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Synthesis and characterization of bis(amidate) rare-earth metal amides and their application in catalytic addition of amines to carbodiimides†

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Two new bis(amidate) lanthanide amides $\{LLn[N(SiMe_3)_2]\cdot THF\}_2$ (H_2L = *N*,*N*′-(cyclohexane-1,2-diyl)-bis(4-*tert*-butyl-benzamide); Ln = Sm(**4**), Yb(**5**)), which were prepared by the treatment of the bridged amide proligand H_2L with $Ln[N(SiMe_3)_2]_3$ in tetrahydrofuran, had been characterized by single-crystal X-ray diffraction and elemental analyses. Both complexes **4** and **5** and the three known isomorphs $\{LRE[N(SiMe_3)_2]\cdot THF\}_2$ (RE = La(**1**), Nd(**2**), Y(**3**)) were successfully employed in the addition of amines to carbodiimides for the first time and were found to be efficient catalysts in the transformation at 60 °C under solvent-free conditions. The Nd-based catalyst **2** showed the highest reactivity and provided various guanidines with good functional group tolerance in high to excellent yields.

Introduction

Guanidines have an important molecular framework, which shares a Y-shaped CN_3 functional group,[1] and are found in many biologically and pharmaceutically active compounds.[2] They are also widely used as ligands in the design of a variety of high efficiency catalysts in many reactions.[3] Meanwhile guanidines themselves as bases could directly catalyze many organic synthesis reactions, such as the Michael reaction, the Henry reaction, the Wittig reaction and the Strecker reaction.[4] Metal catalytic addition of amines to carbodiimides is a well-known methodology in guanidine synthesis, since it is a highly atom-economic reaction, and the commonly used catalysts include main group metal-based catalysts,[5] transition metal-based catalysts[6] and rare-earth metal catalysts.[7]

Rare-earth metal amides have shown highly efficient reactivities in the addition reaction of amines to carbodiimides. Wang firstly employed a simple lanthanide amide $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ to catalyze the reaction using both primary and secondary amines as the substrates and brought out good yields.[7b] This finding aroused several chemists' enthusiasm and many kinds of rare-earth metal amides with different ancillary ligands had been screened for this reaction subsequently, such as indenyl, cyclopentadienyl, pyrrolyl, N-heterocyclic carbene and salen groups.[7c–e,i–l] However, the requirements for some reaction conditions, for example, the relatively high temperature (80–100 °C), the use of organic solvents (benzene, THF, toluene, *etc.*) and a slightly large dosage of the catalysts (0.5–3 mol%), were dissatisfactory and in need of improvement. Thus, seeking new kinds of high efficiency catalysts to realize the addition of amines to carbodiimides, which performed well under mild reaction conditions, is of importance.

Very recently, a bisamide proligand H_2L (H_2L = *N*,*N*′-(cyclohexane-1,2-diyl) bis(4-*tert*-butylbenzamide)) was successfully designed for the preparation of three bridged bis(amidate) rare-earth metal amides $\{LRE[N(SiMe_3)_2]\cdot THF\}_2$ (RE = La(**1**), Nd(**2**), Y(**3**)). The complexes **1–3** had proved to be excellent catalysts for the direct carboxylation by introduction of CO_2 into terminal alkynes at ambient pressure.[8] To further explore the application of these kinds of amides, we prepared two more bis(amidate) rare-earth metal amides $\{LLn[N(SiMe_3)_2]\cdot THF\}_2$ (Ln = Sm(**4**), Yb(**5**)) *via* the treatment of the bridged amide proligand H_2L with $Ln[N(SiMe_3)_2]_3$. Then, five bridged bis(amidate) rare-earth metal amides were screened for the addition of amines to carbodiimides, and it was found that all the complexes are efficient catalysts for the transformation. Fortunately, various guanidines with good functional group tolerance were obtained in high to excellent yields using the highest reactive neodymium catalyst **2** at 60 °C under solvent-free conditions.

Results and discussion

Synthesis and characterization of bridged bis(amidate) rare-earth metal amides

Firstly, three known bridged bis(amidate) lanthanide amides **1–3** $\{LRE[N(SiMe_3)_2]\cdot THF\}_2$ (RE = La(**1**), Nd(**2**), Y(**3**)) were prepared

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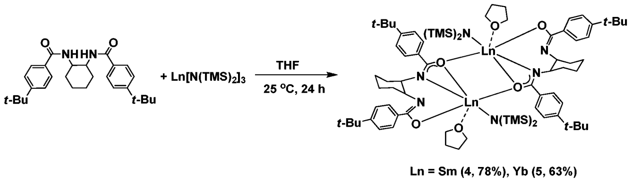
† Electronic supplementary information (ESI) available: General procedures for the preparation of complexes, detailed crystallographic data for complexes **4** and **5**, and figures depicting solid state structures. CCDC 1017172 (**4**) and 1017175 (**5**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5nj00506j



Scheme 1 Synthesis of the bridged bis(amidate) lanthanide amides **4** and **5**.

according to our previous work.[8] In order to see about the effects of central metals on the addition of amines to carbodiimides, the bridged bis(amidate) lanthanide amides **4** and **5** were subsequently prepared by simple metathesis reactions of the proligand H_2L with appropriate lanthanide precursors $Ln[N(SiMe_3)_2]_3$ in THF at room temperature overnight. The outcome of the common silylamine elimination reaction was two desired bridged bis(amidate) lanthanide amides $\{LLn[N(SiMe_3)_2]\cdot THF\}_2$ (Ln = Sm(**4**), Yb(**5**)) in good yields (Scheme 1).

Suitable single crystals of new complexes **4** and **5** were obtained from tetrahydrofuran solution and the solid state structures were determined by X-ray diffraction analysis. As expected, both of them are crystallized in the triclinic crystal system, $P\bar{1}$ space group, and have binuclear centrosymmetric structures with three THF molecules in each unit cell. Since complexes **4** and **5** are isomorphous, only the molecular structure of the Sm-based complex **4** is depicted in Fig. 1 as a representation. It shows that complex **4** is composed of two equivalent subunits with one Sm(III) center for each moiety. Each bridged bis(amidate) group adopts two similar bonding modes, namely κ^2-(N,O):μ-O bonding and monodentate O-bonding modes, to coordinate to each samarium atom. It is the bridged oxygen atom in the κ^2-(N,O):μ-O bound amido group that coordinates to the other samarium atom in the cell to connect two subunits. Each cyclohexane-1,2-diyl group adopts a low-energy state chair conformation to stabilize the whole skeleton of crystals. Fig. 1 shows the structure of the bridged bis(amidate) samarium amide **4** and some selected bond lengths and bond angles. Because of the similarity of the structural features of complexes **4** and **5**, the detailed bond parameters of complex **5** are omitted here.

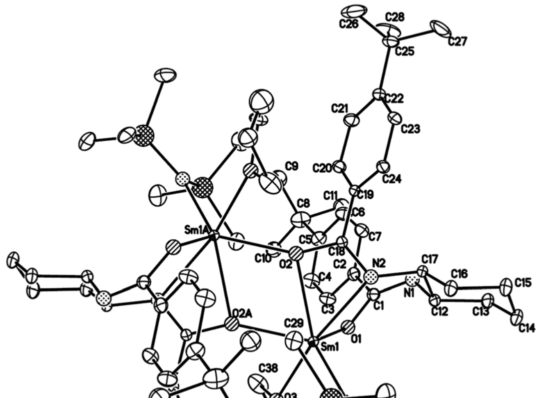
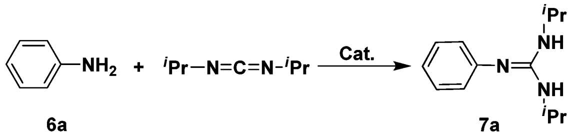


Fig. 1 Structure of bridged bis(amidate) samarium amide **4**, all hydrogen atoms and THF molecules in the unit cell are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Sm(1)–O(1) 2.196(3), Sm(1)–N(3) 2.308(3), Sm(1)–O(2A) 2.364(3), Sm(1)–O(3) 2.494(3), Sm(1)–N(2) 2.500(3), Sm(1)–O(2) 2.550(3), O(1)–Sm(1)–O(3) 79.44(11), O(3)–Sm(1)–O(2A) 76.75(11), O(2A)–Sm(1)–N(2) 117.02(10), N(2)–Sm(1)–O(1) 77.53(11), N(3)–Sm(1)–O(2) 134.62(11), O(2A)–Sm(1)–O(2) 66.13(10).

Synthesis of guanidines by the reaction of amines with carbodiimides catalyzed by bridged bis(amidate) rare-earth metal amides

It is known that there are many successful cases of rare-earth metal amides published regarding the catalytic addition reactions of amines to carbodiimides.[7b–e,i–l] Curiosity evoked us to try bridged bis(amidate) rare-earth metal amides **1–5** in the template reaction of phenylamine (**6a**) with *N*,*N*′-diisopropylcarbodiimide and make clear whether they could perform better. To our delight, an excellent yield of 97% of the target product 1,3-diisopropyl-2-phenylguanidine (**7a**) was obtained using complex **1** as the catalyst (Table 1, entry 1). Immediately, the effects of the central metals on different complexes were tested, and complexes **3** and **5** with smaller ionic radii had the obvious tendency of decreasing reactivities in this transformation (Table 1, entries 1–5). When the dosage of the catalyst was reduced to half of the original, still there was no significant gap between the catalytic reactivities of complexes **1**, **2** and **4** (Table 1, entries 6–8). Until the catalyst loading was cut down to 0.05 mol%, different reactivities between complexes **1**, **2** and **4** emerged (Table 1, entries 9–11).

Table 1 Effects of catalysts, temperature and solvents on the preparation of guanidines



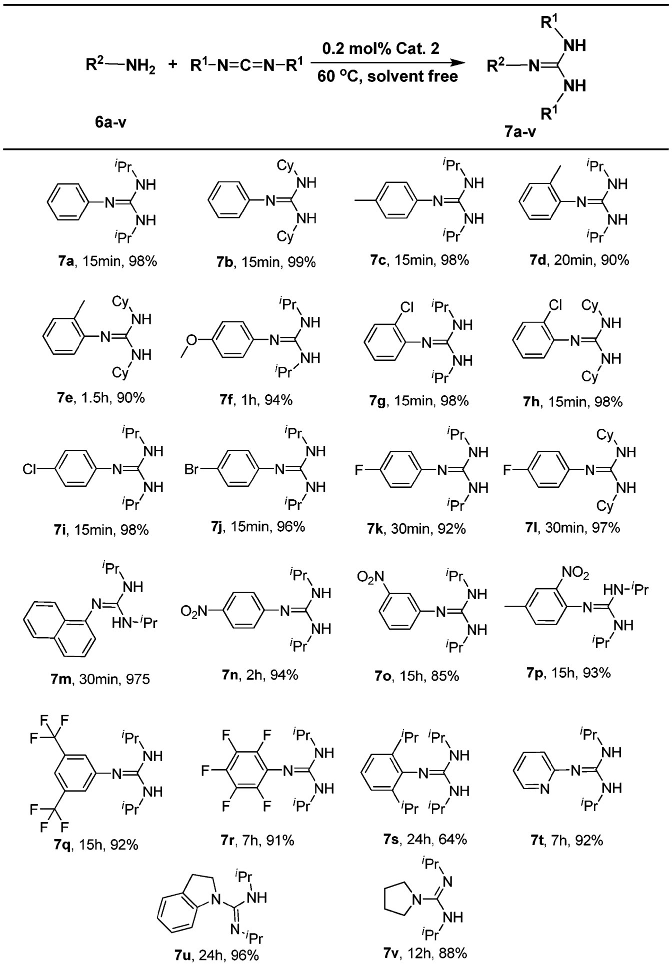
Entry	Cat/mol%	Solvent	*T*/°C	*t*/min	Yield[a]/%
1	**1**/0.25	—	60	15	97
2	**2**/0.25	—	60	15	96
3	**3**/0.25	—	60	15	65
4	**4**/0.25	—	60	15	96
5	**5**/0.25	—	60	15	70
6	**1**/0.125	—	60	30	87
7	**2**/0.125	—	60	30	90
8	**4**/0.125	—	60	30	89
9	**1**/0.05	—	60	30	22
10	**2**/0.05	—	60	30	34
11	**4**/0.05	—	60	30	30
12	**2**/0.15	—	60	15	71
13	**2**/0.2	—	60	15	98
14	**2**/0.2	—	25	15	17
15	**2**/0.2	—	40	15	50
16	**2**/0.2	—	80	15	88
17	**2**/0.2	Tol	60	15	33
18	**2**/0.2	THF	60	15	36
19	**$Nd[N(SiMe_3)_2]_3$**/0.2	—	60	15	67

[a] Isolated yields.

Finally, complex **2** of the central Nd metal with a medium ionic radius was selected to be an ideal catalyst to give us an excellent catalytic outcome in consideration of the efficiency and handy operation, while only 67% of the product was produced in the presence of the corresponding precursor $Nd[N(SiMe_3)_2]_3$ (Table 1, entries 13 and 19). Different temperatures and the addition of polar or nonpolar solvents were also investigated, and the optimal reaction condition was proved to be solvent-free at 60 °C (Table 1, entries 13–18).

Exploration of the substrate scope was carried out soon. Various amines were screened at 60 °C under solvent-free conditions for an appropriate reaction time in the presence of 0.2 mol% catalyst **2** and the results are shown in Table 2. When the substrates on aromatic amines are electron donating groups, excellent yields of guanidines that varied from 90–98% were obtained in short time (Table 2, **7c–f**). The outcome seems much better than the results of previous work.[7c,j] The aromatic amines bearing electron withdrawing groups (EWGs) also gave us excellent yields of 92–98% with high efficiency (Table 2, **7g–l**). It is worthy of note that although the stronger EWGs, the nitro group and the trifluoro group, on phenyl rings retarded the reaction process, good to excellent yields of the corresponding guanidines were still gained as expected (Table 2, **7n–q**). For the same substrate of *p*-nitroaniline, the comparative outcome can be achieved at 110 °C for 36 h with 2 mol% catalyst loading of Wang's catalyst $[\eta^5\text{-}(CH_2)_2(C_9H_6)_2]YN(TMS)_2$[7c] or at 60 °C for 12 h with 2 mol% catalyst $\{(\mu\text{-}\eta^5{:}\eta^1){:}\eta^1\text{-}2\text{-}[(2,4,6\text{-}Me_3C_6H_2)NCH_2][C_4H_3N]SmN(SiMe_3)_2\}_2$,[7i] while Shen got a better result at 60 °C for 12 h with 0.5 mol% catalyst $[4\text{-}OMe\text{-}C_6H_4COCH(CNCHCHN^iPr)]_2$ $YbN(TMS)_2$.[7k] This shows that there are a few electronic effects of substituents on the reaction of amines with carbodiimides, however the steric hindrance has a little effect on the reactivities. For the relatively large sterically hindered 2,6-diisopropyl aniline, the catalytic efficiency markedly decreased to a yield of 64% after 24 h, while aniline and *o*-methyl aniline underwent reaction for 15–20 min to give the corresponding products in 98% and 90% yields, respectively (Table 2, **7a**, **7d** and **7s**). The high efficiency catalyst system also performed excellent in the case of heteroaromatic amines, secondary aromatic amines and alicyclic amines (Table 2, **7t–v**). No obvious effects on the reaction of the substituents of carbodiimide were observed and excellent yields were obtained in all cases of *N*,*N*′-dicyclohexylcarbodiimide (Table 2, **7b**, **7e**, **7h**, and **7l**).

Table 2 Substrate scope for the synthesis of guanidines *via* the treatment of amines with carbodiimides[a]

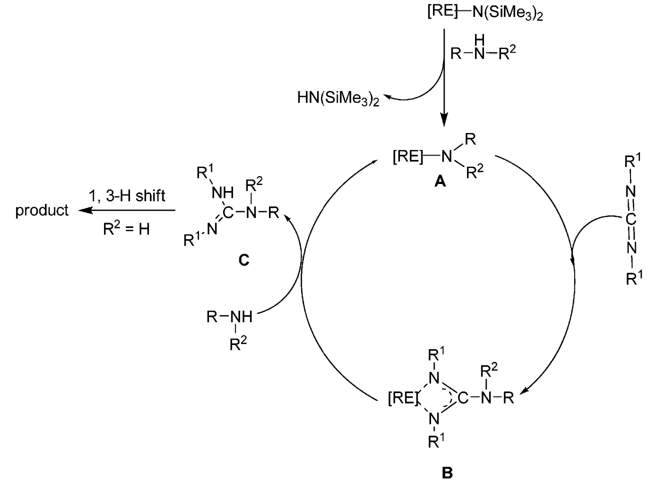


7a, 15min, 98%
7b, 15min, 99%
7c, 15min, 98%
7d, 20min, 90%
7e, 1.5h, 90%
7f, 1h, 94%
7g, 15min, 98%
7h, 15min, 98%
7i, 15min, 98%
7j, 15min, 96%
7k, 30min, 92%
7l, 30min, 97%
7m, 30min, 975
7n, 2h, 94%
7o, 15h, 85%
7p, 15h, 93%
7q, 15h, 92%
7r, 7h, 91%
7s, 24h, 64%
7t, 7h, 92%
7u, 24h, 96%
7v, 12h, 88%

[a] Isolated yields.

Possible mechanism of the synthesis of guanidines by the reaction of amines with carbodiimides catalyzed by bridged bis(amidate) rare-earth metal amides

Based on some literatures,[7b–e,m] we proposed a possible mechanism for our catalytic transformation in Scheme 2. In the first step, in the reaction of substrate amines with the rare-earth metal amides, a new amido intermediate **A** was generated *via* aminolysis. With the introduction of carbodiimide into the RE–N bond, a metal guanidinate species **B** was produced. In the presence of a large amount of amines, the regeneration of **A** was instantly completed and the desired product **C** was achieved. If R^2 is hydrogen atom, generated **C** followed by the 1,3-proton migration released the target guanylated product.



Scheme 2 A possible mechanism for the synthesis of guanidines by the reaction of amines with carbodiimides catalyzed by bridged bis(amidate) rare-earth metal amides.

Conclusion

In summary, totally five bridged bisamidate rare earth metal amides $\{LRE[N(SiMe_3)_2]{\cdot}THF\}_2$ (RE = La(**1**), Nd(**2**), Y(**3**), Sm(**4**), and Yb(**5**); H_2L = *N*,*N*′-(cyclohexane-1,2-diyl)-bis(4-*tert*-butylbenzamide)) had been prepared by the reaction of the bridged amide proligand H_2L with $RE[N(SiMe_3)_2]_3$ in good yields. X-ray structural analysis shows that two new compounds **4** and **5** are isomorphic as the known complexes **1–3** with binuclear centrosymmetric structures. This is the first time that the bridged bisamidate rare earth metal amides were successfully employed in the preparation of valuable guanidines by the reaction of amines with carbodiimides. Complex **2** with the central metal Nd performed the best among those amides and gave us high to excellent yields of guanidines with good tolerance of substituents. It is a convenient access to synthesize important 1,3-disubstituted-2-phenylguanidines and their derivatives. Much effort to make clear the catalytic mechanism and explore new efficient catalysts is still in process in our lab.

Experimental

General procedure

All manipulations and reactions were conducted under a purified argon atmosphere by using vacuum line techniques or in a glovebox. Rare-earth metal precursors $RE[N(SiMe_3)_2]_3$ (RE = La, Nd, Sm, Yb, Y) and the proligand *N*,*N*′-(cyclohexane-1,2-diyl)bis(4-*tert*-butylbenzamide) were prepared according to literature methods.[9] Solvents were distilled from sodium benzophenone ketyl under argon prior to use. Solid amines were degassed before use, and liquid amines were distilled from CaH_2 prior to use. The single crystal X-ray diffraction data were recorded on a Rigaku Mercury CCD X-ray diffractometer. ^1H and ^{13}C NMR spectra were obtained on a Bruker-400 spectrometer in $CDCl_3$. Metal analyses were carried out by a complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. Melting points of the complexes were determined in sealed Ar-filled capillary tubes and are uncorrected.

General procedure for the synthesis of $\{LRE[N(SiMe_3)_2]{\cdot}THF\}_2$

According to our previous work,[8] to a stirred THF solution of $RE[N(SiMe_3)_2]_3$ (1.49 mmol, 10 mL of THF), *N*,*N*′-(cyclohexane-1,2-diyl)-bis(4-*tert*-butylbenzamide) (0.65 g, 1.49 mmol) in 10 mL of THF was slowly added. After the mixture was stirred at 25 °C for 24 h, the solvent was pumped off, and the residue was recrystallized from THF at room temperature to give pure crystals. Characterization data collected for new complexes **4** and **5** are as follows.

$\{LSm[N(SiMe_3)_2]{\cdot}THF\}_2$ (4). Colorless crystals. Yield: 0.95 g (78%). Mp. 294.1–295.5 °C. Anal. Calcd for $C_{76}H_{126}N_6O_6Sm_2Si_4$ (1634.72): C 55.90, H 7.78, N 5.15, Sm 18.42; Found: C 56.05, H 7.85, N 5.20, Sm 18.48. IR: (KBr, cm^{-1}): 2963(w), 2361(m), 2337(m), 1634(m), 1541(s), 1507(w), 1384(s), 1236(s), 1219(s), 1157(vs), 555(m), 505(s).

$\{LYb[N(SiMe_3)_2]{\cdot}THF\}_2$ (5). Colorless crystals. Yield: 0.74 g (63%). Mp. 294.8–296.2 °C. Anal. Calcd for $C_{76}H_{126}N_6O_6Yb_2Si_4$ (1674.75): C 54.39, H 7.57, N 5.01, Yb 20.62; Found: C 54.51, H 7.50, N 5.20, Yb 20.54. IR: (KBr, cm^{-1}): 2963(w), 2361(m), 2337(m), 1634(m), 1541(s), 1507(w), 1384(s), 1236(s), 1219(s), 1157(vs), 505(s).

X-ray structure determination of complexes 4 and 5

Owing to their air and moisture sensitivity, suitable single crystals of complexes **4** and **5** were each sealed in thin-walled glass capillaries. Intensity data were collected on a Rigaku Mercury CCD equipped with graphite-monochromatized Mo Kα (λ = 0.71075 Å) radiation. Details of the intensity data collection and crystal data are given in Tables S1 and S2 in the ESI.† The crystal structures of these complexes were solved by direct methods, expanded by Fourier techniques and refined by using the SHELXL-2013 program.[10] Atomic coordinates and thermal parameters were refined by full matrix least-square analysis on F^2. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically with appropriate isotropic thermal parameters assigned.

General procedure for the synthesis of guanidines by the reaction of amines with carbodiimides

Take complex **2**, for example. A 10.0 mL Schlenk tube under dried argon was charged with complex **2** (0.002 equiv.) and aniline (1.0 equiv.) in turns. After stirring for 10 min, carbodiimide (1.0 equiv.) was added. The resulting mixture was stirred at 60 °C for an appropriate time, then hydrolyzed by water (1 mL), extracted with dichloromethane (3 × 10 mL), and the organic layer was dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under vacuum to afford the target product.

Acknowledgements

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