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Catalytic addition of amines to carbodiimides by bis(β-diketiminate)lanthanide(II) complexes and mechanistic studies

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Catalytic addition of amines to carbodiimides by bis(β-diketiminate)lanthanide(II) complexes and mechanistic studies

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Reduction reactions of bis(β-diketiminate)lanthanide(III) chlorides formed in-situ by reactions of anhydrous $LnCl_3$ with 2 equiv. of sodium salt of the β-diketiminate ligand in THF with Na/K alloy afforded a series of bis(β-diketiminate)lanthanide(II) complexes $LnL_2(THF)_n$ (L = $L^{2,6\text{-}Me2}$ = $[N(2,6\text{-}Me_2C_6H_3)C(Me)]_2CH^-$, n = 1, Ln = Eu (**1**); L = $L^{2,4,6\text{-}Me3}$ = $[N(2,4,6\text{-}Me_3C_6H_2)C(Me)]_2CH^-$, n = 1, Ln = Eu (**2**); L = $L^{2,6\text{-}iPr2}$ = $[N(2,6\text{-}^iPr_2C_6H_3)C(Me)]_2CH^-$, n = 0, Ln = Eu (**3**), Sm (**4**); L = $L^{2,6\text{-}ipr2}{}_{Ph}$ = $[(2,6\text{-}^iPr_2C_6H_3)NC(Me)CHC(Me)N(C_6H_5)]^-$, n = 0, Ln = Eu (**5**), Yb (**6**); L = $L^{2\text{-}Me}$ = $[N(2\text{-}MeC_6H_4)C(Me)]_2CH^-$, n = 1, Ln = Yb (**7**)) in high yields. All the complexes, especially the complexes of Sm^{II} (**4**) and Eu^{II} (**5**), were found to be excellent pre-catalysts for catalytic addition of amines to carbodiimides to multi-substituted guanidines with a wide scope of substrates. The activity depends both on the central metals and the ligands with the active sequence of Yb^{II} < Eu^{II} and Eu^{II} < Sm^{II} and $L^{2,6\text{-}Me2}$ < $L^{2,4,6\text{-}Me3}$ ~ $L^{2,6\text{-}iPr2}$ < $L^{2,6\text{-}ipr2}{}_{Ph}$ for the ligands. The mechanistic study by the isolation of guanidinate species and their reactivity revealed that Eu^{II} monoguanidinate complexes $Eu(L^{2,6\text{-}Me2})[(C_6H_5N)C(NHCy)(NCy)](DME)$ (**8**) and $Eu(L^{2,6\text{-}ipr2}{}_{Ph})[(C_6H_5N)C(NHCy)(NCy)](THF)_2$ (**9**) should be the key active

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intermediates for the systems with Eu^{II} complexes and Yb^{III} bis(guanidinate) complex $Yb(L^{2\text{-}Me})[(C_6H_5N)C(NHCy)(NCy)]_2$ (**11**) for the system using a Yb^{II} complex.

Introduction

Guanidines are an important class of organic compounds, which can serve as synthons for the syntheses of natural products and pharmaceuticals.[1] They can also be applied as ancillary ligands in organometallic chemistry of main, early transition metals and lanthanide metals and as catalysts in organic synthesis.[1a,e,2] Catalytic addition of an amine to a carbodiimide provides a convenient and atom-economical approach for the preparation of multi-substituted guanidines.[3] However, this addition reaction without a catalyst requires forcing conditions.[4] In 2003, Richeson et al first reported the catalytic addition reaction of primary aromatic amines to un-activated carbodiimides induced by "Ti=N" imido species using titanium imido complexes.[5] Then, Hou et al. revealed a half-sandwich Ln alkyl complex could serve as an excellent pre-catalyst for the catalytic addition of both primary and secondary amines with carbodiimides and the reaction was promoted by "Ln-N" amido species.[6] Since then, metal-catalyzed addition of amines to carbodiimides has became one of the interest topics in organometallic chemistry and organic chemistry.[1a,7] Lanthanide metals are particularly attractive, due to their unique character of high coordination numbers and varied size of the metal atom from La to Lu, which are promising for optimizing steric factors in catalysis by varying the size of the metal atom and the number of the ligands. To date,

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vast number of trivalent lanthanide metal (Ln^{III}) complexes have been explored to be efficient catalysts and/or per-catalysts for the catalytic addition reaction, including the complexes containing Ln-C,[6,8] Ln-N,[9] Ln-O,[10] Ln-guanido bonds and lanthanide triflates as well.[11] The catalytic mechanism has also been studied in detail.

Divalent lanthanide (Ln^{II}) complexes have been widely used as one electronic reduction agents or pre-catalysts in various transformations including organic synthesis[12] and polymerization reactions[13] because of their pronounced reductive properties. However, the application of Ln^{II} complexes in catalytic addition of amines to carbodiimides remains poorly explored. In 2008, we reported the first example of the catalytic addition reaction of amines to carbodiimides using Ln^{II} complexes $LnL_2(sol)_x$, where L = $N(TMS)_2$, sol = THF, x = 3, Ln = Sm, Eu, Yb; L = MeC_5H_4, sol = THF, x = 2, Ln = Sm; L = O[2,6-(^{t}Bu)$_2$-4-MeC_6H_2)], sol = THF, x = 2, Ln = Sm, and the proposed reaction pathway including the formation of a trivalent bimetallic bis(amidinate) Sm^{III} species through the reduction-coupling reaction of carbodiimide by the Sm^{II} complex.[12b]

β-Diketiminate anions are well-known to be the useful ligands in stabilizing various organolanthanide complexes including recently developed monoamide[14] and monoborohydride[15] Ln^{III} complexes supported by two β-diketiminate ligands. Besides, the β-diketiminate ligand in a complex itself can also serve as an active group participating various transformations under certain conditions, such as deprotonation,[16] oxidation-coupling,[17] catalytic polymerization of lactones and catalytic addition of amines to carbodiimides[9h,18] as well as reducing a Eu^{III} ion to a

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Eu^{II} ion as a reducing agent.[17] These interesting properties stimulated us to choose bis(β-diketiminate) Ln^{II} complexes for our expanding research on exploring novel and efficient Ln^{II} catalysts/pre-catalysts for catalytic addition reaction of amines to carbodiimides and the detailed reaction mechanism. Here we report the syntheses and catalytic activity of a series of bis(β-diketiminate) Ln^{II} complexes with the three metals of Sm^{II}, Eu^{II} and Yb^{II}, and the possible catalytic mechanism: a divalent active species of (β-diketiminate)Eu^{II}(guanidinate) for the system with Eu^{II} complexes and a trivalent active species of (β-diketiminate)Yb^{III}bis(guanidinate) for the system with a Yb^{II} complex.

Results and discussion

Synthesis and characterization of bis(β-diketiminate) Ln^{II} complexes

The bis(β-diketiminate) Eu^{II} complexes $EuL_2(THF)_n$ (**1**: L = $L^{2,6\text{-Me2}}$ = $[N(2,6\text{-}Me_2C_6H_3)C(Me)]_2CH^-$, n = 1; **2**: L = $L^{2,4,6\text{-Me3}}$ = $[N(2,4,6\text{-}Me_3C_6H_2)C(Me)]_2CH^-$, n = 1; **3**: L = $L^{2,6\text{-iPr2}}$ = $[N(2,6\text{-}^iPr_2C_6H_3)C(Me)]_2CH^-$, n = 0; **5**: L = $L^{2,6\text{-ipr2}}{}_{Ph}$ = $[(2,6\text{-}^iPr_2C_6H_3)NC(Me)CH(Me)N(C_6H_5)]^-$, n = 0) have been reported previously, and they were synthesized by the reaction of $EuCl_3$ with 3 equiv. of sodium salt of the ligand via the reduction of Eu^{III} by a β-diketiminate ion.[17] The same complexes were prepared here in good yields by the reaction of $EuCl_3$ with 2 equiv. of sodium salt of the ligand, followed by treatment with Na/K alloy in one pot synthesis (Scheme 1). The fine crystals were facilely obtained upon crystallization from a mixture of THF and hexane for complexes **1** and **2**, and a mixture of toluene and hexane for complexes **3** and **5**. The identity of complexes **1**-**3** and **5** synthesized

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here was unequivocally established by the satisfactory elemental analyses and the same data of the unit cell of the crystals measured by X-ray crystal analyses as those reported previously.[17] The analogous Sm^{II} and Yb^{II} complexes $LnL_2(THF)_n$ (**4**: L = $L^{2,6\text{-iPr2}}$, Ln = Sm, n = 0; **6**: L = $L^{2,6\text{-ipr2}}{}_{Ph}$, Ln = Yb, n = 0; **7**: L = $L^{2\text{-Me}}$ = $[N(2\text{-}MeC_6H_4)C(Me)]_2CH^-$, Ln = Yb, n = 1) were synthesized similarly in high yields by the same procedure (Scheme 1). However, attempts to synthesize and characterize the Yb^{II} complex bearing $L^{2,6\text{-iPr2}}$ ligand and the Sm^{II} complex with $L^{2,6\text{-ipr2}}{}_{Ph}$ ligand were unsuccessful.

These novel complexes were fully characterized by elemental analyses, ^1H NMR and X-ray crystal structural analysis for complexes **4** and **7**. The ^1H NMR spectra of complexes **4**, **6**, and **7** in C_6D_6 clearly showed the expected set of signals corresponding to the β-diketiminate, indicating that they are diamagnetic Sm^{II} and Yb^{II} complexes. The detailed crystal data and the selected bond distances and angles of complexes **4** and **7** were collected in Tables 1 and 2, respectively. Complex **4** is a four-coordinated homoleptic one in which the central metal Sm^{II} is coordinated by four nitrogen atoms of the two ligands in a distorted tetrahedron (Figure 1). The molecular structure is quite similar to those of complexes **3** and **5** reported[17a] and the known homoleptic bis(β-diketiminate) Yb^{II} complexes.[19] Complex **7** is a THF-solvated five coordinated one, due to the smaller β-diketiminate ligand used in complex **7** compared to that in complex **4**. The coordination polyhedron around the Yb^{II} ion in complex **7** can be described as a distorted trigonal bipyramid (Figure 2), which is similar to those found in complexes **1** and **2** reported.[17] The two nitrogen

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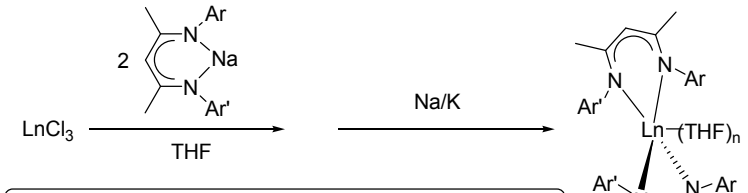
atoms from two ligands respectively occupy the axial sites in an distorted setup to form a N(1)−Ln(1)−N(3) angle of 176.10(19)°. The average Ln−N bond distance in complex **7** is 2.430(6) Å, which is comparable with those found in the reported analogue.[17]



Ar = Ar' = 2,6-$Me_2C_6H_3$, n = 1, Ln = Eu (**1**);
Ar = Ar' = 2,4,6-$Me_3C_6H_2$, n = 1, Ln = Eu (**2**);
Ar = Ar' = 2,6-$^i Pr_2C_6H_3$, n = 0, Ln = Eu (**3**), Sm (**4**);
Ar = 2,6-$^i Pr_2C_6H_3$, Ar' = C_6H_5, n = 0, Ln = Eu (**5**), Yb (**6**);
Ar = Ar' = 2-MeC_6H_4, n = 1, Ln = Yb (**7**).

Scheme 1 Synthesis of bis(β-diketiminate) Ln^{II} complexes.

Catalytic addition of amines to carbodiimides

The reaction of $PhNH_2$ with ^{i}PrNCN^{i}Pr (diisopropylcarbodiimide) as mode reaction was assessed under various conditions (Table 3). Without a catalyst, the reaction did not occur to any detectable degree, even raised reaction temperature to 100 ^{o}C (Table 3, entry 1). Rapid addition was observed by an addition of 0.5 mol% of complex **4** to give the guanidine **12** in a 97% yield at 60 ^{o}C in 8 min (Table 3, entry 2). Other complexes **1**-**3** and **5**-**7** were also effective. The substituents on the nitrogen atom of the β-diketiminate have a great influence on the reactivity with the active sequence of $L^{2,6\text{-}Me2} < L^{2,4,6\text{-}Me3} \sim L^{2,6\text{-}iPr2} < L^{2,6\text{-}ipr2}{}_{Ph}$ (Table 3, entries 3-6). The influence of central metal on activity was also observed in the present catalytic addition reaction. The increasing order in activities is $Eu^{II} < Sm^{II}$ (Table 3, entries 5 and 2) and $Yb^{II} < Eu^{II}$ (Table 3, entries 7 and 6), which is consistent with that reported previously.[12b] It was

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noticed that the Eu^{II} complex **5** with an asymmetric ligand exhibits very high activity. The addition reaction with 0.5 mol% of complex **5** afforded **12** in 99% yield (Table 3, entry 6). The yield of **12** can still be 71% after 30 min even the catalyst amount decreasing to 0.25 mol% (Table 3, entry 9). The reactions in THF or toluene gave **12** in lower yields under the same conditions: 71% for THF and 59% for toluene (Table 3, entries 10 and 11).

Thus, complex **5** was used as a catalyst to evaluate the scope of substrates. A variety of aromatic amines and secondary amines and two carbodiimides of ^{i}PrNCN^{i}Pr and CyNCNCy (dicyclohexylcarbodiimide) were examined. The results are given in Table 4. All the reactions with primary aromatic amines could take place at 60 ^{o}C with use of only 0.5 mol% of complex **5** to yield the corresponding *N,N′,N″*-trisubstituted guanidines **12-30** in excellent yields (Table 4, entries 1-19). The reaction was not influenced by either electron-withdrawing (F-, Cl-, and Br-) or electron-donating substituents (Me- and MeO-) at the phenyl group, showing good functional group tolerance. However, a great influence of steric effects on the catalytic reaction was observed as reported previously.[9a,j,h,10a,b,11b] For example, the reaction of ^{i}PrNCN^{i}Pr with an aromatic amine bearing two bulky substituents on both ortho-positions at the phenyl ring required prolong reaction time to 12 h to afford the corresponding guanidine **26** in good yield (Table 4, entry 15). The reactions with secondary aliphatic amines also went smoothly. In the presence of 0.5 mol% of complex **5**, cyclic secondary amines, pyrolidine and piperidine, could react with ^{i}PrNCN^{i}Pr at 60 ^{o}C to give the corresponding guanidines **27** and **28** in good yields

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after 24 h (Table 4, entries 16 and 17). These results indicated that the Eu^{II} complexes are highly active and compatible with a wide range of substrates.

Mechanistic studies

In our previous work the reaction mechanism for the catalytic addition using a Sm^{II} complex catalyst was proposed to include the formation of a trivalent bimetallic bis(amidinate) Sm^{III} species, as the first step, via the reduction-coupling of carbodiimides by a Sm^{II} complex.[12b] Thus, the active species was a Sm^{III} amide or a Sm^{III} guanidinate complex formed by amine protonolysis for the former or the addition of an amido species to a carbodiimide for the latter. The mechanism was supposed on the basis of a color change of the reaction solution indicative of the transfer of a Sm^{II} ion to a Sm^{III} ion and the reactivity of Sm^{II} complexes with carbodiimides reported previously.[20] To see whether the proposed mechanism is available in the systems with Yb^{II} and Eu^{II} complexes, the detailed reaction mechanism was investigated by the stoichiometric reactions of Ln^{II} complexes (**1, 5** and **7**) with amine, carbodiimide and a mixture of amine and carbodiimide, respectively.

Reaction mechanism catalyzed by Eu^{II} complexes

Reaction of complex 1 with CyNCNCy

The reaction of complex **1** with CyNCNCy was first examined. The reaction between complex **1** and CyNCNCy in a 1:1 molar ratio was conducted in THF at 60 ^{o}C for 24 h. Concentration of the reaction solution led to a yellow tar. Unfortunately, efforts to isolate the product were unsuccessful due to its high solubility in various solvents

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even in hexane.

Reaction of complex 1 with $PhNH_2$

The reaction of complex **1** with $PhNH_2$ in a 1:1 molar ratio was then carried out in THF at 60 ^oC for 24 h. After work up, only complex **1** was recovered completely from the reaction solution, indicating complex **1** did not react with $PhNH_2$ under the reaction conditions.

Reactions of Eu^{II} complexes (1, 5) with a mixture of $PhNH_2$ and CyNCNCy

The reaction of complex **1** with $PhNH_2$ and CyNCNCy in a 1:1:1 molar ratio was conducted at 60 ^oC in THF in an attempt to gain information on the real active species. Stirring for 24 h gave a light red solution, from which red crystals were isolated in 76% yield upon crystallization from a mixture of heptane and DME (dimethoxyethane) at room temperature. Elemental analysis of the crystals is consistent with the formula of a monoguanidinate Eu^{II} complex supported by a β-diketiminate ligand $Eu(L^{2,6\text{-}Me2})[(C_6H_5N)C(NHCy)(NCy)](DME)$ (**8**) (Scheme 2: a). IR spectra exhibited strong absorptions near 1550 and 1510 cm^{-1}, indicating the partial C=N bond character of the β-diketiminate ligands[21] and a C=N stretch approximate 1640 cm^{-1} for the guanidinate ligand.[22] The identity of complex **8** was unequivocally established by an X-ray structure determination. Molecular structure of complex **8** is shown in figure 3 with the selected bond distances and angles. Complex **8** is a six-coordinated monomer, in which the central metal Eu^{II} ion is bound to one β-diketiminate and one guanidinate both in a chelating mode and one DME molecule in a distorted octahedral geometry. As expected, the coordinated guanidinate group forms essentially a planar

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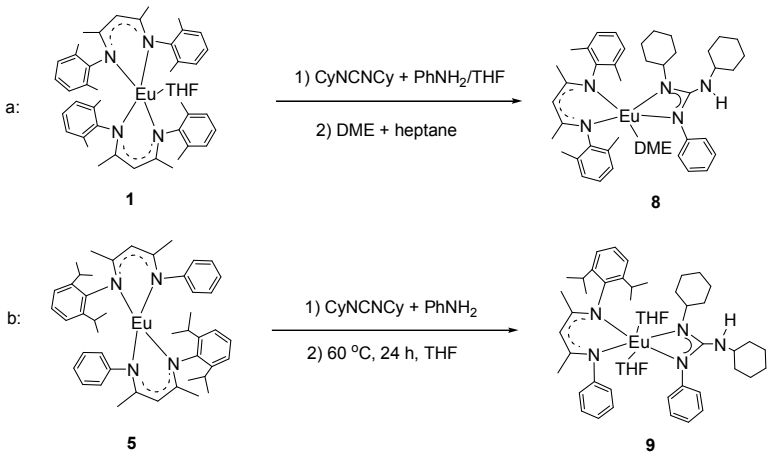
four-member ring with the metal atom [N(3)-C(22)-N(4)-Eu(1)] within experimental errors (the sum of bond angles is 360.04°). The bond angles around C(22) (118.0(5), 122.4(5) and 119.6(4)°, respectively) are consistent with sp^2 hybridization. The C(22)-N(3) bond distance (1.312(6) Å) is shorter than that of the C(22)-N(4) bond distance (1.346(6) Å) and both are significantly shorter than the C(22)-N(5) single-bond distance (1.395(6) Å), indicating that the electrons are delocalized over the N(3)-C(22)-N(4) unit (Figure 3).



Scheme 2 Reaction of complex **1** (**5**) with $PhNH_2$ and CyNCNCy.

The oxidation state of a central metal in a complex can be estimated by Bond Valence Sum (BVS).[23] Indeed, the BVS calculation for Eu in complex **8** gave the value of 2.20, indicating Eu being in the 2+ oxidation state.

The formation of complex **8** could be realized by two possible roads. One is the nucleophilic addition of the amido species, which could be formed directly by the reaction between an amine and complex **1**, to a carbodiimide. The other way is the protonation of a β-diketiminate ligand by a guanidine molecule formed via an attacking of an amine to a carbodiimide coordinated to complex **1**, as amine does not

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react with a carbodiimide without a catalyst. The formation of the amido species directly from complex **1** is not possible, because complex **1** does not react directly with amine as mentioned above. Thus, complex **8** was most probably synthesized by the second road. Although the efforts to isolate the carbodiimide-coordinated Eu^{II} complex were unsuccessful, the similar reaction pathway was reported previously in the catalytic system with a tris(phenolate)Ln^{III} complex, where both a carbodiimide-coordinated tris(phenolate)Ln^{III} complex and a bis(phenolat)Ln^{III}(guaninate) complex via the protonation of a phenolate ligand by a guanidine were successfully isolated.[10c]

To see whether the formation of a monoguanidinate Eu^{II} complex **8** from the system with complex **1** is not a special case, the similar reaction of complex **5** with $PhNH_2$ and CyNCNCy was then carried out under the same conditions. After work up, an analogous Eu^{II} complex $Eu(L^{2,6\text{-}ipr2}{}_{Ph})[(C_6H_5N)C(NHCy)(NCy)](THF)_2$ (**9**) with two coordinated THF molecules, instead of a DME molecule in complex **8**, was obtained in 83% yield (Scheme 2: b). Complex **9** was fully characterized by elemental analysis, IR spectrum and X-ray crystal structural determination. The molecular structure of complex **9**, which is quite similar to that of complex **8**, is shown in Figure 4 with selected bond distances and angles. The bond distances and angles are comparable to those found in complex **8**. The C(24)-N(3) bond distance (1.316(3) Å) is much shorter than that of the C(24)-N(4) bond distance (1.360(3) Å) in the guanidinate unit, and the latter is close to the C(24)-N(5) bond distance (1.388(3) Å), suggesting that the C=N double bond of the guanidinate unit in complex **9** is highly

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localized between the C(24) and N(3) atoms. The average Eu-N (guanidinate N) distance of 2.6032 Å is longer than 2.578 Å in **8**. This may be attributed to the steric demand resulting from the bulky substituents on the arene ring of β-diketiminate ligand in **9**.

The Bond Valence Sum (BVS) for complex **9** was also calculated. The value of 2.09 was obtained indicating Eu in complex **9** being in the 2+ oxidation state. Thus, a monoguanidinate Eu^{II} complex might be the real active species for a Eu^{II} catalyst.

Catalytic activities of complexes 8 and 9.

The catalytic activities of complexes **8** and **9** were further assessed in the addition reaction of $PhNH_2$ to $^{i}PrNCN^{i}Pr$. For comparison the same addition reaction with complexes **1** and **5** was also conducted under the same conditions. A rapid addition of $PhNH_2$ to $^{i}PrNCN^{i}Pr$ was observed at 60 ^{o}C under solvent free condition when 0.5 mol% of complex **8** or complex **9** was added. The reaction using complex **8** within 8 min gave the guanidine **12** in 96% yield, while a 77% yield was achieved by use of complex **1** (Table 5, entries 1 and 2). The higher yield for complex **8**, compared to that for complex **1**, is reasonable because the formation of an active species from its precursor generally needs some time, unless the transformation is fast enough. Complex **9** exhibited the same high level as complex **5** does. Both reactions gave **12** in 83% yields after 5 min (Table 5, entries 3 and 4), indicating that the formation of the active species **9** from complex **5** is very fast.

Suggested mechanism for the catalytic addition by Eu^{II} complexes.

According to the above results, a possible reaction mechanism for the catalytic

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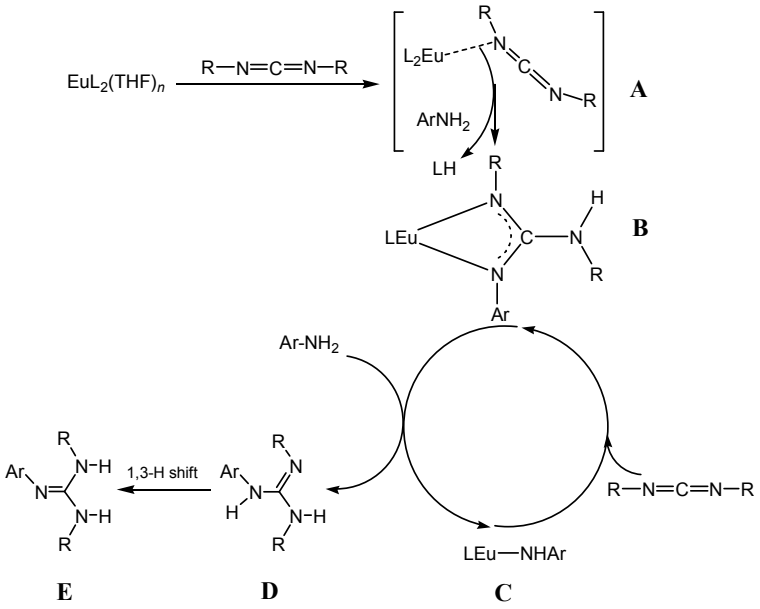
addition of amines to carbodiimides by Eu^{II} complexes could be proposed as shown in Scheme 3. The reaction of a Eu^{II} complex with a carbodiimide would yield the species **A**. The addition of an amine to the carbodiimide, followed by protonation of a β-diketiminate ligand by the formed guanidine afforded the active species **B**. Protonation of **B** by an amine would give the amido species **C** and release the guanidine **D**. Rearrangement of **D** and then 1,3-hydrogen shift led to the more stable isomer **E**. Nucleophilic addition of the amido species **C** to a carbodiimide would regenerate the guanidinate species **B**. The isolation and the reactivity of monoguanidinate Eu^{II} complexes **8** and **9** support the proposed mechanism. Thus, an one-electron reduction reaction by a Eu^{II} ion does not occur here, thereby, the oxidation state of a Eu^{II} ion is not changed during the catalytic addition reaction.



Scheme 3 A possible mechanism for the catalytic addition of amines to carbodiimides by Eu^{II} complexes.

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Reaction mechanism catalyzed by Yb^{II} complexes

Reaction of vomplex 7 with CyNCNCy

To gain information on the reaction mechanism catalyzed by a Yb^{II} complex, the reaction of complex **7** with CyNCNCy was investigated, although the reactivity of Ln^{II} complexes to carbodiimides has been studied in details.[24] An addition of a CyNCNCy solution in THF into an equiv. of complex **7** in THF led to a color change of the reaction mixture gently from dark green to light yellow, indicative of the oxidation of Yb^{II} to Yb^{III}. After work up, the bis(β-diketiminate)Yb^{III}(monoamidinate) complex $Yb(L^{2\text{-}Me})_2[(NHCy)C(C_3H_6OCH)(NCy)]$ (**10**) was obtained as yellow crystals in moderate yield (Scheme 4). Complex **10** is the only isolable product. The identity of complex **10** was confirmed by an X-ray structure determination. The molecular structure is depicted in Figure 5 with selected bond distances and angles. The Yb ion is coordinated by two β-diketiminate and one amidinate ligands, all of which being bound in a κ^2-fashion. The coordination geometry around the Yb ion can be described as highly distorted octahedral geometry. Four nitrogen atoms, N(2), N(3), N(5), and N(6), can be considered to occupy equatorial positions within the octahedron about the Yb ion (the sum of these bond angles is 360.01(9)^o), and the other two nitrogen atoms, N(1) and N(4), occupy axial positions for the angle of N(1)-Yb(1)-N(4) being 164.10(9)^o. The C-N bond distances in the chelating N-C-N unit are nearly equal (1.320(4) and 1.330(4) Å), indicating the delocalization of the π bond in the N-C-N unit.

The present reaction is believed to involve a one-electron reduction of

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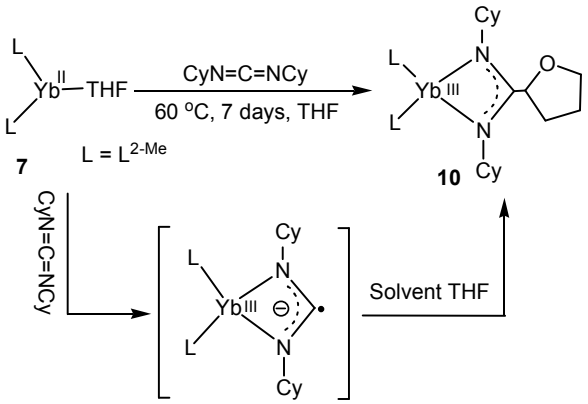
CyN=C=NCy by a Yb^{II} ion to give the corresponding "$C(NCy)_2^{\bullet-}$" radical anionic species , then attacking a THF molecule by the radical anion species to yield complex **10** (Scheme 4). The similar reaction mode was also found in the reactions with Sm^{II} complexes reported previously.[24a]

To see whether the formation of an amidinate Yb^{III} complex was included in the catalytic cycle, the catalytic activity of complex **10** for the addition of $PhNH_2$ to ^{i}PrNCN^{i}Pr was then examined at 60 ^{o}C under solvent free condition using a catalyst amount of 0.5 mol%. The reaction occurred to afford guanidine **12** in a 15% yield within 18 min. However, the yield is much lower than that obtained with complex **7** (Table 5, entries 5 and 6). The much lower reactivity shown by complex **10** indicated that the reaction between complex **7** and a carbodiimide could not be included in the catalytic cycle.



Scheme 4 Formation of **10** by reaction of **7** with CyN=C=NCy.

Reaction of complex 7 with a mixture of $PhNH_2$ and CyNCNCy

The reaction of complex **7** with $PhNH_2$ and CyNCNCy in a molar ratio of 1:1:1 was then conducted in THF at 60 ^{o}C. Unexpectedly, a

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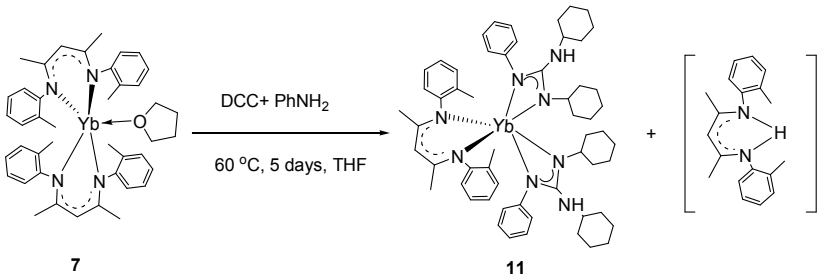
mono(β-diketiminate)Yb^{III}bis(guanidinate) complex $Yb(L^{2\text{-}Me})[(C_6H_5N)C(NHCy)(NCy)]_2$ (**11**) was isolated in rather low yield (40%) (Scheme 5). Complex **11** was confirmed by elemental analysis, IR and X-ray crystal structure analysis. The solid-state structure of complex **11** is depicted in Figure 6 with selected bond distances and angles. The Yb ion is coordinated by one β-diketiminate ligand and two guanidinate anions all in a κ^2-fashion. The coordination geometry around the Yb ion can be described as a highly distorted octahedron. The bond parameters of both Yb-guanidinate and Yb-β-diketiminate units can be compared to those found in the related guanidinate- and β-diketiminate-Yb complexes reported.[9a,10b,c]



7 11

Scheme 5 Formation of **11** by reaction of **7** with $PhNH_2$ and CyN=C=NCy.

The synthesis of complex **11** can be considered to proceed through either a disproportion reaction of a bis(β-diketiminate)Yb^{III}(guanidinate) intermediate **F**, or protonation of a β-diketiminate anion by another molecule of guanidine formed by the reaction of **F** with an amine and a carbodiimide, due to **F** being too crowded to be stable. The intermediate **F** might be formed via a one-electron reduction of a CyN=C=NCy by a Yb^{II} ion to give the radical anionic species "$C(NCy)_2^{\bullet-}$" **G** (as mentioned above), followed by attacking an amine molecule (Scheme 6).

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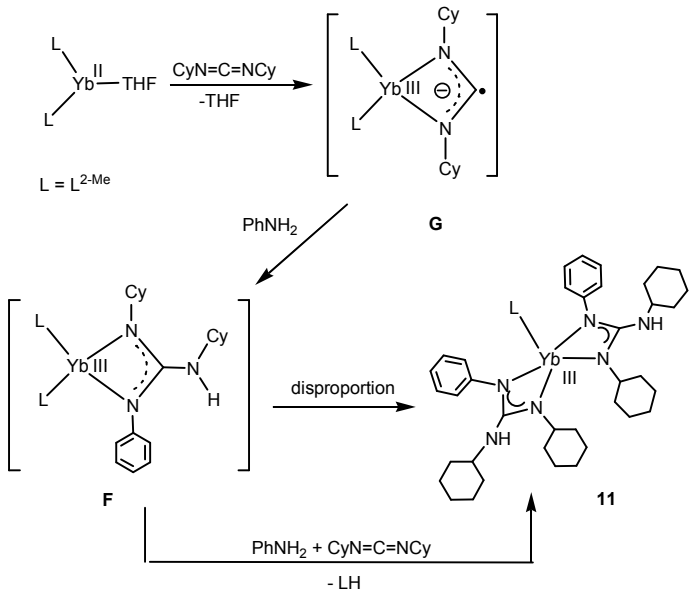

Scheme 6 Formation of **11** by the reaction of **7** with carbodiimide and aniline.

The catalytic activity of complex **11** for the addition reaction of $PhNH_2$ to $^{i}PrNCN^{i}Pr$ was further examined. The reaction proceeded at 60 ^{o}C using 0.5 mol% of complex **11** under solvent free condition to afford guanidine **12** in 60% yield within 18 min. The yield is somewhat higher than that obtained with its precursor complex **7** (Table 5, entries 5 and 7). Thus, complex **11** could be considered to be the real active species for the catalytic system with complex **7**.

Proposed mechanism for the catalytic addition by Yb^{II} complexes.

On the basis of the above results, a possible catalytic cycle for the addition reaction of amines to carbodiimides by Yb^{II} complexes could be proposed in Scheme 7. Reaction of a Yb^{II} complex with a carbodiimide should afford the radical anion intermediate **G′**. Attacking to an amine by **G′** should give the intermediate **F′**. Reaction of **F′** with an another amine and carbodimide, followed by protonation of a β-diketiminate ligand by the guanidine formed should yield the guanidinate species **H**. Protonation of **H** by

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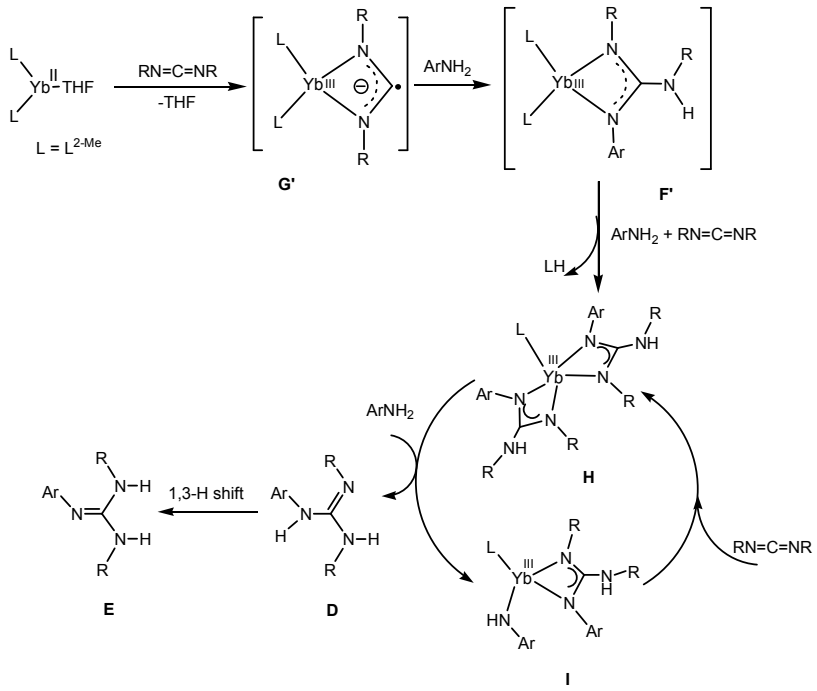
another molecule of amine would generate the amido complex **I** and release the guanidine **D**. Rearrangement of **D** and then 1,3-hydrogen shift would afford **E**. Nucleophilic addition of an amido species to a carbodiimide would regenerate the guanidinate complex **H** (Scheme 7).



Scheme 7 A proposed **m**echanism for addition of amines to carbodiimides catalyzed by Yb^{II} complexes.

Conclusion

Ln^{II} complexes bearing two β-diketiminate ligands **1-7**, which were synthesized by reduction reaction of in-situ formed bis(β-diketiminate) Ln^{III} chlorides, can serve as efficient catalyst precursors for the catalytic addition of amines to carbodiimides to multi-substituted guanidines with a wide range of substrates. The study on the isolation of monoguanidinate Eu^{II} complexes **8** and **9**, and bis(guanidinate) Yb^{III} complex **11**, and their reactivity indicated the present catalytic reactions proceed by

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diverse mechanisms depending on the bis(β-diketiminate)Ln^{II} complexes used. The reaction using a Eu^{II} complex proceeds through the formation of monoguanidinate Eu^{II} species by the reaction of a Eu^{II} complex with an amine and a carbodiimide, protonation of the guanidinate species by an amine, and nucleophilic addition of the resultant amido species to a carbodiimide. The oxidation state of the central metal remains unchanged during the catalytic reaction. The catalytic cycle for the addition reaction using a Yb^{II} complex contains the following steps: formation of a bis(guanidinate) Yb^{III} species formed through one electron reduction of carbodiimide by the Yb^{II} complex and the reaction with amines, then protonation of a β-diketiminate ligand by a guanidine; protonation of the guanidinate species by an amine; nucleophilic addition of the resulted amido species to a carbodiimide.

Experimental Section

General procedures

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, toluene, n-heptane 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. ^{1}H NMR and ^{13}C NMR spectra were run on a Unity Inova-400 spectrometer. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges.

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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 ($L^{2\text{-}Me}H$, $L^{2,6\text{-}Me2}H$, $L^{2,4,6\text{-}Me3}H$, $L^{2,6\text{-}ipr2}H$ and $L^{2,6\text{-}ipr2}{}_{Ph}H$). The preligands $L^{2\text{-}Me}H$, $L^{2,6\text{-}Me2}H$, $L^{2,4,6\text{-}Me3}H$ and $L^{2,6\text{-}ipr2}H$ were prepared by the published method.[17a,25] The asymmetrical preligand $L^{2,6\text{-}ipr2}{}_{Ph}H$ was synthesized by a similar procedure for the synthesis of asymmetrically substituted diimines.[26]

Synthesis of complexes (1–11)

$Eu^{II}(L^{2,6\text{-}Me2})_2(THF)$ (1). A THF solution of $NaL^{2,6\text{-}Me2}$ (14.30 mL, 0.731 M), which was formed by reaction of $L^{2,6\text{-}Me2}H$ with NaH in THF, was added to a slurry of anhydrous $EuCl_3$ (1.35 g, 5.23 mmol) in THF (about 20 mL) at room temperature. The reaction mixture was stirred at room temperature for 24 h. And then a solution of Na/K alloy (0.166 g, 6.79 mmol) in toluene (10 mL) was added. The reaction mixture was stirred for 48 h at room temperature. After the precipitate was removed by centrifugation, the black solution was concentrated to dryness and then about 6 mL THF and 4 mL hexane was added. Crystallization at room temperature afforded red crystals **1** (3.28 g, 72%). Anal. Calcd for $C_{48}H_{62}N_4OEu$ (863.01): C, 66.80; H, 7.24; N, 6.49; Eu, 17.61. Found: C, 66.27; H, 7.45; N, 6.64; Eu, 17.81.

$Eu^{II}(L^{2,4,6\text{-}Me3})_2(THF)$ (2). By the procedure described for **1**, reaction of $EuCl_3$ (1.23 g, 4.76 mmol) with $NaL^{2,4,6\text{-}Me3}$ (11.45 mL, 0.832 M) in THF and then a solution of Na/K alloy (0.152 g, 6.19 mmol) in toluene (10 mL) was added gave **2** as red crystals

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(3.22 g, 76%). Anal. Calcd for $C_{50}H_{66}N_4OEu$ (891.03): C, 67.40; H, 7.47; N, 6.29; Eu, 17.05. Found: C, 66.72; H, 7.61; N, 6.47; Eu, 17.41.

$Eu^{II}(L^{2,6\text{-}ipr2})_2$ (3). A THF solution of $NaL^{2,6\text{-}ipr2}$ (17.68 mL, 0.578 M) in THF was added to a slurry of anhydrous $EuCl_3$ (1.32 g, 5.11 mmol) in THF (about 20 mL) at room temperature. And then a solution of Na/K alloy (0.163 g, 6.64 mmol) in toluene (10 mL) was added. Crystallization at room temperature afforded red crystals **3** (3.64 g, 66%). Anal. Calcd for $C_{58}H_{82}N_4Eu$ (987.28): C, 70.56; H, 8.37; N, 5.67; Eu, 15.39. Found: C, 70.35; H, 8.44; N, 5.68; Eu, 15.53.

$Sm^{II}(L^{2,6\text{-}ipr2})_2$ (4). By the procedure described for **3**, reaction of $SmCl_3$ (1.31 g, 5.10 mmol) with $NaL^{2,6\text{-}ipr2}$ (17.66 mL, 0.578 M) in THF and then a solution of Na/K alloy (0.163 g, 6.63 mmol) in toluene (10 mL) was added gave **4** as black crystals (4.02 g, 80%). Mp: 131−132 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.18−7.07 (m, 12H, Ar*H*), 4.73 (s, 2H, CNC*H*CN), 3.30−3.23 (m, 8H, C*H*$(CH_3)_2$), 1.82 (m, 12H, C*H*$_3$CN), 1.25−1.23 (d, 24H, -(C*H*$_3)_2$), 1.14−1.12 (d, 24H, -(C*H*$_3)_2$) ppm. ^{13}C NMR (101 MHz, C_6D_6): δ 23.82, 23.85, 24.49, 27.96, 90.89, 122.06, 123.33, 139.94, 150.68, 162.86 ppm. IR (KBr, cm^{-1}): 3437 (m), 2961 (w), 2928 (w), 2869 (w), 1622 (w), 1550 (s), 1463 (w), 1439 (w), 1383 (w),1362 (w), 1323 (w), 1277 (w), 1252 (w), 1221 (w), 1171 (w), 1157 (m), 1054 (w), 933 (w), 793 (w), 758 (w), 506 (w). Anal. Calcd for $C_{58}H_{82}N_4Sm$ (985.66): C, 70.68; H, 8.39; N, 5.68; Sm, 15.25. Found: C, 70.41; H, 8.47; N, 5.85; Sm, 15.33.

$Eu^{II}(L^{2,6\text{-}ipr2}{}_{Ph})_2$ (5). By the procedure described for **3**, reaction of $EuCl_3$ (1.04 g, 4.03 mmol) with $NaL^{2,6\text{-}ipr2}{}_{Ph}$ (11.06 mL, 0.728 M) in THF and then a solution of Na/K

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alloy (0.129 g, 5.24 mmol) in toluene (10 mL) was added gave **5** as red crystals (2.71 g, 82%). Anal. Calcd for $C_{46}H_{58}N_4Eu$ (818.92): C, 67.46; H, 7.14; N, 6.84; Eu, 18.56. Found: C, 67.15; H, 7.18; N, 6.55; Eu, 18.63.

$Yb^{II}(L^{2,6\text{-}ipr2}{}_{Ph})_2$ (6). By the procedure described for **1**, reaction of $YbCl_3$ (1.11 g, 3.97 mmol) with $NaL^{2,6\text{-}ipr2}{}_{Ph}$ (10.91 mL, 0.728 M) in THF and then a solution of Na/K alloy (0.127 g, 5.16 mmol) in toluene (10 mL) was added gave **6** as black crystals (2.27 g, 68%). Mp: 163−165 ^{o}C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.23 (s, 4H, Ar*H*), 7.08−6.96 (m, 12H, Ar*H*), 4.83 (s, 2H, CNC*H*CN), 2.98−2.73 (d, 4H, C*H*$(CH_3)_2$), 1.93 (m, 6H, CH_3CN), 1.53 (m, 6H, CH_3CN), 1.06−1.01 (m, 18H, -(CH_3)$_2$), 0.71 (s, 6H, -(CH_3)$_2$) ppm. ^{13}C NMR (101 MHz, C_6D_6): δ 23.78, 23.92, 24.24, 24.65, 25.56, 28.40, 28.56, 96.47, 122.39, 123.85, 124.65, 129.50, 141.13, 141.55, 144.89, 150.77, 162.30, 165.82 ppm. IR (KBr, cm^{-1}): 3441 (m), 2962 (w), 2927 (w), 2868 (w), 1629 (m), 1556 (s), 1541 (w), 1522 (w), 1507 (w),1489 (w), 1457 (w), 1430 (w), 1419 (w), 1369 (w), 1232 (s), 1160 (s), 1027 (w), 753 (w), 665 (w), 506 (m), 424 (w). Anal. Calcd for $C_{46}H_{58}N_4Yb$ (840.03): C, 65.77; H, 6.96; N, 6.67; Yb, 20.06. Found: C, 65.55; H, 6.97; N, 6.58; Yb, 20.11.

$Yb^{II}(L^{2\text{-}Me})_2$(THF) (7). A THF solution of $NaL^{2\text{-}Me}$ (13.64 mL, 0.803 M) which was formed by reaction of $L^{2\text{-}Me}H$ with NaH in THF was added to a slurry of anhydrous $YbCl_3$ (1.53 g, 5.48 mmol) in THF (about 20 mL) at room temperature. And then a solution of Na/K alloy (0.162 g, 5.48 mmol) in toluene (10 mL) was added. After the undissolved portion was removed by centrifugation, the black solution was concentrated to dryness then about 7 mL THF and 1 mL hexane was added.

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Crystallization at room temperature afforded black crystals **7** (4.06 g, 85%). Mp: 141−143 °C. ^{1}H NMR (300 MHz, C_6D_6): δ 7.28 (s, 2H, Ar*H*), 7.18−7.13 (m, 6H, Ar*H*), 7.02−6.97 (m, 4H, Ar*H*), 6.59−6.57 (d, $^{3}J_{HH}$ = 8.0 Hz, 4H, Ar*H*), 5.01 (s, 2H, CH_3CNCH), 2.88 (s, 4H, THF), 2.25 (s, 12H, CH_3−Ar), 1.76 (s, 12H, CH_3CN), 0.98 (s, 4H, THF) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ 17.61, 23.87, 24.50, 67.04, 94.63, 122.44, 124.22, 126.38, 130.01, 130.76, 151.53, 162.96 ppm. IR (KBr, cm^{-1}): 3437 (m), 3062 (w), 2855 (w), 1628 (m), 1555 (m), 1504 (w), 1482 (m), 1438 (w), 1383 (m), 1234 (s), 1158 (s), 1112 (m), 1027 (m), 988 (w), 930 (w), 816 (w), 790 (m), 743 (s), 637 (m), 555 (m), 504 (s), 445 (w). Anal. Calcd for $C_{42}H_{50}N_4OYb$ (799.93): C, 63.06; H, 6.30; N, 7.00; Yb, 21.63. Found: C, 62.97; H, 6.41; N, 6.89; Yb, 21.73.

$Eu^{II}(L^{2,6\text{-}Me2})[(C_6H_5N)C(NHCy)(NCy)](DME)$ (8). A certain amount of aniline (0.20 ml, 10.96 M, 2.2 mmol) was added to a solution of **1** (1.91 g, 2.2 mmol) in THF (20 mL). Then CyNCNCy in THF (2.31 ml, 0.95 M, 2.2 mmol) was added to the mixture. The mixture was stirred at 60 °C for 24 h. After the solvent was removed under reduced pressure, the residue was washed by hexane three times then a certain amount of DME was added to the solution. Then the red solution was concentrated to dryness and 8 mL *n*-heptane was added. Crystallization at room temperature afforded red crystals **8** (1.34 g, 72%). Mp: 134−135 °C. IR (KBr, cm^{-1}): 3441 (m), 2932 (m), 2853 (m), 1626 (m), 1588 (w), 1552 (m), 1506 (w), 1398 (w), 1214 (s), 1155 (s), 764 (w), 692 (w), 668 (w), 638 (m), 555 (m), 504 (s), 457 (w). Anal. Calcd for $C_{44}H_{63}N_5O_2Eu$ (845.96): C, 62.47; H, 7.51; N, 8.28; Eu, 17.96. Found: C, 62.67; H, 7.53; N, 8.43; Eu, 17.81.

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$Eu^{II}(L^{2,6\text{-}ipr2}{}_{Ph})[(C_6H_5N)C(NHCy)(NCy)](THF)_2$ (9). Reaction of **5** (1.45 g, 1.77 mmol) with CyNCNCy (1.87 mL, 0.95 M in THF) and aniline (0.16 mL, 1.77 mmol) in THF (20 mL) was stirred at 60 °C for 24 h. After the solvent was removed under reduced pressure, the residue was washed by hexane three times then about 0.5 mL THF and 6 mL n-hexane were added. Crystallization at room temperature afforded red crystals **9** (1.36 g, 83%). Mp: 152−153 °C. IR (KBr, cm^{-1}): 3454 (m), 3243 (w), 3062 (w), 2932 (m), 2853 (m), 1633 (s), 1588 (m), 1557 (s), 1506 (m), 1488 (w), 1384 (m), 1364 (w), 1277 (w), 1254 (w), 1235 (m), 1158 (m), 1054 (w), 1027 (w), 894 (w), 836 (w), 785 (w), 753 (m), 695 (m), 677 (w), 504 (m). Anal. Calcd for $C_{50}H_{73}N_5O_2Eu$ (928.09): C, 64.71; H, 7.93; N, 7.55; Eu, 16.37. Found: C, 64.64; H, 8.05; N, 7.43; Eu, 16.71.

$Yb^{III}(L^{2\text{-}Me})_2[(NCy)C(CHOC_3H_6)(NCy)]$ (10). Reaction of **7** (0.49 g, 0.56 mmol) with CyNCNCy (0.39 mL, 0.95 M in THF) in THF (20 mL) was stirred at 60 °C for 7 days. After the solvent was removed under reduced pressure, the residue was washed by hexane three times then about 2.5 mL toluene and 2 mL n-hexane were added. Crystallization at room temperature afforded yellow crystals **10** (0.39 g, 70%). Mp: 163−165 °C. IR (KBr, cm^{-1}): 3441 (m), 3063 (w), 2928 (m), 2853 (m), 1628 (s), 1557 (s), 1506 (w), 1482 (w), 1383 (m), 1363 (m), 1281 (m), 1236 (s), 1157 (s), 1112 (m), 1065 (w), 1027 (w), 930 (w), 861 (w), 818 (w), 790 (w), 741 (s), 719 (w), 669 (w), 637 (w), 555 (w), 504 (m), 445 (w). Anal. Calcd for $C_{55}H_{71}N_6OYb$ (1005.22): C, 65.71; H, 7.12; N, 8.36; Yb, 17.22. Found: C, 65.59; H, 7.18; N, 8.31; Yb, 17.40.

$Yb^{III}(L^{2\text{-}Me})[(C_6H_5N)C(NHCy)(NCy)]_2$ (11). Reaction of **7** (1.57 g, 1.95 mmol) with

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CyNCNCy (2.05 mL, 0.95 M in THF) and aniline (0.18 mL, 1.95 mmol) in THF (20 mL) was stirred at 60 ^{o}C for 5 days. After the solvent was removed under reduced pressure, the residue was washed by hexane three times then about 2 mL toluene and 6 mL n-hexane were added. Crystallization at room temperature afforded green crystals **11** (0.82 g, 40%). Mp: 179−180 ^{o}C. IR (KBr, cm^{-1}): 3290 (w), 3244 (w), 3066 (w), 2932 (s), 2852 (m), 2759 (w), 1628 (s), 1587 (s), 1557 (s), 1506 (s), 1447 (w), 1384 (m), 1363 (w), 1349 (w), 1275 (m), 1256 (w), 1179 (w), 1167 (w), 1112 (w), 1084 (w), 1027 (w), 894 (w), 836 (w), 789 (w), 754 (m), 695 (m), 668 (w), 510 (w), 452 (w), 425 (w). Anal. Calcd for $C_{57}H_{77}N_8Yb$ (1047.31): C, 65.37; H, 7.41; N, 10.70; Yb, 16.52. Found: C, 65.41; H, 7.37; N, 10.60; Yb, 16.53.

General Procedure for the Addition Reaction of Amines to Carbodiimides. A 10 mL Schlenk tube under dried argon was charged with **5** (0.0082 g, 0.01 mmol). To the flask were added the aniline ($PhNH_2$) (0.182 mL, 10.96 M, 2.00 mmol), *N,N'*-diisopropylcarbodiimide (^{i}PrNCN^{i}Pr) (0.312 mL, 6.418 M, 2.00 mmol). The resulting mixture was stirred at 60 ^{o}C for 8 min. After the reaction was completed, the reaction mixture was hydrolyzed by water (2 mL), 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 to give the colorless solid **12** (0.4343 g, 99% yield).

X-ray Crystallography. Crystals suitable for X-ray diffraction of complexes **1**−**11** were sealed, respectively, in a thin-walled glass capillary filled with argon for structural analysis. Only the data of the unit cell of the crystals were measured for

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complexes **1**-**3** and **5** (see supporting information Table S1). Crystal structure of complex **6** was not determined for its deterioration in the crystal quality. Diffraction data were collected on a Rigaku Saturn CCD area detector in the ω scan mode using Mo K_α radiation (λ = 0.71075 Å) for complexes **4** and **9** and using Mo K_α radiation (λ = 0.71073 Å) for complexes **7** and **8**, and on an Agilent Xcalibur CCD area detector in the ω scan mode using Cu K_α radiation (λ = 1.54184 Å) for complexe **10** and using Mo K_α radiation (λ = 0.71073 Å) for complexe **11**. The diffracted intensities were corrected for Lorentzpolarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Table 1. 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.[27]

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Notes and references

1 (a) C. Alonso-Moreno, A. Antiñolo, F. Carrillo-Hermosilla and A. Otero, *Chem. Soc. Rev.,* 2014, **43**, 3406–3425; (b) R. G. S. Berlinck, *Nat. Prod. Rep*., 2002, **19**, 617–649; (c) L. Heys, C. G. Moore and P. J. Murphy, *Chem. Soc. Rev*., 2000, **29**, 57–67; (d) R. G. S. Berlinck, *Nat. Prod. Rep*., 1999, **16**, 339-365; (e) R. G. S. Berlinck, *Nat. Prod. Rep*., 1996, **13**, 377–409; (f) G. J. Durant, *Chem. Soc. Rev*., 1985, **14**, 375–398.

2 (a) T. R. M. Rauws and B. U. W. Maes, *Chem. Soc. Rev*., 2012, **41**, 2463−2497; (b) Y. Sohtome and K. Nagasawa, *Chem. Commun*., 2012, **48**, 7777−7789; (c) J. Zhang and X. Zhou, *Dalton Trans*., 2011, **40**, 9637−9648; (d) D. Castagnolo, S. Schenone and M. Botta, *Chem. Rev.,* 2011, **111**, 5247−5300; (e) D. Leow and C.-H. Tan, *Synlett*, 2010, 1589−1605; (f) M. J. Terada, *Synth. Org. Chem. Jpn*., 2010, **68**, 1159−1168; (g) R. G. S. Berlinck, A. C. B. Burtoloso, A. E. Trindade-Silva, S. Romminger, R. P. Morais, K. Bandeira and C. M. Mizuno, *Nat. Prod. Rep*., 2010, **27**, 1871−1907; (h) C. Jones, *Coord. Chem. Rev*., 2010, **254**, 1273−1289; (i) M. P. Coles, *Chem. Commun*., 2009, **45**, 3659−3676; (j) D. Leow and C.-H. Tan, *Chem. - Asian J*., 2009, **4**, 488−507; (k) F. T. Edelmann, *Adv. Organomet. Chem*., 2008, **57**, 183−352; (l) P. Blondeau, M. Segura, R. Pérez-Fernández and J. de Mendoza, *Chem. Soc. Rev*., 2007, **36**, 198−210; (m) C. Schmuck, *Coord. Chem. Rev*., 2006, **250**, 3053−3067; (n) T. Suhs and B. König, *Mini-Rev. Org. Chem*., 2006, **3**, 315−331; (o) T. Ishikawa and T. Kumamoto, *Synthesis*, 2006, 737–752; (p) R. G. S. Berlinck and M. H. Kossuga, *Nat. Prod. Rep*., 2005, **22**, 516−550; (q) J. C. McManus, T. Genski, J. S. Carey and R. J. K. Taylor, *Synlett*, 2003, 369–371; (r) J. C. McManus, J. S. Carey and R. J. K. Taylor, *Synlett*, 2003, 365–368; (s) E. D. Raczyńska, M. K. Cyrański, M. Gutowski, J. Rak, J.-F. Gal, P.-C. Maria, M. Darowska and K. Duczmal, *J. Phys. Org. Chem*., 2003, **16**, 91−106;

View Article Online
DOI: 10.1039/C5DT03674G

(t) M. D. Best, S. L. Tobey and E. V. Anslyn, *Coord. Chem. Rev*., 2003, **240**, 3−15; (u) T. Ishikawa and T. Isobe, *Chem. Eur. J*., 2002, **8**, 552–557; (v) B. Kovacevic and Z. B. Maksic, *Org. Lett*., 2001, **3**, 1523–1526; (w) L. Peterlin-Mašič and D. Kikelj, *Tetrahedron*, 2001, **57**, 7073−7105; (x) P. J. Bailey and S. Pace, *Coord. Chem. Rev*., 2001, **214**, 91−141; (y) M. Costa, G. P. Chiusoli, D. Taffurelli and G. Dalmonego, *J. Chem. Soc. Perkin Trans. 1* 1998, 1541–1546.

3 (a) P. Molina, M. Alajarín, P. Sánchez-Andrada, J. Sanz-Aparicio and M. Martínez-Ripoll, *J. Org. Chem*., 1998, **63**, 2922−2927; (b) R. Chinchilla, C. Nájera and P. Sánchez-Agulló, *Tetrahedron: Asymmetry*, 1994, **5**, 1393−1402.

4 T. P. Hopkins, J. M. Dener, A. M. Boldi, *J. Comb. Chem.,* 2002, **4**, 167−174.

5 T.-G. Ong, G. P. A. Yap and D. S. Richeson, *J. Am. Chem. Soc*., 2003, **125**, 8100−8101.

6 W.-X. Zhang, M. Nishiura and Z. Hou, *Synlett*, 2006, 1213−1216.

7 W.-X. Zhang, L. Xu and Z. Xi, *Chem. Commun*., 2015, **51**, 254−265.

8 (a) P.-H. Wei, L. Xu, L.-C. Song, W.-X. Zhang, and Z. Xi, *Organometallics*, 2014, **33**, 2784–2789; (b) W.-X. Zhang, M. Nishiura and Z. Hou, *Chem. Eur. J*., 2007, **13**, 4037−4051.

9 (a) J. Tu, W. Li, M. Xue, Y. Zhang and Q. Shen, *Dalton Trans.*, 2013, **42**, 5890−5901; (b) J. Chen, Y. Wang and Y. Luo, *Chin. J. Chem.*, 2013, **31**, 1065−1071; (c) Z. Xi, Y. Wang, Y. Yao, B. Wu and Q. Shen, *J. Rare Earths*., 2012, **30**, 909−915; (d) Z. Li, M. Xue, H. Yao, H. Sun, Y. Zhang and Q. Shen, *J. Organomet. Chem*., 2012, **713**, 27−34; (e) F. Han, Q. Teng, Y. Zhang, Y. Wang and Q. Shen, *Inorg. Chem*., 2011, **50**, 2634−2643; (f) C. Liu, S. Zhou, S. Wang, L. J. Zhang, G. Yang, *Dalton Trans.*, 2010, **39**, 8994−8999; (g) Y. Wu, S. Wang, L. Zhang, G. Yang, X. Zhu, Z. Zhou, H. Zhu and S. Wu, *Eur. J. Org. Chem*., 2010, 326−332; (h) R. Jiao, M. Xue, X. Shen, Y. Zhang, Y. Yao and Q. Shen, *Eur. J. Inorg. Chem*., 2010, 2523−2529; (i) Y. Wu, S. Wang, L. Zhang, G. Yang,

View Article Online
DOI: 10.1039/C5DT03674G

X. Zhu, C. Liu, C. Yin and J. Rong, *Inorg. Chim. Acta*., 2009, **362**, 2814−2819; (j) S. Zhou, S. Wang, G. Yang, Q. Li, L. Zhang, Z. Yao, Z. Zhou and H.-B. Song, *Organometallics*, 2007, **26**, 3755−3761. (k) Q. H. Li, S. W. Wang, S. L. Zhou, G. S. Yang, X. C. Zhu and Y. Y. Liu, *J. Org. Chem*., 2007, **72**, 6763−6767.

10 (a) Y. Hong, Y. Zheng, M. Xue, Y. Yao, Y. Zhang and Q. Shen, *Z. Anorg. Allg. Chem*., 2015, **641**, 1230–1237; (b) L. Cai, Y. Yao, M. Xue, Y. Zhang and Q. Shen, *Appl. Organometal. Chem*., 2013, **27**, 366−372; (c) Y. Cao, Z. Du, W. Li, J. Li, Y. Zhang, F. Xu and Q. Shen, *Inorg. Chem*., 2011, **50**, 3729−3737;.

11 (a) X. Zhang, C. Wang, C. Qian, F. Han, F. Xu and Q. Shen, *Tetrahedron*, 2011, **67**, 8790−8799; (b) X. Zhu, Z. Du, F. Xu and Q. Shen, *J. Org. Chem*., 2009, **74**, 6347−6349; (c) S. Kobayashi, M. Sugiura, H. Kitagawa and W. W.-L. Lam, *Chem. Rev*., 2002, **102**, 2227−2302.

12 (a) X. Zhu, F. Xu and Q. Shen, *Chin. J. Chem*., 2009, **27**, 19−22; (b) Z. Du, W. Li, X. Zhu, F. Xu and Q. Shen, *J. Org. Chem*., 2008, **73**, 8966−8972; (c) Z. Zhou, F. Xu, X. Han, J. Zhou and Q. Shen, *Eur. J. Org. Chem*., 2007, 5265–5269; (d) X. Han, F. Xu, Y. Luo and Q. Shen, *Eur. J. Org. Chem*., 2005, 1500–1503; (e) F. Xu, X. Zhu and Q. Shen, *Chin. J. Org. Chem*., 2004, **24**, 872–881; (f) F. Xu, Y. Luo, M. Deng and Q. Shen, *Eur. J. Org. Chem*., 2003, 4728–4730; (g) C. Fan, Y. Tu and X. Hu, *Chem. Eur. J*., 2003, **9**, 4301–4310; (h) J. Collin, N. Giuseppone and P. Van de Weghe, *Coord. Chem. Rev*., 1998, **178–180**, 117–144.

13 (a) S. Yang, Z. Du, Y. Zhang and Q. Shen, *Chem. Commun*., 2012, **48**, 9780–9782; (b) D. T. Dugah, B. W. Skelton and E. E. Delbridge, *Dalton Trans*., 2009, **38**, 1436–1445; (c) P. I. Binda, E. E. Delbridge, H. B. Abrahamson and B. W. Skelton, *Dalton Trans*., 2009, **38**, 2777–2787; (d) E. E. Delbridge, D. T. Dugah, C. R. Nelson, B. W. Skelton and A. H. White, *Dalton Trans*., 2007, **36**,

View Article Online
DOI: 10.1039/C5DT03674G

143−153; (e) H. Zhou, H. Guo, Y. Yao and Q. Shen, *Inorg. Chem*., 2007, **46**, 958−964; (f) M. Deng, Y. Yao, Q. Shen, Y. Zhang and J. Sun, *Dalton Trans*., 2004, **33**, 944−950; (g) D. Cui, T. Tang, J. Cheng, N. Hu, W. Cheng and B. Huang, *J. Organomet. Chem*., 2002, **650**, 84−90; (h) M. Nishiura, Z. Hou, T.-a. Koizumi, T. Imamoto and Y. Wakatsuki, *Macromolecules*, 1999, **32**, 8245−8251; (i) W. J. Evans and H. Katsumata, *Macromolecules*, 1994, **27**, 2330−2332; (j) W. J. Evans and H. Katsumata, *Macromolecules*, 1994, **27**, 4011−4013.

14 (a) Y. Zheng, R. Jiao, X. Shen, M. Xue, Y. Yao, Y. Zhang and Q. Shen, *Appl. Organometal. Chem*., 2014, **28**, 461-470; (b) B. B. Lazarov, F. Hampel and K. C. Hultzsch, *Z. Anorg. Allg. Chem*., 2007, **633**, 2367−2373.

15 X. Shen, M. Xue, R. Jiao, Y. Ma, Y. Zhang and Q. Shen, *Organometallics*, 2012, **31**, 6222−6230.

16 (a) P. Liu, Y. Zhang, Y. Yao and Q. Shen, *Organometallics*, 2012, **31**, 1017−1024; (b) R. Jiao, M. Xue,; X. Shen, Y. Zhang, Y. Yao and Q. Shen, *Eur. J. Inorg. Chem*., **2011**, 1448−1453; (c) S. Bambirra, F. Perazzolo, S. J. Boot, T. J. J. Sciarone, A. Meetsma and B. Hessen, *Organometallics*, 2008, **27**, 704−712; (d) S. T. Liddle and P. L. Arnold, *Dalton Trans*., 2007, **36**, 3305−3313; (e) P. B. Hitchcock, M. F. Lappert and A. V. Protchenko, *Chem. Commun*., 2005, **41**, 951−953; (f) S. Harder, *Angew. Chem., Int. Ed*., 2003, **42**, 3430−3434; (g) A. M. Neculai, H. W. Roesky, D. Neculai and J. Magull, *Organometallics*, 2001, **20**, 5501−5503; (h) Y. Ding, H. Hao, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Organometallics*, 2001, **20**, 4806−4811; (i) P. G. Hayes, W. E. Piers, L. W. M. Lee, K. L. Knight, M. Parvez, M. R. J. Elsegood and W. Clegg, *Organometallics*, 2001, **20**, 2533−2544.

17 (a) X. Shen, Y. Zhang, M. Xue, Q. Shen, *Dalton Trans*., 2012, **41**, 3668–3674; (b) R. Jiao, X.

View Article Online
DOI: 10.1039/C5DT03674G

Shen, M. Xue, Y. Zhang, Y. Yao and Q. Shen, *Chem. Commun*., 2010, **46**, 4118–4120.

18 M. Xue, R. Jiao, Y. Zhang, Y. Yao and Q. Shen, *Eur. J. Inorg. Chem*., 2009, 4110−4118.

19 S. Harder, *Angew. Chem., Int. Ed.,* 2004, **43**, 2714–2718.

20 M. Deng, Y. Yao, Y. Zhang and Q. Shen, *Chem. Commun*., 2004, **40**, 2742–2743.

21 D. S. Richeson, J. F. Mitchell and K. H. Theopold, *J. Am. Chem. Soc*., 1987, **109**, 5868–5870.

22 G. R. Giesbrecht, A. Shafir and J. Arnold, *J. Chem. Soc., Dalton Trans*., 1999, 3601–3604.

23 (a) I. B. Brown and D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci*., 1985, **41**, 244–247; (b) N. E. Brese and M. O'Keeffe, *Acta Crystallogr., Sect. B: Struct. Sci*., 1991, **47**, 192–197; (c) N. N. Thorp, *Inorg. Chem*., 1992, **31**, 1585–1588.

24 (a) G. B. Deacon, C. W. Forsyth, P. C. Junk and J. Wang, *Inorg. Chem*., 2007, **46**, 10022−10030; (b) Z. Du, H. Zhou, H. Yao, Y. Zhang, Y. Yao and Q. Shen, *Chem. Commun*., 2011, **47**, 3595–3597; (c) Z. Du, Y. Zhang, Y. Yao and Q. Shen, *Dalton Trans*., 2011, **40**, 7639−7644.

25 (a) P. H. M. Budzelaar, A. B. v. Oort and A. G. Orpen, *Eur. J. Inorg. Chem*., 1998, 1485−1494; (b) J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabres and S. D. Arthur, *Organometallics*, 1997, **16**, 1514−1516; (c) J. E. Parks and R. H. Holm, *Inorg. Chem*., 1968, **7**, 1408−1416.

26 H. Hamaki, N. Takeda, T. Yamasaki, T. Sasamori and N. Tokitoh, *J. Organomet. Chem*., 2007, **692**, 44−54.

27 G. M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement; University of Gottingen: Gottingen, Germany, 1997.

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DOI: 10.1039/C5DT03674G

Table 1 Crystallographic data for complexes **4**, **7**–**11**

Param	**4**·Toluene	**7**·THF	**8**	**9**	**10**	**11**
Formula	$C_{65}H_{90}N_4Sm$	$C_{46}H_{58}N_4O_2Yb$	$C_{44}H_{63}N_5O_2Eu$	$C_{50}H_{73}N_5O_2Eu$	$C_{55}H_{71}N_6OYb$	$C_{57}H_{77}N_8Yb$
M_w	1077.76	872.00	845.96	928.09	1005.22	1047.31
T (K)	223(2)	223(2)	223(2)	223(2)	223(2)	223(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	C2/c	P 21/n	P 21/c	P-1	P 21/n	P21/c
a (Å)	20.2426(6)	12.149(2)	10.676(2)	11.3940(4)	11.96635(13)	12.4002(4)
b (Å)	16.1891(3)	21.676(4)	16.511(4)	12.9577(5)	17.8687(2)	24.5649(8)
c (Å)	19.2241(5)	16.550(3)	24.986(6)	17.4485(4)	23.4143(3)	20.7771(8)
α (deg)	90	90	90	95.366(3)	90	90
β (deg)	109.222(3)	93.252(6)	93.886(4)	108.726(3)	101.0642(12)	121.754(2)
γ (deg)	90	90	90	91.235(3)	90	90
V (Å^3)	5948.7(3)	4358(2)	4394.0(17)	2425.40(14)	4913.45(10)	5381.6(3)
Z	4	4	4	2	4	4
D_{calcd} (g cm^{-3})	1.203	1.331	1.279	1.271	1.359	1.293
μ (mm^{-1})	1.028	2.189	1.466	1.335	3.853	1.781
F (000)	2280	1792.0	1764.0	974	2084	2180
θ range (deg)	2.76-26.00	3.05-27.50	3.12-27.49	2.90-25.05	3.13-67.08	2.84-25.05
Collcd reflcns	16046	24012	26227	21048	18788	28949
Unique reflcns	5830 [R(int) = 0.0206]	9839 [R(int) = 0.0492]	10002 [R(int) = 0.0418]	8583 [R(int) = 0.0224]	8774 [R(int) = 0.0364]	9531 [R(int) = 0.0908]
GOF	1.052	1.080	1.092	1.068	1.013	0.923
R ($I > 2\sigma(I)$)	0.0268	0.0624	0.0594	0.0221	0.0318	0.0524
Rw	0.0691	0.1252	0.1298	0.0532	0.0775	0.0804

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Table 2 Selected bond distances (Å) and angles (°) for **4** and **7**

	4	**7**
	Bond lengths	
Ln(1)-N(1)	2.5790(16)	2.429(5)
Ln(1)-N(2)	2.5790(16)	2.368(5)
Ln(1)-N(1A/3)	2.5173(16)	2.445(6)
Ln(1)-N(2A/4)	2.5173(17)	2.372(6)
$(Ln\text{-}N)_{av.}$	2.5481(16)	2.507(8)
N(1)-C(2)	1.321(3)	1.326(8)
N(2)-C(4)	1.320(3)	1.319(8)
C(2)-C(3)	1.420(3)	1.403(9)
C(3)-C(4)	1.414(3)	1.398(9)
	Bond angles	
N(1)-Ln(1)-N(2)	76.23(5)	76.25(19)
N(2)-Ln(1)-N(2A/4)	126.98(8)	109.6(2)
N(1A/3)-Ln(1)-N(2A/4)	76.23(5)	76.65(19)
N(1)-Ln(1)-N(1A/3)	142.17(8)	176.10(19)
N(1)-Ln(1)-N(2A/4)	121.84(5)	105.05(19)
N(2)-Ln(1)-N(1A/3)	121.84(5)	106.62(19)
O(1)-Ln(1)-N(4)		125.7(2)

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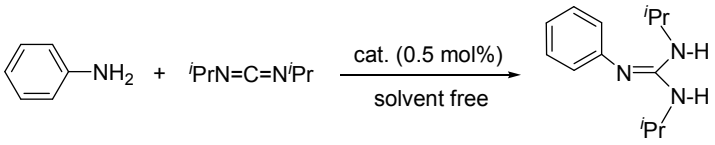
Table 3 Calalytic addition of an aniline to a *N,N′*-diisopropylcarbodiimide by complexes **1**-**7**[a]



Entry	Cat	Temp (°C)	Time (min)	Yield (%)[b]
1	/	100	8	0
2	**4**	60	8	97
3	**1**	60	8	77
4	**2**	60	8	86
5	**3**	60	8	84
6	**5**	60	8	99
7	**6**	60	14	96
8	**7**	60	18	49
9[c]	**5**	60	30	71
10[d]	**5**	60	30	71
11[e]	**5**	60	30	59
12	**5**	r.t.	9	70

[a]Conditions: 2 mmol of aniline, 2 mmol of *N,N′*-diisopropylcarbodiimide. [b]Isolated yields. [c]0.25 mol% catalyst loading. [d]In THF solvent.[e]In toluene solvent.

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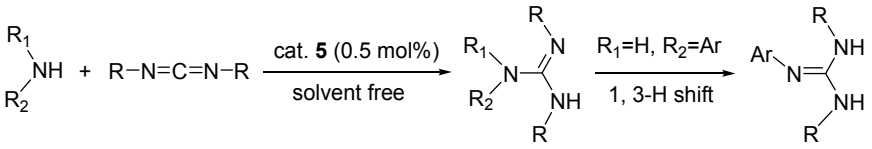
Table 4 Catalytic addition of amines to carbodiimides[a]



Entry	R	R_1R_2NH	Time	Product	Yield (%)[b]
1	^{i}Pr	Ph-NH_2	8 min	**12**	99
2	Cy		10 min	**13**	99
3	^{i}Pr	*p*-F-Ph-NH_2	10 min	**14**	>99
4	Cy		15 min	**15**	98
5	^{i}Pr	*o*-Cl-Ph-NH_2	10 min	**16**	97
6	Cy		20 min	**17**	97
7	^{i}Pr	*o*-Me-Ph-NH_2	10 min	**18**	>99
8	Cy		40 min	**19**	96
9	^{i}Pr	*p*-Me-Ph-NH_2	10 min	**20**	94
10	^{i}Pr	*p*-Cl-Ph-NH_2	10 min	**21**	>99
11	^{i}Pr	*p*-Br-Ph-NH_2	10 min	**22**	97
12	^{i}Pr	*p*-MeO-Ph-NH_2	1 h	**23**	95
13	^{i}Pr	*p*-NO_2-Ph-NH_2	3 h	**24**	84
14	^{i}Pr	1-naPh-NH_2	15 min	**25**	99
15	^{i}Pr	2,6-^{i}Pr$_2$-Ph-NH_2	12 h	**26**	92
16	^{i}Pr	*cyclo*-C_4H_8NH	24 h	**27**	91
17	^{i}Pr	*cyclo*-$C_5H_{10}NH$	24 h	**28**	90
18	^{i}Pr	2,6-Me_2-Ph-NH_2	1.5 h	**29**	>99
19	^{i}Pr	2,4,6-Me_3-Ph-NH_2	2 h	**30**	99

[a]The reaction was performed by treating 2 mmol of amines with 2 mmol of carbodiimides at 60 °C.
[b]Isolated yields.

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Table 5 Addition of $PhNH_2$ to $^{i}PrNCN^{i}Pr$ by complexes **1**, **5** and **7-11**[a]

Entry	Cat	Time (min)	Yield (%)[b]
1	**1**	8	77
2	**8**	8	96
3	**5**	5	83
4	**9**	5	83
5	**7**	18	49
6	**10**	18	15
7	**11**	18	60

[a]The reaction was performed by treating 2 mmol of aniline with 2 mmol of *N,N'*-diisopropylcarbodiimide at 60 °C. [b]Isolated yields.

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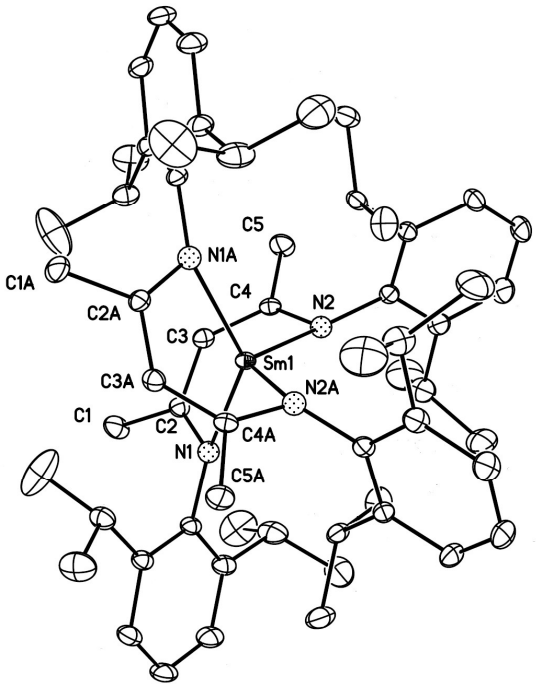

Fig 1. ORTEP diagram of complex **4**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms and a free toluene molecule are omitted for clarity.

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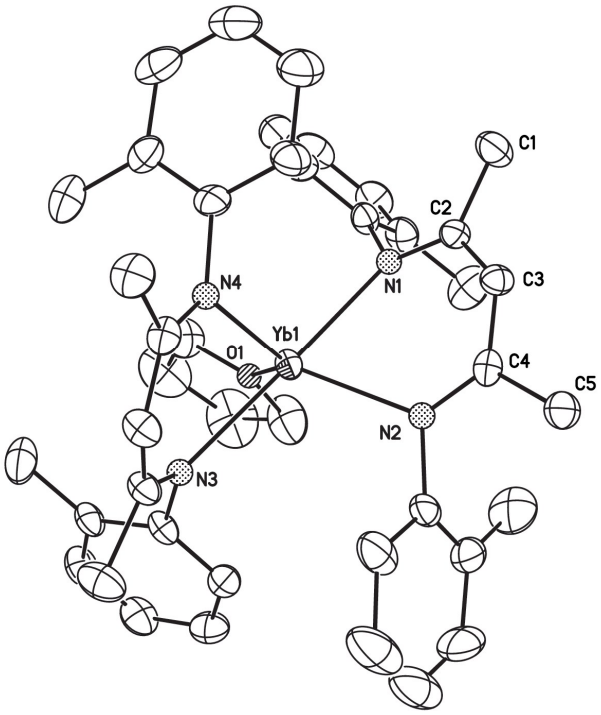

Fig 2. ORTEP diagram of complex **7**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms and a free THF molecule are omitted for clarity.

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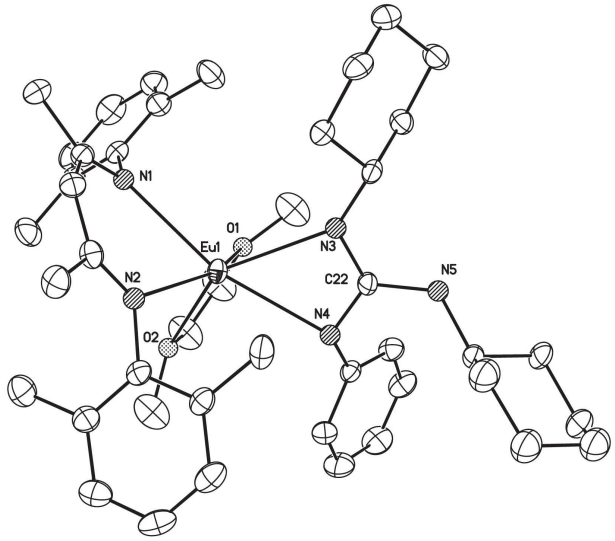

Fig 3. ORTEP diagram of complex **8**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Eu(1)-N(1), 2.604(4); Eu(1)-N(2), 2.518(4); Eu(1)-N(3), 2.568(4); Eu(1)-N(4), 2.588(4); C(22)-N(3), 1.312(6); C(22)-N(4), 1.346(6); C(22)-N(5), 1.395(6); N(3)-C(22)-N(4), 118.0(5); N(3)-C(22)-N(5), 122.4(5); N(4)-C(22)-N(5), 119.6(4); N(1)-Eu(1)-N(2), 71.84(13); N(3)-Eu(1)-N(4), 52.44(13); N(1)-Eu(1)-N(3), 113.96(13); N(2)-Eu(1)-N(4), 117.56(13); N(1)-Eu(1)-N(4), 165.06(14); N(2)-Eu(1)-N(3), 113.76(14).

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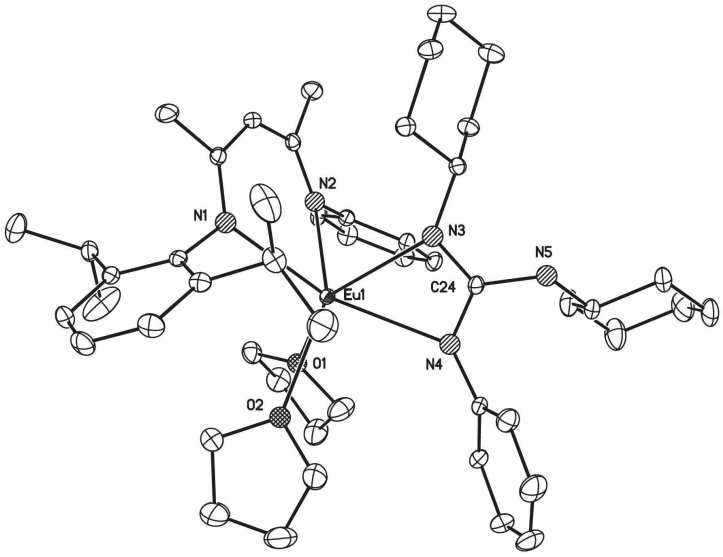

Fig 4. ORTEP diagram of complex **9**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Eu(1)-N(1), 2.5816(16); Eu(1)-N(2), 2.5802(17); Eu(1)-N(3), 2.5847(17); Eu(1)-N(4), 2.6217(16); C(24)-N(3), 1.316(3); C(24)-N(4), 1.360(3); C(24)-N(5), 1.388(3); N(1)-Eu(1)-N(2), 71.98(5); N(3)-Eu(1)-N(4), 52.16(5); N(1)-Eu(1)-N(3), 103.05(5); N(2)-Eu(1)-N(4), 116.09(6); N(1)-Eu(1)-N(4), 151.63(6); N(2)-Eu(1)-N(3), 89.75(6).

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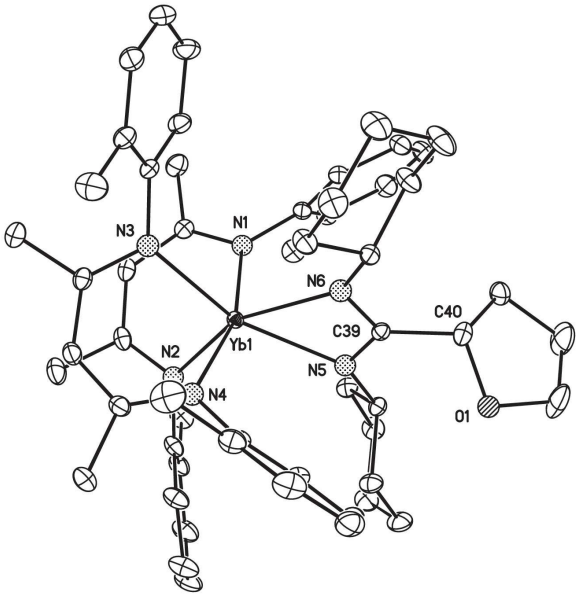

Fig 5. ORTEP diagram of complex **10**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Yb(1)-N(1), 2.371(3); Yb(1)-N(2), 2.365(3); Yb(1)-N(3), 2.360(3); Yb(1)-N(4), 2.363(2); Yb(1)-N(5), 2.342(2); Yb(1)-N(6), 2.332(3); N(5)-C(39), 1.320(4); N(6)-C(39), 1.330(4); C(40)-C(39), 1.533(4); N(1)-Yb(1)-N(2), 76.69(10); N(3)-Yb(1)-N(4), 76.14(9); N(5)-Yb(1)-N(6), 56.99(9); N(6)-Yb(1)-N(3), 101.43(9); N(5)-Yb(1)-N(2), 97.31(9); N(3)-Yb(1)-N(2), 104.28(9); N(4)-Yb(1)-N(1), 164.10(9).

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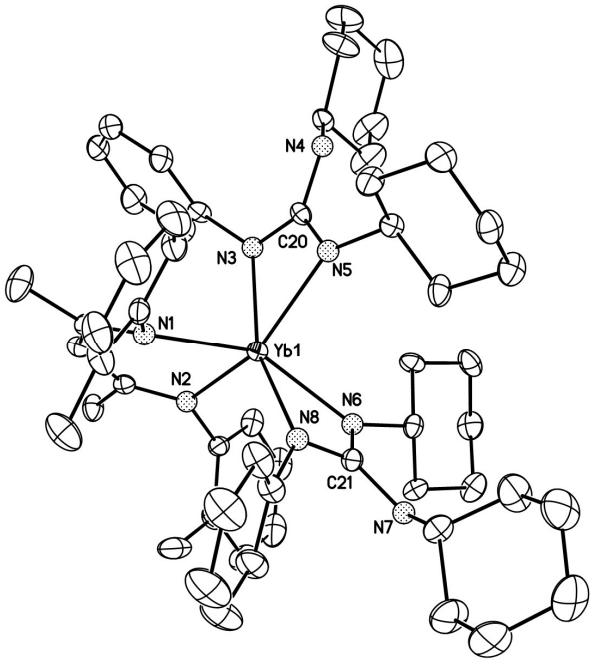

Fig 6. ORTEP diagram of complex **11**. Thermal ellipsoids are drawn at 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Yb(1)-N(1), 2.314(5); Yb(1)-N(2), 2.327(5); Yb(1)-N(3), 2.320(5); Yb(1)-N(5), 2.359(5); Yb(1)-N(6), 2.306(5); Yb(1)-N(8), 2.341(5); N(3)-C(20), 1.342(7); N(5)-C(20), 1.333(8); N(4)-C(20), 1.386(7); N(6)-C(21), 1.336(8); N(8)-C(21), 1.350(8); N(7)-C(21), 1.369(8); N(1)-Yb(1)-N(2), 79.71(17); N(3)-Yb(1)-N(5), 57.57(17); N(6)-Yb(1)-N(8), 57.96(18); N(1)-Yb(1)-N(3), 93.01(18); N(1)-Yb(1)-N(5), 106.07(17); N(1)-Yb(1)-N(6), 148.95(18); N(1)-Yb(1)-N(8), 95.07(19); N(3)-Yb(1)-N(8), 158.61(17).

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Catalytic addition of amines to carbodiimides by bis(β-diketiminate)lanthanide(II) complexes and mechanistic studies

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Text:

Bis(β-diketiminate)lanthanide(II) complexes $L_2Ln(THF)_n$ were found to be excellent pre-catalysts for catalytic addition of amines to carbodiimids and the possible catalytic mechanism was proposed on the basis of the isolation of monoguanidinate Eu(II) and bis(guanidinate) Yb(III) species.

Graphic: