydes have a significant effect on the amidation reactions. The aromatic aldehydes with electron-withdrawing groups at the *p*-position on the phenyl ring give higher yields in comparison with the aldehydes with electron-donating groups, which is consistent with the trend reported in the literature.<sup>4c,d</sup> The properties of the amines also affect the reaction. The yield for the reactions of aldehydes with secondary alkyl amines is higher than those for the reactions with primary aromatic amines under the same reaction conditions. The reactions of aniline with aldehydes give the amide in good isolated yield (Table 3, entries 1–4), whereas the reactions of secondary alkyl amines with aldehydes (except *p*-methylbenzaldehyde) give the corresponding amides with almost quantitative yields under the same reaction conditions. It is worth noting that the amidation of aldehydes with secondary cyclic amines such as pyrrolidine and piperidine proceeded well with the present catalyst to afford the corresponding acylamides in excellent yields (Table 3, entries 9–16). Although the electron-rich *p*-methylbenzaldehyde is less active, the reaction with pyrrolidine can still afford the corresponding amide in 82% isolated yield (Table 3, entry 12). Furthermore, the amidation reactions of

*p*-methylbenzaldehyde with secondary cyclic amines give higher yields than that with linear secondary amines (Table 3, entries 8, 12, and 16), which is different from the catalytic systems reported in the literatures.<sup>15</sup>

## CONCLUSION

In summary, four heterobimetallic lanthanide–potassium complexes stabilized by carbon-bridged bis(phenolate) ligands have been synthesized, and their structural features are provided. It was found that the ionic radii of lanthanide metals have a profound effect on the structures of these complexes. These heterobimetallic complexes are efficient catalysts for the amidation reactions of aldehydes with amines under mild reaction conditions. The new catalysts show good activity and a wide range of substrates to produce amides in good to excellent yields under mild reaction conditions.

## ASSOCIATED CONTENT

**S** Supporting Information. Crystallographic data for complexes **1** to **4** in CIF format and the NMR spectra for complexes **1–4** and all amidation products in PDF format. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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