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Anionic Bridged Bis(amidinate) Lithium Lanthanide Complexes: Efficient Bimetallic Catalysts for Mild Amidation of Aldehydes with Amines

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Abstract: Anionic bridged bis(amidinate) lithium lanthanide complexes have been found to be efficient catalysts for the amidation of aldehydes with amines under mild conditions. The activity follows the order: yttrium < neodymium < europium ≈ ytterbium. The catalysts are available for the formation of benzamides derived from pyrrolidine, piperidine, and morpholine with good to excellent yields. In comparison with the corresponding neutral complexes, the anionic complexes show higher activity and a wider range of scope for the amines. A cooperation of the lanthanide and lithium metals in this process is proposed to contribute to the high activity of the present catalyst.

Keywords: aldehydes; amides; amination; amines; lanthanides

Introduction

The applications of lanthanide complexes in C–N bond formation have became one of the most interesting topics in organic syntheses and lanthanide chemistry.[1] Various lanthanide complexes have been disclosed to be efficient catalysts for these transformations, including hydroamination/cyclization,[2] guanylation of amines,[3] cyclotrimerization of benzonitrile,[4] addition of amines to nitriles,[5] homocoupling of isocyanides with terminal alkynes,[6] Mannich-type reaction of hydroxy ketones,[7] monoaddition of terminal alkynes to nitriles[8] etc.

The synthesis of aromatic and aliphatic amides is of significant importance in organic synthesis as amides constitute an essential motif in polymers, natural products and pharmaceuticals.[9] The direct amidation of aldehydes with amines is the most desired approach to amides as economical and available starting materials. Various successful examples have been reported for this process.[10–14] Recently, a direct amidation from alcohols and amines *via* aldehyde intermediates was also reported.[15] However, all the approaches published require harsh conditions including the use of peroxide[10] or equivalent alkali metal amides *via* the Cannizzaro reaction.[16] Very recently, the pioneer work by Seo and Marks has explored that the homoleptic lanthanide amido complexes $Ln[N(SiMe_3)_2]_3$ are efficient catalysts for the amidation of aldehydes with amines under mild conditions without the use of peroxide. But the catalysts are not successful for the amidation of aldehydes with secondary cyclic amines.[17] Thus, the development of new lanthanide catalysts with high activity and broad scope of substrates is still required in amide synthesis.

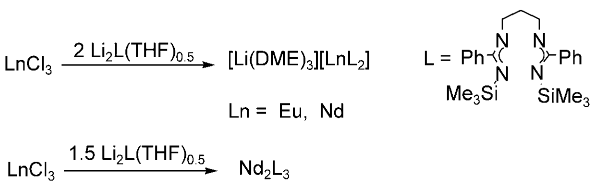
Multinuclear metal complexes offer a possibility of unique and more selective catalytic transformations by facilitating cooperative effects between active sites, and heterobimetallic complexes of a lanthanide and an alkali metal have been well known to be versatile catalysts, which enable transformations that have never been possible using monometallic catalysts of the lanthanides.[1a] These successful examples of bimetallic catalysts in homogeneous catalyses prompted us to seek new efficient bimetallic catalysts for the mild amidation of aldehydes with amines. Here we report a new class of bimetallic catalyst $[Li(DME)_3][LnL_2]$ {L = $[Me_3SiNC(Ph)N(CH_2)_3NC(Ph)NSiMe_3]$},[18] which shows high activity and a broad scope of reactants including secondary cyclic amines.

Results and Discussion

Anionic complexes Eu **III** and Nd **IV**, and neutral complex Nd **VII** were synthesized by the metathesis reaction of the corresponding chloride with the lithium salt according to the literature method[18] as shown in Scheme 1. The complexes of Eu and Nd were further characterized by X-ray crystal structure analysis.[19] The molecular structures, which are isostructural to those of the analogous with Yb and Y,[18] are shown in Figure 1. Both complexes are composed of a separated ion-pairs: an anion $[LnL_2]^-$ and a cation $[Li(DME)_3]^+$ (DME = 1,2-dimethoxylethane). Complex **VII** was characterized by elemental analysis and IR spectroscopy.

The other complexes were prepared by a published method,[18] and the complexes used here are listed in Scheme 2.

With the complexes in hand, the catalytic activity of these complexes for the reaction of benzaldehyde **1a** with *N*-methylbenzylamine **2a** was first examined at 25 °C with 2 mol% catalyst loading based on metal. For comparison, the activity of Li_2L was also tested. As shown in Table 1, all complexes, except the chlo-



Scheme 1.

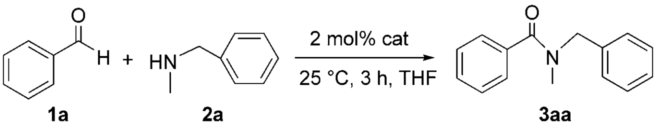
$[Li(DME)_3][LnL_2]$ Ln = Yb **I**, Y **II**, Eu **III**, Nd **IV**

$[Ln_2L_3]$ Ln = Yb **V**, Y **VI**, Nd **VII**

$LYbCl(THF)_2$ **VIII**

Scheme 2.

Table 1. Amidation of **1a** with **2a** catalyzed by various complexes.[a]



Entry	Molar ratio (**1a**/**2a**)	Catalyst	mol% of catalyst[b]	Time [h]	Yield [%][c]
1	3:1	**I**	2	3	98
2	3:1	**II**	2	3	78
3	3:1	**III**	2	3	96
4	3:1	**IV**	2	3	86
5	3:1	**V**	1	3	76
6	3:1	**VI**	1	3	52
7	3:1	Li_2L	2	3	34
8	3:1	**VIII**	2	3	2

[a] Amine was first added to the catalyst solution, and after 30 min, aldehyde was added.

[b] Based on lanthanide metal.

[c] Isolated yield based on amine.

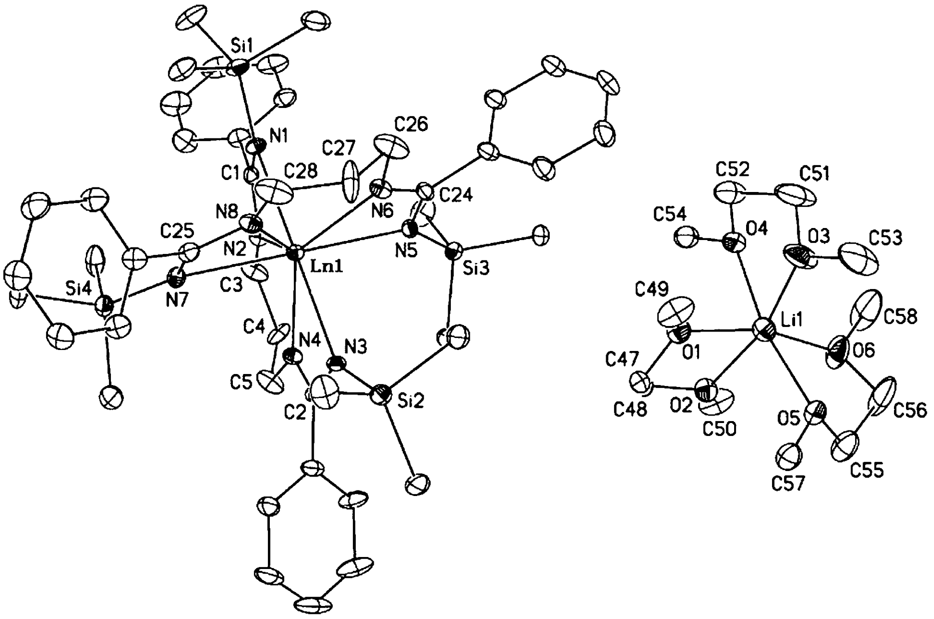
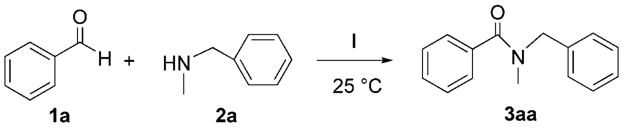


Figure 1. X-ray crystal structures of **III** (*left*) and **IV** (*right*).

Table 2. Optimization of the amidation of **1a** with **2a** catalyzed by **I**.[a]



Entry	Molar ratio (**1a**/**2a**)	Catalyst	mol% of catalyst[b]	Time [h]	Yield [%][c]
1	1:1	THF	2	3	39
2	2:1	THF	2	3	75
3	3:1	THF	2	3	98
4[d]	3:1	THF	2	3	80
5	3:1	THF	1	3	55
6	3:1	THF	0.5	3	15
7	3:1	THF	2	2	85
8	3:1	toluene	2	3	85
9	3:1	–	2	3	68

[a] Amine was first added to the catalyst solution, and after 30 min, aldehyde was added.

[b] Based on lanthanide metal.

[c] Isolated yield based on amine.

[d] Aldehyde was first added to the catalyst solution, after 30 min, amine was added.

ride **VIII**, serve as the catalysts for this transformation yielding the desired product **3aa** in moderate to excellent yields depending on the complexes used after 3 h. Anionic lanthanide complexes containing lithium metal show the highest activity, while the lithium complex Li_2L is the least active one (Table 1, entries 1–8). Lanthanide metals have a remarkable effect on the activity, and the active order of $Y < Nd < Eu \approx Yb$ is observed (Table 1, entries 1–4).

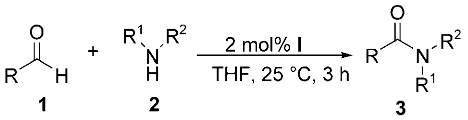
Optimization experiments were then conducted using **I**. The results indicate that an excess of aldehyde (3 equiv.) is required for getting the product in a high yield (Table 2, entries 1–3). The feeding sequence of reactants is crucial. Good yields can only be obtained with the following sequence: the amine is first added into a catalyst solution for 30 min then the aldehyde is added. Otherwise, the yield drops down (Table 2, entries 3 and 4). The yield increases with an increase in catalyst loading (Table 2, entries 3, 5 and 6), and the reaction with 2 mol% of **I** can afford excellent results (Table 2, entry 3). THF is a better solvent than toluene (Table 2, entries 3 and 8). The reaction proceeds in solvent-free conditions affording **3aa** in low yield (Table 2, entry 9). The reaction carried out in THF at 25 °C using 2 mol% of **I** affords the product in 85% yield for 2 h and in almost quantitative yield for 3 h (Table 2, entries 3 and 7).

With the reaction conditions optimized (Table 2, entry 3), we then screened various aldehydes and amines to explore the generality and scope of the reaction (Table 3).

All the reactions proceeded smoothly to afford the corresponding amides in good to excellent yields. The aromatic aldehydes with electron-withdrawing groups at the *p*-position on the ring give higher yields relative to the aldehydes with electron-donating groups (Table 3, entries 1–4 and 9–19). The reaction with a primary aromatic amine (aniline) proceeded smoothly to give the amide in good yield. However, aniline derivatives with either electron-withdrawing or electron-donating groups on the ring give lower yields versus unsubstituted aniline (Table 2, entries 5–7). The reaction with benzylamine also proceeds, however, affording the product in low yield, which may be attributed to catalyst deactivation by the water produced *via* imine formation. The yield can be improved by using 4 mol% of catalyst (Table 3, entry 8). The formation of several benzamides derived from pyrrolidine **2f**, piperidine **2g** and morpholine **2h**, with **1a**, respectively, occurs with good to excellent yields and is completed within 3 h at 25 °C using 2 mol% **I**. For example, *p*-chlorobenzaldehyde, **1c**, is almost quantitatively converted to *N*-(*p*-chlorobenzoyl)pyrrolidine, **3cf** (Table 3, entry 11), and **1a** is transformed to the corresponding benzoylpyrrolidine **3af** in 90% yield (Table 3, entry 9). In comparion with the yields obtained with the homoleptic $Ln[N(SiMe_3)_2]_3$ catalyst reported[17](Table 3, entry 20), the present catalyst is more efficient for this amidation. The reaction with an electron-rich aromatic aldehyde is less active and affords lower yield (Table 3, entry 12). We are pleased to find that the bimetallic catalyst can also afford benzoylpiperidines **3ag–3cg**, in 93–96% yields (Table 3, entries 13–15) and benzoylmorpholines **3ah–3ch** in 85–95% yields (Table 3, entries 17–19).

The desired results obtained for the amidation of aldehydes with secondary cyclic amines using the present catalyst prompted us to re-examine the activity of the corresponding monometallic complexes **V**–**VII** to probe the cooperative effect of lithium and lanthanide metals in the amidation reaction. The reaction of **1a** with **2f** was chosen as a probe reaction (Table 4). For comparison, the same reactions with Li_2L and with a mixture of Li_2L and **VII**, respectively, were also examined (Table 4, entries 4 and 8). The reactions with monometallic complexes **V**, **VI**, and **VII** affords the amide in yields of around 30% (Table 4, entries 1–3), whereas the reactions with anionic complexes (**I**, **II**, **IV**) provide the amide in much higher yields (90–61%, Table 4, entries 5–7). The lithium complex Li_2L was not efficient under the same conditions (Table 4, entry 4). A mixture system of Li_2L and **VII** afforded the product in the yield almost equal to the sum of the values obtained with respective **VII** and Li_2L and lower than that for the system with the anionic complex (Table 4, entries 5 and 8). The high activity of the anionic complex may be attributed to a cooperation effect resulted from lanthanide and lithi-

Table 3. Complex **I**-catalyzed amidation of aldehydes with amines.[a]



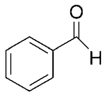
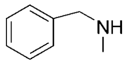
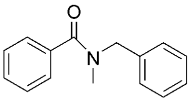
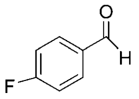
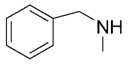
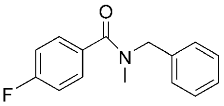
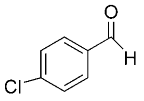
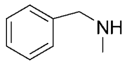
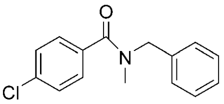
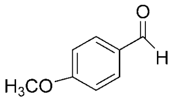
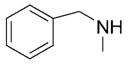
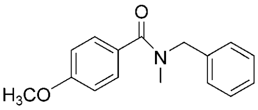
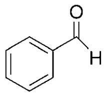
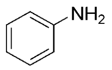
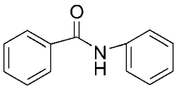
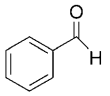
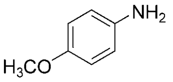
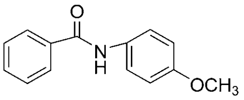
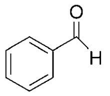
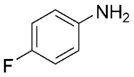
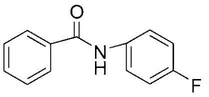
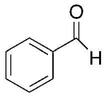
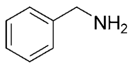
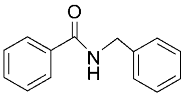
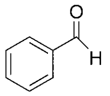
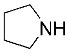
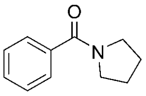
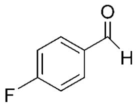
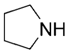
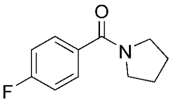
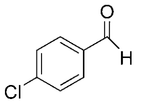
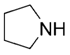
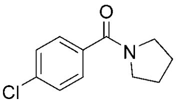
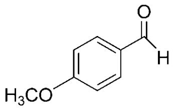
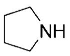
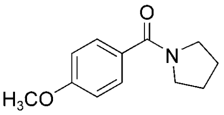
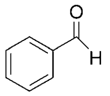
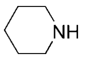
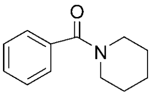
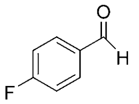
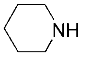
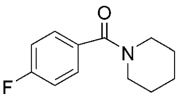
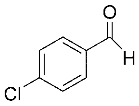
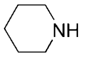
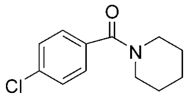
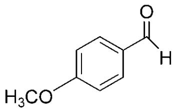
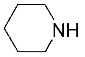
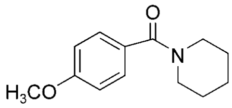
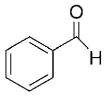
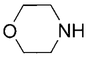
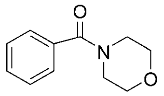
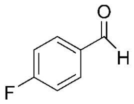
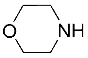
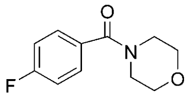
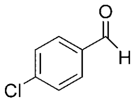
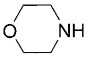
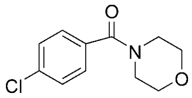
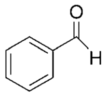
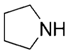
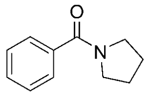
Entry	Aldehyde	Amine	Amide	Yield [%][b]
1	**1a** 	**2a** 	**3aa** 	96
2	**1b** 	**2a** 	**3ba** 	99
3	**1c** 	**2a** 	**3ca** 	97
4	**1d** 	**2a** 	**3da** 	70 (88[c])
5	**1a** 	**2b** 	**3ab** 	80
6	**1a** 	**2c** 	**3ac** 	55
7	**1a** 	**2d** 	**3ad** 	50
8	**1a** 	**2e** 	**3ae** 	55 (80[c])
9	**1a** 	**2f** 	**3af** 	90
10	**1b** 	**2f** 	**3bf** 	98
11	**1c** 	**2f** 	**3cf** 	97
12	**1d** 	**2f** 	**3df** 	56
13	**1a** 	**2g** 	**3ag** 	93
14	**1b** 	**2g** 	**3bg** 	96

Table 3. (Continued)

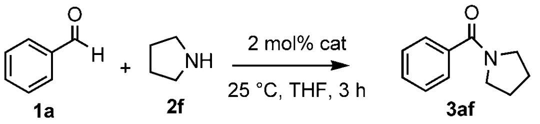
Entry	Aldehyde		Amine		Amide		Yield [%][b]
15	**1c**		**2g**		**3cg**		94
16	**1d**		**2g**		**3dg**		60
17	**1a**		**2h**		**3ah**		85
18	**1b**		**2h**		**3bh**		89
19	**1c**		**2h**		**3ch**		95
20	**1a**		**2f**		**3af**		38[d]

[a] Amine was first added to the catalyst solution, and after 30 min, aldehyde was added.
[b] Isolated yield based on amine.
[c] 4 mol% **I**.
[d] Ref.[17]

um metals in amidation reaction of aldehydes with amines.

According to the mechanism of amidation proposed by Seo and Marks, the active species for amidation is an amino-alkoxide, which is formed by the reaction of the precatalyst the amido complex with aldehyde *in situ*, and then regenerated by the reaction of alkoxide with amino alcohol.[17] So, alcohols are one of the by-products, as the aldehyde in this process acts as not only a reactant but also as an oxidant. The other by-product suggested by them is esters, which are formed by the Tishchenko reaction catalyzed by lanthanide alkoxide, as homoleptic lanthanide amide has been proven to be a highly efficient catalyst for the Tishchenko reaction.[20] In our case, the alcohol is really detected by ^{1}H NMR in a yield as high as that of amide (see Supporting Information), and the ester is also found as a by-product. To further assess the catalytic behavior of the present catalysts, the activity of complexes **I** and **V**, respectively, for the Tishchenko reaction of **1a** was then examined under the same conditions as those for Table 5. After 3 h the ester was isolated in the yields of 37% for **I** and 25% for **V**, indicating **I** and **V** are much less efficient than Ln(NTMS)$_3$ reported[20] for the Tishchenko reaction. Then, the reaction of benzyl benzoate with 1 equivalent of **2f** in the presence of 2 mol% of **I** and **V**, and without catalyst, respectively, was tested to see whether the amide can be formed by this transformation. After work-up amide **3af** was isolated in 10%, 6%, and 2% yields, respectively, at 25 °C for 3 h, indicating that the transformation goes sluggishly. Thus, the amount of amide formed from the reaction of esters with amines need not be considered during the amidation of aldehydes with amines.

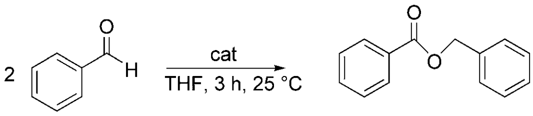
Table 4. Activity for amidation of **1a** with **2f** catalyzed by monometallic and bimetallic catalysts.[a]



Entry	Catalyst	Yield [%][b]	Entry	Catalyst	Yield [%][b]
1	**V**	27	5	**I**	90
2	**VII**	24	6	**IV**	78
3	**VI**	20	7	**II**	61
4	Li$_2$L	25	8[c]	**VII**+Li$_2$L	42

[a] Amine was first added to the catalyst solution, and after 30 min, aldehyde was added.
[b] Isolated yield based on amine.
[c] 2 mol% **VII**+ 2 mol% Li$_2$L.

Table 5. Activity for Tishchenko reaction catalyzed by **I** and **V**.



Entry	Catalyst	mol% of catalyst	Time [h]	Yield [%][a]
1	**I**	2	3	37
2	**V**	1	3	25

[a] Isolated yield based on aldehyde.

According to the above results and the fact that the activity of the anionic complex is much higher than that of a mixture of the corresponding neutral complex and the lithium complex (Table 4, entries 5 and 8), it is supposed that in our case the mechanism is quite similar to that suggested by Seo and Marks,[17] but the precatalyst, the anionic amido complex, is assumed to form by the reaction of anionic complex with amine, and the bimetallic amino-alkoxide **A** is the active species. The active species is formed by the reaction of the anionic amido complex with the aldehyde and regenerated by the reaction of the bimetallic alkoxide **B** with the amino alcohol as shown in Scheme 3. The cooperation of lanthanide and lithium metals makes the substrates more reactive in both reactions of **A** with aldehydes and of **B** with amino alcohols. As a result the bimetallic catalyst is more efficient relative to the monometallic one.

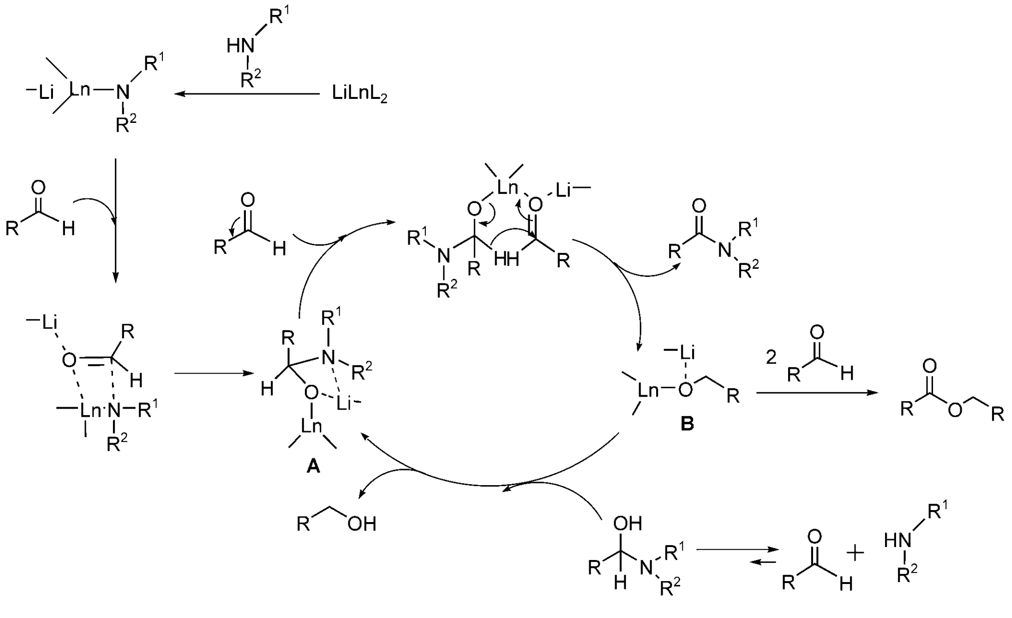
Conclusions

In summary, we have developed anionic bridged bis(amidinate) lithium lanthanide complexes as a new class of bimetallic catalysts for the amidation of aldehydes with amines. The new catalysts show high activity and wide range of scope to produce amides in good to excellent yields under mild conditions. A cooperation effect between the lanthanide and the alkali metal was proposed.

Experimental Section

General Remarks

All manipulations and reactions were performed under a purified argon atmosphere using standard Schlenk techniques. Solvents were degassed and distilled from sodium benzophenone ketyl prior to use. [Li(DME)$_3$] [LnL$_2$] (Ln = Yb **I**, Y **II**), Ln$_2$L$_3$ (Ln = Yb **V**, Y **VI**,) and LYbCl(THF)$_2$ (**VIII**) [L = Me$_3$SiNC(Ph)N(CH$_2$)$_3$NC(Ph)NSiMe$_3$] were prepared according to the literature.[18] All aldehydes and amines were predried, sublimed, recrystallized or distilled before use. Melting points were determined in sealed Ar-filled capillary tubes, and are not corrected. ^{1}H and ^{13}C NMR spectra were recorded on a Unity Inova-400 spectrometer. Chemical shifts (δ) were reported in ppm. HR-MS were recorded on a GCT-TOF instrument.



Scheme 3.

General Procedure for the Synthesis of Complexes $[Li(DME)_3][LnL_2]$(Ln=Nd, Eu) (Taking $[Li(DME)_3][NdL_2]$ (IV) as an Example)

A stirred suspension of $NdCl_3$ (0.37 g, 1.5 mmol) in THF (20 mL) was treated with $LLi_2(THF)_{0.5}$ (1.41 g, 3 mmol) in THF (15 mL). The reaction mixture was stirred at room temperature for 48 h, and the solvent was removed under vacuum. The residue was extracted with toluene (40 mL) and the volume of the extract was reduced to 10 mL followed by an addition of DME (1 mL). Cooling to 0 °C afforded **IV** as light-blue crystals; yield: 1.14 g (60%): mp 186–189 °C. IR (KBr pellet): $\nu = 2961$ (m), 1625 (m), 1540 (m), 1487 (m), 1446 (m), 1374 (m), 1250 (w), 1190 (w), 980 (w), 903 (w), 833 (w), 779 (w), 700 cm^{-1} (m); anal. calcd. for $C_{58}H_{98}LiN_8O_6Si_4Nd$ (MW: 1266.98): C 54.98, H 7.80, N 8.84, Nd 11.38%; found: C 54.04, H 7.35, N 9.47, Nd 11.54%. Monoclinic, $P3_1$ $a = 15.7981(11)$ Å, $b = 15.7981(11)$ Å, $c = 24.2228(19)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$, $V = 5235.6(7)$ Å^3, $Z = 3$, $D_x = 1.206$ g cm^{-3}, 12717 independent reflections. $R = 0.0723$ and wR_2 was 0.1873.

General Procedure for the Synthesis of Complex Nd_2L_3 (VII)

A solution of $LLi_2(THF)_{0.5}$ (1.41 g, 3 mmol) in THF (30 mL) was added to a stirring suspension of $NdCl_3$ (0.50 g, 2 mmol) in THF (25 mL). Complex **VII** was obtained as blue crystals by the published procedure;[18] yield: 0.79 g (48%). IR (KBr pellet): $\nu = 2958$ (m), 1633 (m), 1601 (m), 1537 (m), 1383 (m), 1210 (w), 1058 (w), 890 (w), 839 (w), 781 (w), 756 (w), 700 cm^{-1} (m); anal. calcd. for $C_{73}H_{112}N_{12}O_2Si_6Nd_2$ (MW: 1646.74): C 53.24, H 6.86, N 10.21, Nd 17.52; found: C 53.77, H 7.26, N 9.87, Nd 17.04%.

General Procedure for the Synthesis of Amides from the Reaction of Aldehydes with Amines Catalyzed by Complex I (Product *N*-Benzyl-*N*-methylbenzamide 3aa as an Example)

A 30-mL of Schlenk flask was charged with the solution of complex **I** (2.00 mL, 0.02 mmol). *N*-Methylbenzylamine was added (0.13 mL, 1.00 mmol), after stirring for 0.5 h, benzaldehyde was then added (0.3 mL, 3.00 mmol). The resulting mixture was stirred at 25 °C for 3 h, filtered through a small plug of silica gel to remove the catalyst. The crude product was purified by column chromatography: (ethyl acetate: petroleum ether = 1:5); yield: 216 mg (98%).

General Procedure for the Synthesis of Benzyl Benzoate from the Reaction of Benzaldehyde Catalyzed by Complex I and V (Taking I as an Example)

A 30-mL of Schlenk flask was charged with the solution of complex **I** (2.00 mL, 0.02 mmol). Benzaldehyde was then added (0.2 mL, 2.00 mmol). The resulting mixture was stirred at 25 °C for 3 h, filtered through a small plug of silica gel to remove the catalyst. The crude product was purified by column chromatography: (ethyl acetate:petroleum ether = 1:10); yield: 78 mg (37%).

General Procedure for the Synthesis of Amides from the Reaction of Pyrrolidine with Benzyl Benzoate Catalyzed by Complex I and V (Taking I as an Example)

A 30-mL of Schlenk flask was charged with the solution of complex **I** (2.00 mL, 0.02 mmol). pyrrolidine was added (0.08 mL, 1.00 mmol), after stirring for 0.5 h, benzyl benzoate was then added (0.18 mL, 1.00 mmol). The resulting mixture was stirred at 25 °C for 3 h, filtered through a small plug of silica gel to remove the catalyst. The crude product was purified by column chromatography: (ethyl acetate: petroleum ether = 1:3); yield: 18 mg (10%).

Acknowledgements

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