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Enol-functionalized *N*-heterocyclic carbene lanthanide amide complexes: Synthesis, molecular structures and catalytic activity for addition of amines to carbodiimides

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ABSTRACT

Reaction of $LnCl_3$ (Ln = Y, Nd, Sm and Yb) with enol-functionalized imidazolium salt H_2LBr (L = 4-OMe-$C_6H_4COCH\{C(NCHCHN^iPr)\}$) and $NaN(TMS)_2$ at a molar ratio of 1:4:1 in THF at room temperature afforded the corresponding novel enol-functionalized *N*-heterocyclic carbene (NHC) lanthanide amides $L_2LnN(TMS)_2$ (Ln = Y (**1**), Nd (**2**), Sm (**3**), Yb (**4**)) in 37–40% yields. Molecular structures of **1**–**4** were determined by X-ray structure analyses. All complexes adopt monomeric structures where each 5-coordinated metal is coordinated by two NHC ligands and one amido group.in distorted trigonal bipyramid geometry. All complexes, especially Yb complex (**4**), were found to be highly active pre-catalysts for the catalytic addition of amines to carbodiimides giving guanidines. The system with **4** shows good functional group tolerance and a wide scope of amines including primary and secondary cyclic amines.

1. Introduction

N-heterocyclic carbene ligands (NHC)s with a pendant anionic group have attracted increasing attention in organolanthanide chemistry [1], as these ligands are hemilable and covalently bond to metal with the tunable electronic and steric factors, which has potential in homogeneous catalyzes. Several anionic-functionalized NHC ligands were explored including alkoxo- [2,3], aryloxo- [4–7], amido- [2,7–9], indenyl- [10], fluorenyl- [11], xylene- [12], salicylaldiminato- [13] and 2,4,6-trimethylphenyl- [14,15] functionalized NHCs, and various lanthanide derivatives supported by these NHCs ligands were successfully synthesized and characterized [2–15]. Moreover, the alkoxy-functionalized NHC yttrium amide complex was reported to be a bifunctional catalyst of a combination of Lewis acid and base functionalities for lactide polymerization [2]. The lanthanide bis(alkyl)complexes bearing either fluorenyl- or indenyl- functionalized NHC were found to be efficient catalysts for syndiotactically enriched highly 3,4-selective polymerization of isoprene in the presence of aluminum alkyls and organoborate [16] and for the homo- and co-polymerization of ethylene and norbornene [11], and the CCC-pincer 2,6-xylenyl bis(carbene) lanthanide dibromides exhibited high activity and cis-1,4 selectivity in the polymerization of isoprene upon activation with AlR_3 and $[Ph_3C][B(C_6F_5)_4]$ [17].

Enol-functionalized NHC ligands, which are another kind of O-containing anionic-functionalized NHCs, have the advantages of easy to prepare and enable enhance the stability of metal-NHC bonding through the formation of six-membered metal-heterocycles. These ligands have been successfully used in the syntheses of NHC complexes of late-transition metals Pd [18,19], Ni [18,20,21] and Fe [22]. In continuation of our work [4–7,13] we were interested in understanding the potential of this kind of NHC ligands in the chemistry of organolanthanide metals. For this purpose, we designed and synthesized lanthanide amide complexes bearing the enol-functionalized NHC ligand L (L = 4-OMe-$C_6H_4COCH\{C(NCHCHN^iPr)\}$) and evaluated the catalytic activity of these new amide complexes for catalytic addition of amines to carbodiimides. Here we report details of the synthesis and molecular structures of new complexes $L_2LnN(TMS)_2$ (Ln = Y (**1**), Nd (**2**), Sm (**3**), Yb (**4**)) and the catalytic behavior of **1**–**4**.

2. Results and discussion

2.1. Synthesis and structural characterization of $L_2LnN(TMS)_2$ (Ln = Y (**1**), Nd (**2**), Sm (**3**), Yb (**4**))

The enol-functionalized imidazolium salt H_2LBr was synthesized by a published method [22]. Reaction of YCl_3 with 5

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equivalents of $NaN(TMS)_2$ in THF at room temperature, then treatment with two equivalents of H_2LBr did not allow to isolate the target product as pure crystals, but the powders which were insoluble even in THF. However, decreasing the molar ratio of YCl_3/$NaN(TMS)_2$/H_2LBr from 1:5:2 to 1:4:1 led to the isolation of pink crystals in 37% yield easily upon crystallization from toluene. Elemental analysis of the crystals is consistent with the formula of $L_2YN(TMS)_2$ (**1**) (Scheme 1). The ^{13}C NMR spectra of the crystals revealed the characteristic signals of the ylidene carbons at 188.37 and 187.94 ppm, which are comparable to the values reported previously for the NHC-containing Y complexes [9,10]. The appearance of the characteristic signals of the carbene carbon indicates the formation of a direct Y-$C_{carbene}$ linkage. Complex **1** was further confirmed by an X-ray crystal structure analysis.

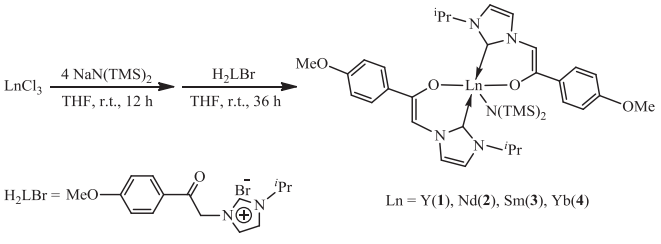
The success in the preparation of complex **1** promoted us to prepare the analogous complexes with other lanthanide metals. Thus, the similar reactions with $NdCl_3$, $SmCl_3$ and $YbCl_3$ were conducted. All reactions went smoothly to give the corresponding complexes $L_2LnN(TMS)_2$ (Ln = Nd (**2**), Sm (**3**), Yb (**4**)) as blue crystals for **2**, light yellow and yellow crystals for **3** and **4** in the yields similar to that for complex **1** (Scheme 1). The $C_{carbene}$ resonate in ^{13}C NMR spectroscopy of complexes **2**–**4** could not be detected as the cases for the NHC complexes of the corresponding lanthanide metals reported previously [7,9,10,12]. The confirmation of complexes **2**–**4** were unequivocally established by X-ray crystal structure analyses.

The low yield of complexes **1**–**4** might be attributed to the shortage of the amount of $NaN(TMS)_2$ and H_2LBr used. Attempts to improve the yield by use of the right molar ratio were unsuccessful. All reactions, which were conducted at 60 °C, 0 °C and −78 °C, respectively, afforded the powders, which were insoluble in normal solvents including THF. The poor solubility of the powders prevented from the purification of the product, and from the full characterization. The reason for it has not been clarified. Although the yields of complexes **1**–**4** are somewhat low, the syntheses of **1**–**4** are reproducible.

Complexes **1**–**4** are very sensitive to air and moisture, but thermal stable. They did not decompose up to 150 °C. All complexes are freely soluble in THF and toluene, but not soluble in hexane.

Single crystals of **1**–**4** suitable for X-ray diffraction were obtained by crystallization from toluene. X-ray diffraction analyses revealed **1**–**4** are isostructural and each of them being a monomer as shown in Fig. 1. The selected bond lengths and angles are listed in Table 1.

The central metal in each complex coordinates to two chelating enol-functionalized NHC ligands and one $-N(TMS)_2$ group. The coordination geometry around each 5-coordinated metal can be best described as a distorted trigonal bipyramid with the two carbene carbon atoms (C(3) and C(18)) and one nitrogen atom N(5) occupying the apical positions and the two enolate oxygen atoms at the axial sites. The sum of the angles in the plane of Ln-C(3)-C(18)-N(5) is 359.97(14)o for **1**, 359.88(13)o for **2**, 359.99(13)o for **3**, and 359.99(13)o for **4** and the angles of O(1)-Ln-O(3) deviate from 180°



Scheme 1. Synthesis of complexes **1**–**4**.

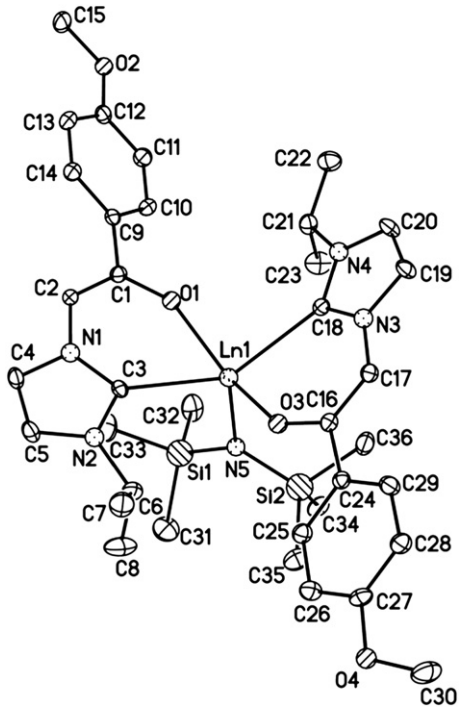


Fig. 1. Molecular structures of complexes **1**–**4**.

to 150.41(13)o for **1**, 147.70(12)o for **2**, 147.90(12)o for **3**, and 152.87(11)o for **4**. The average Ln-$C_{carbene}$ bond lengths (2.512(5) for **1**, 2.621(4) for **2**, 2.581(5) for **3**, 2.463(4) for **4**) in **1**–**4** are compared to each other when the differences in ion radius among these metals were considered. The values can also be comparable with those found in the related lanthanide NHC complexes [7,12,13].

The Ln–O and Ln–N bond distances in each complex fall in the range of the Ln-alkoxide and Ln–N bond distances found in Ln-alkoxide [2,3] and Ln-amide complexes [9].

2.2. Catalytic activity of complexes 1–4 for addition of amines to carbodiimides

Guanidines are important structural motifs found in many biologically and pharmaceutically active compounds. An addition of amine to carbodiimide provides a convenient and atom-economical approach to multisubstituted guanidines. However,

Table 1
Selected bond distances (Å) and angles (deg) for complexes **1**–**4**.

	1	2	3	4
Ln(1)-O(3)	2.141(3)	2.220(3)	2.206(3)	2.116(3)
Ln(1)-O(1)	2.160(3)	2.247(3)	2.219(3)	2.136(3)
Ln(1)-N(5)	2.261(4)	2.356(4)	2.312(4)	2.212(3)
Ln(1)-C(3)	2.512(5)	2.619(4)	2.579(4)	2.453(4)
Ln(1)-C(18)	2.513(4)	2.624(4)	2.584(5)	2.473(4)
O(3)-Ln(1)-O(1)	150.40(13)	147.70(12)	147.90(12)	152.87(11)
O(3)-Ln(1)-N(5)	103.06(13)	103.61(12)	106.97(12)	101.99(11)
O(1)-Ln(1)-N(5)	106.41(13)	108.35(12)	105.12(12)	105.08(11)
O(3)-Ln(1)-C(3)	93.17(14)	93.78(12)	74.15(13)	93.41(12)
O(1)-Ln(1)-C(3)	74.80(14)	72.04(12)	92.36(12)	76.40(12)
N(5)-Ln(1)-C(3)	108.83(13)	108.30(13)	116.69(14)	108.40(13)
O(3)-Ln(1)-C(18)	75.53(13)	72.48(12)	92.32(13)	76.64(12)
O(1)-Ln(1)-C(18)	92.49(13)	94.09(12)	73.21(13)	92.02(12)
N(5)-Ln(1)-C(18)	118.85(14)	121.82(13)	114.80(13)	118.28(13)
C(3)-Ln(1)-C(18)	132.29(14)	129.76(13)	128.50(13)	133.31(13)

the addition reaction without a catalyst requires harsh condition. Thus, catalytic addition of amines to carbodiimides by metal complexes under mild conditions has attracted increasing attention [23–43]. Lanthanide amides are one of the most efficient pre-catalysts for this transformation [29–31]. To assess the chemistry behavior of complexes **1**–**4**, catalytic addition of aniline to *N,N′*-diisopropylcarbodiimide (^{i}PrN=C=N^{i}Pr) by **4** was conducted under various conditions. The results are listed in Table 2.

The catalytic addition of aniline to ^{i}PrN=C=N^{i}Pr with 0.5 mol% of **4** can proceed either in toluene or in THF at 60 °C to give the guanidine **5** in almost quantitative yield. However, the reaction in toluene is faster than that in THF (Table 2, entries 3 and 12). The best result was obtained when the reaction proceeded under solvent free condition (Table 2, entry 11). The addition reaction can also proceed at 20 °C although the reaction rate is lower (Table 2, entries 3–5). The activity of **4** is extremely high. For example, the yield of **5** can still reached to 97% at 60 °C after 36 h, even the catalyst loading decreased to 0.1 mol% (Table 2, entry 7).

Complexes **1**–**3** were also effective in this reaction. The activity of Y complex (**1**) is almost equal to that of Yb complex (**4**), whilst the activities of Sm (**3**) and Nd (**2**) complexes were somewhat lower than that of **4** (Table 2, entries 3, 8, 9 and 10). The active sequence of Nd < Sm < Y ∼ Yb observed here is opposite to the trend reported previously for half-sandwich lanthanide metal complexes [36] and for lanthanide amides [29–31], but consistent with that found for the Ln(OAr)$_3$(THF)$_2$ reported [43]. This may be because of the more crowded coordination sphere around the metal compare to complexes **2** and **3**, which makes the reaction between **4** and an amine easier.

Complex **4** was then chosen as a precatalyst for the addition reaction of various amines including primary and secondary amines to carbodiimides at 60 °C under solvent free condition. Representative results are summarized in Table 3.

Complex **4** is a very efficient precatalyst which showed good functional group tolerance. The reaction was not influenced by either electron-withdrawing or electron-donating substituents, or the position of the substituents at the phenyl ring (Table 3, entries 1–11). The reaction with a steric bulky amine proceeded somewhat slowly to yield the product **6t** in 71% yield after 24 h (Table 3, entry 20), which is often observed with the other lanthanide complexes [29,30]. Various cyclic secondary amines could react with ^{i}PrN=C=N^{i}Pr and CyN=C=NCy (*N,N′*-dicyclohexylcarbodiimide) at 60 °C affording the corresponding tetrasubstituted guanidines in excellent yields (Table 2, entries 12–17).

A double catalytic addition reaction of diamines to two equivalents of carbodiimides is a direct method to biguanidines. Thus, the reaction of 1,4-diaminobenzene to two equivalents of ^{i}PrN=C=N^{i}Pr was also tried. The reaction went smoothly to yield the biguanidines **7a** in 92% yield after 0.5 h (Scheme 2. (Eq. (1))). The same reaction with 1,3-diaminobenzene yielded the biguanidine **7b** in 93% yield after 0.5 h (Scheme 2. (Eq. (2))).

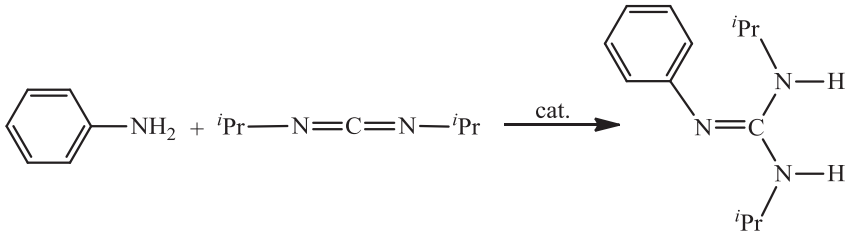
A catalytic cycle which was suggested previously [29,30,35,36] could be proposed for the present transformation. Complex **4** reacts with an amine to yield an amide species, which reacts further with a carbodiimide to afford the guanidinate species. Protonolysis of the guanidinate species by another amine molecule regenerates the amide species and releases the guanidine.

3. Experimental section

3.1. General considerations

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl under pure argon prior to use. H_2LBr (L = 4-OMe-C_6H_4COCH{C(NCHCHN^{i}Pr)}) [22] and NaN(TMS)$_2$ [44] were synthesized according to the literature methods. Elemental analysis was performed by direct combustion on a Carlo-Erba EA-1110 instrument. IR spectra were recorded on a Magna-IR 550

Table 2
Catalytic addition of aniline to ^{i}PrN=C=N^{i}Pr by complexes **1**–**4**

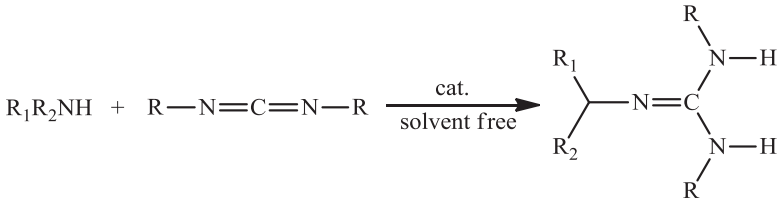


5

Entry[a]	Cat.	Catalyst loading (mol%)	Temp (°C)	Time (h)	Yield (%)[b]
1	**4**	0.5	60	0.5	79
2	**4**	0.5	60	1	82
3	**4**	0.5	60	3	98
4	**4**	0.5	20	4	60
5	**4**	0.5	20	12	>99
6	**4**	0.25	60	24	98
7	**4**	0.1	60	36	97
8	**1**	0.5	60	3	>99
9	**2**	0.5	60	3	23
10	**3**	0.5	60	3	35
11[c]	**4**	0.5	60	0.25	98
12[d]	**4**	0.5	60	24	>99

[a] General condition: in 1 mL toluene.
[b] Isolated yield.
[c] Solvent free.
[d] The concentration of ^{i}PrN=C=N^{i}Pr is 1.9 mol/L in THF.

Table 3
Catalytic addition of amines to carbodiimides by complex **4**



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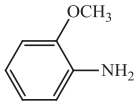
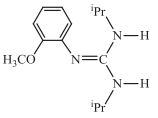
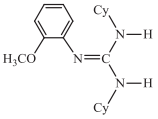
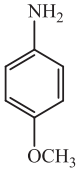
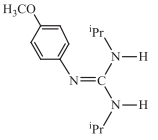
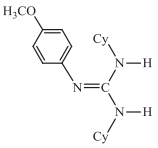
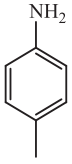
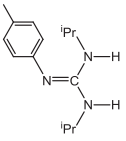
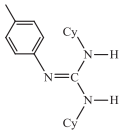
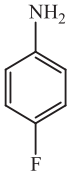
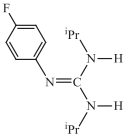
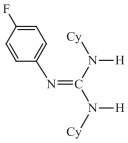
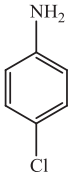
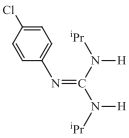
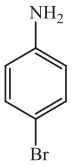
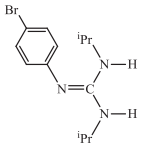
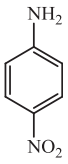
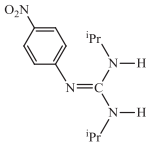
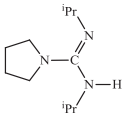
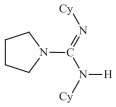
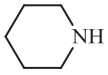
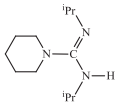
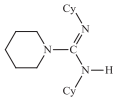
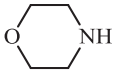
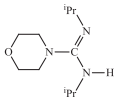
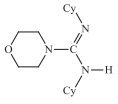
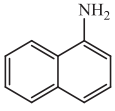
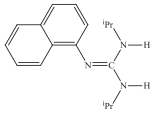
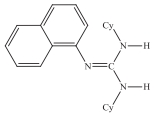
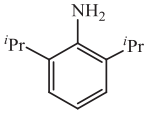
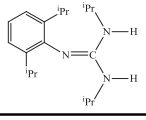
Entry[a]	R	Amines	Time (h)	**6**	Product structure	Yield (%)[b]
1	^{i}Pr		0.5	**6a**		>99
2	Cy		0.5	**6b**		94
3	^{i}Pr		2	**6c**		97
4	Cy		2	**6d**		>99
5	^{i}Pr		0.5	**6e**		98
6	Cy		0.5	**6f**		96
7	^{i}Pr		0.5	**6g**		95
8	Cy		0.5	**6h**		91
9	^{i}Pr		0.5	**6i**		>99

Table 3 (*continued*)

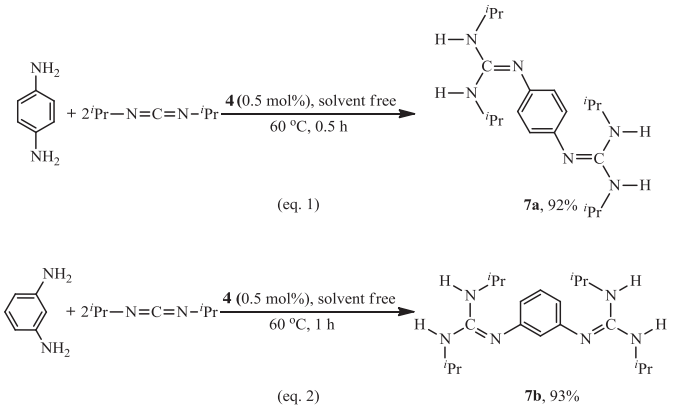
Entry[a]	R	Amines	Time (h)	**6**	Product structure	Yield (%)[b]
10	^{i}Pr		2	**6j**		96
11	^{i}Pr		12	**6k**		82
12	^{i}Pr		12	**6l**		95
13	Cy		12	**6m**		96
14	^{i}Pr		12	**6n**		93
15	Cy		12	**6o**		94
16	^{i}Pr		12	**6p**		96
17	Cy		12	**6q**		92
18	^{i}Pr		4	**6r**		98
19	Cy		6	**6s**		97
20	^{i}Pr		24	**6t**		71

[a] General condition: solvent free, catalyst loading is 0.5 mol %.
[b] Isolated yield.

spectrometer as KBr pellets. ^{1}H NMR and ^{13}C NMR were measured on a VNMRS-300 and an INOVA-400 spectrometer in d-C_6D_6. Melting points were measured in sealed Ar-filled capillary tubes and are uncorrected.

3.2. Preparation of $L_2YN(TMS)_2$ (**1**)

The solution of $NaN(TMS)_2$ (8.58 mL, 1.17 M, 10.04 mmol) in THF was slowly added into the THF solution of anhydrous YCl_3 (0.49 g,



Scheme 2. Catalytic addition of diamines to a carbodiimide.

2.51 mmol) at room temperature. The reaction mixture was stirred over 12 h, then H_2LBr (0.85 g, 2.51 mmol) was added and stirred for additional 36 h. The suspension was centrifuged to remove the NaCl and evaporated to dryness and extracted with about 15 mL of toluene. Concentrating the toluene solution and cooling at 0 °C led to the isolation of pink crystals of **1** (0.71 g, 37%) after several days. m.p.: 151–153 °C. Anal. Calc. for $C_{36}H_{52}N_5O_4Si_2Y$: C, 56.60; H, 6.86; N, 9.17%. Found: C, 56.92; H, 6.89; N, 8.74%. ^{1}H NMR (C_6D_6, 400 MHz): δ (ppm), 7.73 (d, 4H, $J = 8.4$, 4 × PhH), 6.82 (d, 4H, $J = 8.4$, 4 × PhH), 6.21 (s, 2H, 2 × C═CH), 6.18 (s, 2H, 2 × NCH), 6.10 (s, 2H, 2 × NCH), 5.49–5.34 (m, 2H, 2 × $(CH_3)_2CH$), 3.30 (s, 6H, 2 × CH_3O), 1.15 (s, 12H, 2 × $(CH_3)_2CH$), 0.30 ppm (s, 18H, 2 × $Si(CH_3)_3$). ^{13}C NMR (C_6D_6, 101 MHz): δ (ppm), 188.37, 187.94 (Y-$C_{carbene}$), 159.71 (O–C═C), 151.90 (Ar), 151.88 (Ar), 134.11(Ar), 127.17(Ar), 120.14 (NC═CN), 113.61 (NC═CN), 101.78 (C═CN), 54.79 (OCH_3), 52.02 ($CH(CH_3)_2$), 23.88 ($CH(CH_3)_2$), 5.29, 4.84, 2.58 ($Si(CH_3)_3$). IR (KBr, cm^{-1}): 3428 (w), 2955 (m), 2835 (w), 1605 (s), 1507 (s), 1423 (m), 1399 (m), 1247 (vs), 1157 (vs), 1099 (m), 1033 (s), 934 (s), 840 (s), 739 (m), 683 (w), 504 (w).

3.3. Preparation of $L_2NdN(TMS)_2$ (**2**)

Complex **2** was prepared by the procedure described for the synthesis of complex **1**, except $NdCl_3$ (0.63 g, 2.51 mmol), $NaN(TMS)_2$ (8.58 mL, 1.17 M, 10.04 mmol) and H_2LBr (0.85 g, 2.51 mmol) were used. Blue crystals of complex **2** were isolated (0.72 g, 36%). m.p.: 154–156 °C. Anal. Calc. for $C_{36}H_{52}N_5O_4Si_2Nd$: C, 52.78; H, 6.40; N, 8.55%. Found: C, 52.69; H, 6.21; N, 8.38%. IR (KBr, cm^{-1}): 3380 (w), 2955 (vs), 2894 (w), 1606 (w), 1446 (s), 1399 (m), 1250 (vs), 1181 (s), 1157(s), 1062 (m), 935 (s), 842 (s), 7784 (m), 685 (m), 504 (m).

3.4. Preparation of $L_2SmN(TMS)_2$ (**3**)

Complex **3** was prepared by the procedure described for the synthesis of complex **1**, except $SmCl_3$ (0.64 g, 2.49 mmol), $NaN(TMS)_2$ (8.51 mL, 1.17 M, 9.96 mmol) and H_2LBr (0.85 g, 2.51 mmol) were used. Light yellow crystals of complex **3** were isolated (0.72 g, 38%). m.p.: 151–153 °C. Anal. Calc. for $C_{36}H_{52}N_5O_4Si_2Sm$: C, 52.39; H, 6.35; N, 8.49%. Found: C, 52.47; H, 6.32; N, 8.26%. IR (KBr, cm^{-1}): 3442 (w), 2955 (m), 2836 (w), 1604 (s), 1506 (s), 1423 (m), 1252 (s), 1160 (s), 1097 (w), 1032 (m), 934 (m), 843 (s), 744 (m), 683 (m), 504 (s).

3.5. Preparation of $L_2YbN(TMS)_2$ (**4**)

Complex **4** was prepared by the procedure described for the synthesis of complex **1**, except $YbCl_3$ (0.70 g, 2.51 mmol), $NaN(TMS)_2$ (8.58 mL, 1.17 M, 10.04 mmol) and H_2LBr (0.85 g, 2.51 mmol) were used. Yellow crystals of complex **4** were isolated (0.72 g, 40%). m.p.: 148–150 °C. Anal. Calc. for $C_{36}H_{52}N_5O_4Si_2Yb$: C, 50.99; H, 6.18; N, 8.26%. Found: C, 49.99; H, 6.08; N, 7.79%. IR (KBr, cm^{-1}): 3490 (w), 2955 (m), 2835 (w), 1605 (s), 1508 (s), 1423 (m), 1252 (s), 1160 (s), 1097 (w), 1032 (m), 934 (m), 843 (s), 744 (m), 683 (m), 504 (s).

3.6. General procedure for the direct synthesis of guanidines from the reaction of aromatic amines with carbodiimides catalyzed by $L_2LnN(TMS)_2$ (Ln = Y, Nd, Sm, Yb)

A 10.0 mL Schlenk tube under dried argon was charged with $L_2LnN(TMS)_2$ (0.005 equiv.), aromatic amines (1.0 equiv.), and toluene (1 mL). To the mixture was added carbodiimides (1.0 equiv.). The resulting mixture was stirred at 20 °C or at 60 °C for a fixed interval, as shown in Tables 2or 3. Then the reaction mixture was hydrolyzed by water (1 mL), extracted with dichloromethane (3 × 10 mL), dried over anhydrous Na_2SO_4, and filtered. After the solvent was removed under reduced pressure, the final products were further purified by washing with diethyl ether or hexane.

3.7. General procedure for the direct synthesis of guanidines from the reaction of secondary amines with carbodiimides catalyzed by $L_2YbN(TMS)_2$

A 10.0 mL Schlenk tube under dried argon was charged with complex **4** (0.005 equiv.) and secondary amines (1.0 equiv.). To this mixture was added carbodiimides (1.0 equiv.). The resulting mixture was stirred at 60 °C for the desired time, as shown in Table 3. The reaction mixture was then hydrolyzed with water (0.5 mL), extracted with hot hexane (3 × 15 mL), dried over anhydrous Na_2SO_4, and filtered. After the solvent was removed under vacuum, the final products were obtained.

3.8. Synthesis of *N,N′*-1,4-phenylenebis (*N,N′*-diisopropylguanidine) (**7a**)

A 10 mL Schlenk tube was charged with complex **4** (0.0136 g, 0.016 mmol), *N,N′*-diisopropylcarbodiimide (1.0 mL, 6.42 mmol) and 1,4-diaminobenzene (0.3469 g, 3.21 mol) under dried argon. The resulting mixture was stirred at 60 °C for 0.5 h. The reaction mixture was extracted with ether and filtered to give a clean solution. After removing the solvent under vacuum, the residue was recrystallized in ether to provide a white solid **7a** (1.0650 g, 92% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm), 6.76 (s, 4H), 3.75 (br, 4H),1.15–1.13 (d, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm), 151.2, 143.9, 124.7, 43.4, 23.5.

3.9. Synthesis of *N,N′*-1,3-phenylenebis (*N,N′*-diisopropylguanidine) (**7b**)

Product **7b** was obtained by the procedure described for the synthesis of **7a**, except complex **4** (0.0094 g, 0.011 mmol), *N,N′*-diisopropylcarbodiimide (0.69 mL, 4.43 mmol) and 1,3-diaminobenzene (0.2398 g, 2.22 mol) were used. And a white solid **7b** was isolated (1.0764 g, 93% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm), 7.15–7.10 (t, $J = 7.8$ Hz, 1H), 6.46–6.43 (d, $J = 7.7$ Hz, 2H), 6.38 (s, 1H), 3.73 (m, 4H), 1.15–1.13 (d, $J = 6.4$ Hz, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm), 151.4, 150.1, 129.9, 118.8, 117.3, 43.3, 23.4.

3.10. X-ray crystallography

A suitable single crystal was sealed in a thin-walled glass capillary for X-ray structural analysis. Diffraction data were

Table 4
X-ray crystallographic data for complexes **1**–**4**.

	1·C_7H_8	**2**·C_7H_8	**3**·1.5C_7H_8	**4**·C_7H_8
Formula	$C_{43}H_{60}N_5O_4Si_2Y$	$C_{43}H_{60}N_5NdO_4Si_2$	$C_{46.50}H_{64}N_5O_4Si_2Sm$	$C_{43}H_{60}N_5O_4Si_2Yb$
Mol wt	856.05	911.38	963.56	940.18
Temp (K)	223(2)	223(2)	223(2)	223(2)
λ (Å)	0.71075	0.71075	0.71075	0.71075
Cryst syst	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.4258(10)	13.3828(10)	13.9743(2)	13.4293(8)
b (Å)	14.3307(7)	14.4345(8)	14.6298(11)	14.2974(7)
c (Å)	14.4583(3)	14.4906(2)	15.5233(10)	14.401
α (deg)	61.918(8)	61.855(8)	85.391(11)	61.923(6)
β (deg)	68.731(9)	69.664(10)	64.371(8)	68.556(6)
γ (deg)	85.954(12)	85.900(12)	61.799(8)	86.069(8)
V (Å^3)	2270.1(2)	2299.9(2)	2490.8(2)	2252.73(17)
Z (Å^3), D_{calcd} (g/mL)	2, 1.252	2, 1.316	2, 1.285	2, 1.386
μ (mm^{-1})	1.381	1.224	1.270	2.173
F(000)	904	946	1000	966
Cryst size (mm)	0.35 × 0.25 × 0.20	0.60 × 0.40 × 0.30	0.60 × 0.40 × 0.20	0.60 × 0.50 × 0.30
θ range (deg)	3.02–25.50	3.00–25.50	3.13–25.50	3.04–25.50
Total no. of rflns	19,526	19,640	20,254	19,246
no. of indep rflns	8403	8500	9201	8334
R_{int}	0.0646	0.0451	0.0460	0.0500
GOF	1.038	1.091	1.145	1.028
R1, wR2 ($I > 2\sigma(I)$)	0.0708, 0.1681	0.0482, 0.1137	0.0519, 0.1066	0.0373, 0.0787
R1, wR2 [all data]	0.0992, 0.1854	0.0570, 0.1195	0.0597, 0.1107	0.0420, 0.0806

collected on a Rigaku Mercury CCD area detector at 223(2) K. The structure was solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were treated as idealized contributions. The structures were refined using SHELXTL-97 programs Crystal data, collection details and main refinement parameters are given in Table 4.

4. Conclusion

The novel enol-functionalized NHC lanthanide amide complexes $L_2LnN(TMS)_2$ (Ln = Y (**1**), Nd (**2**), Sm (**3**), Yb (**4**)) were synthesized and structurally characterized. Complex **4** was found to be an excellent precatalyst for catalytic addition of primary and secondary cyclic amines to carbodiimides, leading to efficient formation of a series of guanidine derivatives. The catalytic system has a wide scope of substrates.

Acknowledgements

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Appendix A. Supplementary material

CCDC 860025 (for **1**), -860026 (for **2**), -860027 (for **3**) and -860028 (for **4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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