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Bridged bis(amidinate) lanthanide aryloxides: syntheses, structures, and catalytic activity for addition of amines to carbodiimides†

Jing Tu, Wenbo Li, Mingqiang Xue,* Yong Zhang and Qi Shen*

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Various lanthanide aryloxide complexes supported by bridged bis(amidinate) ligand L, LLnOAr(DME) (L = $Me_3SiNC(Ph)N(CH_2)_3NC(Ph)NSiMe_3$, DME = dimethoxyethane, Ln = Y, Ar = 2,6-$(Me)_2C_6H_3$ (**1**), 2,6-$(^iPr)_2C_6H_3$ (**2**), 2,6-$(^tBu)_2$-4-$(Me)C_6H_2$ (**3**); Ar = 2,6-$(^tBu)_2$-4-$(Me)C_6H_2$, Ln = Nd (**4**), Sm (**5**), Yb (**6**)) were synthesized, and complexes **1**, **2** and **4–6** were characterized by single crystal X-ray diffraction. All the complexes are efficient precatalysts for catalytic addition of amines to carbodiimides. The catalytic activity is influenced by lanthanide metals and the aryloxide groups (Nd (**4**) ~ Sm (**5**) < Y (**3**) ~ Yb (**6**) and -2,6-$(Me)_2C_6H_3$ < -2,6-$(^iPr)_2C_6H_3$ < -2,6-$(^tBu)_2$-4-$(Me)C_6H_2$). The catalytic addition reaction with **3** showed a good scope of substrates. The mechanism investigation revealed the real active intermediate being the monoguanidinate complexes supported by an aryloxide and an amidine-functionalized amidinate group, L'Ln[O2,6-$(^tBu)_2$-4-$(Me)C_6H_2$][RNCNHRN(Ar')] (L' = $Me_3SiNHC(Ph)N(CH_2)_3NC(Ph)NSiMe_3$, R = ^iPr, Ar' = phenyl, Ln = Yb (**8**), Y (**11**); R = Cy, Ar' = phenyl, Ln = Yb (**10**), Y (**12**); R = ^iPr, Ar' = 4-ClC_6H_4, Ln = Yb (**9**)), which were isolated from the reactions of **6** (or **3**) with amine and carbodiimide in a molar ratio of 1 : 1 : 1 and structurally characterized. The Ln-active group in the present precatalyst is a Ln–amidinate species, not the Ln–OAr group.

Introduction

The catalytic formation of the C–N bond by metal complexes is an active subject in organic synthesis and organometallic chemistry of main, transition and lanthanide metals.[1,2] Guanidines are the important structural motifs found in many biologically and pharmaceutically active compounds,[3] and catalytic addition reaction of the amine N–H bond to carbodiimide provides a straightforward and atom-economical route for the preparation of multi-substituted guanidines.[4] However, this addition reaction without a catalyst requires harsh conditions.[5] Therefore, exploring efficient metal catalysts for catalytic addition of amines to carbodiimides has received much current interest.[6] Particularly, the utility of lanthanide complexes as precatalysts has attracted much attention. A variety of lanthanide complexes containing M–C,[7a,b] M–N bond,[6h,7c–e] divalent lanthanide complexes[7f,g] as well as lanthanide triflates[7h,i] have been explored to be efficient catalysts for this process and the real active intermediate, lanthanide–guanidinate species has been well documented.[7j,k] Very recently, we have reported lanthanide trisaryloxides, $Ln(OAr)_3(THF)_2$ can act as efficient catalyst precursors for the catalytic addition of amines to carbodiimides yielding multi-substituted guanidines, which represents the first example of metal catalyst containing metal–aryloxide (alkoxide) moiety. The detailed mechanism study revealed the Ln–OAr group is an active group and the corresponding monoguanidinate species formed *via* protonation of OAr group by *in situ* formed guanidine.[8a] In comparison with lanthanide alkyl and amide complexes lanthanide aryloxides are easier to access and less sensitive to air and moisture. Thus, investigation of the influence of ancillary ligands on the reactivity of Ln–aryloxide species may be rewarding, as the ancillary ligands around the center metal may play a key role in modification of the catalytic behavior of the Ln–OAr active group. Bridged bis(amidinate) L (L = $Me_3SiNC(Ph)N(CH_2)_3NC(Ph)NSiMe_3$) ligand has shown the ability to provide a suitable coordination environment, which allows the synthesis of various isolable lanthanide complexes containing Ln–BH_4,[9a] Ln–N[9b–d] and Ln–O[9e] bonds. These complexes serve as well-defined single-site catalysts for polymerization of ε-caprolactone and L-lactide in a living fashion and

Key Laboratory of Organic Synthesis of Jiangsu Province, Department of Chemistry and Chemical Engineering, Dushu Lake CampusSoochow University, Suzhou 215123, People's Republic of China. E-mail: qshen@suda.edu.cn, xuemingqiang@suda.edu.cn; Fax: +(86) 512-65880305; Tel: +(86) 512-65882806

†Electronic supplementary information (ESI) available. CCDC 915745 (for **1**), 915744 (for **2**), 915746 (for **4**), 915747 (for **5**), 915748 (for **6**), 915741 (for **7**), 915742 (for **8**) and 915743 (for **9**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt33069a

the amide complexes are efficient catalysts for catalytic addition of amines to aromatic nitriles to monosubstituted amidines.[9] Ligand L in all these catalytic reactions serves as a spectator ligand and does not participate in the transformations. Therefore, we tried to synthesize a series of lanthanide aryloxides with different sized aryloxide groups and lanthanide metals using L as the ancillary ligand, LLn(OAr), and assessed their activity for catalytic addition of amines to carbodiimides to guanidinates. It was found that the target complexes LLn(OAr)(DME) (Ln = Y, Ar = 2,6-$(Me)_2C_6H_3$ (**1**); Ar = 2,6-$(^iPr)_2C_6H_3$ (**2**); Ar = 2,6-$(^tBu)_2$-4-$(Me)C_6H_2$ (**3**) and Ar = 2,6-$(^tBu)_2$-4-$(Me)C_6H_2$, Ln = Nd (**4**); Sm (**5**); Yb (**6**)) could be prepared in high yields and all these complexes show higher activity for addition of amines to carbodiimides than the corresponding $Ln(OAr)_3(THF)_2$. A detailed investigation of the mechanism revealed the active group here is the Ln–amidinate species of the L, not the Ln–OAr species as the cases with $Ln(OAr)_3(THF)_2$. Here we report the results. The isolation and characterization, as well as the activities of the real active intermediates L′Ln[RNCNHRN(Ar′)](OAr) are also presented.

Results and discussion

Synthesis of bis(amidinate) lanthanide aryloxides

The ytterbium aryloxide complex bearing the bridged bis(amidinate) ligand L, LYb[O2,6-$(^iPr)_2C_6H_3$](DME) (L = $Me_3SiNC(Ph)N(CH_2)_3NC(Ph)NSiMe_3$), has been reported previously.[9e] The analogous aryloxide complexes LY[O2,6-$(Me)_2C_6H_3$](DME) (**1**); LY[O2,6-$(^iPr)_2C_6H_3$](DME) (**2**) and LLn[O2,6-$(^tBu)_2$-4-$(Me)C_6H_2$]-(DME) (Ln = Y (**3**); Nd (**4**); Sm (**5**); Yb (**6**)) were prepared similarly in high yields by the reaction of $LLnCl(THF)_2$ with NaOAr in THF and followed by treatment with toluene and DME (Scheme 1).

Complexes **1–6** were characterized by elemental analysis, IR and NMR spectroscopy for Y complexes **1–3**. The molecular structures of **1**, **2** and **4–6** were determined. X-ray single-crystal structure analyses revealed that complexes **1**, **2** and **4–6** are isostructural and isomorphous. Their selected bond lengths and angles are summarized in Table 1, and only the ORTEP drawing of **6** is shown in Fig. 1. The ORTEP drawing of complexes **1**, **2**, **4** and **5** are given in the ESI (Fig. S20–S23†).

The central metal in each complex coordinates to four nitrogen atoms from the bis(amidinate) ligand, three oxygen atoms from one OAr group and one DME molecule. The coordination geometry around each metal center can be described as a distorted trigonal bipyramid, when each amidinate ligand is considered to be point donors located at the central carbon atoms. Each center carbon atom (C1 and C2) of the two amidinate groups and one oxygen atom (O3) occupy equatorial positions, while two oxygen atoms (O1 and O2) locate on axial sites with the angle of O(1)–Ln(1)–O(2) of 157.32(9)° for **6**, (154.65(16)° for **1**, 149.68(9)° for **2**, 142.66(7)° for **4** and 143.37(6)° for **5**). The molecular structures of **1**, **2** and **4–6** are quite similar to that of LYb[O2,6-$(^iPr)_2C_6H_3$](DME) reported previously.[9e]

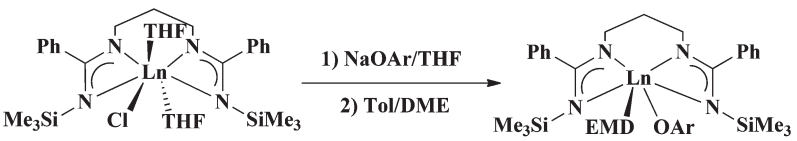
The C–N bond distances in the chelating N–C–N unit are nearly equal and the average value, 1.33 Å, indicates the delocalization of the π bond in the N–C–N unit. The bond parameters within the two amidinate ligands and within the Yb–N–C–N units compare well with those found in LYb[O2,6-$(^iPr)_2C_6H_3$](DME) and the related complexes reported.[9,11]

The Ln–O(OAr) bond distance in **6** is 2.110(2) Å and the value is almost consistent with those found in **1**, **2**, **4** and **5** (Table 1), when the differences in the ionic radii among these metals are considered (2.105(4) Å for **1**, 2.095(2) Å for **2**, 2.212(2) Å for **4** and 2.189(2) Å for **5**). The value is comparable to those of the analogue LYb[O2,6-$(^iPr)_2C_6H_3$](DME) and the lanthanide aryloxides.[8]

Catalytic activity of 1–6 for catalytic additions of amines to carbodiimides

The catalytic activity of **1–6** in the addition of $PhNH_2$ to *N*,*N*′-diisopropylcarbodiimide ($^iPrNCN^iPr$) was assessed under the conditions as shown in Table 2. All complexes were found to be efficient precatalysts. However, the differences in the activity among them were observed. The activities of Y (**3**) and Yb (**6**) complexes are higher than those of Nd (**4**) and Sm (**5**) complexes (Table 2, entries 3–6). The aryloxide group also has a great influence on the activity with the activity trend of -2,6-$(Me)_2C_6H_3$ < -2,6-$(^iPr)_2C_6H_3$ < -2,6-$(^tBu)_2$-4-$(Me)C_6H_2$ (Table 2, entries 1–3), which is consistent with the size of the aryloxide groups. Such an active sequence is as same as that reported for the systems with $Ln(OAr)_3(THF)_2$.[8a] Thus, complexes **3** and **6** show the highest activity, while complex **1** has the lowest one among the six complexes.

To compare the model, reactions with Y[O2,6-$(Me)_2C_6H_3]_3(THF)_2$, Y[O2,6-$(^iPr)_2C_6H_3]_3(THF)_2$ and Y[O2,6-



Ln = Y, Ar = 2,6-$(Me)_2C_6H_3$ (1); 2,6-$(^iPr)_2C_6H_3$ (2);

Ar = 2,6-$(^tBu)_2$-4-$(Me)C_6H_2$, Ln =Y (3); Nd (4); Sm (5); Yb (6).

Scheme 1 Preparations of LLn(OAr)(DME).

Table 1 Selected bond distances (Å) and angles (°) for **1**, **2** and **4–6**

Bond lengths	1	2	4	5	6
Ln(1)–N(1)	2.516(5)	2.509(3)	2.559(2)	2.541(2)	2.586(3)
Ln(1)–N(2)	2.319(5)	2.328(3)	2.443(3)	2.415(2)	2.263(3)
Ln(1)–N(3)	2.524(5)	2.488(3)	2.674(3)	2.652(2)	2.510(3)
Ln(1)–N(4)	2.317(6)	2.382(3)	2.422(3)	2.399(2)	2.290(3)
Ln(1)–C(1)	2.832(6)	2.839(4)	2.911(3)	2.884(2)	2.860(4)
Ln(1)–O(1)	2.105(4)	2.095(2)	2.212(2)	2.189(2)	2.110(2)
Ln(1)–C(2)	2.820(7)	2.819(4)	2.974(3)	2.946(2)	2.794(4)
N(1)–C(1)	1.330(8)	1.341(5)	1.339(4)	1.336(3)	1.333(4)
N(2)–C(1)	1.318(8)	1.314(5)	1.307(4)	1.311(3)	1.325(5)
N(3)–C(2)	1.335(8)	1.341(5)	1.338(4)	1.331(3)	1.328(5)
N(4)–C(2)	1.296(8)	1.337(5)	1.314(4)	1.312(3)	1.306(5)
Bond angles					
O(3)–Ln(1)–C(1)	116.88(17)	116.33(10)	128.22(7)	127.39(6)	110.30(10)
O(3)–Ln(1)–C(2)	113.62(17)	116.60(10)	110.99(8)	111.09(7)	115.84(10)
C(2)–Ln(1)–C(1)	124.07(19)	119.50(11)	112.50(8)	113.23(7)	119.88(12)
O(2)–Ln(1)–C(1)	90.93(17)	88.60(12)	90.02(8)	89.97(6)	81.45(10)
O(2)–Ln(1)–C(2)	88.1(2)	88.10(12)	92.65(8)	91.55(7)	83.30(11)
O(3)–Ln(1)–O(2)	66.42(14)	65.48(8)	61.18(6)	61.81(6)	66.83(9)
O(1)–Ln(1)–O(2)	154.65(16)	149.68(9)	142.66(7)	143.37(6)	157.32(9)
N(2)–Ln(1)–N(1)	55.32(19)	55.41(11)	53.57(8)	54.13(7)	54.62(10)
N(4)–Ln(1)–N(3)	54.77(17)	55.56(11)	52.33(8)	52.68(7)	55.50(11)

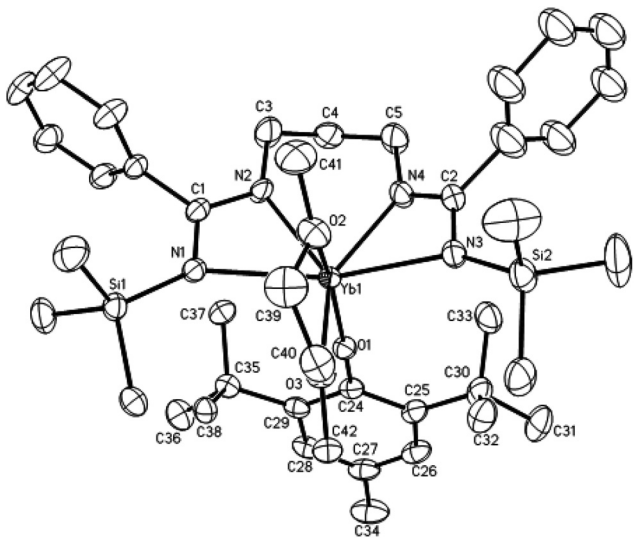
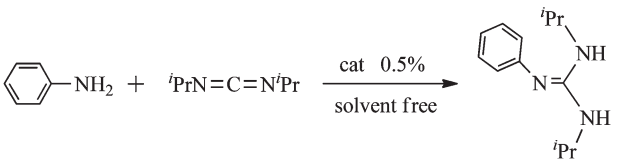


Fig. 1 ORTEP diagram of the molecular structure of **6**. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms are omitted for clarity.

Table 2 Addition of $PhNH_2$ to $^{i}PrNCN^{i}Pr$ by complexes **1–6**, **8** and **11**[a]



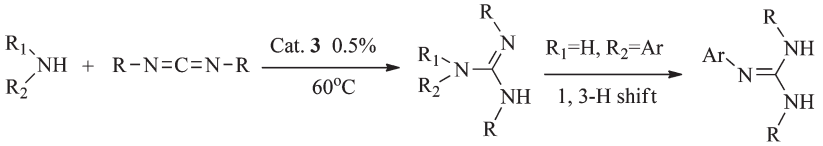
Entry	Cat	Temp/°C	Time/h	Yield[b](%)
1	**1**	60	0.25	78
2	**2**	60	0.25	87
3	**3**	60	0.25	95
4	**4**	60	0.25	67
5	**5**	60	0.25	69
6	**6**	60	0.25	92
7	**3**	60	0.5	>99
8	**3**	r.t.	2	92
9	$Y[O2,6\text{-}(Me)_2C_6H_3]_3(THF)_2$	60	24	13
10	$Y[O2,6\text{-}(^{i}Pr)_2C_6H_3]_3(THF)_2$	60	4	58
11	$Y[O2,6\text{-}(^{t}Bu)_2\text{-}4\text{-}(Me)C_6H_2]_3(THF)_2$	60	0.5	98
12	**8**	60	0.25	97
13	**11**	60	0.25	99

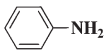
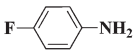
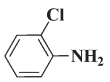
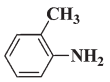
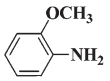
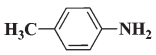
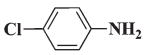
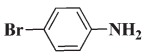
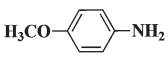
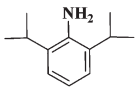
[a] 1 mmol of aniline, 1 mmol of *N*,*N*′-diisopropylcarbodiimide. [b] Isolated yields.

$(^{t}Bu)_2$-4-$(Me)C_6H_2]_3(THF)_2$, respectively, were also conducted. It is worth noting that the complexes with L ligand show higher activity in comparison with the corresponding aryloxides complexes without the L ligand. For example, the model reactions with $Y[O2,6\text{-}(Me)_2C_6H_3]_3(THF)_2$ and $Y[O2,6\text{-}(^{i}Pr)_2C_6H_3]_3(THF)_2$ afforded the guanidine in 13% yield after 24 h and 58% yield after 4 h, respectively, while the yields increased to 78% and 87% after 0.25 h when **1** and **2** were used instead. Also, the same reaction with complex **3** yielded the product in 95% yield after 0.25 h, while to get the same yield the reaction time needed to be extended to 0.5 h, when $Y[O2,6\text{-}(^{t}Bu)_2\text{-}4\text{-}(Me)C_6H_2]_3(THF)_2$ was used (Table 2, entries 1–3 and 9–11). The reaction with **3** can even proceed at room temperature and the yield of the product is as high as 92% after 2 h at the catalyst loading of 0.5 mol% (Table 2, entry 8).

Complex **3** was chosen as a catalyst precursor for the catalytic addition of various primary and secondary amines to carbodiimides. Representative results are summarized in Table 3. As shown in Table 3, complex **3** is an efficient catalyst precursor with a wide scope of amines and it is robust. The reaction is

Table 3 Catalytic additions of amines to carbodiimides[a]



Entry	R	R_1R_2NH	Time/h	Product	Yield[b](%)
1	^{i}Pr		0.5	13	>99
2	Cy		0.5	14	99
3	^{i}Pr		0.5	15	>99
4	Cy		0.5	16	>99
5	^{i}Pr		0.5	17	93
6	Cy		0.5	18	96
7	^{i}Pr		0.5	19	90
8	Cy		0.5	20	93
9	^{i}Pr		0.5	21	92
10	Cy		0.5	22	98
11	^{i}Pr		0.5	23	>99
12	^{i}Pr		0.5	24	>99
13	^{i}Pr		0.5	25	>99
14	^{i}Pr		2	26	95
15	^{i}Pr		24	27	98
16	^{i}Pr		24	28	80
17	^{i}Pr		24	29	95
18	^{i}Pr		24	30	92
19	^{i}Pr		24	31	91

[a] The reaction was performed by treating 1 equiv. of amines with 1 equiv. of carbodiimides at 60 °C. [b] Isolated yields.

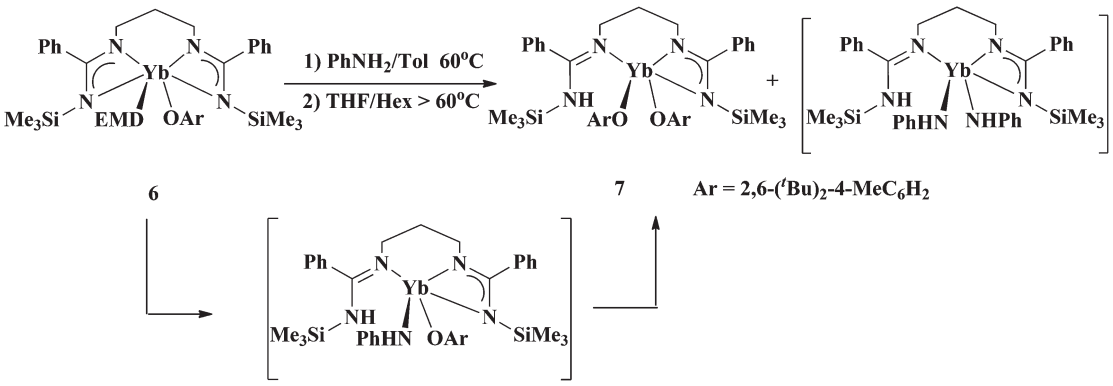
not influenced by either electron-withdrawing or electron-donating substituents at the phenyl ring of aromatic amines. Primary and secondary amines both could be used for this reaction. However, the reaction with a bulky amine, 2,6-diisopropylaniline, is less active, this may be attributed to the steric hindrance. The same phenomenon has also been observed for the systems with other lanthanide catalysts reported.[7d,10]

Mechanistic studies

The stoichiometric reactions of **6** with ^{i}PrNCN^{i}Pr and $PhNH_2$, and the reaction of **6** (or **3**) with a mixture of amine and carbodiimide, respectively, were conducted in order to gain information about the real active species and the reaction pathways.

Reaction of 6 with ^{i}PrNCN^{i}Pr

The coordination of carbodiimide to the center metal of $Ln(OAr)_3(THF)_2$ is known to be the first key step in the catalytic addition of amine to carbodiimide using $Ln(OAr)_3(THF)_2$ as a precatalyst.[8a] Therefore, the reaction of **6** with ^{i}PrNCN^{i}Pr in a 1 : 1 molar ratio was firstly carried out in toluene at 60 °C to see whether the coordinated DME molecule in **6** could be replaced by a ^{i}PrNCN^{i}Pr molecule. However, after stirring for 24 h, no reaction was observed and complex **6** was recovered completely from the reaction solution.



Scheme 2 Reaction of **6** with $PhNH_2$.

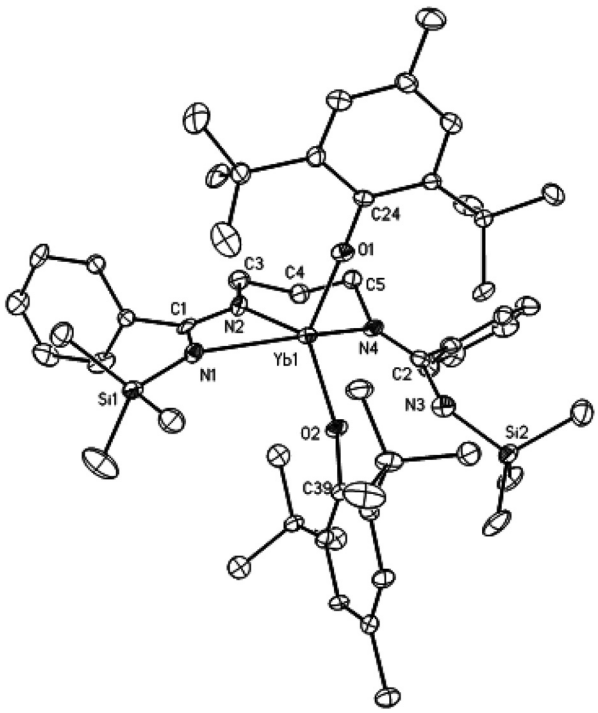


Fig. 2 Molecular structure of **7**. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms are omitted for clarity.

Table 4 Selected bond distances (Å) and angles (°) for **7**

Bond lengths			
Ln(1)–N(1)	2.415(8)	Ln(1)–O(2)	2.069(6)
Ln(1)–N(2)	2.260(9)	N(1)–C(1)	1.358(13)
Ln(1)–N(4)	2.416(8)	N(2)–C(1)	1.345(13)
Ln(1)–C(1)	2.777(10)	N(3)–C(2)	1.415(14)
Ln(1)–O(1)	2.066(7)	N(4)–C(2)	1.321(14)
Bond angles			
O(1)–Ln(1)–O(2)	126.7(3)	O(2)–Ln(1)–N(4)	91.8(3)
O(1)–Ln(1)–C(1)	114.7(3)	N(1)–Ln(1)–N(2)	58.0(3)
O(2)–Ln(1)–C(1)	114.2(3)	N(2)–C(1)–N(1)	114.2(9)
O(1)–Ln(1)–N(4)	94.0(3)		

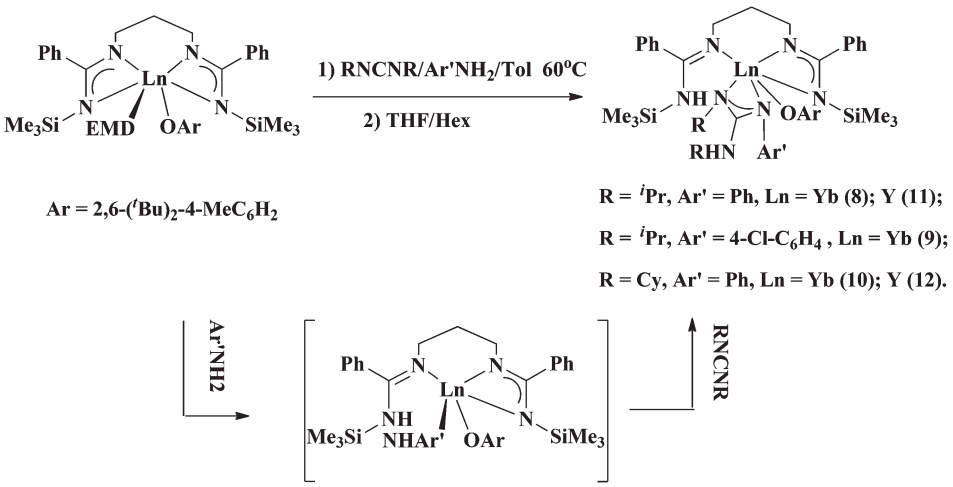
Reaction of 6 with $PhNH_2$

The reaction of **6** with $PhNH_2$ at a molar ratio of 1 : 1 was then carried out in toluene at 60 °C. The reaction took place smoothly to afford a pale yellow solution, from which light yellow crystals were isolated in 42% yield. The crystals were characterized by elemental analysis, IR and X-ray crystal structure determination to be the bis-aryloxide complex supported by a newly formed amidine-functionalized monoamidinate ligand L′, L′Yb[O2,6-(^{t}Bu)$_2$-4-(Me)C$_6$H$_2$]$_2$ (**7**) (L′ = Me$_3$SiNHC(Ph)N(CH$_2$)$_3$NC(Ph)NSiMe$_3$) (Scheme 2).

The formation of **7** is unexpected, probably due to the disproportionation of the *in situ* formed monoamide complex {L′Yb(NHC$_6$H$_5$)[O2,6-(^{t}Bu)$_2$-4-(Me)C$_6$H$_2$]} *via* the protonation of one amidinate group of L in **6** by $PhNH_2$ (Scheme 2), as the protonation of an amidinate group in lanthanide amidinate complex by amine to the corresponding amide complex has been documented.[9d] Probing the reaction of **3** with $PhNH_2$ in 1 : 1 molar ratio at room temperature by NMR revealed the formation of the Y-NHPh species (ESI: Fig. S25–S26†). However, efforts to isolate the bisamido complex have not been successful.

The molecular structure of **7** is shown in Fig. 2 and the selective bond distances and angles are given in Table 4.

Complex **7** is a monomer. The bond parameters in the part of Yb–N1–C1–N2 (Table 4) are comparable with those found in complexes **1**, **2** and **4–6** and the related bridged amidinate complexes reported.[7] Whilst, the distances of the C2–N3 bond (1.415(14) Å) and the C2–N4 bond (1.321(14) Å) fall in the range of C–N single and C═N double bonds, respectively, and the bond distance of Yb–N4 of 2.416(8) Å is indicative of a donating bonding, the N3 atom is out of the coordination sphere. The bond parameters of the YbL′ unit, which is quite different from those in **6**, indicates the L′ in **7** is a newly formed monoanionic amidine-functionalized amidinate group. Thus, the Yb center in **7** is five-coordinate and bound to two aryloxide ligands and three N atoms of the amidinate fragment. The coordinated geometry around the center Yb metal can be described as a distorted trigonal pyramid, when the amidinate ligand is considered to be point donor located at the central carbon atom (C1). The distances of two Ln–O



Scheme 3 Reactions of **6** (or **3**) with amines and carbodiimides.

bonds, 2.066(7) and 2.069(6) Å, are almost equivalent and the values are comparable with those in complexes **1**, **2** and **4–6**.

Reactions of 6 (or 3) with a mixture of amine and carbodiimide

The Ln–guanidinate species has proven to be the real active intermediate for addition of amines to carbodiimides.[7j,k] Thus, the reaction of **6** (or **3**) with equivalents of amine and carbodiimide was conducted in an attempt to see whether the monoguanidinate complex, the real active intermediate for this catalytic reaction, could be isolated *via* the insertion of a carbodiimide into the *in situ* formed monoamide complex mentioned above. NMR experiments for the reaction of **3** with $PhNH_2$ and $^{i}PrNCN^{i}Pr$ at room temperature indicated the corresponding Y-guanidinate species was formed (ESI: Fig. S27–S29†). Then, the reaction of **6** with $PhNH_2$ and $^{i}PrNC$-$N^{i}Pr$ in a molar ratio of 1 : 1 : 1 at 60 °C in toluene was tested. The reaction went easily to give a light yellow solution, from which yellow crystals were isolated upon crystallization from a mixture of THF and hexane in high yield. The crystals were characterized by X-ray crystal structure determination to be the expected monoguanidinate complex supported by the L′ and the -O2,6-(^{t}Bu)$_2$-4-(Me)C_6H_2 ligands, L′Yb[O2,6-(^{t}Bu)$_2$-4-(Me)-C_6H_2][^{i}PrNCNH^{i}PrN(Ph)] (**8**) (Scheme 3). Treatments of **6** with either 4-$ClC_6H_4NH_2$ and $^{i}PrNCN^{i}Pr$ or $PhNH_2$ and CyNCNCy both afforded the corresponding monoguanidinate complexes L′Yb[O2,6-(^{t}Bu)$_2$-4-(Me)C_6H_2][^{i}PrNCNH^{i}PrN(4-ClC_6H_4)] (**9**) and L′Yb[O2,6-(^{t}Bu)$_2$-4-(Me)C_6H_2][CyNCNHCyN(Ph)] (**10**). Also, the analogous Y complexes L′Y[O2,6-(^{t}Bu)$_2$-4-(Me)C_6H_2][^{i}PrNCN-H^{i}PrN(Ph)] (**11**) and L′Y[O2,6-(^{t}Bu)$_2$-4-(Me)C_6H_2][CyNCNHCy-N(Ph)] (**12**) could be prepared similarly by reactions of **3** with $PhNH_2$ and carbodiimides as shown in Scheme 3.

According to the NMR experiments (both for the reactions of **3** with $PhNH_2$ and with $PhNH_2$ and $^{i}PrNCN^{i}Pr$) the pathway for the preparations of monoguanidinate complexes of **8–12** could be proposed as follows: **3** (or **6**) reacted firstly with amine to yield the monoamide complex, which added immediately to carbodiimide affording the monoguanidinate complex (Scheme 3).

The molecular structures of complexes **8–12** were determined by X-ray crystal structure analyses. The results revealed that **9–12** and **8** are isostructural, although the detailed bond parameters for complexes **11** and **12** could not be given due to the poor quality of their single crystals. The selective bond distances and angles for complexes **8** and **9** are given in Table 5 and only the ORTEP drawing of **8** is shown in Fig. 3. The ORTEP drawing of **9** is given in the ESI (Fig. S24†).

Complex **8** is a monomer. The center metal Yb coordinates to one L′, one guanidinate ligand, and one OAr group. The coordination number of the center metal is 6 and the coordination geometry around the center metal can be

Table 5 Selected bond distances (Å) and angles (°) for **8** and **9**

	8	**9**		**8**	**9**
Bond lengths					
Ln(1)–N(1)	2.384(7)	2.423(6)	N(1)–C(1)	1.345(11)	1.339(9)
Ln(1)–N(2)	2.300(7)	2.287(6)	N(2)–C(1)	1.324(11)	1.321(9)
Ln(1)–N(4)	2.419(7)	2.459(5)	N(3)–C(2)	1.372(12)	1.355(9)
Ln(1)–N(5)	2.328(7)	2.343(5)	N(4)–C(2)	1.320(11)	1.290(8)
Ln(1)–N(6)	2.384(8)	2.368(5)	N(5)–C(45)	1.340(11)	1.349(8)
Ln(1)–O(1)	2.083(6)	2.086(4)	N(6)–C(45)	1.350(12)	1.339(8)
Bond angles					
O(1)–Ln(1)–C(1)	110.3(3)	112.06(19)	N(4)–Ln(1)–O(1)	89.8(2)	91.26(18)
O(1)–Ln(1)–C(45)	126.2(3)	120.00(18)	N(2)–C(1)–N(1)	113.7(8)	114.7(6)
N(5)–Ln(1)–N(6)	56.8(3)	56.80(18)	N(4)–C(2)–N(3)	120.2(9)	120.7(6)
N(1)–Ln(1)–N(2)	57.0(2)	56.7(2)	N(5)–C(45)–N(6)	112.9(9)	113.0(6)
C(1)–Ln(1)–C(45)	110.8(3)	116.21(19)			

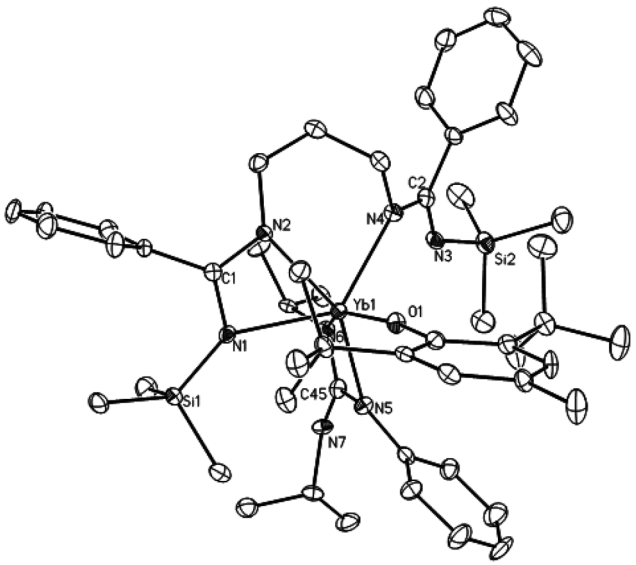
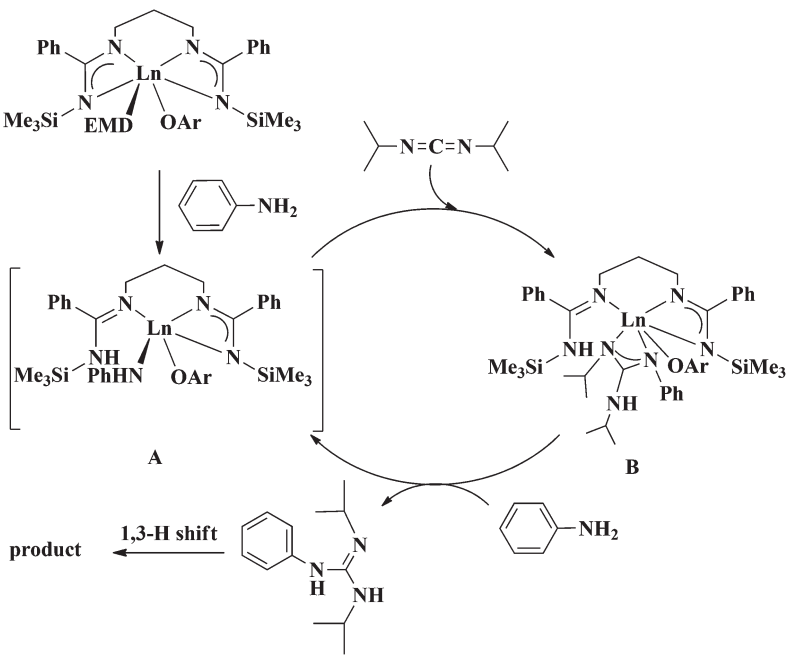


Fig. 3 ORTEP diagram of the molecular structure of **8**. Thermal ellipsoids are drawn at the 30% probability level. All hydrogen atoms and lattice solvent molecules are omitted for clarity.

described as a distorted trigonal pyramid when the amidinate and the guanidinate ligands both are considered to be point donors located at the central carbon atoms (C1 and C45, respectively). The bond parameters of the unit of YbL′ and the distance of Yb–O1 bond (Table 5) are well comparable with those in complex 7 (Table 4). As expected, the coordinated guanidinate group forms essentially a planar four-member ring with the metal atom within experimental errors. The bond angles around C45 are consistent with sp^2 hybridization. The bond distances of C45–N5 (1.340(11) Å) and C45–N6 (1.350(12) Å) are almost equivalent and significantly shorter than the C–N single-bond distances, indicating that the electrons are delocalized over the N–C–N unit. The bond parameters of Yb–guanidinate unit (Table 5) are compared to those in the related guanidinate Yb complexes reported.[7k,8a]

As it stated that no reaction was observed between $PhNH_2$ and $^{i}PrNCN^{i}Pr$ at 60 °C for 24 h. In contrast, addition of 0.25 mol% of **8** led to rapid addition of $PhNH_2$ to $^{i}PrNCN^{i}Pr$ to give the guanidine in 92% yield. The activities of the intermediates of **8** and **11** were found to be the same as those of the catalyst precursors **6** and **3** (Table 2, entries 12–13 and 6). According to the above results, a possible reaction pathway for the catalytic addition of amines to carbodiimides by LLn(OAr)(DME) could be proposed in Scheme 4. The protonation reaction between LLn(OAr)(DME) and an amine should simply yield an amido species **A**. Nucleophilic addition of the amido species **A** to a carbodiimide would afford directly the guanidinate species **B**. Protonation of **B** by another molecule of amine would regenerate the amido species **A** and release the guanidine.

Thus, the active group in the precatalysts **1–6** is the amidinate group of L ligand, not the OAr group as the systems with $Ln(OAr)_3(THF)_2$. This may be because the Ln–amidinate bond is more reactive than the Ln–OAr bond for the protonation reaction, even the amidinate group is from a bridged bis(amidinate) ligand. To the best of our knowledge this is the first example of a catalytic addition of amines to carbodiimides by a precatalyst containing the Ln-bridged amidinate active group.



Scheme 4 Mechanism for addition of amines to carbodiimides catalyzed by LLn(OAr)DME.

Conclusion

A series of bridged bis(amidinate) lanthanide aryloxides, LLn(OAr)(DME) (**1–6**) can be easily prepared by the reaction of $LLnCl(THF)_2$ with the corresponding sodium aryloxide in high yields. All the complexes can serve as efficient catalyst precursors for addition of amines to carbodiimides to multi-substituted guanidines in excellent yields with a wide range of amines. The study on the isolation and structure characterization of guanidinate complexes of **8–12** and their activity for catalytic addition of amines to carbodiimides revealed that the present catalytic reaction proceeds through the protonation of an amidinate group of the precatalyst (**1–6**) by amine, then the nucleophilic addition of the formed amide species to a carbodiimide, followed by amine protonolysis of the resultant guanidinate species.

Experimental section

All preparations and manipulations involving air- and moisture-sensitive complexes were carried out under an inert atmosphere of purified argon using standard Schlenk techniques. The solvents of THF, DME (dimethoxyethane), toluene and *n*-hexane were dried and distilled from sodium/benzophenone ketal prior to use. [D_6]Benzene was dried over fresh Na chips in a glovebox for NMR reactions. Carbodiimides and amines were purchased from TCI and were used as supplied. The ligand precursor LH_2 (LH_2 = $Me_3SiNHC(Ph)N(CH_2)_3NC(Ph)NHSiMe_3$) and $LLnCl(THF)_2$ were prepared according to the literature procedure.[11] ^{1}H NMR and ^{13}C NMR spectra were run on a Bruker DPX-300 or a Unity Inova-400 spectrometer. Lanthanide analyses were performed by EDTA titration with a xylenol orange indicator and a hexamine buffer. Elemental analyses were performed by direct combustion using a Carlo-Erba EA 1110 instrument. The Infrared spectra were recorded on a Magna-IR 550 spectrometer as KBr pellets.

Synthesis of LY[O2,6-$(Me)_2C_6H_3$](DME) (1)

Following modified literature routes,[9e] a solution of Na[O2,6-$(Me)_2C_6H_3$] (0.48 g, 3.0 mmol) in THF (30 mL) was slowly added to a stirring solution of $LYCl(THF)_2$ (2.08 g, 3.0 mmol) in a Schlenk flask. The reaction mixture was stirred at room temperature overnight. The residual NaCl was removed by centrifugation, the solvent evaporated *in vacuo*, and the solid residue extracted with toluene (30 mL). The resulting pale yellow solution was concentrated and a small amount of DME was added. Then the mixture was filtered, and the solution was slowly concentrated at room temperature, cooled to −30 °C, and left overnight. The crystalline precipitate was washed with cold hexane and dried *in vacuo* at room temperature. Complex **1** was obtained as colorless crystals. Yield: 1.85 g (85%). M.p.: 125–127 °C (decomp.). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.36 (2 H, d, J = 7.3 Hz, –ArH), 7.21 (7 H, d, J = 12.9 Hz, –ArH), 7.08 (4 H, m, –ArH), 3.28 (10 H, m, $-CH_3OC_2H_4OCH_3$), 3.03 (6 H, s, $-CH_2$), 2.77 (6 H, s, $-OC_6H_3(CH_3)_2$), 0.07 (18 H, m, $-SiMe_3$). IR (KBr, cm^{-1}): 3648 (m), 3338 (m), 3062 (m), 2953 (m), 2872 (m), 1605 (s), 1540 (m), 1432 (m), 1360 (m), 1280 (m), 1233 (m), 1158 (s), 1053 (m), 998 (s), 887 (w), 777 (m), 750 (m), 701 (m), 553 (m). Calcd for $C_{42}H_{61}N_4O_3Si_2Y$ (815.04): C, 61.89; H, 7.54; N, 6.87; Y, 10.91. Found: C, 61.67; H, 7.38; N, 6.92; Y, 11.03.

Synthesis of LY[O2,6-$(^iPr)_2C_6H_3$](DME) (2)

By the procedure described for **1**, reaction of Na[O2,6-$(^iPr)_2C_6H_3$] (0.70 g, 3.5 mmol) with a solution of $LYCl(THF)_2$ (2.43 g, 3.5 mmol) gave **2** as colorless crystals. Yield: 2.26 g (83%). M.p.: 126–127 °C (decomp.). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.33 (2 H, d, J = 7.5 Hz, –ArH), 7.21 (5 H, m, –ArH), 7.07 (6 H, m, –ArH), 3.83 (8 H, s, $-CH_3OC_2H_4OCH_3$), 3.00 (2 H, s, $-CH_3OC_2H_4OCH_3$), 1.54 (8 H, d, J = 6.8 Hz, $-CH_2$ and $-CH(CH_3)_2$), 1.38 (12 H, m, $-OC_6H_3[CH(CH_3)_2]_2$), 0.06 (18 H, m, $-SiMe_3$). ^{13}C NMR (101 MHz, C_6D_6): δ = 128.3, 127.9, 122.9, 116.4, 69.5, 48.2, 33.0, 25.4, 25.2, 24.6. IR (KBr, cm^{-1}): 3690 (m), 3352 (m), 3060 (m), 2955 (m), 1609 (s), 1572 (m), 1540 (m), 1432 (m), 1343 (m), 1280 (m), 1239 (m), 1157 (s), 1043 (m), 998 (s), 887 (w), 833 (m), 778 (m), 751 (m), 701 (m), 555 (m). Calcd for $C_{39}H_{61}N_4O_3Si_2Y$ (779.01): C, 60.13; H, 7.89; N, 7.19; Y, 11.41. Found: C, 59.89; H, 7.64; N, 7.12; Y, 11.21.

Synthesis of LY[O2,6-$(^tBu)_2$-4-$(Me)C_6H_2$](DME) (3)

By the procedure described for **1**, reaction of Na[O2,6-$(^tBu)_2$-4-$(Me)C_6H_2$] (0.75 g, 3.1 mmol) with a solution of $LYCl(THF)_2$ (2.15 g, 3.1 mmol) gave **3** as colorless crystals. Yield: 2.24 g (88%). M.p.: 120–121 °C (decomp.). ^{1}H NMR (400 MHz, C_6D_6): δ = 7.35 (4 H, m, –ArH), 7.04 (12 H, s, –ArH), 3.32 (10 H, m, $-CH_3OC_2H_4OCH_3$), 2.46 (3 H, m, $-CH_2$), 2.13 (3 H, s, $-CH_2$), 1.88 (21 H, m, $-OC_6H_2[C(CH_3)_3]_2CH_3$), 0.07 (18 H, m, $-SiMe_3$). IR (KBr, cm^{-1}): 3647 (m), 3414 (m), 3326 (m), 2954 (m), 1645 (w), 1603 (s), 1569 (m), 1490 (m), 1431 (m), 1384 (m), 1362 (m), 1233 (m), 1216 (m), 1158 (s), 1073 (m), 957 (s), 832 (w), 776 (m), 701 (m), 503 (m). Calcd for $C_{42}H_{67}N_4O_3Si_2Y$ (821.08): C, 61.44; H, 8.22; N, 6.82; Y, 10.83. Found: C, 61.19; H, 8.41; N, 6.68; Y, 10.56.

Synthesis of LNd[O2,6-$(^tBu)_2$-4-$(Me)C_6H_2$](DME) (4)

By the procedure described for **1**, reaction of Na[O2,6-$(^tBu)_2$-4-$(Me)C_6H_2$] (0.85 g, 3.5 mmol) with a solution of $LNdCl(THF)_2$ (2.61 g, 3.5 mmol) gave **4** as light purple crystals. Yield: 2.39 g (78%). M.p.: 121–122 °C (decomp.). IR (KBr, cm^{-1}): 3648 (m), 3415 (m), 3338 (m), 2957 (m), 1669 (m), 1646 (w), 1607 (s), 1569 (m), 1490 (m), 1433 (m), 1384 (m), 1363 (m), 1231 (m), 1216 (m), 1158 (s), 1120 (m), 1028 (s), 860 (w), 777 (m), 701 (m), 504 (m). Calcd for $C_{42}H_{67}N_4O_3Si_2Nd$ (876.42): C, 57.56; H, 7.71; N, 6.39; Nd, 16.46. Found: C, 57.39; H, 7.81; N, 6.68; Nd, 16.65.

Synthesis of LSm[O2,6-$(^tBu)_2$-4-$(Me)C_6H_2$](DME) (5)

By the procedure described for **1**, reaction of Na[O2,6-$(^tBu)_2$-4-$(Me)C_6H_2$] (0.94 g, 3.9 mmol) with a solution of $LSmCl(THF)_2$ (2.93 g, 3.9 mmol) gave **5** as pale yellow crystals. Yield: 2.79 g (81%). M.p.: 119–120 °C (decomp.). IR (KBr, cm^{-1}): 3429 (m),

2957 (m), 1636 (w), 1607 (s), 1540 (m), 1490 (m), 1431 (m), 1384 (m), 1363 (m), 1231 (m), 1215 (m), 1157 (s), 1120 (m), 860 (w), 779 (m), 701 (m), 504 (m). Calcd for $C_{42}H_{67}N_4O_3Si_2Sm$ (882.54): C, 57.16; H, 7.65; N, 6.35; Sm, 17.04. Found: C, 57.19; H, 8.41; N, 6.58; Sm, 17.26.

Synthesis of LYb[O2,6-(^{t}Bu)$_2$-4-(Me)C$_6$H$_2$](DME) (6)

By the procedure described for **1**, reaction of Na[O2,6-(^{t}Bu)$_2$-4-(Me)C$_6$H$_2$] (0.73 g, 3.0 mmol) with a solution of LYbCl(THF)$_2$ (2.32 g, 3.0 mmol) gave **6** as pale yellow crystals. Yield: 2.31 g (85%). M.p.: 130–133 °C (decomp.). IR (KBr, cm^{-1}): 3648 (m), 3422 (m), 3334 (m), 2955 (m), 1646 (w), 1603 (s), 1569 (m), 1490 (m), 1431 (m), 1384 (m), 1363 (m), 1232 (m), 1216 (m), 1158 (s), 1120 (m), 968 (s), 860 (w), 747 (m), 701 (m), 505 (m). Calcd for $C_{42}H_{67}N_4O_3Si_2Yb$ (905.22): C, 55.73; H, 7.46; N, 6.19; Yb, 19.12. Found: C, 55.67; H, 7.64; N, 6.12; Yb, 19.21.

Synthesis of L′Yb[O2,6-(^{t}Bu)$_2$-4-(Me)C$_6$H$_2$]$_2$ (7)

A certain amount of aniline (0.32 ml, 10.96 M, 3.5 mmol) was added to a solution of **6** (3.06 g, 3.5 mmol) in toluene (30 mL), which was stirred at 100 °C for 12 h. After the solvent was removed under reduced pressure, and the residue was extracted with hot THF. The resulting pale yellow solution was concentrated and a certain amount of hexane was added. Then the mixture was filtered, and the solution was slowly concentrated at room temperature. Single crystals of **7** suitable for X-ray analysis were obtained after about one day. Yield: 1.54 g (42%). M.p.: 109–110 °C (decomp.). IR (KBr, cm^{-1}): 3443 (m), 2958 (m), 2361 (m), 1637 (w), 1436 (m), 1384 (w), 1232 (m), 1155 (s), 1068 (s), 700 (m), 639 (m), 555 (w), 503 (m). Calcd for $C_{53}H_{81}N_4O_2Si_2Yb$ (1035.44): C, 61.48; H, 7.88; N, 5.41; Yb, 16.71. Found: C, 61.78; H, 7.64; N, 5.64; Yb, 16.57.

Synthesis of L′Yb[O2,6-(^{t}Bu)$_2$-4-(Me)C$_6$H$_2$][(C$_6$H$_5$N)C(NH^{i}Pr)-N^{i}Pr](THF) (8)

A certain amount of aniline (0.27 ml, 10.96 M, 3.0 mmol) was added to a solution of **6** (2.63 g, 3.0 mmol) in toluene (20 mL). Then ^{i}PrNCN^{i}Pr (0.47 ml, 6.418 M, 3.0 mmol) was added to the mixture. The mixture was stirred at 60 °C for 12 h. After the solvent was removed under reduced pressure, the residue was washed by hexane twice then extracted with THF to give a yellow solution, in which a certain amount of hexane was added. The mixture was allowed to crystallize at room temperature and light yellow crystals were obtained after about one day (2.95 g, 89% yields). M.p.: 111–113 °C (decomp.). IR (KBr, cm^{-1}): 3646 (m), 2961 (m), 2866 (w), 2355 (m), 1645 (w), 1615 (s), 1441 (m), 1383 (w), 1247 (m), 1156 (s), 1122 (s), 1068 (s), 1003 (w), 862 (w), 836 (w), 751 (m), 695 (m), 500 (m). Calcd for $C_{55}H_{86}N_7O_2Si_2Yb$ (1106.53): C, 59.69; H, 7.28; N, 8.86; Yb, 15.64. Found: C, 59.39; H, 7.38; N, 8.99; Yb, 16.01.

Synthesis of L′Yb[O2,6-(^{t}Bu)$_2$-4-(Me)C$_6$H$_2$][(4-Cl-C$_6$H$_4$N)C-(NH^{i}Pr)N^{i}Pr](THF) (9)

By the procedure described for **8**, reaction of **6** (3.06 g, 3.5 mmol) with ^{i}PrNCN^{i}Pr (0.54 ml, 6.418 M, 3.5 mmol) and 4-chloroaniline (0.37 g, 3.5 mmol) in toluene (20 mL) gave **9** as pale yellow crystals. Yield: 3.27 g (82%). M.p.: 104–105 °C (decomp.). IR (KBr, cm^{-1}): 3456 (m), 2968 (m), 2869 (w), 2363 (m), 1637 (w), 1608 (s), 1491 (m), 1384 (w), 1243 (m), 1155 (s), 1090 (s), 859 (w), 836 (w), 639 (w), 555 (w), 504 (m). Calcd for $C_{55}H_{85}ClN_7O_2Si_2Yb$ (1140.97): C, 57.89; H, 6.98; N, 8.59; Yb, 15.17. Found: C, 57.54; H, 7.32; N, 9.01; Yb, 15.59.

Synthesis of L′Yb[O2,6-(^{t}Bu)$_2$-4-(Me)C$_6$H$_2$][(C$_6$H$_5$N)C(NHCy)-NCy](THF) (10)

By the procedure described for **8**, reaction of **6** (3.50 g, 4.0 mmol) with CyNCNCy (2.38 ml, 1.677 M, 4.0 mmol) and aniline (0.36 ml, 10.96 M, 4.0 mmol) in toluene (20 mL) gave **10** as pale yellow crystals. Yield: 4.04 g (85%). M.p.: 117–118 °C (decomp.). IR (KBr, cm^{-1}): 3424 (m), 2935 (m), 2869 (w), 1613 (s), 1358 (w), 1164 (s), 1062 (s), 837 (w), 755 (m), 700 (m), 630 (w), 500 (m). Calcd for $C_{61}H_{94}N_7O_2Si_2Yb$ (1186.66): C, 61.74; H, 7.98; N, 8.26; Yb, 14.58. Found: C, 61.62; H, 8.12; N, 8.26; Yb, 14.75.

Synthesis of L′Y[O2,6-(^{t}Bu)$_2$-4-(Me)C$_6$H$_2$][(C$_6$H$_5$N)C(NH^{i}Pr)-N^{i}Pr](THF) (11)

To expand the scope and elucidate the mechanistic details for these transformations, we examined other potential catalyst precursors using the same method for **8**. Reaction of **3** (3.28 g, 4.0 mmol) with ^{i}PrNCN^{i}Pr (0.62 ml, 6.418 M, 4.0 mmol) and aniline (0.36 ml, 10.96 M, 4.0 mmol) in toluene (20 mL) gave **11** as colorless crystals. Yield: 3.19 g (80%). M.p.: 102–103 °C (decomp.). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 7.36 (2 H, s, –ArH), 7.29 (6 H, m, –ArH), 6.93 (9 H, m, –ArH), 3.56 (4 H, s, –OC$_4$H$_8$), 3.39 (4 H, m, –CH$_2$N), 2.86 (2 H, s, –NH), 2.43 (3 H, s, –OC$_6$H$_2$[C(CH$_3$)$_3$]$_2$CH$_3$), 1.82 (18 H, s, –OC$_6$H$_2$[C(CH$_3$)$_3$]$_2$CH$_3$), 1.39 (4 H, s, –OC$_4$H$_8$), 1.22 (2 H, s, –NCH), 1.10 (2 H, s, –CHH), 0.87 (12 H, s, –NCH(CH$_3$)$_2$), 0.18 (18 H, m, –SiMe$_3$). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 179.4, 167.4, 164.3, 161.6, 151.7, 150.8,149.5, 139.5,137.6, 135.1, 129.6, 128.3, 128.0, 127.7, 125.9, 67.8, 46.5, 44.8, 43.2, 35.4, 32.8, 25.8, 23.2, 21.7. IR (KBr, cm^{-1}): 3648 (m), 2957 (m), 2871 (w), 2360 (m), 1645 (w), 1615 (s), 1439 (m), 1386 (w), 1239 (m), 1155 (s), 1123 (s), 1071 (s), 1003 (w), 859 (w), 836 (w), 750 (m), 699 (m), 500 (m). Calcd for $C_{55}H_{86}N_7O_2Si_2Y$ (1022.39): C, 64.61; H, 8.48; N, 9.59; Y, 8.70. Found: C, 64.48; H, 8.51; N, 9.63; Y, 8.86.

Synthesis of L′Y[O2,6-(^{t}Bu)$_2$-4-(Me)C$_6$H$_2$][(C$_6$H$_5$N)C(NHCy)NCy]-(THF) (12)

Reaction of **3** (3.69 g, 4.5 mmol) with CyNCNCy (2.68 ml, 1.677 M, 4.5 mmol) and aniline (0.41 ml, 10.96 M, 4.5 mmol) in toluene (20 mL) gave **12** as colorless crystals. Yield: 4.07 g (82%). M.p.: 116–117 °C (decomp.). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 7.22 (6 H, d, J = 7.4 Hz, –ArH), 7.12 (6 H, d, J = 3.0 Hz, –ArH), 6.89 (5 H, s, –ArH), 4.00 (1 H, s, –NH), 3.56 (4 H, s, –OC$_4$H$_8$), 3.36 (4 H, s, –CH$_2$N), 2.83 (1 H, s, –NH), 2.40 (3 H, s, –OC$_6$H$_2$[C(CH$_3$)$_3$]$_2$CH$_3$), 1.79 (18 H, s, –OC$_6$H$_2$[C(CH$_3$)$_3$]$_2$CH$_3$), 1.43 (4 H, d, J = 10.2 Hz, –OC$_4$H$_8$), 1.35 (2 H, s, –NCH), 1.10 (2 H, d, J = 11.1 Hz, –CHH), 0.85 (20 H, d, J = 0.9 Hz, –NC$_6$H$_{11}$), 0.16 (18 H, m, –Si(CH$_3$)$_3$). ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 179.0, 167.3, 163.4, 161.3, 151.5, 150.2, 149.0, 139.2, 137.3, 134.8,

Table 6 Crystallographic data for complexes **1**, **2** and **4–9**

Compound	**1** (toluene)	**2**	**4**	**5**	**6**	**7**	**8**·(THF)	**9**·(THF)
Formula	$C_{42}H_{61}N_4O_3Si_2Y$	$C_{39}H_{61}N_4O_3Si_2Y$	$C_{42}H_{67}N_4O_3Si_2Nd$	$C_{42}H_{67}N_4O_3Si_2Sm$	$C_{42}H_{67}N_4O_3Si_2Yb$	$C_{53}H_{81}N_4O_2Si_2Yb$	$C_{55}H_{86}N_7O_2Si_2Yb$	$C_{55}H_{85}ClN_7O_2Si_2Yb$
Fw	815.04	779.01	876.42	882.53	905.22	1035.44	1106.53	1140.97
T/K	200(2)	100(2)	200(2)	173(2)	223(2)	223(2)	223(2)	223(2)
λ/Å	0.7107	0.71070	0.71070	0.71073	0.71075	0.71075	0.71075	0.71075
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	*Pcab*	*P*21/*c*	*P*21/*n*	*P*21/*n*	*P*21/*c*	*P*212121	*P*21/*n*	*P*21/*c*
Crystal size/mm	0.80 × 0.40 × 0.30	0.60 × 0.20 × 0.20	0.30 × 0.16 × 0.15	0.70 × 0.25 × 0.20	0.50 × 0.40 × 0.30	0.80 × 0.60 × 0.40	0.40 × 0.20 × 0.10	0.80 × 0.30 × 0.10
a/Å	8.6929(2)	24.6655(11)	9.0793(2)	9.0917(4)	22.7177(9)	13.244(4)	13.980(2)	18.079(2)
b/Å	52.4298(17)	8.6830(3)	14.3645(3)	14.3482(7)	9.1356(3)	19.003(6)	26.110(3)	18.777(2)
c/Å	19.5627(7)	20.0629(7)	33.6538(8)	33.7910(17)	21.8886(9)	21.832(6)	17.139(3)	18.448(2)
α (°)	90	90	90	90	90	90	90	90
β(°)	90	106.124(4)	95.124(2)	95.344(2)	91.3490(10)	90	111.891(4)	109.725(3)
γ(°)	90	90	90	90	90	90	90	90
V/Å^3	8916.0(5)	4127.9(3)	4371.59(17)	4388.9(4)	4541.5(3)	5495(3)	5804.8(14)	5895.1(13)
Z/Å^3	8	4	4	4	4	4	4	4
D_{calcd}/g cm^{-3}	1.214	1.254	1.332	1.336	1.324	1.252	1.266	1.286
μ/mm^{-1}	1.40	1.510	1.283	1.433	2.151	1.785	1.696	1.716
F(000)	3456	1656	1836	1844	1876	2164	2316	2380
θ_{range}/°	2.82–25.50	2.84–25.50	2.81–25.50	2.27–25.50	3.02–27.48	3.00–25.50	3.02–25.50	3.12–25.50
Total no. of rflns	84 018	28 966	29 627	131 137	32 573	19 391	28 075	29 491
No. of indep rflns	8290	7688	8114	8156	10 281	9737	10 714	10 935
R_{int}	0.1233	0.0408	0.0479	0.0448	0.0303	0.0475	0.1050	0.0817
GOF	1.193	1.072	1.032	1.129	1.072	1.094	1.188	1.173
R [$I > 2\sigma(I)$]	0.0986	0.0515	0.0335	0.0254	0.0375	0.0585	0.0984	0.0705
wR	0.1725	0.1216	0.0620	0.0607	0.0827	0.1428	0.1410	0.1494
Largest diff. peak and hole/e Å^{-3}	1.012, −1.904	1.551, −1.507	0.612, −0.574	1.404, −0.412	1.553, −0.930	2.888, −1.122	0.644, −0.903	1.906, −1.601

129.3, 128.0, 127.7, 123.5, 122.7, 121.0, 67.8, 56.0, 51.5, 49.2, 47.8, 35.6, 33.6, 32.4, 26.0, 24.9, 21.3. IR (KBr, cm^{-1}): 3432 (m), 2941 (m), 2870 (w), 1615 (s), 1355 (w), 1158 (s), 1067 (s), 837 (w), 750 (m), 700 (m), 639 (w), 504 (m). Calcd for $C_{61}H_{94}N_7O_2Si_2Y$ (1102.52): C, 66.45; H, 8.59; N, 8.89; Y, 8.06. Found: C, 66.28; H, 8.64; N, 8.95; Y, 8.32.

General procedure for the reaction of amines with carbodiimides catalyzed by 3

A 10 mL Schlenk tube under dried argon was charged with **3** (0.005 equiv.) and a certain amount of amines and carbodiimides. The resulting mixture was stirred at room temperature or 60 °C for the desired time, as shown in Tables 2 and 3. After the reaction was completed, the reaction mixture was hydrolyzed by water, extracted with dichloromethane (3 × 10 mL), dried over anhydrous Na_2SO_4, and filtered. Then the solvent was removed under reduced pressure, and the final products were further purified by crystallization from *n*-hexane.

X-ray crystallography

Crystals suitable for X-ray diffraction of complexes **1**, **2** and **4–9** were sealed, respectively, in a thin-walled glass capillary filled with argon for structural analysis. Diffraction data were collected on an Agilent Xcalibur CCD area detector in the ω scan mode using Mo Kα radiation (λ = 0.71070 Å) for complexes **1**, **2** and **4**, on a Bruker APEX-II CCD area detector in the ω scan mode using Mo Kα radiation (λ = 0.71073 Å) for complex **5** and on a Rigaku Saturn CCD area detector in the ω scan mode using Mo Kα radiation (λ = 0.71075 Å) for complexes **6–9** (see the ESI†). The diffracted intensities were corrected for Lorentz-polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 6 respectively. The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. The structures were refined using SHELXL-97 programs. CCDC 915745 (for **1**), 915744 (for **2**), 915746 (for **4**), 915747 (for **5**), 915748 (for **6**), 915741 (for **7**), 915742 (for **8**), 915743 (for **9**) contain the supplementary crystallographic data for this paper.

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