

Dalton Transactions

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Journal Name

ARTICLE

Synthesis and characterization of bridged bis(amidato) rare earth metal amides and their applications in C-N bond formation reactions

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Bei Zhao^{*}, Yang Xiao, Dan Yuan, Chengrong Lu, Yingming Yao^{*}

Based on three bisamide proligands H_2L^n ($n = 1-3$) ($H_2L^1 = [(Me_3C_6H_2CONHCH_2)_2CH_2]$, $H_2L^2 = [(Me_3C_6H_2CONHCH_2)_2C(CH_3)_2]$, $H_2L^3 = [Me_3C_6H_2CONH(CH_2)_2NCH_3]$), eight bis(amidato) trivalent rare-earth metal amides $\{L^n RE[N(TMS)_2]_2\}$ ($n = 1$, RE = La (1), Sm (2), Nd (3), Y (4)); $n = 2$, RE = La (5), Nd (6)); $n = 3$, RE = La (7), Nd (8); TMS = SiMe₃) were successfully synthesized by treatment of H_2L^n with $RE[N(TMS)_2]_3$ in 1:1 molar ratio. Complexes 3, and 5-8 were characterized by single-crystal X-ray diffraction, and NMR characterization was carried out for La complexes 1, 5, 7 and Y complex 4. These complexes exhibited high catalytic activities in both the direct amidation of aldehydes and the addition of amines with carbodiimine. It was found that the bis(amidato) rare earth metal amides bearing different linkers have different effects on the transformations and lanthanum and neodymium complexes performed better than others.

Introduction

Organolanthanide amides are important rare earth metal complexes with rich reactivities^[1]. In general, the catalytic performance of the organolanthanide amides can be effectively controlled by changing the metal center or auxiliary ligand^[2]. In recent years, amidato groups, whose steric and electric effects can be easily tuned, attracted great attention in lanthanide chemistry^[3]. Several amidato rare-earth metal amides have been successfully prepared and proved to be useful catalysts for ring opening polymerization of lactones^[3a-c] and some valuable transformations including C-C bond^[3d-e], C-P bond^[3f] and C-N bond^[3g-h, j] formation. To further explore the application of auxiliary amidato ligand in homogenous rare-earth metal catalysts, the synthesis and characterization of bridged bis(amidato) rare-earth metal amides and their applications were investigated and up to now, only four successful cases were reported in the field^[3b, e, i, j]. Thus, three new series of bridged bis(amidato) rare-earth metal amides were designed, prepared and well characterized in this report.

Amides are one type of important nitrogen-containing compounds, have unique physiological activities and are key structural elements in the study of drug chemistry and biochemistry^[4]. Moreover, amide derivatives can also serve as ancillary ligands in the field of coordination chemistry^[5]. In 2008, Marks found that the direct amidation of aldehydes and amines to yield amides can be catalyzed by neutral

$La[N(TMS)_2]_3$, a simple and easily available lanthanide amide, without using any oxidants, bases, heat or light^[6]. This finding evoked chemists to pay constant attention to this transformation and many kinds of rare-earth metal amides with different ancillary ligands were found to be the efficient catalysts^[7]. However, a relative large catalyst loading (5 mol%) and the relative narrow substrate scope were usually observed and are in need of improvement. Recently, Schafer's group found yttrium amidato complexes can catalyze this conversion in a very short time, but the yields of many products were still not good enough^[3h]. Thus, our new bridged bis(amidato) lanthanide amides were tested, which were found to be efficient catalysts in the direct amidation of aldehydes.

The addition of amines and carbodiimine is a popular atom economic method to construct guanidines. However, the synthesis of the guanidine compounds need harsh conditions in the absence of catalyst^[8]. Over the past decade, a large number of studies showed that many rare earth metal organic complexes with diverse structures can catalyze the addition of amines and carbodiimides, including rare earth metal alkyl, amino and alkyl (aryl) oxy compounds with different ancillary ligands, such as cyclopentadienyl^[9a-c], indenyl^[9d-f], amino^[9g-i], pyrrolyl^[9j], guanidine^[9k], N-heterocyclic carbene^[9l], salen^[9m], β -diketiminato^[9n], and amidine group^[9o-p]. Very recently, our group found that cyclohexyl bridged bis(amidato) trivalent rare earth metal amides were efficient catalysts in the addition reaction of amines and carbodiimine at 60 °C under solvent-free conditions^[3j]. To get insight into the structure-activity relationship of the bridged bis(amidato) rare earth metal

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou 215123, People's Republic of China

*To whom correspondence should be addressed. Email: zhaobei@suda.edu.cn; yaoym@suda.edu.cn

amides in the guanidination, new bridged bis(amidato) lanthanide amides were also tested in this study.

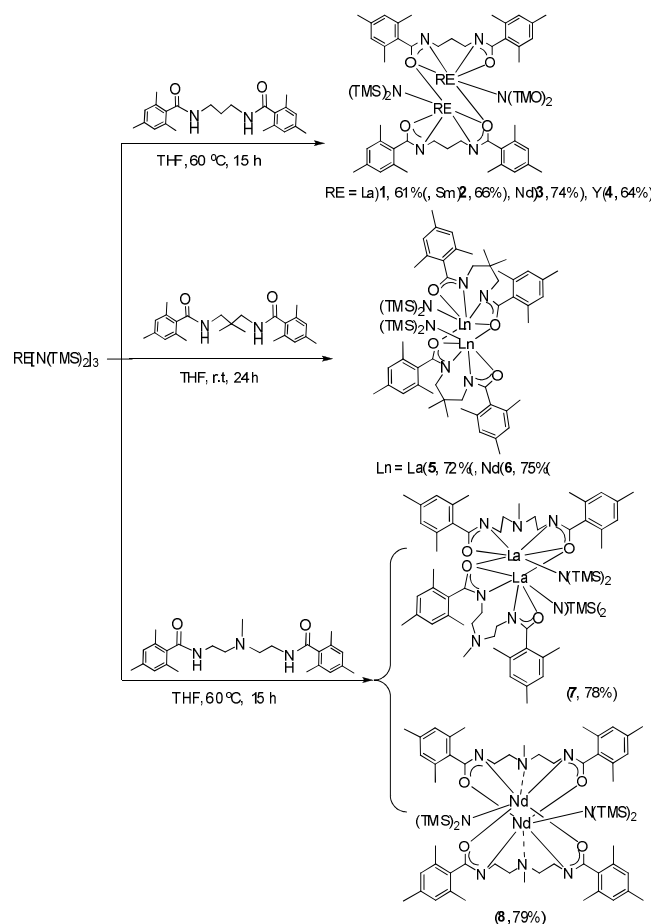
Results and discussion

Syntheses and characterization of bridged bis(amidato) rare-earth metal amides.

To further explore the reactivity of bridged bis(amidato) rare earth metal amides, eight target complexes $\{L^n RE[N(TMS)_2]_2\}_2$ ($n = 1$, RE = La (**1**), Sm (**2**), Nd (**3**), Y (**4**)); $n = 2$, RE = La (**5**), Nd (**6**)); $n = 3$, RE = La (**7**), Nd (**8**)) bearing different bridged bis(amidato) groups were successfully synthesized by treatment of suitable rare earth metal precursors $RE[N(SiMe_3)_2]_3$ with bridged bis(amidato) proligands^[10] H_2L^n ($n = 1-3$) ($H_2L^1 = [(Me_3C_6H_2CONHCH_2)_2CH_2]$, $H_2L^2 = [(Me_3C_6H_2CONHCH_2)_2(CH_3)_2C]$, $H_2L^3 = [Me_3C_6H_2CONH(CH_2)_2]_2NCH_3$) (Scheme 1) according to literature methods^[11]. Disappearance of the corresponding N-H signals of proligands in the 1H NMR spectra of lanthanum and yttrium complexes confirms the occurrence of metathesis. All complexes are air and moisture sensitive, and complexes **1-6** are soluble in both toluene and THF, while complexes **7** and **8** are soluble in THF, and slightly soluble in toluene.

Crystals of complex **3** suitable for X-ray diffraction were obtained from toluene solution at room temperature. The solid structure of complex **3** is depicted in Figure 1 and the details of the crystallographic data are summarized in TS 1 (See ESI, Table 1). It is a centrosymmetric binuclear structure with one toluene molecule in each unit cell. The Nd center is six coordinated by two oxygen atoms and two nitrogen atoms from the carbon bridged bis(amidato) ligand L^1 , one oxygen atom from a second ligand L^1 and one nitrogen atom from $-N(TMS)_2$ group. The bridged bis(amidato) group adopts a coordination mode named $\kappa^4-(N,O):\mu-O$, in which ligand L^1 not only chelates one metal center but also bridges two metal centers via an oxygen atom. When taking the metal center Nd as the spiro atom, each amidato subunit in one bridged ligand constitutes a planar quadrilateral since the sum of these bond angles of Nd1-O1-C1(93.1(5) $^\circ$), O1-C1-N1(117.2(8) $^\circ$), C1-N1-Nd1(97.4(5) $^\circ$) and N1-Nd1-O1(51.7(2) $^\circ$) is 359.5 $^\circ$, and the same for the other metal center Nd2. The spatial configuration of the metal center Nd can be described as a distorted pentagon cone for N3 is the vertex. The average bond lengths of C-O and C-N are 1.308 Å and 1.269 Å, respectively, indicating the electron delocalization in amidato subunit. In comparison, the bond length of Nd1- κ -N2 (2.430(8) Å) was significantly shorter than the bond length of Nd- κ -N4 (2.694 (5)Å) in anionic amidate rare earth metals complex $Li(THF)Nd[C_6H_5C(O)NC_6H_3^iPr_2]_4$; while the bond length of Nd1- κ -O2 (2.397(6) Å) is very close to the bond length of Nd- κ -O4 (2.385 (5) Å) in the above anionic complex^[3c]. The bond lengths of Nd1- κ -N1 (2.491(7) Å), Nd1- κ -O1 (2.554(5)Å), Nd1A- μ -O1 (2.384(6) Å) in complex **3** were slightly shorter than the corresponding bond lengths of Nd1- κ -N2 (2.526 (5)Å), Nd1- κ -O2 (2.593(4)Å) and Nd1A- μ -O2(2.443(6) Å) in the cyclohexyl bridged bis(amidato) neodymium amide $\{^tBuC_6H_4CONH(C_6H_{10})NHCOC_6H_4^tBu\}Nd[N(TMS)_2]_2THF\}_2$ ^[3e].

These data suggest that the whole molecule of complex **3** is more compact and the surrounding of the metal center may be more open due to the flexible unbranched C3 linker in the bis(amidato) ligand. This structural characters of complex **3** probably result in improved catalytic reactivity (*vide infra*).



Scheme 1. Preparation of rare earth metal amides supported by bridged bis(amidato) ligands

Crystals of complexes **1**, **2** and **4** were obtained from toluene solution using the same method as that for complex **3**. Unfortunately, unsatisfactory results from X-ray diffraction were obtained and only the skeletons of the molecular structures of **1**, **2** and **4** could be determined. However, NMR spectra of complexes **1** and **4** and the elemental analysis results of complexes **1**, **2** and **4** are informative. Thus, it can be deduced that the molar ratio of the ligand L^1 to the metal center and the amido group is 1:1:1. Therefore, it is presumed that the solid structures of complexes **1-4** are isostructural.

Crystals of complexes **5** and **6** suitable for X-ray diffraction were obtained from THF-hexane solutions after several days at room temperature. The molecular structure of complex **5** was monoclinic, P12/c1 space group with two free THF molecules in every unit cell, while isostructural complex **6** belongs to P1c1 space group with two *n*-hexane molecules in every unit cell. The molecular structure of complex **5** is a representative example, which is shown in Figure 2, and details of the crystallographic data are summarized in TS 1 (See ESI, Table 1).

It is shown that the metal center is six coordinated with two amidato groups, one silylamido ligand and a bridged oxygen atom from the other amidato group. Though the coordination modes of bridged bis(amidato) group L^2 are almost the same as those in complex **3**, the location of silylamido groups is on the same side of the square plane of La1-O2-La1A-O2A. The bond lengths of La1-N1 bond (2.492 (3) Å) and La1-O1 bond (2.471 (3) Å) of amidato ligand adopting κ^2 -(N,O) coordination mode are shorter than the bond lengths of La1-N2 bond (2.706 (3) Å) and La1-O2 bond (2.579 (3) Å) of amidato ligand adopting κ -(N,O): μ -O coordination mode, which is consistent with the bond lengths of complex **3**. The bond parameters in complex **6** are similar to the corresponding values in complex **5**, taking into account the difference in ionic radii.

Aminolysis of $\text{Ln}[\text{N}(\text{TMS})_2]_3$ (Ln = La, Nd) with proligand H_2L^3 [$\text{Me}_3\text{C}_6\text{H}_2\text{CONH}(\text{CH}_2)_2\text{NCH}_3$] yielded two desired complexes $\{\text{L}^3\text{Ln}[\text{N}(\text{TMS})_2]_2\}$ (Ln = La(**7**), Nd(**8**)). Suitable crystals for X-ray diffraction determination were obtained from toluene solution at room temperature and details of the crystallographic data are collected in TS 1 (See ESI, Table 1). The solid structure of complex **7** is depicted in Fig. 3. The coordination modes of bridged bis(amidato) groups in complex **7** are consistent with those in complexes **1-6**. It crystallizes in the monoclinic crystal system, P21/n space group. The spatial configuration of the metal center can be described as a distorted pentagonal pyramid, with N3 as the vertex. Similar to complexes **5** and **6**, silylamido groups in complex **7** are located at the same side of the coordination plane of La1-O2-La1A-O2A. It is noteworthy that the bridging nitrogen atoms do not coordinate to the lanthanum centers.

Though neodymium complex **8** is supported by the same ligand L^3 as lanthanum complex **7**, it crystallizes in the triclinic crystal system, P-1 space group, and has a binuclear centrosymmetric structure with a coordination number of six. As shown in Fig. 4, the neodymium atom is coordinated with two nitrogen atoms from an amidato group, a nitrogen atom that bridges two amidato groups, two oxygen atoms from the other amidato ligand, and a nitrogen atom from the silylamido group. The bis(amidato) group adopts a bridging mode in complex **8**, that is, the nitrogen atom coordinate to one neodymium atom, while the oxygen atom in the same fragment coordinate to the other metal center in the unit cell. The bridging fashion is one of the possible coordination modes of amidato ligands in organometallics^[12], and to the best of our knowledge, this is the first case reported in lanthanide chemistry. The average bond lengths of C-O and C-N are 1.291 Å and 1.301 Å, which shows significant electron delocalization in the amidato fragment. The average bond length of Nd-O bond is 2.346 Å, which is shorter than Nd- κ -O bond lengths of complex **3** (2.397 Å) and complex **6** (2.400 Å). The Nd-N average bond length of 2.500 Å is slightly longer than the Nd- κ -N bond lengths of complex **3** (2.430 Å) and complex **6** (2.463 Å). The spatial configuration of the metal center can be described as a distorted triangular prism and the dihedral angle of the planes consisting of N1A, N2A, N3A and N4A, O1, O3 is 9.6°.

The different coordination modes of the same ligand in complexes **7** and **8** may be attributed to the different ionic radii between La and Nd and the relative bulky bridged bis(amidato) donor H_2L^3 .

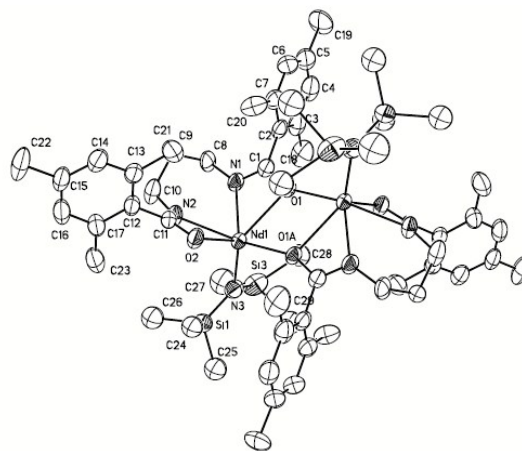


Figure 1. Molecular structure of complex **3**-toluene. Hydrogen atoms and toluene molecules are omitted for clarity.

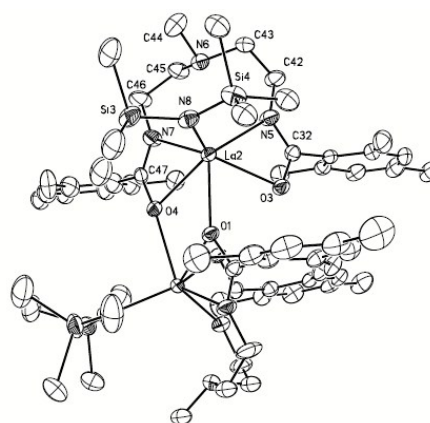
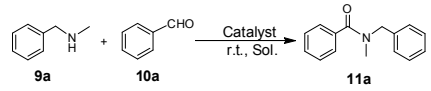


Figure 3. Molecular structure of one independent molecule of complex **7**-toluene. Hydrogen atoms and toluene molecules are omitted for clarity.

17). Finally, the optimal condition was determined to be 1 mol% complex **1** as the catalyst in THF at room temperature for 3 hrs (Table 1, entry 12).

Table 1. Condition screening of the amidation of **9a** with **10a** catalyzed by various bridged bis(amidato) rare earth amides^a



entry	Molar ratio (9a/10a)	Cat.	Catalyst loading (mol%) ^b	Solvent	Time/h	Yield(%) ^c
1	1:1	3	1	THF	3	46
2	1:2	3	1	THF	3	80
3	1:3	3	1	THF	3	92
4	1:3	3	1	THF	0.5	72
5	1:3	3	1	THF	1	85
6	1:3	3	1	THF	6	93
7	1:3	3	1	-	3	88
8	1:3	3	1	CH ₂ Cl ₂	3	45
9	1:3	3	2.5	Tol	3	91
10	1:3	3	2.5	Et ₂ O	3	94
11	1:3	3	2.5	THF	3	98
12	1:3	1	1	THF	3	98
13	1:3	2	1	THF	3	91
14	1:3	4	1	THF	3	90
15	1:3	5	1	THF	3	96
16	1:3	7	1	THF	3	68
17	1:3	1	0.5	THF	3	92

^a Amine was first added to the solution of catalyst, and aldehyde was added 30 min later. The concentration of amine was 0.8 mol·L⁻¹. ^b Based on the catalyst amount. ^c GC yield based on the amount of amine.

Figure 4. Molecular structure of complex **8**-2toluene. Hydrogen atoms and toluene molecules are omitted for clarity.

Catalytic activities of complexes **1-5** and **7** in the amidation of amines and aldehydes.

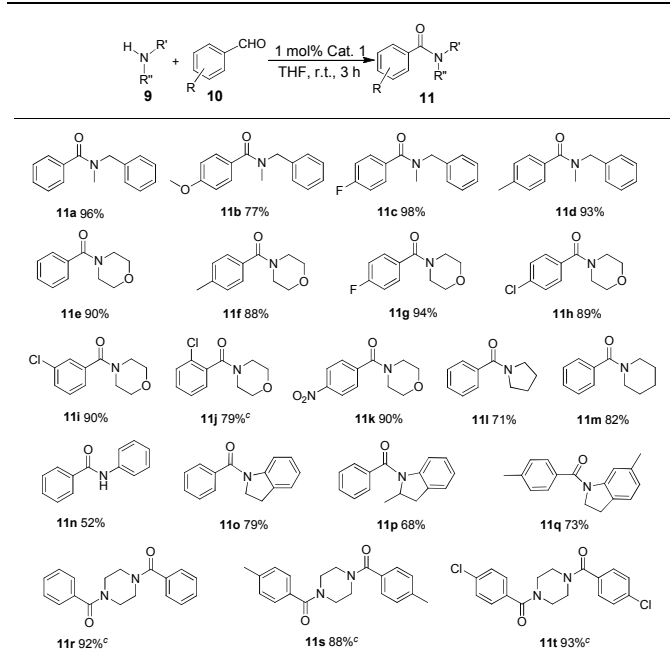
Direct reaction of amine and aldehyde has attracted increasing attention because of its high efficiency in the formation of amide bonds^[13]. In 2006, Wang's group successfully introduced LnCl₃ and Ln[N(TMS)₂]₂(μ-Cl)Li(THF)₃ to catalyze the reaction of aldehydes and amides, though the substrate scope was limited^[14]. Before long, Marks developed neutral Ln[N(TMS)₂]₃ as the single component catalyst, which showed limitations in catalyzing reactions of aliphatic amines^[6]. Recently, Schafer's contributions in this transformation using yttrium amidate complexes as the catalyst shortened the reaction time to only 5 min, and catalytic activities of rare earth metal amides are found to largely depend on the auxiliary ligands^[3h]. Despite so many reports, no lanthanide bimetallic complex has been applied in catalyzing the amidation reactions. To explore the potential bimetallic synergistic effect of the bis(amidato) rare earth metal amides, their performance as catalysts for the amidation of *N*-methyl benzylamine and benzaldehyde was examined and the results are listed in Table 1.

It is found that the amidation was smoothly catalyzed by complexes **1-5** and **7** in THF at room temperature. Even though the main side reaction named Tishchenko reaction was also accelerated under the same reaction conditions, the increasing amount of benzaldehyde was beneficial to amidation, as the yield of the desired amide increased from 46 to 92% (Table 1, entries 1-3). The reaction time and the solvent had a great influence on the reaction outcome and under optimized conditions, the reaction in THF for 3 hours was the best choice (Table 1, entries 3-11). The central metal had somewhat effect on the reaction and the La complex **1** exhibited the highest activity (Table 1, entries 3 and 12-14). The ligand effect was also observed in this catalytic system. For the same lanthanum amides, the yield of the reaction catalyzed by complex **7** bearing the relative bulky ligand L³ was only 68%, while the reaction was basically complete when complexes **1** and **5** bearing the amidato ligands L¹ and L² were used as the catalysts (Table 1, entries 12 and 15-16). It is presumed that the relative crowded surrounding of lanthanum in complex **7** hindered the approaching of aldehyde to the metal center. The attempt to reduce the amount of catalyst by half failed because the yield dropped apparently (Table 1, entries 12 and

Subsequently, the reaction of various amines and aldehydes were investigated and the results are shown in Table 2. It can be seen that electronically varied aldehydes underwent the transformation with *N*-methyl benzylamine smoothly and the yield of the desired amides were excellent except for the substrate *p*-methoxy benzaldehyde (Table 2, **11a-11d**). Several secondary cyclic amines, such as morpholine, tetrahydropyrrole, and piperidine were investigated and the yields were satisfying, ranging from 71-94% (Table 2, **11e-11m**), which are comparable with previous reports^[7]. Though the chlorine atom adjacent to carbonyl group in *o*-chlorobenzaldehyde decelerated the reaction process, the yield of the corresponding amide increased when the amount of catalyst loading was doubled (Table 2, **11j**). If *N*-methyl benzylamine was replaced with aniline, the yield of amide dramatically dropped to 52% (Table 2, **11a** and **11n**), meanwhile the main byproduct imine was observed in GC determination. It may be ascribed to the less nucleophilic nature of aniline comparing to that of aliphatic amine. With benzopyrrole and its derivatives as the substrate amine, the yields were better (Table 2, **11o-11q**). To our delight, the

results of bisamidation of piperazine were excellent in the presence of 2 mol% catalyst **1**, which was less reported in previous work (Table 2, **11r-11t**).

Table 2. Substrate scope for the amidation^{a,b}



^a Reaction conditions: amine (1.0 mmol), aldehydes (3.0 mmol), catalyst **1** (0.01 mmol), THF (0.8 mL). ^b Isolated yield based on amine. ^c Catalyst **1** (0.02 mmol).

Catalytic activities of complexes **1-4**, **6** and **8** in the guanidination of DIC and amines.

Guanidine is an important structural unit of some drugs due to their physiological activity in antibacterial, enzyme inhibitors, antiviral and so on^[15]. Guanidine and its derivatives were also commonly used as ligands in coordination chemistry^[16]. Moreover, guanidine itself was found to be efficient catalyst in organic synthesis^[17]. Hence, great progress was made in the synthetic method of guanidine and its derivatives^[18].

Encouraged by our previous work^[3], the catalytic activities of bis(amidato) rare earth metal amides **1-4**, **6** and **8** in the addition of aniline and diisopropyl carbodiimide (DIC) were investigated and the results are summarized in Table 4. The addition gave rise to the expected guanidines, up to 96% yields at 60 °C after 15 min (Table 3, entries 1-6). The central metal had little effect on the transformation, while the relative bulky ligand, especially L³ had great influence on the outcome, as the yield dramatically dropped to 52% (Table 3, entries 1-6). The coordinating THF was not an ideal solvent and the optimal condition is solvent free (Table 3, entries 1, 5, and 7-9). At ambient temperature, the satisfying yield of 92% was only obtained after 3 h in the presence of easily prepared catalyst **3** (Table 3, entries 10 and 11). Even though the amount of catalyst **3** was reduced to half, the yield of guanidine maintained (Table 3, entries 1 and 12). So, the optimal condition for the model reaction of aniline and DIC is as

follows: 0.25 mol% catalyst **3**, at 60 °C for 15 min under solvent-free conditions.

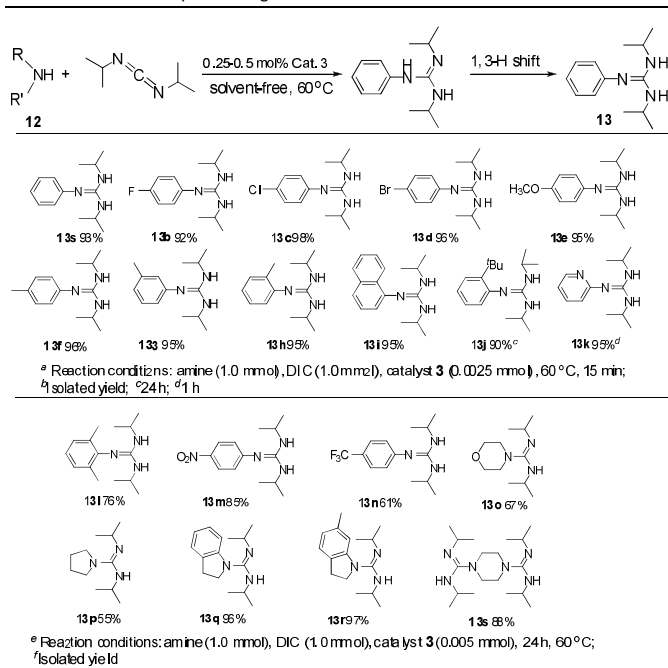
Various amines were screened at 60 °C under solvent-free conditions for appropriate reaction time in the presence of catalyst **3** and the results are shown in Table 4. It was found that the electronic effect of less sterically hindered substituents, such as halides, methyl and methoxy groups had no significant influence on the guanidination of substituted anilines and DIC. The target guanidine can be easily obtained in excellent yields in a time as short as 15 min (Table 4, **13a-13i**). However, the reaction time needs to be prolonged to 24 h for *o*-*tert*-butylaniline, and 1 h for pyridine-2-amine to afford the corresponding guanidine in 90% and 95% yields, respectively (Table 4, **13j** and **13k**). As for the substrates bearing the strong electron withdrawing group, for example, nitro and trifluoromethyl group, or the *ortho* disubstituted substrate 2,6-methylaniline, the yields of products dropped to 61-76% in the presence of 0.5 mol% catalyst **3** for 24 h (Table 4, **13l-13n**). The catalytic system was also suitable for some cyclic secondary amines, such as pyrrole and morpholine (Table 4, **13o-13r**). It also provides a convenient access to bisguanidine in a high yield using 0.5 mol% catalyst **3** for 24 h (Table 4, **13s**). All results presented here are comparable to those of reactions catalyzed by cyclohexyl bridged bis(amidato) neodymium amides^[3].

Table 3. Condition screening of the guanidination of DIC and amines^a

Reaction scheme for Table 3: Aniline (12a) reacts with diisopropyl carbodiimide (DIC) in the presence of a catalyst to form a guanidine intermediate, which then undergoes a 1,3-H shift to form the final guanidine product (13a).

Entry	Cat.	Catalyst loading (mol%) ^b	Solvent	Temp (°C)	Time (min)	Yield (%) ^b
1	3	0.5	-	60	15	96
2	1	0.5	-	60	15	91
3	2	0.5	-	60	15	96
4	4	0.5	-	60	15	88
5	6	0.5	-	60	15	93
6	8	0.5	-	60	15	52
7	3	0.5	Hex	60	15	80
8	3	0.5	Tol	60	15	52
9	3	0.5	THF	90	15	34
10	3	0.5	-	25	15	70
11	3	0.5	-	25	180	92
12	3	0.25	-	60	15	94

^a Reaction conditions: amine (1.0 mmol), DIC (1.0 mmol), catalyst **3** (0.0025 mmol); ^b Isolated yield.

Table 4. Substrate scope for the guanidination

Conclusions

In summary, overall eight bis(amidato) rare earth metal amides have been successfully prepared and well characterized through the reactions of the different bridged amide proligands H_2L^n with appropriate $RE[N(TMS)_2]_3$ in good yields. It is noteworthy that the spatial structures of these complexes depend on the diverse structures of ligands and the ionic radii of the metal centers. It is the first example that the bridged bis(amidato) rare earth metal amides were successfully introduced in the preparation of amides from the direct amidation of amines with aldehydes. Aliphatic secondary amines and diamines also underwent the transformation smoothly using La complex **1** as the catalyst and the target amides were obtained in moderate to excellent yields with some substituent tolerance. Furthermore, the catalytic system also performed well in the addition of amines and DIC. Neodymium precatalyst **3** can be used to promote reactions of electronically and sterically varied amines with DIC under appropriate conditions. Direct comparison of other previously published rare earth metal amido complexes with complexes **1** and **3** bearing carbon bridged bis(amidato) group showed that the catalytic activities of **1** and **3** are superior with respect to the reduced amount of precatalysts and the relative wide substrate scope. Many efforts to investigate catalytic mechanisms and develop new efficient catalysts are still in process in our lab.

Experimental section

All experiments were performed by using standard Schlenk or glove-box techniques, with rigorous exclusion of traces of moisture and air. After being dried over, THF, toluene and *n*-hexane were purified by distillation from sodium/benzophenoneketyl. Benzene- d_6 , THF- d_8 and toluene- d_8 were dried with sodium sand. All commercially available chemicals (aldehydes, amines, and DIC) were dried with CaH_2 and distilled in vacuum or atmospheric pressure prior to use. NMR spectra were recorded using a Bruker-400 MHz spectrometer in $CDCl_3$, benzene- d_6 , THF- d_8 or toluene- d_8 at room temperature, unless otherwise stated. The crystal structures were resolved by direct method equipped with graphite-monochromatized Mo $K\alpha$ ($\lambda = 0.71075 \text{ \AA}$) radiation after measuring and collecting data on a Rigaku Mercury CCD X-ray diffractometer. All the non-hydrogen atomic coordinates and anisotropic thermal parameters went on with correction by the full matrix least squares method and refined by using the SHELXL-1997 program^[19]. The C, H, and elemental analyses of rare-earth metal complexes were performed in the element analyzer of the Carlo Erba 1110 and determination of infrared absorption spectrum was implemented in the vertex 70 Fourier transform infrared spectrometer, scanning range from 400-4000 cm^{-1} .

Synthesis of $\{L^1Ln[N(SiMe_3)_2]\}_2$ (**1-4**)

To a solution of $Ln[N(SiMe_3)_2]_3$ (1 mmol) in THF (10 mL), a THF suspension (10 mL) of proligand H_2L^1 (1 mmol) was added slowly at 25 °C and the mixture was stirred for 15 h under 60 °C. After THF was removed under vacuum, the solid residue was washed with *n*-hexane to remove silylamine, which was recrystallized in toluene. After several days, suitable crystals were obtained in 61%-74% yield.

$\{L^1La[N(SiMe_3)_2]\}_2$ (1**):** colourless crystals, yield 61%; 1H NMR (400 MHz, d_8 -Tol): 6.79-6.61 (m, 8H, ArH), 3.08-3.03 (m, 4H, CH_2N), 2.74-2.69 (m, 4H, CH_2N), 2.41-2.12 (m, 40H, CH_2 , $ArCH_3$), 0.32 (s, 30H, $SiCH_3$), 0.08 (s, 6H, $SiCH_3$); ^{13}C NMR (100 MHz, d_8 -THF): 177.89, 135.72, 134.35, 132.44, 127.10, 46.34, 33.34, 32.39, 19.65, 18.65, 3.77, 3.50, 1.22; IR (ν , cm^{-1}): 2957 (w), 2923 (w), 1627 (s), 1613 (s), 1544 (m), 1459 (m), 1435 (m), 1399 (m), 1377 (m), 1340 (m), 1251 (m), 1179 (m), 1143 (m), 931 (s), 847 (s); Anal. calcd for $C_{58}H_{92}La_2N_6O_4Si_4$ (1327.54 $g \cdot mol^{-1}$): C 52.47, H 6.99, N 6.33, La 20.93; Found: C 52.19, H 6.84, N 6.13, La 20.78.

$\{L^1Sm[N(SiMe_3)_2]\}_2$ (2**):** colourless crystals, yield 66 %; IR (ν , cm^{-1}): 2954 (w), 2921 (w), 1625 (s), 1612 (s), 1540 (m), 1457 (m), 1438 (m), 1397 (m), 1374 (m), 1342 (m), 1249 (m), 1179 (m), 1140 (m), 930 (s), 845 (s); Anal. calcd for $C_{58}H_{92}Sm_2N_6O_4Si_4$ (1354.47 $g \cdot mol^{-1}$): C 51.58, H 6.87, N 6.22, Sm 22.27; Found: C 51.44, H 6.68, N 6.16, Sm 20.78.

$\{L^1Nd[N(SiMe_3)_2]\}_2$ (3**):** blue crystals, yield 74%; IR (ν , cm^{-1}): 2953 (w), 2919 (w), 1624 (s), 1612 (s), 1540 (m), 1457 (m), 1434 (m), 1397 (m), 1374 (m), 1342 (m), 1249 (m), 1177 (m), 1140 (m), 929 (s), 845 (s); Anal. calcd for $C_{58}H_{92}Nd_2N_6O_4Si_4$ (1334.46 $g \cdot mol^{-1}$): C 52.06, H 6.93, N 6.28, Nd 21.56; Found: C 52.33, H 6.78, N 5.94, Nd 21.19.

$\{L^1Y[N(SiMe_3)_2]\}_2$ (4**):** colourless crystals, yield 64%; 1H NMR (400 MHz, d_8 -THF): 6.81(s, 8H, ArH), 2.93-2.91(m, 8H, CH_2N), 2.40-2.39(m, 4H, CH_2), 2.30-2.20(m, 36H, $ArCH_3$), 0.12 (s, 24H,

SiCH₃), 0.05 (s, 4H, SiCH₃), 0.04 (s, 4H, SiCH₃), -0.07 (s, 4H, SiCH₃); IR (ν, cm⁻¹): 2950 (w), 2916 (w), 1622 (s), 1612 (s), 1540 (m), 1457 (m), 1430 (m), 1397 (m), 1371 (m), 1342 (m), 1249 (m), 1177 (m), 1140 (m), 929 (s), 845 (s); Anal. calcd for C₅₈H₉₂Y₂N₆O₄Si₄ (1226.44 g·mol⁻¹): C 56.75, H 7.55, N 6.85, Y 14.49; Found: C 56.40, H 7.43, N 6.77, Y 14.39.

Synthesis of {L²Ln[N(SiMe₃)₂]}₂ (5 and 6)

To a solution of Ln[N(SiMe₃)₂]₃ (1 mmol) in THF (10 mL), a THF solution (10 mL) of H₂L² (1 mmol) was added slowly at 25 °C and the mixture was stirred for 24 h under room temperature. After THF was removed under vacuum, the solid residue was washed with hexane to remove silylamine, which was recrystallized in hexane-THF. After several days, suitable crystals were obtained in 72% yield for **5** and 75% yield for **6**.

{L²La[N(SiMe₃)₂]}₂ (**5**): colourless crystals, yield 72%; ¹H NMR (400 MHz, d₈-THF): 6.78 (s, 8H, ArH), 2.73 (s, 8H, CH₂), 2.24 (d, J = 10.5 Hz, 36H, ArCH₃), 0.70 (s, 12H, CH₃), 0.14 (s, 24H, Si-CH₃), 0.04 (s, 12H, Si-CH₃); ¹³C NMR (100 MHz, d₈-THF): 179.4, 135.7, 134.2, 132.6, 127.0, 66.7, 57.8, 35.1, 24.9, 24.8, 24.2, 24.0, 23.8, 23.6, 23.4, 19.6, 18.9, 3.5, 1.2; IR (ν, cm⁻¹): 2951 (w), 2919 (w), 1627 (s), 1612 (s), 1535 (m), 1437 (m), 1377 (m), 1341 (s), 1248 (m), 1212 (m), 1180 (m), 1141 (m), 930 (s), 846 (s); Anal. calcd for C₆₂H₁₀₀La₂N₆O₄Si₄ (1382.50 g·mol⁻¹): C 53.82, H 7.20, N 5.88, La 20.20; Found: C 53.58, H 7.13, N 5.89, La 19.92.

{L²Nd[N(SiMe₃)₂]}₂ (**6**): light blue crystals, yield 75%; IR (ν, cm⁻¹): 2953 (w), 2919 (w), 1625 (s), 1612 (s), 1540 (m), 1457 (m), 1435 (m), 1397 (m), 1375 (m), 1343 (m), 1249 (m), 1177 (m), 1128 (m), 930 (m), 846 (s); Anal. calcd for C₆₂H₁₀₀Nd₂N₆O₄Si₄ (1390.51 g·mol⁻¹): C 53.41, H 7.23, N 6.03, Nd 20.69; Found: C 53.01, H 6.97, N 5.80, Nd 20.40.

Synthesis of {L³Ln[N(SiMe₃)₂]}₂ (7 and 8)

To a solution of Ln[N(TMS)₂]₃ (1 mmol) in THF (10 mL), a THF solution (10 mL) of H₂L³ (1 mmol) was added slowly at 25 °C and the mixture was stirred for 24 h under 60 °C. Then THF was removed under vacuum, the residue was washed by *n*-hexane for several times. After that, the powder was dissolved in mixed toluene-hexane and recrystallized at room temperature. The crystals of complexes **7** and **8** were isolated in 78% and 79% yield, respectively.

{L³La[N(SiMe₃)₂]}₂ (**7**): colourless crystals, yield 78%; ¹H NMR (400 MHz, C₆D₆): 6.85 (s, 8H, ArH), 2.91-2.71 (m, 8H, CH₂-N), 2.61-2.08 (m, 50H, CH₂, ArCH₃), 0.31 (s, 36H, Si-CH₃); IR (ν, cm⁻¹): 2950 (w), 2917 (w), 2852 (w), 1631 (m), 1612 (m), 1541 (s), 1436 (m), 1395 (m), 1340 (s), 1248 (m), 1181 (m), 1141 (m), 958 (m), 927 (m), 884 (m), 847 (s); Anal. calcd. for C₆₂H₁₀₂La₂N₈O₄Si₄ (2825.04 g·mol⁻¹): C 52.69, H 7.28, N 7.93, La 19.69; Found: C 52.36, H 7.03, N 7.57, La 19.36.

{L³Nd[N(SiMe₃)₂]}₂ (**8**): blue crystals, yield 79%; IR (ν, cm⁻¹): 2953 (w), 2916 (w), 2852 (w), 1635 (m), 1612 (m), 1541 (s), 1436 (m), 1396 (m), 1341 (m), 1249 (m), 1180 (m), 1140 (m), 982 (m), 928 (m), 884 (m), 846 (s); Anal. calcd. for C₆₂H₁₀₂Nd₂N₈O₄Si₄ (1418.53 g·mol⁻¹): C 52.28, H 7.23, N 7.88, La 20.25; Found: C 52.56, H 6.94, N 7.74, La 20.06.

General procedure for the amidation of amines and aldehydes:

Take complex **1** as an example. A Schlenk tube was charged with complex **1** (0.01 mmol), *N*-methylbenzylamine (1.0 mmol)

and 0.8 mL of THF successively, then the mixture was stirred at room temperature for half an hour. Aldehyde (3.0 mmol) was added, and the mixture was continued to be stirred for another 3 h. The reaction was quenched by ethyl acetate and the target product was separated and purified by column chromatography.

General procedure for the guanidination of DIC and amines:

Take complex **3** as an example. Complex **3** (0.0025 mmol) and aniline (1.0 mmol) was added into a Schlenk tube and stirred for a while. After complex **3** was dissolved in aniline, DIC (1.0 mmol) was added by syringe. The resulting mixture was stirred at 60 °C for an appropriate time, then quenched by water (2 mL), extracted with dichloromethane (3 × 10 mL). The organic layer was dried over anhydrous Na₂SO₄, filtered, and the solvent was removed under vacuum to give the target product.

Notes:

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of China. Fax: +86-512-65880305; Tel: +86-512-65880305; E-mail: zhaobei@suda.edu.cn,† the information that supplementary of crystallographic data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or e-mail: deposit@ccdc.cam.ac.uk. [CCDC: 1402613 (3), 1402611 (5), 1402612 (6), 1407220 (7), 1402610(8)]

Acknowledgments:

We gratefully acknowledge financial supports from the National Natural Science Foundation of China (Grant Nos. 21172165, 21132002, 21372172 and 21572151), PAPD, the Major Research Project of the Natural Science Foundation of the Jiangsu Higher Education Institutions (Project 14KJA150007), and the Qing Lan Project.

References

- 1 C. T. Qian, C. H. Wang and Y. F. Chen, *Acta Chim. Sinica*, 2014, **72**, 883.
- 2 (a) C. H. Huang, *Rare earth Coordination Chemistry: Fundamentals and applications*, John Wiley & Sons, Inc., Singapore, 2010; (b) L. C. Song and B. Q. Wang, *The principle and application of Organolanthanide chemistry*, Higher Education Press, Beijing, 2012.
- 3 (a) Q. W. Wang, F. R. Zhang, H. B. Song and G. F. Zi, *J. Organomet. Chem.*, 2011, **696**, 2186-2192; (b) F. R. Zhang, J. X. Zhang, H. B. Song and G. F. Zi, *Inorg. Chem. Commun.*, 2011, **14**, 72-74; (c) X. L. Hu, C. R. Lu, B. Wu, H. Ding, B. Zhao, Y. M. Yao and Q. Shen, *J. Organomet. Chem.*, 2013, **732**, 92-101; (d) H. Ding, C. R. Lu, X. L. Hu, B. Zhao, B. Wu and Y. M. Yao, *Synlett*, 2013, **24**, 1269-1274; (e) H. Cheng, B. Zhao, Y. M. Yao and C. R. Lu, *Green Chem.*, 2015, **17**, 1675-1682; (f) L. Zhao, H. Ding, B. Zhao, Y. M. Yao and C. R. Lu, *Polyhedron*, 2014, **83**, 50-59; (g) L. J. E. Stanlake and L. L. Schafer, *Organometallics*, 2009, **28**, 3990-3998; (h) J. A. Thomson and L. L. Schafer, *Dalton Trans.*, 2012, **41**, 7897-7904; (i) J. L.

- Brown, M. B. Jones, and A. J. Gaunt, *Inorg. Chem.*, 2015, **54**, 4064-4075; (j) H. Cheng, Y. Xiao, C. R. Lu, B. Zhao, Y. R. Wang and Y. M. Yao, *New J. Chem.*, 2015, **39**, 7667-7671.
- 4 (a) A. B. Reitz, R. W. Tuman, C. S. Marchione, A. D. J. Jordan, C. R. Bowden and B. E. Maryanoff, *J. Med. Chem.*, 1989, **32**, 2110-2116; (b) T. J. Baker, N. W. Luedtke, Y. Tor and M. Goodman, *J. Org. Chem.*, 2000, **65**, 9054-9058.
- 5 (a) M. C. Wood, D. C. Leitch, C. S. Yeung, J. A. Kozak and L. L. Schafer, *Angew. Chem. Int. Ed.*, 2007, **46**, 354-358; (b) A. L. Reznichenko and K. C. Hultsch, *Organometallics*, 2010, **29**, 24-27.
- 6 S. Y. Seo and T. J. Marks, *Org. Lett.*, 2008, **10**, 317-319.
- 7 (a) J. F. Wang, J. M. Li, F. Xu and Q. Shen, *Adv. Synth. Catal.*, 2009, **351**, 1363-1370; (b) C. W. Qian, X. M. Zhang, J. M. Li, F. Xu, Y. Zhang and Q. Shen, *Organometallics*, 2009, **28**, 3856-3862; (c) C. W. Qian, X. M. Zhang, Y. Zhang and Q. Shen, *J. Organomet. Chem.*, 2010, **695**, 747-752; (d) J. M. Li, F. Xu, Y. Zhang and Q. Shen, *J. Org. Chem.*, 2009, **74**, 2575-2577; (e) C. Y. Cai, L. Li, F. Xu and Q. Shen, *Chinese Sci. Bull.*, 2010, **55**, 3641-3643; (f) Y. J. Wu, S. W. Wang, L. J. Zhang, G. S. Yang, X. C. Zhu, Z. H. Zhou, H. Zhu and S. H. Wu, *Eur. J. Org. Chem.*, 2010, 326-332; (g) B. Xu, L. L. Huang, Z. J. Yang, Y. M. Yao, Y. Zhang and Q. Shen, *Organometallics*, 2011, **30**, 3588-3595. (h) C. Wang, L. L. Huang, M. Lu, B. Zhao, Y. R. Wang, Y. Zhang, Q. Shen and Y. M. Yao, *RSC Adv.*, 2015, **5**, 94768.
- 8 (a) M. K. T. Tin, G. P. A. Yap and D. S. Richeson, *Inorg. Chem.*, 1998, **37**, 6728-6730; (b) M. K. T. Tin, N. Thirupathi, G. P. A. Yap and D. S. Richeson, *J. Chem. Soc., Dalton Trans.*, 1999, **17**, 2947-2951.
- 9 (a) W. X. Zhang, M. Nishiura and Z. M. Hou, *Synlett*, 2006, **8**, 1213-1216; (b) W. X. Zhang, M. Nishiura and Z. M. Hou, *Chem. Eur. J.*, 2007, **13**, 4037-4051; (c) L. Xu, Z. T. Wang, W. X. Zhang and Z. F. Xi, *Inorg. Chem.*, 2012, **51**, 11941-11948; (d) S. L. Zhou, S. W. Wang, G. S. Yang, Q. Li, L. J. Zhang, Z. J. Yao, Z. Zhou and H. B. Song, *Organometallics*, 2007, **26**, 3755-3761; (e) Y. B. Wang, Y. Y. Lei, S. H. Chi and Y. J. Luo, *Dalton Trans.*, 2013, **42**, 1862-1871; (f) Y. J. Luo, Y. B. Wang and J. Chen, *Chin. J. Chem.*, 2013, **31**, 1065-1071; (g) Q. H. Li, S. W. Wang, S. L. Zhou, G. S. Yang, X. C. Zhu and Y. Y. Liu, *J. Org. Chem.*, 2007, **72**, 6763-6767; (h) Z. Du, W. Li, X. Zhu, F. Xu and Q. Shen, *J. Org. Chem.*, 2008, **73**, 8966-8972; (i) Y. J. Wu, S. W. Wang, L. J. Zhang, G. S. Yang, X. C. Zhu, C. Liu, C. W. Yin and J. W. Rong, *Inorg. Chim. Acta.*, 2009, **262**, 2814-2819. (j) C. Liu, S. L. Zhou, S. W. Wang, L. J. Zhang and G. S. Yang, *Dalton Trans.*, 2010, **39**, 8994-8999; (k) X. M. Zhang, C. Y. Wang, C. W. Qian, F. B. Han, F. Xu and Q. Shen, *Tetrahedron*, 2011, **67**, 8790-8799; (l) F. B. Han, Q. Q. Teng, Y. Zhang, Y. R. Wang and Q. Shen, *Inorg. Chem.*, 2011, **50**, 2634-2643; (m) Z. Li, M. Q. Xue, H. S. Yao, H. M. Sun, Y. Zhang and Q. Shen, *J. Organomet. Chem.*, 2012, **713**, 27-34; (n) L. X. Cai, Y. M. Yao, M. Q. Xue, Y. Zhang and Q. Shen, *Appl. Organometal. Chem.*, 2013, **27**, 366-372; (o) P. H. Wei, L. Xu, L. C. Song, W. X. Zhang and Z. F. Xi, *Organometallics*, 2014, **33**, 2784-2789; (p) J. Tu, W. Li, M. Xue, Y. Zhang and Q. Shen, *Dalton Trans.*, 2013, **42**, 5890-5901.
- 10 (a) D. C. Leitch, P. R. Payne, C. R. Dunbar and L. L. Schafer, *J. Am. Chem. Soc.*, 2009, **131**, 18246-18247; (b) M. W. Drover, L. L. Schafer and J. A. Love, *Organometallics*, 2015, **34**, 1783-1786.
- 11 (a) D. C. Bradley, J. S. Ghotra and F. A. Hart, *J. Chem. Soc., Dalton Trans.*, 1973, 1021-1023. (b) S. P. Anthony, K. Basavaiah and T. P. Radhakrishnan, *Cryst. Growth. Des.*, 2005, **5**, 1663-1666.
- 12 A. V. Lee and L. L. Schafer, *Eur. J. Inorg. Chem.*, 2007, 2243-2255.
- 13 Y. Xiao, Q. Y. Wang, B. Zhao and Y. M. Yao, *Chin. J. Org. Chem.*, 2015, 1598-1614 (in Chinese).
- 14 L. J. Zhang, S. W. Wang, S. L. Zhou, G. S. Yang and E. Sheng, *J. Org. Chem.*, 2006, **71**, 3149-3153.
- 15 (a) J. M. Humphrey and A. R. Chamberlin, *Chem. Rev.*, 1997, **97**, 2243-2266; (b) K. Ekoue-Kovi and C. Wolf, *Chem. Eur. J.*, 2008, **14**, 6302-6315.
- 16 T. E. Frank, *Chem. Soc. Rev.*, 2012, **41**, 7657-7672.
- 17 (a) M. P. Coles, *Chem. Commun.*, 2009, 3659-3676; (b) T. Ishikawa, *Chem. Pharm. Bull.*, 2010, **58**, 1555-1564; (c) X. Fu and C. H. Tan, *Chem. Commun.*, 2011, **47**, 8210-8222; (d) J. E. Taylor, S. D. Bull and J. M. J. Williams, *Chem. Soc. Rev.*, 2012, **41**, 2109-2121.
- 18 (a) W. H. Zhang and Z. M. Hou, *Org. Biomol. Chem.*, 2008, **6**, 1720-1730; (b) A. M. Carlos, A. Antonio, C. H. Fernando and O. Antonio, *Chem. Soc. Rev.*, 2014, **43**, 3406-3425; (c) W. X. Zhang, L. Xu and Z. F. Xi, *Chem. Commun.*, 2015, **51**, 254-265; (d) L. Xu, W. X. Zhang and Z. F. Xi, *Organometallics*, 2015, **34**, 1787-1801.
- 19 G. M. Sheldrick, SHELXL-1997, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

Graphic Abstract

Synthesis and characterization of bridged bis(amidato) rare earth metal amides and their applications in C-N bond formation reactions

Bei Zhao*, Yang Xiao, Dan Yuan, Chengrong Lu, Yingming Yao*

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science,
Soochow University, Suzhou 215123, PR China

Eight bis(amidato) rare-earth metal amides were successfully synthesized and well characterized, which exhibited high catalytic activities in both the direct amidation of aldehydes and the addition of amines with carbodiimine.

