

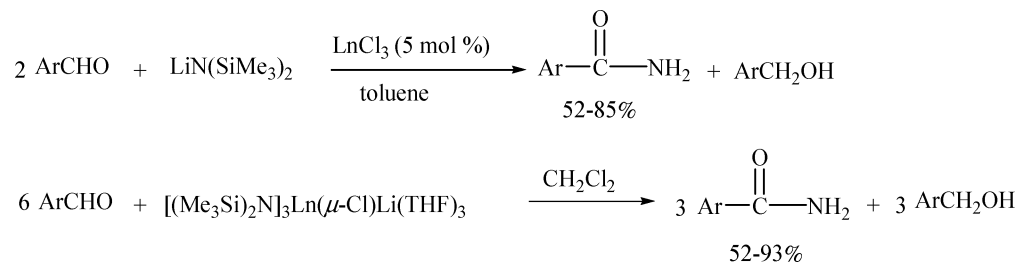
Cannizzaro-Type Disproportionation of Aromatic Aldehydes to Amides and Alcohols by Using Either a Stoichiometric Amount or a Catalytic Amount of Lanthanide Compounds

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Aromatic aldehydes can be directly converted to the corresponding amides and alcohols in good to excellent yields by the treatment of aromatic aldehydes with lithium amide $\text{LiN}(\text{SiMe}_3)_2$ in the presence of catalytic lanthanide chlorides LnCl_3 or by the treatment of aromatic aldehydes with a stoichiometric amount of lanthanide amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ at ambient temperature. The effects of solvents, substituents on the phenyl ring, and lanthanide metals on the reaction have been examined. The mechanism of the disproportionation reaction was proposed based on the experimental results.

Introduction

Aromatic and aliphatic amides are of significant importance in organic chemistry as integral parts of polymers, natural products, and pharmaceuticals. In general, amides are synthesized from amines and activated carboxylic acid derivatives with the same oxidation level as the resulting products.¹ Another attractive method is the aminocarbonylation of olefins with carbon monoxide and amines in the presence of late transition metal catalysts.² So far, very few direct methods for the transformation of aldehydes to amides have been reported. One method is the Beckmann rearrangement,³ which has been long

recognized as an extremely valuable and versatile method for the preparation of amides or lactams. But the Beckmann rearrangement needs high temperature or the use of strong Bronsted or Lewis acids.⁴ Other methods include a tandem reaction through which the amides are produced by the treatment of aldehydes with iodine and H_2O_2 ⁵ or the direct oxidative amination of aldehydes,⁶ which requires the use of a stoichiometric or an excess amount of expensive transition metals such as palladium and ruthenium as catalysts. Ishihara and Yano recently reported the synthesis of carboxamides through a Cannizzaro reaction by using lithium *N,N*-diisopropylamide (LDA) as a catalyst, and Abaee et al. found that the Cannizzaro reaction can be facilitated by a magnesium bromide ethyl etherate and trimethylamine system.⁷

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Recently, lanthanide amides $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ ($\text{Ln} = \text{Y}$, lanthanide), which can either be prepared from a simple one-step synthesis in very high yields or are commercially available, have received much attention for their applications as active catalysts for Tishchenko reactions,⁸ intramolecular alkene and alkyne hydroaminations,⁹ hydrosilylations,¹⁰ and ring-opening polymerizations of ϵ -caprolactone and δ -valerolactone.¹¹ We have recently reported that lanthanide amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ can work as efficient catalysts for the aldol-condensation reaction¹² and the stereoregularity of polymeric methyl methacrylate.¹³ The lanthanide amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ have been proven to be valuable starting materials in lanthanide chemistry because of the facile cleavage of the silylamine group.¹⁴ As part of our continuous interests in developing lanthanide compounds as catalysts or initiators in organic synthesis, we have tried to study the catalytic activity of lanthanide amides on the Baylis–Hillman reaction of aromatic aldehydes with methyl acrylate. To our surprise, the corresponding aromatic amides and alcohols, instead of the expected Baylis–Hillman reaction products, were isolated.

In this paper, we wish to report a Cannizzaro-type disproportionation reaction of aromatic aldehydes to the corresponding amides and alcohols by using stoichiometric or catalytic amounts of the lanthanide compounds. The reaction provides a very simple and efficient method for the preparation of aromatic amides.

Results and Discussion

To select a favorable reaction condition, the reaction of 2 equiv of 4-nitrobenzaldehyde with lithium amide $\text{LiN}(\text{SiMe}_3)_2$ catalyzed by YCl_3 under different conditions was examined (Table 1). At first, different solvents such as dichloromethane, benzene, toluene, diethyl ether, and THF were used to initiate the reaction. It was found that toluene and benzene were the most suitable solvents for the reaction. The isolated yield of the amide was only 40% when THF was used as a solvent. No amide could be obtained when the reaction was performed in CH_2Cl_2 , which may be a result of the lithium amide $\text{LiN}(\text{SiMe}_3)_2$ reacting with the CH_2Cl_2 . A lower conversion was observed upon heating the reaction mixture to 70 °C or from performing the reaction at 0 °C when the reactions were carried out in toluene. The mole ratios of the catalyst to 4-nitrobenzaldehyde have some influences on the isolated yields of the reaction. For example, the yields changed from 78% to 85% as the catalyst to lithium amide mole ratios were changed from 2% to 10% when the reaction was performed in toluene at room temperature. The experimental data indicated that the reaction was not

TABLE 1. Conditions and Results of the Reaction

$$2 \text{ O}_2\text{N}-\text{C}_6\text{H}_4-\text{CHO} + \text{LiN}(\text{SiMe}_3)_2 \xrightarrow[2. \text{H}_2\text{O}]{1. \text{YCl}_3 (2-10 \text{ mol } \%)}$$

ratio ^a	T (°C)	solvent	cat. (%)	t (d)	yield of 2g ^b (%)
1:1	rt	toluene	5	2	40
2:1	rt	toluene	5	2	85
3:1	rt	toluene	5	2	85
2:1	rt	C ₆ H ₆	5	2	85
2:1	rt	Et ₂ O	5	2	65
2:1	rt	THF	5	2	40
2:1	rt	CH ₂ Cl ₂	5	2	0
2:1	rt	hexane	5	2	32
2:1	rt	toluene	0	2	47
2:1	rt	toluene	2	2	78
2:1	rt	toluene	10	2	80
2:1	0	toluene	5	2	48
2:1	70	toluene	5	2	40
2:1	rt	toluene	5	1	75
2:1	rt	toluene	5	3	88

^a Ratio of aldehyde/lithium amide. ^b Isolated yield based on the lithium amide.

completed when the reaction time was less than 2 days. Only a little increase in yield was observed when the reaction was prolonged. From Table 1, it could also be found that the amount of aldehyde had a remarkable influence on the formation of the amide, and this provided a useful clue to understanding the reaction mechanism. The results showed that only a 40% yield of amide could be obtained when the aldehyde to lithium amide ratio was 1:1. A satisfactory yield of amide was obtained when the ratio of aldehyde to lithium amide reached 2:1. The yield of amide had almost not been changed when the aldehyde to lithium amide ratio was 3:1. Thus, the suitable condition was selected by the treatment of 2 equiv of the aldehyde with lithium amide $\text{LiN}(\text{SiMe}_3)_2$ catalyzed by 5% YCl_3 in toluene at room temperature for 2 days.

A variety of aromatic aldehydes could be successfully converted to the corresponding amides in good to excellent yields (Table 2), and almost the same amount of the corresponding alcohols could be isolated as well. As shown in Table 2, whether the R groups on the phenyl ring were electron-donating groups (such as $\text{CH}_3\text{O}-$, CH_3- , $(\text{CH}_3)_2\text{N}-$) or the R groups on the phenyl ring were electron-withdrawing groups (such as $\text{O}_2\text{N}-$, $\text{F}_3\text{C}-$, $\text{X}-$), the isolated yields were satisfactory. But the yields of the corresponding amides having electron-withdrawing groups were higher than those having electron-donating groups even though the reaction time was prolonged. For example, when the aldehyde was the 4-nitrobenzaldehyde, the yield of the product could reach as high as 85%, but when the substituents were 4- $\text{CH}_3\text{O}-$ or 4- $(\text{CH}_3)_2\text{N}-$, the yields of the products were only 58 or 52%, respectively, indicating electronic effects from the substituted groups on the reactions.

The influence of the rare earth metal on the yields of the products was also investigated, and the results are given in Table 3. It was found that lanthanide chlorides generally had good catalytic activities on the reaction, but the catalytic activity of PrCl_3 was relatively poor compared to that of other LnCl_3 catalysts. The results are in accordance with the Lewis acidity of the Ln^{3+} cations.¹⁵ The results (Tables 2 and 3) are also in

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TABLE 2. Results of Reactions of Aldehydes with Lithium Amide LiN(SiMe₃)₂ Catalyzed by YCl₃^a

$$2 \text{ Ar-CHO} + \text{LiN(SiMe}_3)_2 \xrightarrow[2. \text{ H}_2\text{O}]{1. \text{ YCl}_3 (5 \text{ mol } \%)}$$

$$\text{Ar-C(=O)-NH}_2 + \text{ArCH}_2\text{OH}$$

Ar—	<i>t</i> (d)	product of 2	yield of 2 ^b (%)	product of 3	yield of 3 ^b (%)
C ₆ H ₅ —	3	2a	56 (18) ^c	3a	62 (21) ^c
4-CH ₃ C ₆ H ₄ —	3	2b	62	3b	65
4-CH ₃ OC ₆ H ₄ —	3	2c	58	3c	60
4-ClC ₆ H ₄ —	2	2e	76	3e	78
4-BrC ₆ H ₄ —	2	2f	82	3f	78
4-O ₂ NC ₆ H ₄ —	2	2g	85	3g	85
4-F ₃ CC ₆ H ₄ —	2	2j	83	3j	81
4-Me ₂ NC ₆ H ₄ —	3	2k	52	3k	50

^a Reaction conditions: solvent, toluene; temperature, room temperature.
^b Isolated yield based on the lithium amide. ^c Isolated yields in the absence of YCl₃ are shown in parentheses.

TABLE 3. The Influence of the Lanthanide Metal on the Reaction^a

$$2 \text{ O}_2\text{N-C}_6\text{H}_4\text{-CHO} + \text{LiN(SiMe}_3)_2 \xrightarrow[2. \text{ H}_2\text{O}]{1. \text{ LnCl}_3 (5 \text{ mol } \%)}$$

$$\text{O}_2\text{N-C}_6\text{H}_4\text{-C(=O)-NH}_2 + \text{O}_2\text{N-C}_6\text{H}_4\text{-CH}_2\text{OH}$$

Ln	none	Y	Pr	Nd	Sm	Eu	Dy	Ho	Yb
yield of 2g ^b (%)	47	85	60	82	78	70	75	80	85

^a Reaction conditions: reaction time, 2 d; solvent, toluene; temperature, room temperature. ^b Isolated yield based on the lithium amide.

agreement with the electronic effects of the substituents on the phenyl ring, suggesting that the higher the Lewis acidity of the catalysts and the more electronegative the substituents on the phenyl ring are, the more favorable are the transformations of aldehydes to amides and alcohols.

To collect some evidence for understanding the reaction mechanism, several reactions were performed. A lower yield of the product was obtained when 4-nitrobenzaldehyde was treated with lithium amide LiN(SiMe₃)₂ in the absence of LnCl₃, indicating that the reaction might involve the cooperation of the lanthanide metal. Because the reaction of lithium amide with LnCl₃ could afford the lanthanide amides Ln[N(SiMe₃)₂]₃,¹³ it was proposed that lanthanide amides Ln[N(SiMe₃)₂]₃ might be the active initiators. To test this hypothesis, a reaction of yttrium amide Y[N(SiMe₃)₂]₃ with 6 equiv of 4-nitrobenzaldehyde was carried out in toluene at room temperature. The amide was isolated in an 82% yield, which was almost the same as the result initiated by YCl₃. The result confirms that lanthanide amides Ln[N(SiMe₃)₂]₃ are the active initiators. When yttrium amide [(Me₃Si)₂N]₃Y(μ-Cl)Li(THF)₃ instead of Y[N(SiMe₃)₂]₃ was used, the isolated yield of amide could reach 88%. Thus, different solvents were used to test the reaction, and good to excellent yields of products could be obtained. When the reaction was performed in CH₂Cl₂, the isolated yield of amide was as high as 93%, suggesting that lanthanide amides [(Me₃-

TABLE 4. Results of Reactions of Aromatic Aldehydes with Stoichiometric Amount of Yttrium Amide [(Me₃Si)₂N]₃Y(μ-Cl)Li(THF)₃^a

$$6 \text{ Ar-CHO} + 1 \text{ equiv. of } [(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y}(\mu\text{-Cl})\text{Li}(\text{THF})_3 \xrightarrow[2. \text{ H}_2\text{O}]{1.}$$

$$3 \text{ Ar-C(=O)-NH}_2 + 3 \text{ ArCH}_2\text{OH}$$

Ar—	solvent	<i>t</i> (d)	product of 2	yield of 2 ^b (%)	product of 3	yield of 3 ^b (%)
4-O ₂ NC ₆ H ₄ —	CH ₂ Cl ₂	2	2g	93	3g	88
4-O ₂ NC ₆ H ₄ —	C ₆ H ₆	2	2g	88	3g	80
4-O ₂ NC ₆ H ₄ —	toluene	2	2g	88	3g	80
4-O ₂ NC ₆ H ₄ —	Et ₂ O	2	2g	70	3g	72
4-O ₂ NC ₆ H ₄ —	THF	2	2g	47	3g	50
C ₆ H ₅ —	CH ₂ Cl ₂	3	2a	58	3a	62
4-CH ₃ C ₆ H ₄ —	CH ₂ Cl ₂	3	2b	68	3b	70
4-CH ₃ OC ₆ H ₄ —	CH ₂ Cl ₂	3	2c	58	3c	55
2-CH ₃ OC ₆ H ₄ —	CH ₂ Cl ₂	3	2d	57	3d	59
4-ClC ₆ H ₄ —	CH ₂ Cl ₂	2	2e	78	3e	76
4-BrC ₆ H ₄ —	CH ₂ Cl ₂	2	2f	82	3f	78
2-Furyl—	CH ₂ Cl ₂	2	2h	77	3h	70
C ₆ H ₅ CH=CH—	CH ₂ Cl ₂	3	2i	52	3i	58
4-F ₃ CC ₆ H ₄ —	CH ₂ Cl ₂	2	2j	90	3j	85
4-Me ₂ NC ₆ H ₄ —	CH ₂ Cl ₂	2	2k	56	3k	50
2,4-Cl ₂ C ₆ H ₃ —	CH ₂ Cl ₂	2	2l	91	3l	80
2,4-(Me ₂ O) ₂ C ₆ H ₃ —	CH ₂ Cl ₂	3	2m	65	3m	60

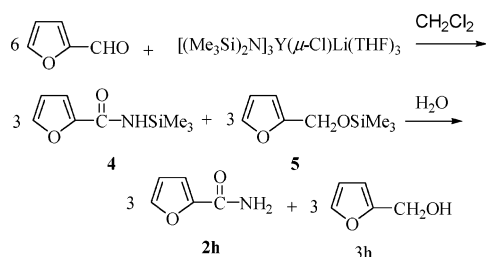
^a Reaction condition: temperature, room temperature. ^b Isolated yield based on the lanthanide amide.

Si)₂N]₃Ln(μ-Cl)Li(THF)₃ are more solvent compatible than the lithium amide (Table 4). So, it can be seen that the catalytic activity of yttrium amide [(Me₃Si)₂N]₃Y(μ-Cl)Li(THF)₃ is almost the same as that of the yttrium amide Y[N(SiMe₃)₂]₃. Therefore, a variety of aromatic aldehydes were treated with a stoichiometric amount of yttrium amide [(Me₃Si)₂N]₃Y(μ-Cl)Li(THF)₃ in CH₂Cl₂ at room temperature, and the corresponding amides and alcohols were obtained in good to high yields (Table 4). It was not surprising that the yields of **2a–m** and **3a–m** were higher than those of reactions initiated by YCl₃, especially when the aromatic aldehydes were those having electron-withdrawing groups, which are in accordance with the results of Table 2. It is noteworthy that when commercial benzaldehyde or 4-trifluoromethylbenzaldehyde was treated with a stoichiometric amount of yttrium amide [(Me₃Si)₂N]₃Y(μ-Cl)Li(THF)₃, the corresponding benzamide or 4-trifluoromethylbenzamide can be isolated in 55 and 89% yields, respectively, suggesting that a small amount of impurities in the aldehydes only have a little influence on the reaction. Other lanthanide amides showed a similar high reactivity on the reaction. For example, reactions of 1 equiv of ytterbium amide [(Me₃Si)₂N]₃Yb(μ-Cl)Li(THF)₃ or europium amide [(Me₃Si)₂N]₃Eu(μ-Cl)Li(THF)₃ with 6 equiv of 4-nitrobenzaldehyde afforded the corresponding amide in yields of 85 and 75%, respectively.

When a mixture of an electron-deficient aldehyde such as 4-nitrobenzaldehyde and an electron-rich aldehyde such as 4-methoxybenzaldehyde was treated with a stoichiometric amount of yttrium amide [(Me₃Si)₂N]₃Y(μ-Cl)Li(THF)₃, a mixture of 4-nitrobenzamide, 4-nitrobenzyl alcohol, 4-methoxybenzamide, and 4-methoxybenzyl alcohol was isolated in 48, 39, 37, and 42% yields, respectively. This result cannot explain how the hydride transfers in the reaction. To search for the reaction mechanism, another experiment was carried out to investigate the mechanism of the reaction by the treatment of 6 equiv of 2-furylaldehyde with yttrium amide [(Me₃Si)₂N]₃Y-

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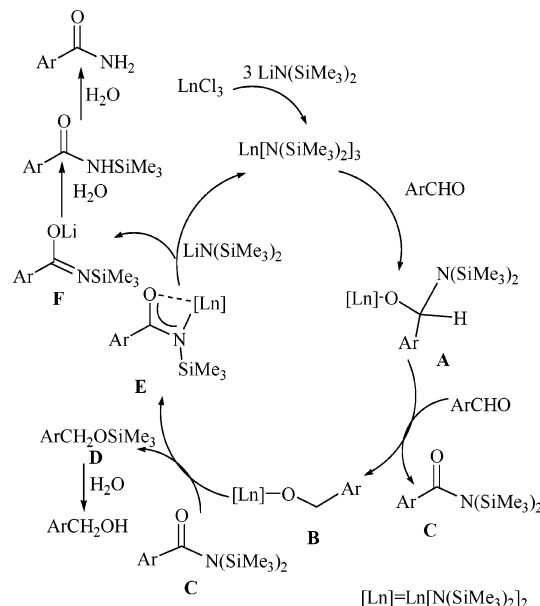
SCHEME 1



$(\mu\text{-Cl})\text{Li}(\text{THF})_3$ in CH_2Cl_2 , and the reaction mixture was examined by GCT-MS after 12 h. Almost equal amounts of *N*-trimethylsilyl furan-2-carbamide (**4**) and furfuryl trimethylsilyl ether (**5**) could be detected in GCT-MS spectra, and the corresponding furan-2-carbamide and furfuryl alcohol were isolated after hydrolysis of the reaction mixture with 1N HCl (Scheme 1, Table 4). It is interesting to note that when the aldehyde having the electron-withdrawing group on the phenyl ring, such as 4-nitrobenzaldehyde, was used in the reaction, only the corresponding amide (**2g**), not *N*-trimethylsilyl 4-nitrobenzamide, and 4-nitrobenzyl trimethylsilyl ether (**6**) could be detected by GCT-MS, indicating an electron effect on the reaction. These results suggested that a half equivalent of the aldehydes might be used to produce the amides, while the other half amount of the aldehydes might be transferred to the alcohols. To test this conclusion, 6 equiv of PhCDO was treated with 1 equiv of yttrium amide $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ in CH_2Cl_2 for 2 days. Almost the same amount of deuterated benzyl trimethylsilyl ether $\text{PhCD}_2\text{OSiMe}_3$ and *N*-trimethylsilyl benzamide PhCONHSiMe_3 were detected by GCT-MS spectra. The above results confirmed a conclusion that the hydride was transferred from one molecule of PhCHO to the second molecule of PhCHO in the reaction.

When the lanthanide amides were considered the efficient active catalysts for the Tishchenko reaction,⁸ it was assumed that the lanthanide amides might activate aldehydes to afford the corresponding Tishchenko esters, which might then react with lanthanide amides to give the corresponding amides and alcohols. To test this possibility, reactions of yttrium amide $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ with a variety of esters such as benzyl benzoate and benzyl acetate were performed under the same conditions, but no amides could be isolated, which indicated that the esters were not the intermediates of the reactions to the amides. Therefore, the *N,N*-bis(trimethylsilyl) benzamide might be the most likely intermediate.⁸ When the aromatic aldehydes were changed to aliphatic aldehydes such as phenylacetaldehyde or butyraldehyde, the expected products of the reactions could not be isolated, for the reactions gave a complex mixture.

On the basis of the above-described evidences, the following mechanism of the disproportionation reaction was proposed (Scheme 2). The reaction of lithium amide with LnCl_3 generated the lanthanide amide $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$, which is coordinated by the aldehyde. The addition of $-\text{N}(\text{SiMe}_3)_2$ in lanthanide amide $\text{Ln}[\text{N}(\text{SiMe}_3)_2]_3$ to a carbonyl group gave the intermediate **A**, which transferred a hydride to the second molecule of the aldehyde to give a lanthanide alkoxide **B** and the *N,N*-bis(trimethylsilyl) benzamide **C**. The lanthanide alkoxide **B** reacted with the *N,N*-bis(trimethylsilyl) benzamide **C** to give trimethylsilyl ether **D** and the intermediate **E**,¹⁶ which then reacted with lithium amide $\text{LiN}(\text{SiMe}_3)_2$ to give $\text{Ar}-\text{C}(\text{OLi})=\text{NSiMe}_3$ **F** and lanthanide amides. Hydrolysis of $\text{Ar}-\text{C}(\text{OLi})=\text{NSiMe}_3$

SCHEME 2. Proposed Mechanism for the Disproportionation Reaction Catalyzed by LnCl_3 

F and trimethylsilyl ether **D** afforded the corresponding amide and benzyl alcohol.

Conclusions

In summary, we for the first time found that a variety of aromatic amides can be directly synthesized simply by the treatment of aromatic aldehydes with lithium amide, catalyzed by commercially available LnCl_3 , or by the treatment of aromatic aldehydes with a stoichiometric amount of lanthanide amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ in good to high yields. The results showed that the reaction had a tolerance for a variety of substituents on the phenyl ring, solvents, and different lanthanide compounds, such as LnCl_3 or $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$. The results also indicated that the lanthanide amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ are more solvent compatible than the lithium amides, and the reactions initiated by the lanthanide amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ gave more satisfactory results than those catalyzed by LnCl_3 . Because the disproportionation reaction can be initiated by inexpensive and commercially available LnCl_3 or easily prepared lanthanide amides $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Ln}(\mu\text{-Cl})\text{Li}(\text{THF})_3$ and because of the good solvent compatibility of the lanthanide amides, the disproportionation reaction provides a novel and simple method for the preparation of amides compared with the method using LDA as a catalyst.^{7a} Further investigations on the use of this disproportionation reaction by using other lanthanide compounds are in progress.

Experimental Section

General Procedure for the Direct Synthesis of Amides from the Reaction of Aromatic Aldehydes with Lithium Amide Catalyzed by LnCl_3 . A 30-mL Schlenk tube under dried argon was charged with lithium amide $\text{LiN}(\text{SiMe}_3)_2$ (0.168 g, 1.0 mmol), YCl_3 (0.010 g, 0.05 mmol), and toluene (10 mL). To the mixture was added 4-nitrobenzaldehyde (0.303 g, 2.0 mmol). After stirring

(16) This kind of coordination mode has been proven in lanthanide chemistry, see: Evans, W. J.; Fujimoto, C. H.; Ziller J. W. *Organometallics* **2001**, *20*, 4529.

the reaction for 2 or 3 days at room temperature, diluted hydrochloric acid (0.1 M, 1 mL) was then added and the mixture was extracted with ethyl acetate, dried over anhydrous MgSO_4 , and filtered. After the solvents were evaporated, the residue was purified by silica gel column chromatography by using a mixture of *n*-hexane and ethyl acetate (1:1, v/v) as an eluent to give 4-nitrobenzamide (**2g**) as a pale yellow solid in 85% yield (0.141 g) and 4-nitrobenzyl alcohol (**3g**) as a yellow solid in 85% yield (0.130 g). This compound can also be prepared in 47% yield in the absence of YCl_3 by using similar procedures as those used above.

The amides (**2a–g**, **2j**, and **2k**) and alcohols (**3a–g**, **3j**, and **3k**) were prepared following similar procedures as those used for the preparation of **2g** by alternating aldehydes and were fully characterized. In some cases, the amides were isolated directly by silica gel column chromatography after the completion of the reaction and evaporation of the solvent, without hydrolysis of the reaction mixture. Their physical and spectral data can be read in Supporting Information.

General Procedure for the Direct Synthesis of Amides from the Reaction of Aromatic Aldehydes with a Stoichiometric Amount of Lanthanide Amides. A 30-mL Schlenk tube under dried argon was charged with yttrium amide $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y}(\mu\text{-Cl})\text{-Li}(\text{THF})_3$ (0.249 g, 0.3 mmol) and dichloromethane (10 mL). To the mixture was added 4-nitrobenzaldehyde (0.272 g, 1.8 mmol). After stirring the mixture for 2 days at room temperature, the reaction mixture was hydrolyzed by 1N HCl, extracted with ethyl acetate, dried over anhydrous MgSO_4 , and filtered. Then the solvent was evaporated and purified by silica gel column chromatography by using a mixture of *n*-hexane and ethyl acetate (1:1, v/v) as an eluent to give 4-nitrobenzamide (**2g**) as a pale yellow solid in 93% yield (0.139 g) and 4-nitrobenzyl alcohol (**3g**) as a yellow solid in 88% yield (0.121 g).

The amides (**2a–m**) and alcohols (**3a–m**) were prepared following similar procedures as those used for the preparation of

2g by alternating aldehydes or lanthanide amides and were fully characterized. In some cases, the amides were isolated directly by silica gel column chromatography after the completion of the reaction and evaporation of the solvent, without hydrolysis of the reaction mixture. Their physical and spectral data were reported in Supporting Information.

The commercial aldehydes such as benzaldehyde or 4-trifluoromethylbenzaldehyde can also be used directly for the preparation of the corresponding amides in 55 and 89% yield, respectively, following the procedures similarly used above.

When a mixture of 4-nitrobenzaldehyde and 4-methoxybenzaldehyde was treated with a stoichiometric amount of yttrium amide $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y}(\mu\text{-Cl})\text{-Li}(\text{THF})_3$, a mixture of the corresponding 4-nitrobenzamide, 4-nitrobenzyl alcohol, 4-methoxybenzamide, and 4-methoxybenzyl alcohol was isolated in 48, 39, 37, and 42% yields, respectively, following the procedures similarly used above.

GCT-MS Analyses. The reaction of 6 equiv of 2-furylaldehyde or 4-nitrobenzaldehyde or PhCDO with yttrium amide $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{Y}(\mu\text{-Cl})\text{-Li}(\text{THF})_3$ in CH_2Cl_2 was performed independently, and the reaction mixture was examined by GCT-MS after 12 h.

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Supporting Information Available: Characterization spectra and data of the compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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