Inorganic Chemistry

Activation of Carbodiimide and Transformation with Amine to Guanidinate Group by Ln(OAr)₃(THF)₂ (Ln: Lanthanide and Yttrium) and Ln(OAr)₃(THF)₂ as a Novel Precatalyst for Addition of Amines to Carbodiimides: Influence of Aryloxide Group

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Supporting Information

ABSTRACT: Reaction of $Ln(OAr^{1})_{3}(THF)_{2}$ ($Ar^{1} = [2,6-({}^{t}Bu)_{2}-4-MeC_{6}H_{2}]$ with carbodiimides (RNCNR) in toluene afforded the RNCNR coordinated complexes ($Ar^{1}O$)_{3}Ln(NCNR) (R = ${}^{i}Pr$ (isopropyl), Ln = Y (1) and Yb (2); R = Cy (cyclohexyl), Ln = Y (3)) in high yields. Treatment of 1 and 2 with 4-chloroaniline, respectively, at a molar ratio of 1:1 yielded the corresponding monoguanidinate complex ($Ar^{1}O$)_2Y[(4-Cl-C₆H₄N)C(NHⁱPr) NⁱPr] (THF) (4) and ($Ar^{1}O$)_2Yb[(4-Cl-C₆H₄N)C(NHⁱPr)NⁱPr]



(THF) (5). Complexes 4 and 5 can be prepared by the reaction of $Ln(OAr^1)_3(THF)_2$ with RNCNR and amine in toluene at a 1:1:1 molar ratio in high yield directly. A remarkable influence of the aryloxide ligand on this transformation was observed. The similar transformation using the less bulky yttrium complexes $Y(OAr^2)_3(THF)_2$ ($Ar^2 = [2,6-(^iPr)_2C_6H_3]$) or $Y(OAr^3)_3(THF)_2$ ($Ar^3 = [2,6-Me_2C_6H_3]$) did not occur. Complexes $Ln(OAr^1)_3(THF)_2$ were found to be the novel precatalysts for addition of RNCNR with amines, which represents the first example of catalytic guarylation by the lanthanide complexes with the Ln-O active group. The catalytic activity of $Y(OAr^1)_3(THF)_2$ was found to be the same as that of monoguanidinate complex 4, indicating 4 is one of the active intermediates in the present process. The other intermediate, amide complex ($Ar^1O_2Ln[(2-OCH_3-C_6H_4NH)(2-OCH_3-C_6H_4NH_2)]$ (6), was isolated by protonolysis of 4 with 2-OCH_3-C_6H_4NH_2. All the complexes were structurally characterized by X-ray single crystal determination.

INTRODUCTION

Activation and transformation of small molecules mediated by lanthanide complexes are one of the most interesting topics in organometallic chemistry and coordination chemistry of lanthanide metals.¹ Carbodiimides, as one of the members of heterocumulene family, have attracted increasing attention for lanthanide metal based reactivity studies.² For example, insertion reactions of carbodiimides into lanthanide metal Ln-C^{2b,3c}or $Ln-N^{2c-g}$ bonds have been explored to afford lanthanide(III) complexes with a substituted propiolamidine group or a substituted guanidinate RNC(NHR')NR ligand. More interestingly, an atom economic method for the synthesis of substituted guanudines or propiolamidine has been developed by the combination of the insertion reaction and the following protonolysis.³ Recently, the activation and transformation of carbodiimides in different modes have been documented with divalent lanthanide complexes by Deacon and Junks' group, and our group. These reduction reactions of carbodiimides by divalent lanthanide complexes were found to afford an oxalamidinate,^{4a,c} a formamidinate, a linked formamidinate,^{4b} or a diamidocarbene species^{4d} depending on the divalent lanthanide complex and/or

the carbodiimides used. Similarly, a direct synthetic way to guanidines or propiolamidine was also explored using divalent lanthanide complexes as the precatalysts.^{3g}

Lanthanide aryloxides are well-known to serve as catalysts in many reactions, such as enantioselective alkylation of aldehydes, asymmetric epoxidation of unsaturated ketones, decarboxylation of carboxylic acids,^{5a,b} intramolecular hydroalkoxylation,^{5c} polymerization of lactones and lactides,^{6a–d} and copolymerization of carbon dioxide with epoxides,^{6e} and so forth. However, no report concerning the activation and transformation of carbodiimides by a Ln-O active group has been found until now. In continuation of our work, we studied the reactivity of Ln(OAr)₃-(THF)₂ (Ln = lanthanide and yttrium metals) toward carbodiimides. It was found that the aryloxide ligand has a remarkable influence on the reactivity. A carbodiimide coordinated complex (Ar¹O)₃Ln(RNCNR) can be isolated when the aryloxide is a bulky [2,6-(^fBu)₂-4-MeC₆H₂] (OAr¹). In contrast, no carbodiimide-coordinated complexes could be isolated using the less bulky

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Scheme 1. Reaction of $Ln(OAr)_3(THF)_2$ with Carbodiimide: the Influence of Aryloxide Ligand







lanthanide tris(aryloxides) complexes as $Ln(OAr^2)_3(THF)_2$ ($OAr^2 = [2,6-({}^iPr)_2C_6H_3]$) or $Ln(OAr^3)_3(THF)_2$ ($OAr^3 = [2,6-Me_2C_6H_3]$). The carbodiimide-coordinated complex can further react with an equivalent of amine to afford the corresponding lanthanide bis(aryloxide) guanidinate, which reacts with amine to yield the corresponding lanthanide bis(aryloxide) amide. Complexes $Ln(OAr^1)_3(THF)_2$ were found to serve as a novel precatalysts for guanylation of amines with carbodiimides to substituted guanidines. Here we report the results.

RESULTS AND DISCUSSION

Synthesis and Structures of $(Ar^{1}O)_{3}Ln(RNCNR) R = {}^{i}Pr$, Ln = Y (1) and Yb (2); R = Cy, Ln = Y (3). A series of lanthanide aryloxides were synthesized according to the literature method, including $Ln(OAr^{1})_{3}(THF)_{2}$ $(Ar^{1} = [2,6-({}^{t}Bu)_{2}-4-MeC_{6}H_{2}]$ Ln = Y and Yb), $Y(OAr^{2})_{3}(THF)_{2}$ $(Ar^{2} = [2,6-({}^{t}Pr)_{2}-4-MeC_{6}H_{2}]$ C_6H_3]) and Y(OAr³)₃(THF)₂ (Ar³ = [2,6-Me₂C₆H₃]).⁷ Treatment of $Y(OAr^1)_3(THF)_2$ with N_iN' -diisopropylcarbodiimide (ⁱPrNC-N'Pr) in a molar ratio of 1:2 at 60 °C in toluene gave a light yellow solution from which the 'PrNCN'Pr coordinated complex $(Ar^{1}O)_{3}Y(^{i}PrNCN^{i}Pr)$ (1) was isolated in a high yield (Scheme 1). Following the same procedure, the analogous Yb complex $(Ar^{1}O)_{3}Yb(^{i}PrNCN^{i}Pr)$ (2) can facilely be synthesized via the replacement of the coordinated tetarhydrofuran (THF) molecule by a 'PrNCN'Pr molecule (Scheme 1). The similar reaction of $Y(OAr^1)_3(THF)_2$ with N,N'-dicyclohexylcarbodiimide (CyNCNCy) worked smoothly, and the corresponding complex $(Ar^{1}O)_{3}Y(CyNCNCy)$ (3) was also prepared in 80% vield (Scheme 1).

However, the analogous reactions using the less bulky complexes, $Y(OAr^2)_3(THF)_2$ and $Y(OAr^3)_3(THF)_2$, did not occur, and the starting yttrium complexes were recovered. In both cases



Figure 1. ORTEP diagram of the molecular structures of complexes 1 and 2 (Ln = Y(1), Yb (2)). Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms are omitted for clarity.



Figure 2. ORTEP diagram of the molecular structure of complex 3. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms and lattice solvent molecules are omitted for clarity.

no replacement of the coordinated THF molecules by a carbodiimide was observed (Scheme 1). Complexes 1-3 are well soluble in toluene. They are thermostable and do not decompose until 110 °C.

As expected, the complexes 1-3 will completely convert to a THF-solvate $Y(OAr^1)_3(THF)_2$ via replacement of a carbodiimide by THF molecules, when putting them in a THF solution and stirring for 12 h at room temperature (Scheme 2).

The molecular structures of 1-3 were determined and are shown in Figures 1 and 2, respectively, as complexes 1 and 3 are isostructural. X-ray structure determination shows that 1 and 2 featuring the donating coordinated ⁱPrN=C=NⁱPr moiety are both solvent-free monomers with the central metal atom bonded to three aryloxide groups and one carbodiimide molecule. The coordination geometry around the each metal can be described as a distorted-tetrahedral geometry. The Ln(1)–N(1) distances are 2.443(3) Å for 1 and 2.392(3) Å for 2, which are comparable with each other when the difference in ion radius between Y and Yb was considered and both are in the range of Ln-N donated bonding (Table 1). Because no analogous complexes can be found in the literature, the bond distances concerning carbo-

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 1-3

	1	2	3
	Bond Length	S	
Ln (1)-O (1)	2.063(2)	2.038(2)	2.079(2)
Ln (1)-O (2)	2.098(2)	2.062(2)	2.091(2)
Ln (1)-O (3)	2.125(2)	2.091(2)	2.092(2)
Ln(1)-N(1)	2.443(3)	2.392(3)	2.462(3)
N (1)-C (46)	1.250(5)	1.260(5)	1.255(5)
N (2)-C (46)	1.182(5)	1.172(5)	1.191(5)
	Bond Angles	5	
O (1)–Ln (1)–O (2)	108.66(9)	108.74(9)	115.27(9)
O (1)–Ln (1)–O (3)	116.16(8)	116.40(9)	114.42(10)
O (2)–Ln (1)–O (3)	127.89(9)	127.92(10)	115.75(10)
C (46)–N (1)–Ln (1)	110.0(2)	109.7(3)	112.6(3)
N (2)-C (46)-N (1)	170.0(5)	170.5(5)	172.5(4)
C (46)–N (1)–C (47)	118.0(3)	116.9(3)	118.2(7)
C (46)–N (2)–C (50)	147.7(4)	149.0(5)	136.9(4)

Scheme 3. Formation of 4 (5) by Reaction of 1 (2) with 4-Chloroaniline



diimides moiety can only be compared with those in Cp₃Y- $({}^{i}PrNCN{}^{i}Pr)$.^{2b} The Ln-N bond distance is shorter than the corresponding value found in Cp₃Y(${}^{i}PrNCN{}^{i}Pr)$ (2.547(6) Å). A significant structural feature in these adducts is the apparent elongation of the one C=N double bond in the carbodiimide moiety (C(46)=N(1) 1.250(5) Å and C(46)=N(2) 1.182(5) Å). The elongation of C=N double bond indicates clearly that the coordinated carbodiimide has been activated. The bond parameters about the part of (Ar¹O)₃Ln compare well with those found in Ln(OAr¹)₃(THF)₂. The crystal structure of **3** is exactly similar to those of **1** and **2**.

Reaction of 1 or 2 with 4-Chloroaniline: Synthesis and Molecular Structures of the Monoguanidinate Complexes $(Ar^{1}O)_{2}Ln[(4-Cl-C_{6}H_{4}N)C(NH'Pr)N'Pr](THF)$ (Ln = Y (4); Yb (5)). Heating 1 in a toluene solution did not lead to the product $(Ar^{1}O)_{2}Y[(^{i}PrN)_{2}C(OAr^{1})]$ via the insertion of $^{i}PrNCN^{i}Pr$ into the Y-OAr¹ bond as the case of the reaction of $Ti(O'Pr)_4$ with carbodiimide,⁸ but the starting substrate recovered. However, 1 could react with 4-chloroaniline (4-Cl-C₆H₄NH₂), at a molar ratio of 1:1 clearly to give a light yellow solution. Evaporation and crystallization from toluene solution resulted in the yellow crystals of monoguanidinate complex $(Ar^{1}O)_{2}Y[(4-Cl-C_{6}H_{4}N)]$ C(NH'Pr)N'Pr](THF) (4) (Scheme 3), which were fully characterized including elemental analysis, ¹HNMR spectroscopy, and X-ray single crystal structure determination. The analogous Yb complex $(Ar^1O)_2$ Yb[(4-Cl-C₆H₄N)C(NH'Pr)N'Pr](THF) (5) could also be isolated by the same procedure in good yield as dark red crystals (Scheme 3).

As is well-known, primary aromatic amines do not react with carbodiimide to a guanidine without catalyst under mild conzditions.⁹ Consequently, the formation of guanidinate species here should be attributed to the activation of carbodiimide via its coordination to the metal of $Ln(OAr^1)_3(THF)_2$ as confirmed by the elongated C=N double bond distance in 1, followed by the formation of an intermediate A via the coordination of amine. The formation of A makes it favorable to realize the addition of amine to the coordinated carbodiimide and to release a phenol via protonolysis by in situ formed guanidine concomitantly in an intramolecular transformation mode (Scheme 3). Further study revealed that complex 4 can also be synthesized in high yield by the reaction of $Y(OAr^1)_3(THF)_2$ with ^{*i*}PrNCN'Pr and

Scheme 4. Reaction of Ln(OAr)₃(THF)₂ with 4-Cl-C₆H₄N₂ and ⁱPrNCNⁱPr





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

4-Cl-C₆H₄NH₂ at a 1:1:1 molar ratio in toluene in one pot synthesis (Scheme 4). Neither the less bulky aryloxides, Y- $(OAr^2)_3(THF)_2$, nor Y $(OAr^3)_3(THF)_2$ could react with ^{*i*}PrNC-N^{*i*}Pr and 4-Cl-C₆H₄NH₂, only the starting materials were recovered for both reactions (Scheme 4).

These results indicated that the formation of a carbodiimide coordinated complex as the first step is crucial for the transformation of carbodiimide with amine to a guanidinate group, that is, the activation of a carbodiimide molecule by $Y(OAr^1)_3$ - $(THF)_2$ is the basis for its further transformation with amine. Although the insertion of carbodiimide into the Ln-N bond to a guanidinate group is well documented and becomes a general method for synthesis of lanthanide guanidinate complexes.^{2c-h} To our best knowledge, this is the first example of activation of carbodiimide and transformation with amine to a guanidinate species mediated by an Ln-O active group.

Molecular structures of complexes 4 and 5 are depicted in Figure 3. The crystal structure determination of complexes 4 and 5 revealed that they are isostructural, in which each center metal is bonded to two aryloxide ligands and one guanidinate unit, forming a distorted-tetragonal pyramidal geometry (Figure 3). As expected, the coordinated guanidinate group forms essentially a planar four-member ring with the metal atom within experimental errors. The bond angles around C(37) are consistent with sp² hybridization. The C($\overline{37}$)–N(1) bond distance (1.342(4) Å in 4, 1.332(5) Å in 5) and C(37)-N(2) bond distances (1.342(4) Å in 4, 1.350(5) Å in 5) are almost equivalent and significantly shorter than the C-N single-bond distance, indicating that the electrons are delocalized over the N-C-N unit (Table 2). The bond distances of the Y-N(1) (2.403(2) Å in 4) and Yb-N(1)(2.362(3) Å in 5) are significantly longer than that of the Y(1)-N(2) (2.299(2) Å in 4) and Yb(1)-N(2)

	4	5		4	5
		Bond Lei	ngths		
Ln (1)-O (1)	2.0859(19)	2.058(3)	Ln (1)-N (1)	2.403(2)	2.362(3)
Ln (1)-O (2)	2.1024(19)	2.076(2)	Ln(1)-N(2)	2.299(2)	2.254(3)
Ln (1)-O (3)	2.386(2)	2.347(2)	N (1)-C (37)	1.342(4)	1.332(5)
N (2)-C (37)	1.342(4)	1.350(5)	N (3)-C (37)	1.366(4)	1.368(5)
		Bond Ar	ngles		
O (2)–Ln (1)–O (3)	86.97(8)	86.89(9)	N (2)-C (37)-N (1)	113.8(2)	113.2(3)
O (2)–Ln (1)–N (2)	99.33(8)	98.89(11)	N (2)-C (37)-N (3)	120.4(3)	120.9(3)
N (2)–Ln (1)–N (1)	57.08(8)	57.98(11)	N (1)-C (37)-N (3)	125.6(3)	125.7(3)
O(3)-Ln(1)-N(1)	91.72(8)	91.63(10)			

Fable 2. Selected Bond Distances	(Å) and Angles	(deg) for	Comp	lexes	4 - 3	5
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Table 3. Catalytic Guanylation of an Aniline with an $N_s N'$ -Diisopropylcarbodiimide^{*a*}



entry	Cat.	catalyst loading (mol %)	R	temp/ °C	time/ h	product	yield(%) ^b
1	4	1	Н	10	0.5	7	95
2	4	0.5	Н	rt	1	7	87
3	4	0.5	Η	60	0.5	7	99
4	4	0.5	Cl	60	0.5	8	96
5	$Y(OAr^1)_3(THF)_2$	1	Η	10	0.5	7	63
6	$Y(OAr^1)_3(THF)_2$	0.5	Η	60	0.5	7	98
7	$Y(OAr^2)_3(THF)_2$	0.5	Η	60	4	7	58
8	$Y(OAr^3)_3(THF)_2$	0.5	Н	60	24	7	13
9	$Nd(OAr^1)_3(THF)_2$	0.5	Н	60	0.5	7	50
10	$Sm(OAr^1)_3(THF)_2$	0.5	Η	60	0.5	7	67
11	$Yb(OAr^1)_3(THF)_2$	0.5	Н	60	0.5	7	85
^a 1 mm	ol of 4-chloroanilir	ne or anil	ine	1 mm	ol of N	J.N'-diise	opropylcar-

"1 mmol of 4-chloroaniline or aniline, 1 mmol of *N*,*N*'-diisopropylcarbodiimide. ^b Isolated yields.

(2.254(3) Å in 5). This may be due to the steric hindrance of the benzene group at N(1) stretching the Ln-N(1) bonds.

Catalytic Activity of 4 for Addition of Amines to RNCNR and Isolation and Characterization of Amide Complex $(Ar^{1}O)_{2}Y[(2-OCH_{3}-C_{6}H_{4}NH)(2-OCH_{3}-C_{6}H_{4}NH_{2})]$ (6) via the Protonolysis of 4 by 2-OCH₃-C₆H₄NH₂. As is well-known, an amide and a guanidinate intermediates are the true catalyst species for catalytic formation of a guanidine compound by lanthanide amide or alkyl complexes.^{3c} Thus, the catalytic activity of 4 for addition of aniline to carbodiimide was tested. Addition of 1 mol % 4 into the mixture of 'PrNCN'Pr and PhNH₂ at 10 °C under solvent free condition led to rapid formation of the $N_{i}N'_{i}$ N''-trisubstituted guanidine 7 in 95% yield after 0.5 h (Table 3, entry 1). Even when the amount of 4 decreased to 0.5 mol %, the reaction at room temperature can still afford 7 in 87% yield after 1 h (Table 3 entry 2). Raising the temperature to 60 °C led to increasing the yield and shortening the reaction time (Table 3, entry 3). Similarly, the reaction of 4-chloroaniline (4-Cl-C₆H₄NH₂)



Figure 4. ORTEP diagram of the molecular structures of complexes 6. Thermal ellipsoids are drawn at 30% probability level. All hydrogen atoms are omitted for clarity.

with 'PrNCN'Pr using 0.5 mol % of 4 at 60 °C worked well, and the guanidine 8 was obtained in 96% yield (Table 3, entry 4).

These positive results prompted us to isolate the intermediate amide complex by protonolysis of 4 with amines. The reaction of 4 with excess $2\text{-OCH}_3\text{-}C_6\text{H}_4\text{NH}_2$ at room temperature in toluene took place rapidly leading to a color change from light yellow to darkish; the corresponding structurally characterizable amide complex **6** (Figure 4) was isolated from the solution (Scheme 5).

The isolation of **6** suggests that the catalytic formation of a guanidine compound proceeds by the following pathways. Complex **4** reacts with amine to afford the corresponding amide intermediate, then nucleophilic addition of the amido species to a carbodiimide, followed by amine protonolysis of the resultant guanidinate species.

X-ray crystal structure analysis revealed that the center metal ion of **6** is bonded to two aryloxide ligands and two oxygen atoms and two nitrogen atoms from the two amido groups in a distorted-octahedral geometry (Figure 4). The Y(1)-N(1) bond distance of 2.268(3) Å compares well with those found in the yttrium amide complexes,^{10,11} while the bond distance of



Table 4. Selected Bond Distances (Å) and Angles (deg) for Complex 6

6							
	Bond	Lengths					
	Dona	Deliguis					
Y (1)-O (1)	2.132(2)	Y (1)-O (4)	2.553(3)				
Y (1)-O (2)	2.118(2)	Y(1)-N(1)	2.268(3)				
Y (1)-O (3)	2.495(2)	Y(1)-N(2)	2.483(3)				
	Bond Angles						
O (2)-Y (1)-O (1)	159.7(2)	O (3)-Y (1)-O (4)	69.45(8)				
O (2)-Y (1)-O (3)	87.64(9)	N(1)-Y(1)-N(2)	136.44(12)				
O (1)-Y (1)-O (3)	157.14(9)						

Y(1)-N(2) (2.483(3) Å) is much longer and falls into Y–N donating bonds (Table 4).¹¹ The sum of the angles of O(1)– Y(1)-O(2), O(2)-Y(1)-O(3), O(3)-Y(1)-O(4), and O-(4)-Y(1)-O(1) is 360.8°, suggesting that the four oxygen atoms are almost in a plane. The angle formed by two N atoms and the central metal is 136.44°.

Ln(OAr¹)₃(THF)₂ as an Efficient Precatalysts for Addition of Amines to Carbodiimides. Given that 4 was synthesized directly by the reaction of $Y(OAr^1)_3(THF)_2$ with amine and carbodiimide, the catalytic activity of $Y(OAr^1)_3(THF)_2$ for addition of aniline to carbodiimide was then tested under solvent free conditions. As shown in Table 3, $Y(OAr^{1})_{3}(THF)_{2}$ exhibits high activity for the addition of aniline to ⁱPrNCNⁱPr and the corresponding 7 was isolated in 97% yield with the amount of 0.5 mol % of $Y(OAr^1)_3(THF)_2$ at 60 °C for 0.5 h (Table 3, entry 6). The activity of $Y(OAr^1)_3(THF)_2$ is almost the same as that of 4, indicating 4 is the true active species. Aryloxide group has a remarkable influence on the activity. The complexes with the less bulky ligands Y(OAr²)₃(THF)₂ and Y(OAr³)₃(THF)₂ showed very low activity (Table 3, entries 6-8). This is expected because neither $Y(OAr^2)_3(THF)_2$ nor $Y(OAr^3)_3(THF)_2$ can react with a mixture of amine and carbodiimide in a 1:1:1 molar ratio at 80 °C to a guanidinate species as demonstrated above. The influence of the central metals on the activity was clearly observed with the increasing trend of Y > Yb > Sm > Nd (Table 3, entries 6, 9–11). The complex $Y(OAr^1)_3(THF)_2$ was then chosen as a precatalyst for addition reaction of various aromatic primary amines with carbodiimides. As shown in Table 5, a wide range of substituted amines could be used for this reaction, including the amines with either electron-withdrawing or electron-donating substituents (Table 5, entries 1-11). The present catalytic guanylation was suggested to proceed through the formation of guanidinate species by reaction of $Y(OAr^{1})_{3}(THF)_{2}$ with amine and carbodiimide in a 1:1:1 molar ratio, followed by protonolysis of the

resultant guanidinate species by amine. The nucleophilic addition of an amido species formed to a carbodiimide^{3c} to regenerate the guanidinate species as shown in Scheme 6.

CONCLUSION

Activation of carbodiimide and transformation with amine to guanidinate group was explored with the bulky complexes $Ln(OAr^{1})_{3}(THF)_{2}$ (Ln = Y and Yb; $Ar^{1} = [2,6-({}^{t}Bu)_{2}-4-$ MeC₆H₂]), and the corresponding monoguanylate complexes $(Ar^{1}O)_{2}Ln[(4-Cl-C_{6}H_{4}N)C(NH^{i}Pr)N^{i}Pr]$ (Ln = Y (4); Yb (5)) were isolated and structurally characterized. The analogous transformation does not occur using the less bulky complexes $Y(OAr^{2})_{3}(THF)_{2}$ (Ar² = [2,6-(ⁱPr)_{2}C_{6}H_{3}]) or $Y(OAr^{3})_{3}$ - $(THF)_2 (Ar^3 = [2,6-Me_2C_6H_3])$. Thus, $Ln(OAr^1)_3 (THF)_2$ were first found to be the efficient precatalysts for guanylation of amine with carbodiimide under mild conditions, and the active species in this process are the corresponding monoguanidinate complexes 4 and the amide complex $(Ar^{1}O)_{2}Y[(2-OCH_{3}-C_{6}H_{4}$ NH)(2-OCH₃-C₆H₄NH₂)] (6), which was formed by protonolysis of 4 by 2-OCH₃-C₆H₄NH₂. The activity is greatly influenced by aryloxide group with the sequence of [2,6- $({}^{t}Bu)_{2}$ -4-MeC₆H₂] > Ar² = [2,6-(${}^{t}Pr)_{2}C_{6}H_{3}$] > Ar³ = [2,6-Me₂C₆H₃]. The results presented here indicate that the robust lanthanide tris(aryloxide) exhibits wide reactivity to small molecules.

EXPERIMENTAL SECTION

Materials and Methods. All operations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified argon or nitrogen using standard Schlenk techniques. The solvents THF, toluene, and *n*-hexane were dried and distilled from sodium benzophenone ketal under argon prior to use. $Ln(OAr^1)_3$ - $(THF)_2$, $Ln(OAr^2)_3(THF)_2$, and $Ln(OAr^3)_3(THF)_2$ were prepared according to the literature procedure.⁷ ¹H NMR and ¹³C NMR spectra were recorded on a 300 MHz or 400 MHz instrument and processed using MestReNova software. Elemental analyses were performed by direct combustion using a Carlo-Erba EA 1110 instrument. The IR spectra were recorded on a Magna-IR 550 spectrometer as KBr pellets. All yields of lanthanide complexes were calculated based on ligands and were crystallized yield only for the first time.

 $(Ar^{1}O)_{3}Y('PrNCN'Pr)$ (**1**). A certain amount of ⁱPrNCNⁱPr (0.32 g, 2.57 mmol) was added to a solution of Y(OAr¹)₃(THF)₂ (2.29 g, 2.57 mmol) in toluene (20 mL) in a Schlenk tube. The mixture was stirred at 60 °C for 12 h. After the solvent was removed under reduced pressure, the residue was extracted with hexane to give a white powder: 1.9 g (85%), and the white powder was dissolved in toluene and filtered to give a clean solution. Single crystals of **1** suitable for X-ray analysis were obtained from toluene at room temperature for about 1 day. ¹H NMR (400 MHz,

		$Ar-NH_2 + R-N=C=N-R - \frac{Y(O)}{2}$	$\frac{\operatorname{Ar}^{1}_{3}(\operatorname{THF})_{2}}{60^{\circ} \operatorname{C}} \xrightarrow{0.5\%} \operatorname{Ar}_{3}$		
entry	R	Ar-NH ₂	time/h	R product	Yield(%) ^b
1	Су	NH ₂	1	9	96
2	ⁱ Pr	cı حر	1	10	96
3	Су		2	11	95
4	ⁱ Pr		0.5	12	97
5	Су		1	13	93
6	ⁱ Pr		1	14	83
7	ⁱ Pr		1	15	90
8	^{<i>i</i>} Pr	H ₃ C-NH ₂	1	16	96
9	ⁱ Pr		1	8	90
10	ⁱ Pr		3	17	92
11	ⁱ Pr	NH ₂	1	18	90

 Table 5. Catalytic Addition of Primary Aromatic Amines to Carbodiimides^a

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

Scheme 6. Mechanism for Addition of Amines to Carbodiimides Catalyzed by $Y(OAr^1)_3(THF)_2$



 $C_6D_6){:}\ \delta$ 7.13 (s, 6 H, $OC_6H_2[C(CH_3)_3]_2CH_3),$ 3.37 (s, 2 H, $CH_2(CH_3)_2),$ 2.31 (s, 9 H, $OC_6H_2[C(CH_3)_3]_2CH_3),$ 1.64 (s, 54 H,

 $\begin{array}{l} {\rm OC}_6{\rm H}_2[{\rm C}({\rm CH}_3)_3]_2{\rm CH}_3), \ 0.91 \ (d, \ 12 \ {\rm H}, \ {\rm CH}({\rm CH}_3)_2); \ ^{13}{\rm C} \ {\rm NMR} \\ (101 \ {\rm MHz}, \ {\rm C}_6{\rm D}_6) \ 154.38, \ 132.03, \ 126.40, \ 122.73, \ 122.58, \ 122.34, \\ 120.64, \ 119.50, \ 45.38, \ 30.03, \ 27.47, \ 18.46, \ 16.00; \ {\rm IR} \ ({\rm KBr}, \ {\rm cm}^{-1}): \\ 3648({\rm m}), \ 3359({\rm w}), \ 2957({\rm s}), \ 2915({\rm s}), 2871({\rm s}), \ 2361({\rm w}), \ 2112({\rm s}), \\ 1747({\rm w}), \ 1615({\rm m}), 1418({\rm s}), \ 1386({\rm m}), \ 1360({\rm m}), 1238({\rm s}), \ 1158({\rm s}), \\ 1120({\rm m}), \ 922({\rm w}), \ 890({\rm w}), \ 861({\rm m}), \ 830({\rm s}), \ 640({\rm w}), \ 534({\rm m}), \ 504({\rm w}); \\ {\rm Anal. \ Calcd \ for} \ C_{52}{\rm H}_{83}{\rm N}_2{\rm O}_3{\rm Y} \ (873.11): \ {\rm C}, \ 71.53; \ {\rm H}, \ 9.58; \ {\rm N}, \ 3.21. \\ {\rm Found:} \ {\rm C}, \ 71.18; \ {\rm H}, \ 9.78; \ {\rm N}, \ 3.94. \end{array}$

 $(Ar^{1}O)_{3}Yb(^{i}PrNCN^{i}Pr)$ (2). A certain amount of ⁱPrNCNⁱPr (0.28 g, 2.21 mmol) was added to a solution of Yb(OAr¹)₃(THF)₂ (1.99 g, 2.21 mmol) in toluene (20 mL). The reaction mixture was subsequently worked up by the method described above. Red crystals of 2 were obtained in 78% yield (1.65 g). IR (KBr, cm⁻¹): 3652(m), 3345(w), 2945(s), 2909(s),2881(s), 2120(s), 1621(m), 1425(s), 1387(m), 1367-(m),1239(s), 1155(s), 1123(m), 931(w), 893(w), 861(m), 838(s), 776(w), 646(w), 537(m); Anal. Calcd for C₅₂H₈₃N₂O₃Yb (957.24): C, 65.24; H, 8.74; N, 2.93. Found: C, 65.86; H, 8.82; N, 2.79.

 $(Ar^{1}O)_{3}Y(CyNCNCy)$ (**3**). By the procedure described for **1**, reaction of $Y(OAr^{1})_{3}(THF)_{2}$ (2.54 g, 3.11 mmol) with CyNCNCy (0.64 g, 3.11 mmol) gave **3** as colorless crystals. Yield: 2.66 g (82%). ¹H NMR (400 MHz, $C_{6}D_{6}$): δ 7.13 (s, 6H, $OC_{6}H_{2}[C(CH_{3})_{3}]_{2}CH_{3}$), 3.04 (s, 2H, Cy), 2.29 (s, 9H, $OC_{6}H_{2}[C(CH_{3})_{3}]_{2}CH_{3}$), 1.95–1.74 (m, 4H), 1.66 (d, 54H, $OC_{6}H_{2}[C(CH_{3})_{3}]_{2}CH_{3}$), 1.95–1.74 (m, 4H), 1.66 (d, 54H, $OC_{6}H_{2}[C(CH_{3})_{3}]_{2}CH_{3}$), 1.47 (d, 4H, Cy), 1.31 (d, 2H, Cy), 1.17 (d, 4H, Cy), 1.10–0.95 (m, 4H, Cy), 0.89 (dd, 2H, Cy). ¹³C NMR (101 MHz, $C_{6}D_{6}$): δ 159.94, 137.63, 131.24, 126.16, 124.94, 57.33, 35.48,

Tab	le	6. (Crystal	lograpl	hic Da	ata for	Comp	lexes	1-	6
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	1	2	3	4	5	6
formula	C ₅₂ H ₈₃ N ₂ O ₃ Y	C ₅₂ H ₈₃ N ₂ O ₃ Yb	C ₆₅ H ₉₉ N ₂ O ₃ Y	C54H81ClN3O3Y	C ₅₄ H ₈₁ ClN ₃ O ₃ Yb	$C_{44}H_{63}N_2O_4Y$
mol wt	873.11	957.24	1045.37	944.58	1028.71	772.87
λ (Å)	0.71075	0.71075	0.71075	0.71075	0.71075	0.71075
cryst syst	monoclinic	monoclinic	triclinic	triclinic	triclinic	monoclinic
space group	$P2_{1}/c$	P2 ₁ /c	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$	$P2_{1}/n$
cryst size (mm)	$0.80\times0.40\times0.15$	$0.80\times0.20\times0.20$	$0.55\times0.40\times0.15$	$0.50\times0.30\times0.30$	$0.60\times0.18\times0.12$	$0.70\times0.30\times0.20$
a (Å)	15.5829(18)	15.5373(12)	14.2961(4)	9.8439(7)	9.8319(5)	14.7013(17)
b (Å)	17.9753(19)	17.9224(13)	14.8441(5)	11.2519(9)	11.2382(6)	17.9628(16)
c (Å)	18.564(2)	18.5630(15)	15.7236(6)	24.409(2)	24.3593(15)	16.8390(18)
α (deg)	90	90	79.534(5)	83.406(7)	83.370(4)	90
β (deg)	103.940(3)	103.976(2)	75.579(5)	80.859(5)	80.871(4)	110.551(3)
γ (deg)	90	90	71.112(4)	76.620(6)	76.612(4)	90
$V(Å^3)$	5046.8(10)	5016.1(7)	3038.96(18)	2588.3(4)	2576.5(2)	4163.8(8)
$Z(\text{\AA}^3)$, $D_{\text{calcd}} (g/mL)$	4, 1.149	4, 1.268	2, 1.142	2, 1.212	2, 1.326	4, 1.233
$\mu \ (\mathrm{mm}^{-1})$	1.196	1.905	1.003	1.221	1.910	1.442
F (000)	1888	2012	1132	1012	1074	1648
θ range (deg)	3.11-27.47	3.00-25.50	3.08-25.50	3.10-25.50	3.10-25.50	3.01-25.50
total no. of rflns	27663	25325	26299	22313	21011	20176
no. of indep rflns	11447	9295	11250	9531	9482	7721
R _{int}	0.0530	0.0414	0.0594	0.0395	0.0340	0.0552
GOF	1.104	1.108	1.072	1.049	1.104	1.154
R1,wR2 $(I > 2\sigma(I))$	0.0695, 0.1462	0.0399, 0.0748	0.0702, 0.1513	0.0520, 0.1230	0.0377, 0.0781	0.0681, 0.1122
R1, wR2 (all data)	0.0997, 0.1636	0.0484, 0.0788	0.0844, 0.1592	0.0617, 0.1283	0.0427, 0.0807	0.0923, 0.1211

 $\begin{array}{l} 34.74,\, 33.03,\, 25.10,\, 21.53;\, IR\,\, (KBr,\, cm^{-1}):\, 3627(m),\, 3420(m),\, 2932(s),\\ 2858(m),\,\, 2871(s),\,\, 2120(s),\,\, 1627(w),\,\, 1432(m),\,\, 1397(w),\,\, 1362(w),\\ 1231(s),\, 1154(s),\, 1045(w),\, 922(w),\, 867(m),\, 774(w),\, 623(w),\, 503(w);\\ Anal.\,\, Calcd\,\, for\,\, C_{65}H_{99}N_2O_3Y\,\,(1045.37):\,\, C,\,\, 74.68;\,\, H,\,\, 9.55;\,\, N,\,\, 2.68.\\ Found:\,\, C,\, 73.97;\,\, H,\, 9.78;\,\, N,\, 2.86.\\ \end{array}$

 $(Ar^{1}O)_{2}Y[(\mathbf{4}-Cl-C_{6}H_{4})NC(NH^{i}Pr)N^{i}Pr](\mathbf{4})$. A certain amount of 4-chloroaniline (0.38 g, 3 mmol) was added to a solution of $Yb(OAr^{1})_{3}(THF)_{2}$ (2.67 g, 3 mmol) in toluene (20 mL) in a Schlenk tube. Then ⁱPrNCNⁱPr (0.38 g, 3 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 extracted with hexane to give a white powder, yield: 2.35 g (83%), and the white powder was dissolved with toluene and filtered to give a clean solution. Single crystals of 4 suitable for X-ray analysis were grown in toluene at room temperature for about 1 day. ¹H NMR (400 MHz, C₆D₆): 7.21 (s, 4 H, OC₆H₂[C(CH₃)₃]₂CH₃), 7.06 (d, 2 H, ClC₆H₄N), 6.87 (d, 2 H, ClC₆H₄N), 3.61 (d, 4 H, OC₄H₈), 3.57 (s, 1 H, CH(CH₃)₂NH), 3.26-3.04 (m, 2 H, CH(CH₃)₂), 2.35 (s, 6 H, OC₆H₂-[C(CH₃)₃]₂CH₃), 1.61 (s, 36 H, OC₆H₂[C(CH₃)₃]₂CH₃), 1.27 (d, 6 H, $CH(CH_3)_2$, 1.10 (s 4 H, OC_4H_8), 0.68 (d, 6 H, $CH(CH_3)_2$); ¹³C NMR (101 MHz, C₆D₆): δ 164.51, 160.29, 149.15, 137.68, 129.33, 129.09, 128.57, 126.14, 125.62, 124.44, 45.98, 44.68, 35.31, 32.26, 30.49, 25.26, 24.85, 23.57, 21.57; IR (KBr, cm⁻¹): 3422(m), 2961(m), 2872(w), 2360(m), 1637(w), 1431(w), 1398(w), 1243(s), 1156(s), 1044.6(w), 861(w), 639(w), 555(w), 504(m); Anal. Calcd for C₅₄H₈₁ClN₃O₃Y (944.58): C, 68.66; H, 8.64; N, 4.45. Found: C, 68.93; H, 8.71; N, 3.70.

 $(Ar^{1}O)_{2}Yb[(4-Cl-C_{6}H_{4})NC(NH^{1}Pr)N^{1}Pr]$ (**5**). By the procedure described for 4, reaction of Yb(OAr¹)₃(THF)₂ (2.63 g, 2.7 mmol) with ⁱPrNCNⁱPr (0.34 g, 2.7 mmol) and 4-chloroaniline (0.34 g, 2.7 mmol) gave **5** as dark red crystals. Yield: 1.82 g (72%). IR (KBr, cm⁻¹): 3428(m), 2957(m), 2879(w), 2364(m), 1632(w), 1438(w), 1396(w), 1245(s), 1151(s), 870(w), 644(w), 561(w), 507(m); Anal. Calcd for C₅₄H₈₁ClN₃O₃Yb (1028.71): C, 63.05; H, 7.94; N, 4.08. Found: C, 62.02; H, 7.86; N, 4.21.

 $(Ar^{1}O)_{2}Y[(2-OCH_{3}-C_{6}H_{4}NH)(2-OCH_{3}-C_{6}H_{4}NH_{2})]$ (**6**). A certain amount of 2-methoxyaniline (0.21 g, 1.7 mmol) was added to a solution of **4** (1.57 g, 1.7 mmol) in toluene (20 mL) in a Schlenk tube. The mixture was stirred at room temperature for 18 h. The volatiles were removed under reduced pressure, and the residue was extracted with *n*-hexane. Removing the *n*-hexane solution by centrifugation led to gray solids. Single crystals of **6** suitable for X-ray analysis were grown in toluene and hexane mixed solvent at room temperature for about 1 week. The crystallization of **6** was accompanied with guanidine generated by the amine protonolysis of **4**, so we could not obtain a pure sample of **6** suitable for the ¹H NMR, ¹³C NMR, IR, and elemental analysis.

General Procedure for the Reaction of Amines with Carbodiimides Catalyzed by 4 and $Y(OAr^1)_3(THF)_2$. A 10 mL Schlenk tube under dried argon was charged with the related catalysts (0.01 equiv.), amines, and carbodiimides. The resulting mixture was stirred at 10 or 60 °C for the desired time, as shown in Table 3 and Table 5. After the reaction was completed, the reaction mixture was hydrolyzed by water, extracted with dichloromethane (3 × 10 mL), dried over anhydrous Na₂SO₄, and filtered. Then the solvent was removed under reduced pressure, and the final products were further purified by recrystallization from *n*-hexane.

X-ray Crystallography. Crystals suitable for X-ray diffraction of complexes **1**–**6** were sealed in a thin-walled glass capillary filled with argon for structural analysis. Diffraction data were collected on a Rigaku Mercury CCD area detector in the ω scan mode using Mo K α radiation (λ = 0.71075 Å); all data collection temperature is 223(2) K. 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. 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 SHELXTL-97 programs.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic data of complexes **1**–**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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