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Cyclopentadienyl-Free Rare-Earth Metal Amides [{(CH_2SiMe_2){(2,6-$i$$Pr_2C_6H_3$)N}$_2$}Ln{N($SiMe_3$)$_2$}(THF)] as Highly Efficient Versatile Catalysts for C–C and C–N Bond Formation

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Keywords: Lanthanides / N,O ligands / Amides / Amidines

Efficient methods have been developed for the direct synthesis of amides from aldehydes and a straightforward route to propiolamidines using cyclopentadienyl-free rare-earth metal amides [{(CH_2SiMe_2){(2,6-$i$$Pr_2C_6H_3$)N}$_2$}Ln{N($SiMe_3$)$_2$}(THF)] [Ln = Yb (**1**), Y (**2**), Dy (**3**), Sm (**4**), Nd (**5**)] as versatile catalysts. The results indicate that in the direct synthesis of amides from aldehydes the catalysts have the activity order **2** > **1** ~ **3** ~ **4** ~ **5**. These methods have the advantage of easy preparation of the catalysts, low catalyst loading, high conversion of substrates to products, mild reaction conditions, and compatibility with a wide range of substrates.

Introduction

The catalytic formation of C–C and C–N bonds is an active subject in modern organic synthesis. Amides are important functional groups in polymers, natural products, and pharmaceuticals.[1] Their value in organic, biological, and materials chemistry mandates the development of more efficient methods for their synthesis.[1] In general, amides can be produced from the reaction between carboxylic acids or their derivatives and amines.[1b,2] Rovis and Bode and their co-workers reported amidation using *N*-heterocyclic carbenes (NHCs) as catalysts.[3] We have reported an amidation process for the preparation of the primary amides using lanthanide chlorides ($LnCl_3$) as catalysts in the reaction of aromatic aldehydes with LiN($SiMe_3$)$_2$ or lanthanide amides [{(Me_3Si)$_2$N}$_3$Ln(μ-Cl)Li(THF)$_3$] as stoichiometric reagents reacting with aldehydes.[4] The reactivity of lanthanide complexes that incorporate amido and enolate mixed ligands towards aromatic aldehydes has been studied very recently.[5] Seo and Marks developed a catalytic amidation of aldehydes with amines catalyzed by homoleptic lanthanide amido complexes Ln[N($SiMe_3$)$_2$]$_3$ (Ln = La, Sm, Y).[6a] Ishihara and Yano reported the direct synthesis of *N*-alkylcarboxamides and *N*,*N*-dialkylcarboxamides by Haller–Bauer (HB) and Cannizzaro-type reactions in the presence of LDA (lithium *N*,*N*-diisopropylamide) as catalyst.[6b] Abaee et al. reported a Cannizzaro reaction facilitated by magnesium bromide–diethyl ether.[6c] Rare-earth metal amido complexes as catalysts for the catalytic transformation of aldehydes to the corresponding amides remain to be further explored.[7]

Propiolamidines [RN=C(C≡CR′)(NHR)] are important amidine derivatives and have received considerable attention over the past decade due to their applications in biological and pharmacological systems,[8] but they can rarely be obtained directly because of their high sensitivity to hydrolysis due to their unique chemical and structural properties.[9] The addition of terminal alkynes to carbodiimides could, in principle, provide a straightforward route to propiolamidines. We have found that the [ethylenebis(η^5-indenyl)][bis(trimethylsilyl)amido]lanthanide(III) complexes {[(EBI)LnN(TMS)$_2$]; EBI = ethylenebis(indenyl); Ln = Y, Sm, and Yb} exhibited diverse catalytic activities on the addition of the C–H bond of terminal alkynes and the N–H bond of amines to carbodiimides.[9b] Other precatalysts such as half-sandwich rare-earth metal complexes bearing silylene-linked cyclopentadienyl-amido ligands[9a] and LiN($SiMe_3$)$_2$[10] for the catalytic addition of the C–H bond of the terminal alkynes to carbodiimides have been reported. Shen and co-workers recently found that divalent lanthanide complexes are active precatalysts for the addition of the C–H bond of terminal alkynes to carbodiimides.[11]

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However, the catalytic synthetic route to propiolamidines with cyclopentadienyl-free rare-earth metals amides as catalysts remains limited.

We recently reported the synthesis of a series of tetracoordinated rare-earth metal amides with the general formula $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Ln\{N(SiMe_3)_2\}(THF)]$ [Ln = Yb (**1**), Y (**2**), Dy (**3**), Sm (**4**), Nd (**5**)] (Figure 1) and found that these complexes exhibited high catalytic activity and selectivity in the cyclotrimerization of aromatic isocyanates and a high catalytic activity for the guanylation of aromatic and heterocyclic amines.[12]

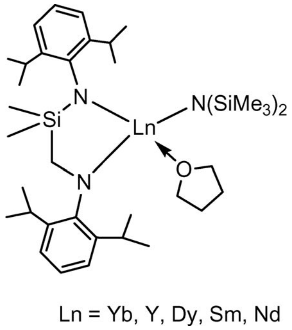


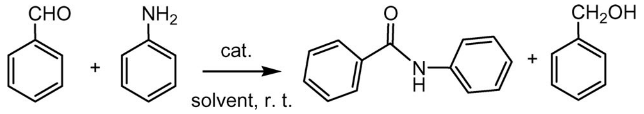
Figure 1. The catalysts $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Ln\{N(SiMe_3)_2\}(THF)]$ described in this paper.

As part of our continuing interest in developing rare-earth metal amides as diverse catalysts for the catalytic formation of C–C and C–N bonds in organic synthesis[4,9b,12] we have studied the catalytic activity of the cyclopentadienyl-free lanthanide amides **1**–**5** in the catalytic amidation of aldehydes with amines and the catalytic addition of the C–H bond of terminal alkynes to carbodiimides. We report the results herein.

Results and Discussion

The catalytic activity of the rare-earth metal amides $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Ln\{N(SiMe_3)_2\}(THF)]$ [Ln = Yb (**1**), Y (**2**), Dy (**3**), Sm (**4**), Nd (**5**)] in the amidation reaction of aldehydes with amines was investigated by performing the reaction of aniline with benzaldehyde as a model reaction under various reaction conditions. The results are given in Table 1.

Table 1. Reaction of aniline with benzaldehyde catalyzed by $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Ln\{N(SiMe_3)_2\}(THF)]$ [Ln = Yb (**1**), Y (**2**), Dy (**3**), Sm (**4**), Nd (**5**)].[a]



Entry	PhCHO/ PhNH$_2$	Ln (catalyst loading [mol-%])	Solvent	Yield [%] [b]
1	1:1	Nd (3)	toluene	15
2	2:1	Nd (3)	toluene	53
3	3:1	Nd (3)	toluene	68
4	1:1	Nd (3)	THF	18
5	2:1	Nd (3)	THF	49
6	3:1	Nd (3)	THF	65
7	1:1	Nd (5)	toluene	37
8	2:1	Nd (5)	toluene	73
9	3:1	Nd (5)	toluene	85
10	3:1	Sm (5)	toluene	86
11	3:1	Dy (5)	toluene	87
12	3:1	Y (5)	toluene	99
13	3:1	Yb (5)	toluene	83
14	3:1	Y (1)	toluene	25
15	3:1	Y (2)	toluene	54
16	3:1	Y (3)	toluene	89

[a] Room temperature, 12 h. [b] Isolated yields of amides based on aniline.

The above results reveal that the amidation reaction of benzaldehyde with aniline could work in toluene or THF at room temperature in the presence of the catalysts $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Ln\{N(SiMe_3)_2\}(THF)]$ [Ln = Yb (**1**), Y (**2**), Dy (**3**), Sm (**4**), Nd (**5**)]. The results indicate that the yields of the reaction can be improved by changing the mole ratio of aldehyde to aniline from 1:1 to 3:1. For example, the yields of the amides could be raised from 15 to 68% in toluene and 18 to 65% in THF in the presence of 3 mol-% catalyst (Table 1, entries 1–6), which indicates that solvent has little effect on the reaction, similar to observations of other amidation reactions.[6] When the catalyst loading was fixed at 5 mol-%, the yields of the reaction improved from 37 to 85% by changing the mole ratio of aldehyde to aniline from 1:1 to 3:1 (Table 1, entries 7–9), which indicates that the results of the reaction are significantly influenced by the catalyst loading. Different lanthanide amides $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Ln\{N(SiMe_3)_2\}(THF)]$ [Ln = Yb (**1**), Y (**2**), Dy (**3**), Sm (**4**), Nd (**5**)] exhibited good-to-excellent catalytic activity in the amidation reaction of aldehyde and aniline when the catalyst loading was 5 mol-% and the ratio of aldehyde to aniline was 3:1 (Table 1, entries 9–13). The complexes **1**, **3**, **4**, and **5** exhibited similar catalytic activity with the yttrium complex **2** showing the highest activity (Table 1, entry 12). This observation contrasts the results obtained with the homoleptic lanthanide amido catalysts $Ln[N(SiMe_3)_2]_3$, in which the lanthanum complex exhibited the highest catalytic activity,[6a] and the heterobimetallic lanthanide/sodium phenoxide catalytic systems, in which the samarium complex displayed the highest activity.[7] With yttrium, the catalyst loading had a similar effect on the yields of the amides, for example, when the catalyst loading was changed, the yield of the reaction changed greatly (Table 1, entries 12 and 14–16). Thus, the optimized reaction conditions for the following experiments were selected as a 3:1 mole ratio of aldehyde to amine, 5 mol-% catalyst loading, toluene as solvent, and room temperature.

The effects of the rare-earth metal and reaction time on the isolated yields of the amide were further investigated under the optimized conditions. A plot of the isolated yields of amide against reaction time is shown in Figure 2 and shows that 1) different rare-earth metal amides

[{(CH_2SiMe_2){(2,6-$i$$Pr_2C_6H_3$)N}$_2$}Ln{N($SiMe_3$)$_2$}(THF)] [Ln = Yb (**1**), Y (**2**), Dy (**3**), Sm (**4**), Nd (**5**)] have different catalytic activities (complexes **1**, **3**, **4**, and **5** exhibited similar activity with the yttrium complex **2** exhibiting the highest activity of the five catalysts examined and 2) the highest conversion of the substrates to the amide could be achieved in 120 min. Thus, a reaction time of 2 h and complexes **2** and **5** as catalysts were selected for the following studies for comparison.

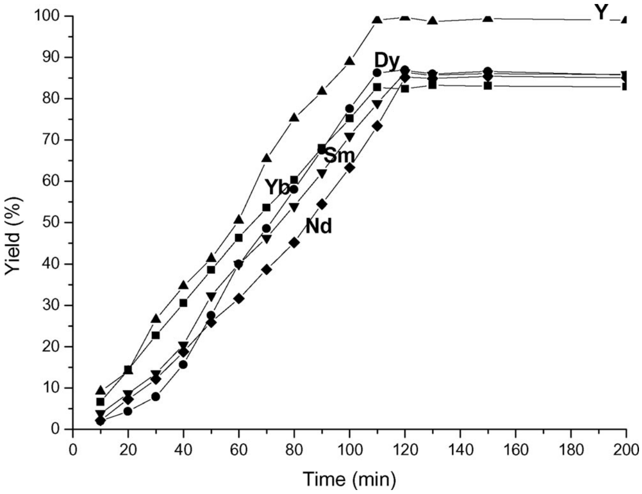


Figure 2. Amide yield vs. reaction time for the different catalysts **1**–**5**.

The reactions of a variety of aldehydes with different amines were evaluated under the optimized reaction conditions. The results are presented in Table 2.

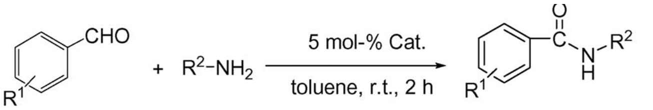
As shown in Table 2, a wide range of substituted aldehydes and amines are suitable for the reaction. The substituents on the phenyl ring could be either electron-withdrawing or -donating groups, for example, CH_3, CH_3O, *i*Pr, HO, and Cl, and good-to-excellent yields of the products can be obtained. The results indicate that the catalysts examined have advantages in comparison with those we used in our previous work[4] and the LDA catalytic system, which requires the transformation of the amines to the corresponding lithium amides.[6b] When the more sterically hindered 2,6-diisopropylaniline was employed in the reaction, the yields of the reactions were low (Table 2, entries 4, 9, 14, and 19); the yields of the isolated amides were improved by raising the reaction temperature to 80 °C and by prolonging the reaction time to 12 h (Table 2, entries 4 and 9), which indicates that steric effects have a significant effect on the results of the reaction. When the same amine was treated with different aldehydes (Table 2, entries 1, 6, 11, and 17), good-to-excellent yields of the amides were obtained, regardless of the electronic nature of the substituents on the aryl groups of the aldehydes. Relatively low yields of amides were isolated when 4-chloroaniline, which has an electron-withdrawing group on the phenyl ring, reacted with benzaldehyde (compare the results of entries 1–3 with those of entry 5, entries 6–8 with 10, entries 17 and 18 with 20, and entries 21 and 22 with entry 23), which suggests that the more electron-deficient amines disfavor the reaction. Only 26 and 28% yields of the corresponding products were isolated when the heterocyclic amine pyrrole was used in the reaction (Table 2, entry 16), probably due to the low reactivity of the aromatic pyrrole ring. Note that good-to-excellent results were obtained when 2-hydroxybenzaldehyde was allowed to react with either electron-rich or -deficient amines (Table 2, entries 21–23), which suggests that the catalysts tolerate the hydroxy group and the catalysts Ln[N($SiMe_3$)$_2$]$_3$[6a] and LDA[6b] systems with which the reactions of 2-hydroxybenzaldehyde with amines were not examined. From Table 2 we also note that the reactions catalyzed by the yttrium catalyst **2** generally give higher yields of products than those catalyzed by the neodymium catalyst **5**, which further demonstrates that the yttrium complex exhibits higher catalytic activity than other catalysts.

The satisfactory results obtained for the construction of C–N bonds encouraged us to explore the use of these complexes as versatile catalysts in C–C coupling reactions. The catalytic addition of terminal alkynes to carbodiimides could provide a straightforward route to the biologically and pharmaceutically useful propiolamidines and as reports on cyclopentadienyl-free rare-earth metal amido complexes as catalysts in this type of reaction are rare we have studied the reaction of diisopropylcarbodiimide and phenylacetylene in the presence of [{(CH_2SiMe_2){(2,6-$i$$Pr_2C_6H_3$)N}$_2$}-Ln{N($SiMe_3$)$_2$}(THF)] [Ln = Yb (**1**), Y (**2**), Dy (**3**), Sm (**4**), Nd (**5**)] as catalysts. The results are given in Table 3.

From Table 3 we can see that the catalyst loading and reaction temperature both have a significant effect on the yields of the reaction (Table 3, entries 1–8) in either toluene or THF. For example, when the catalyst loading was increased from 1 to 3 mol-%, the yields increased accordingly from 34 to 71% in THF (Table 3, entries 1–3) and from 36 to 70% in toluene (Table 3, entries 5–7). When the reaction temperature was raised from room temperature to 60 °C in the presence of 3 mol-% catalyst, the yields of the products increased from 71 to 89% in THF (Table 3, entries 3 and 4) and from 70 to 87% in toluene (Table 3, entries 7 and 8). The reaction of phenylacetylene with *N*,*N*′-diisopropylcarbodiimide can be catalyzed by all the complexes screened and the yields of the reaction were satisfactory (Table 3, entries 4 and 9–12) when the reactions were carried out at 60 °C in THF in the presence of 3 mol-% catalyst loading, which indicates that the central metal of the complexes has little influence on the activities of the catalysts. These results contrast those obtained in the amidation reaction of aldehydes in which the yttrium complex exhibited higher catalytic activity than the other complexes. Therefore catalyst **4**, 3 mol-% catalyst loading, a reaction temperature of 60 °C, and THF as solvent were selected as the reaction conditions for the following experiments.

The results indicate that the reactions proceed smoothly to produce the corresponding propiolamidines regardless of the electronic properties of the substituents on the phenyl ring of the aromatic alkynes (Table 4, entries 1–9). The sub-

Table 2. Amidation of different aldehydes with different amines catalyzed by $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Ln\{N(SiMe_3)_2\}(THF)]$ [Ln = Y (**2**) or Nd (**5**)].[a]



R^1 = H, CH_3, Cl, CH_3O, OH; R^2 = C_6H_5, $CH_3C_6H_4$, 2,6-iPrC_6H_3, ClC_6H_4

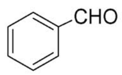
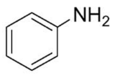
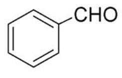
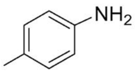
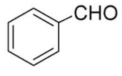
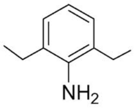
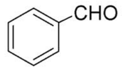
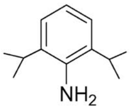
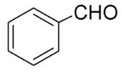
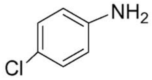
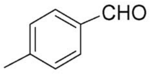
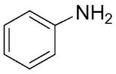
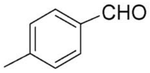
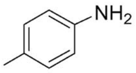
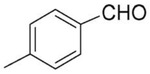
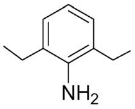
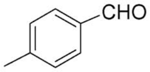
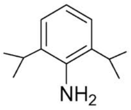
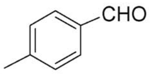
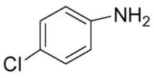
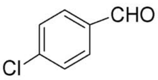
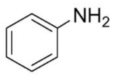
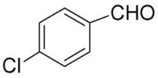
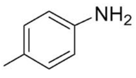
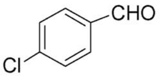
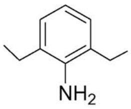
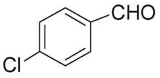
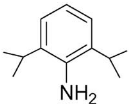
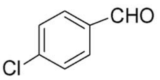
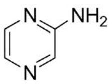
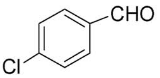
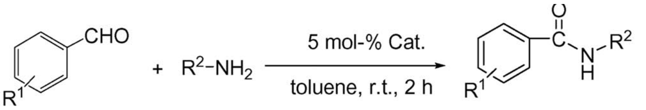
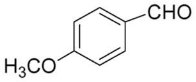
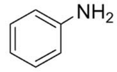
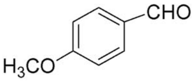
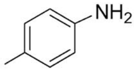
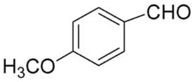
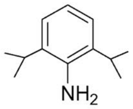
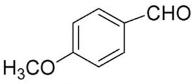
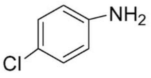
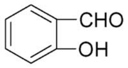
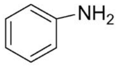
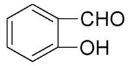
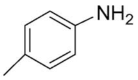
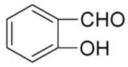
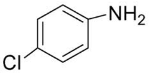
Entry	Aldehydes	Amines	Ln	Temp. / °C	Time/h	Yield (%)[b]	Product
1			**Nd**	r.t.	2	85	**6**
			Y	r.t.	2	99	
2			**Nd**	r.t.	2	82	**7**
			Y	r.t.	2	95	
3			**Nd**	r.t.	2	78	**8**
			Y	r.t.	2	87	
4			**Nd**	r.t. (80)	2 (12)	9 (30)	**9**
			Y	r.t. (80)	2 (12)	25 (49)	
5			**Nd**	r.t.	2	35	**10**
			Y	r.t.	2	74	
6			**Nd**	r.t.	2	77	**11**
			Y	r.t.	2	83	
7			**Nd**	r.t.	2	72	**12**
			Y	r.t.	2	89	
8			**Nd**	r.t.	2	64	**13**
			Y	r.t.	2	75	
9			**Nd**	r.t. (80)	2 (12)	14 (36)	**14**
			Y	r.t. (80)	2 (12)	52 (77)	
10			**Nd**	r.t.	2	44	**15**
			Y	r.t.	2	73	
11			**Nd**	r.t.	2	90	**16**
			Y	r.t.	2	89	
12			**Nd**	r.t.	2	93	**17**
			Y	r.t.	2	97	
13			**Nd**	r.t.	2	94	**18**
			Y	r.t.	2	96	
14			**Nd**	r.t.	2	20	**19**
			Y	r.t.	2	45	
15			**Nd**	r.t.	2	57	**20**
			Y	r.t.	2	79	
16			**Nd**	r.t.	2	26	**21**
			Y	r.t.	2	28	

Table 2. *(Continued).*

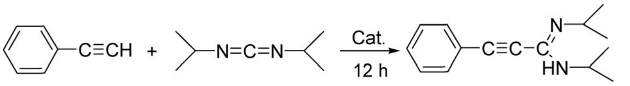


R^1 = H, CH_3, Cl, CH_3O, OH; R^2 = C_6H_5, $CH_3C_6H_4$, 2,6-*i*PrC_6H_3, ClC_6H_4

Entry	Aldehydes	Amines	Ln	Temp. / °C	Time/h	Yield (%)[b]	Product
17			**Nd**	rt	2	91	**22**
			Y	r.t.	2	90	
18			**Nd**	r.t.	2	79	**23**
			Y	r.t.	2	83	
19			**Nd**	r.t.	2	25	**24**
			Y	r.t.	2	47	
20			**Nd**	r.t.	2	29	**25**
			Y	r.t.	2	49	
21			**Nd**	r.t.	2	87	**26**
			Y	r.t.	2	98	
22			**Nd**	r.t.	2	89	**27**
			Y	r.t.	2	98	
23			**Nd**	r.t.	2	42	**28**
			Y	r.t.	2	67	

[a] Reagents: 3 equiv. of aldehyde, 1 equiv. of amine, 5 mol-% catalyst, toluene. [b] Isolated yield based on amine (see ref.[8]).

Table 3. Reaction of *N,N′*-diisopropylcarbodiimide with phenylacetylene catalyzed by [{(CH_2SiMe_2){(2,6-*i*$Pr_2C_6H_3$)N}$_2$}Ln{N($SiMe_3$)$_2$}(THF)] [Ln = Yb (**1**), Y (**2**), Dy (**3**), Sm (**4**), Nd (**5**)].[a]



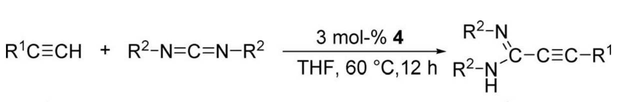
Entry	Ln (catalyst loading [mol-%])	Solvent	*T* [°C]	Yield [%][b]
1	**Sm** (1)	THF	r.t.	34
2	**Sm** (2)	THF	r.t.	52
3	**Sm** (3)	THF	r.t.	71
4	**Sm** (3)	THF	60	89
5	**Sm** (1)	toluene	r.t.	36
6	**Sm** (2)	toluene	r.t.	49
7	**Sm** (3)	toluene	r.t.	70
8	**Sm** (3)	toluene	60	87
9	**Yb** (3)	THF	60	87
10	**Y** (3)	THF	60	88
11	**Dy** (3)	THF	60	83
12	**Nd** (3)	THF	60	86

[a] Reagents: 1 equiv. of phenylacetylene, 1 equiv. of *N,N′*-diisopropylcarbodiimide. [b] Isolated yield.

stituents could be electron-donating groups such as CH_3 and CH_3O, or electron-withdrawing groups such as Cl and Br. The yields of the corresponding propiolamidine obtained from the reactions of *N,N′*-dicyclohexylcarbodiimide with terminal alkynes or substituted phenylacetylene were slightly lower than those obtained in the reactions of *N,N′*-diisopropylcarbodiimide with terminal alkynes or substituted phenylacetylene under the same conditions, probably due to steric effects arising from the more bulky cyclohexyl group in the carbodiimide (Table 4, entries 1–9). The fact that the reactions of substituted phenylacetylene with electron-withdrawing groups such as 1-ethynyl-4-bromobenzene and 4-chloro-1-ethynylbenzene with carbodiimides (Table 4, entries 3–5) were somewhat easier than those of the electron-rich substituted alkyne 4-ethynylanisole with carbodiimides (Table 4, entries 6 and 7) is probably due to the different acidities of the terminal alkynes, which may favor the alkyne–amido exchange process in the catalytic initiation step. These results indicate that the catalytic activities of the cyclopentadienyl-free lanthanide amides in the addition of alkynes to carbodiimides can be compared with those of half-sandwich yttrium alkyl complexes,[9a] lithium amide LiN(TMS)$_2$,[10] and lanthanide(II) complexes.[11] However, when an aliphatic alkyne was treated with *N,N′*-diisopropylcarbodiimide under the same conditions, a relatively low yield of the corresponding product was isolated (Table 4, entry 10).

The mechanism proposed for the amidation of aldehydes is as follows (Scheme 1). Interaction of the amine with lanthanide amide gives the new amido intermediate **A** through an acid–base exchange reaction.[13] Coordination of an aldehyde molecule to the central metal of **A** followed by addition of the amido group to the carbonyl group produces

Table 4. Addition of alkynes to carbodiimides catalyzed by $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Sm\{N(SiMe_3)_2\}(THF)]$ (**4**).[a]

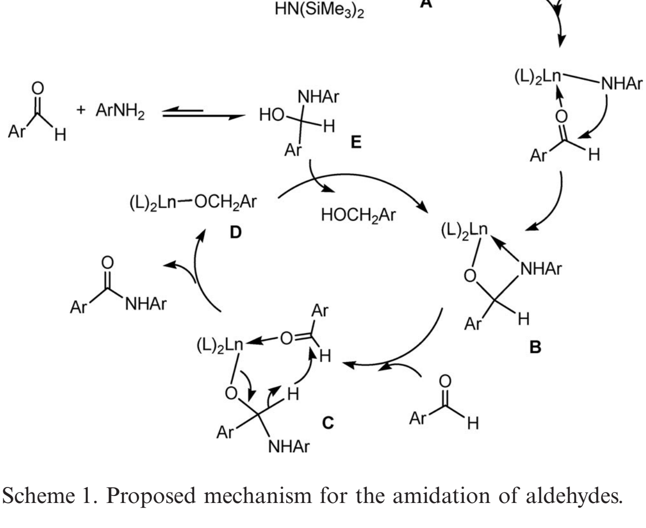


$R^1 = C_6H_5$, $4\text{-}BrC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}CH_3C_6H_4$, $n\text{-}C_3H_7$; R^2 = Cy, *i*Pr

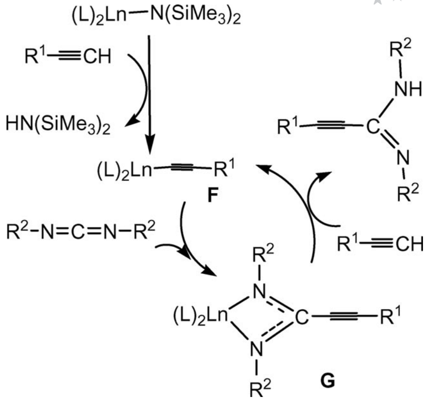
Entry	R^1	R^2	Product	Yield [%][b]
1	C_6H_5	*i*Pr	**29**	89
2	C_6H_5	Cy	**30**	87
3	$4\text{-}BrC_6H_4$	*i*Pr	**31**	97
4	$4\text{-}BrC_6H_4$	Cy	**32**	93
5	$4\text{-}ClC_6H_4$	*i*Pr	**33**	96
6	$4\text{-}CH_3OC_6H_4$	*i*Pr	**34**	81
7	$4\text{-}CH_3OC_6H_4$	Cy	**35**	78
8	$4\text{-}CH_3C_6H_4$	*i*Pr	**36**	76
9	$4\text{-}CH_3C_6H_4$	Cy	**37**	69
10	$n\text{-}C_3H_7$	*i*Pr	**38**	58

[a] Reagents: 1 equiv. of terminal alkyne, 1 equiv. of carbodiimide. [b] Isolated yield.

the intermediate **B**, which transfers a hydride to another aldehyde molecule as indicated in **C** to give an alkoxy intermediate **D** and the product amide. The hydride transfer process has been proved previously by treatment of deuteriated C_6H_5CDO with $[\{(Me_3Si)_2N\}_3Y(\mu\text{-}Cl)Li(THF)_3]$.[4] The intermediate **D** reacts with intermediate **E**, which is produced by the addition of amine to aldehyde, to produce **B** finishing the catalytic cycle. The mechanism for the formation of propiolamidine would be similar to the one proposed in our previous work (Scheme 2).[9b] Interaction of the lanthanide amide with terminal alkyne produces the intermediate **F**, which then reacts with the carbodiimide to produce the amidinate species **G** by an insertion reaction.[14] **G** reacts with a terminal alkyne to give the final product propiolamidine finishing the catalytic cycle. However, another mechanism and the involvement of other intermediates in the catalytic cycle cannot be ruled out.



Scheme 1. Proposed mechanism for the amidation of aldehydes.



Scheme 2. Proposed mechanism for the amidation of propiolamides.

Conclusions

We have developed efficient methods for the direct amidation of aldehydes with amines and a straightforward route to propiolamidines using the cyclopentadienyl-free rare-earth metal amides $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Ln\{N(SiMe_3)_2\}(THF)]$ (Ln = Yb, Y, Dy, Sm, Nd) as versatile catalysts. These methodologies have the advantage of easy preparation of the catalysts, low catalyst loading, high conversion of substrates to products, mild reaction conditions, and compatibility with a wide range of substrates and solvents. The results indicate that the yttrium complex is the most efficient catalyst of the catalysts examined in the amidation of aldehydes with amines with the Yb, Dy, Sm, and Nd complexes displaying similar catalytic activities. Examination of the reactions of terminal alkynes with carbodiimides using the catalysts $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Ln\{N(SiMe_3)_2\}(THF)]$ (Ln = Yb, Y, Dy, Sm, Nd) indicates that all these complexes exhibit similar catalytic activities. To the best of our knowledge this is the first application of readily accessible cyclopentadienyl-free rare-earth metal amides as catalysts in the preparation of propiolamidines.

Experimental Section

General Procedure for the Direct Synthesis of Amides by the Reaction of Aniline with Benzaldehyde Catalyzed by $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Nd\{N(SiMe_3)_2\}(THF)]$ (6 as an Example): A 30 mL Schlenk tube under dried argon was charged with the neodymium amide $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}NdN(SiMe_3)_2\}(THF)]$ (**5**; 0.037 g, 0.0463 mmol) and toluene (10 mL). Aniline (0.086 g, 0.926 mmol) and benzaldehyde (0.295 g, 2.778 mmol) were added to the flask. The resulting mixture was stirred at room temperature for 2 h and then hydrolyzed with water (1 mL) and extracted with dichloromethane (3 × 10 mL). The extracts were dried with anhydrous $MgSO_4$ and filtered. After removing the solvent under reduced pressure, the final product could be isolated as white crystals by washing the crude product with diethyl ether (10 mL) or by recrystallization from THF; yield 0.155 g, 85%; m.p. 57–58 °C. IR (neat): $\tilde{\nu}$ = 3331, 3059, 3028, 2961, 2889, 1738, 1576, 1526, 1314, 1281, 1260, 1192, 868, 760, 693 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.46 (s, 1 H, NH), 7.93 (d, *J* = 7.8 Hz, 2 H), 7.50 (t, *J* = 6.6 Hz, 3 H), 7.40 (t, *J* = 8.1 Hz, 2 H), 7.24 (t, *J* = 9.6 Hz, 3 H) ppm. ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ = 160.1, 131.1, 128.8, 128.5, 125.6, 120.5 ppm. HRMS (EI): calcd. for $C_{13}H_{11}NO$ $[M]^+$ 197.0841; found 197.0849.

General Procedure for the Synthesis of Propiolamidines by the Reaction of *N*,*N*′-Diisopropylcarbodiimide with Phenylacetylene Catalyzed by $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Sm\{N(SiMe_3)_2\}(THF)]$ (Compound 23 as an Example): A 30 mL Schlenk tube under dried argon was charged with the samarium amide $[\{(CH_2SiMe_2)\{(2,6\text{-}i\text{Pr}_2C_6H_3)N\}_2\}Sm\{N(SiMe_3)_2\}(THF)]$ (**4**; 0.098 g, 0.122 mmol) and THF (10 mL). *N*,*N*′-Diisopropylcarbodiimide (0.317 g, 2.4 mmol) and phenylacetylene (0.248 g, 2.4 mmol) were added to the flask and the resulting mixture was stirred at 60 °C for 12 h. After removing the solvent under reduced pressure, the residue was extracted with hexane and filtered to give a clean solution. The solvent was evaporated under vacuum and the final product was obtained as white crystals by recrystallization from *n*-hexane or by silica gel column chromatography using *n*-hexane/ethyl acetate (1:6, v/v) as eluent; yield 0.488 g, 89%. IR (neat): $\tilde{\nu}$ = 3325, 2874, 2214, 1462, 1439, 1385, 1250, 1169 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.16–1.26 (m, 12 H, CH_3), 3.92–4.00 (m, 2 H, CH), 7.35–7.37 (m, 3 H, C_6H_5), 7.48–7.51 (m, 2 H, C_6H_5) ppm. ^{13}C NMR (75.0 MHz, $CDCl_3$): δ = 21.6, 23.9, 24.3, 47.8, 52.5, 92.1, 118.4, 129.1, 129.2, 131.9, 132.0, 139.7, 141.6 ppm. HRMS (EI): calcd. for $C_{15}H_{21}N_2$ $[M + H]^+$ 229.1705; found 229.1695.

Supporting Information (see also the footnote on the first page of this article): Full experimental details and characterization of all products.

Acknowledgments

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