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Cyclopentadienyl-Like Ligand as a Reactive Site in Half-Sandwich Bis(amidinato) Rare-Earth-Metal Complexes: An Efficient Application in Catalytic Addition of Amines to Carbodiimides

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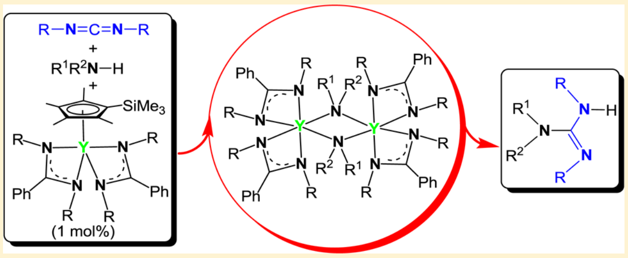
Supporting Information

ABSTRACT: A series of mixed Cp′/bis(amidinato) (Cp′ = η^5-$C_5Me_4(SiMe_3)$) lanthanide complexes were synthesized by the 1:2 acid−base reaction between $Cp'Ln(CH_2SiMe_3)_2(THF)$ (Ln = Y, Dy, Er, Lu) and amidines. These Cp′/bis(amidinato) complexes showed excellent catalytic activity for the addition of amines to carbodiimides, yielding the corresponding guanidines. Isolation, structural characterization, and catalytic application of the binuclear lutetium amido complex showed clearly that the catalytic cycle was initiated by the dissociation of Cp′. These results demonstrated that Cp′, for the first time, acted as a reactive site to yield the active Ln−N species.



INTRODUCTION

The study on the stabilizing ability of different types of supporting ligands toward the same metal center in the stoichiometric and catalytic process is of great importance in the ligand design and elucidation of some reaction processes.[1,2] Their stabilizing ability is significantly dependent on the acidity and basicity of ligands, the steric hindrance, the coordination environment, etc. Therefore, the design and synthesis of organometallic complexes with mixed ligands, such as Cp/amidinate, are in great demand in order to probe the difference of their stabilizing ability. Hou et al. found the reaction of terminal alkynes with half-sandwich yttrium complexes bearing a silylene-linked Cp-amido ligand and propiolamidinate could release propiolamidines at high temperatures, in which the Cp-amido ligand remained bonded to yttrium.[3] Very recently, we communicated a comparative study on the stabilizing ability between $C_5Me_4(SiMe_3)$ (Cp′ for short) and propiolamidinate in half-sandwich bis(propiolamidinato) lanthanides, in which Cp′ was found to dissociate from the rare-earth-metal center via competition with a propiolamidinate.[4] Herein we report the synthesis and structural characterization of various half-sandwich bis(amidinato) lanthanide complexes. Furthermore, these lanthanide complexes can serve as excellent catalyst precursors for the addition reaction of various amines to carbodiimides (also known as guanylation reactions of amines or hydroaminations of carbodiimides). Many catalysts including transition-metal, main-group-metal, and rare-earth-metal complexes are reported for the guanylation reaction because of the atom-economical preparation of guanidines.[5−9] In the case of rare-earth-metal catalyst precursors, the rare-earth-metal complexes having Ln−C or Ln−N bonds usually serve as precursors to yield the active Ln−N species. As far as we are aware, this type of half-sandwich bis(amidinato) rare-earth-metal complex is the first example of an η^5-cyclopentadienyl-like ligand acting as a reactive site to yield the active Ln−N species.

RESULTS AND DISCUSSION

Synthesis and Structure of Rare-Earth-Metal Complexes Bearing Cp′/Bis(amidinates). The 1:2 acid−base reaction between $Cp'Y(CH_2SiMe_3)_2(THF)$ (**1-Y**, Cp′ = $C_5Me_4(SiMe_3)$) and the amidine $PhC({=}NPh)(NHPh)$ in toluene at room temperature for 12 h yielded the mono-Cp′ bis(amidinato) yttrium complex $Cp'Y\{PhC(NPh)_2\}_2$ (**2**) in 94% isolated yield (Scheme 1). The analogous mono-Cp′ bis(amidinato) rare-earth-metal complexes $Cp'Ln\{PhC(NAr)_2\}_2$ (**3**, Ln = Y, Ar = 4-MeC_6H_4; **4**, Ln = Dy, Ar = Ph; **5**, Ln = Er, Ar = Ph; **6**, Ln = Lu, Ar = Ph; **7**, Ln = Lu, Ar = 4-MeC_6H_4) were prepared similarly in high yields by the acid−base reactions between $Cp'Ln(CH_2SiMe_3)_2(THF)$ (Ln = Y, Dy, Er, Lu) and amidines $PhC({=}NAr)(NHAr)$ (Scheme 1). The diamagnetic complexes **2**, **3**, **6**, and **7** were characterized by ^1H NMR and ^{13}C NMR spectroscopy.

All of these half-sandwich bis(amidinato) lanthanide complexes **2**−**7** were structurally characterized by X-ray

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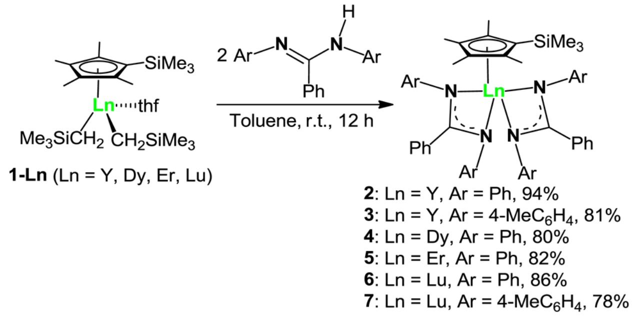
Scheme 1. Synthesis of Rare-Earth-Metal Complexes Bearing Mono-Cp′ and Bis(amidinates) via Acid–Base Reaction



diffraction analyses. Their selected bond lengths and angles are summarized in Table 1, and only the ORTEP drawings of **3** and **7** are shown in Figures 1 and 2, respectively. In the case of the bis(amidinate) complexes **2**–**7**, the Ln^{3+} ion is bonded to one η^5-Cp′ and two η^2-amidinate ligands; thus, the coordination number of their metal centers is 6. These complexes **2**–**7**, which crystallize in the monoclinic $P2_1/c$ space group, are isostructural and isomorphous. The Y–N bond lengths (2.341(3)–-2.471(4) Å) in **2** and **3** are comparable with those of Cp′Y[(^{i}PrN)$_2$CCH$_2$TMS]$_2$ (2.376–2.411 Å).[10]

Catalytic Application in Addition of Amines to Carbodiimides. *Condition Screening.* As a control experiment, no reaction took place when a mixture of aniline and *N*,*N*′-diisopropylcarbodiimide (^{i}PrN=C=N^{i}Pr, DIC) was heated to 140 °C for 24 h in C_6D_5Cl (Table 2, entry 1). In contrast, when 1 mol % of complexes **2**–**7** were involved, the guanylation between aniline and DIC proceeded at 80 °C to provide the corresponding guanidine **8a** (Table 2, entries 2–7). Among them, **3** shows the best catalytic activity, possibly owing to the effect of the ionic radii and substitution effect on the aromatic ring. The catalytic activity of **3** is comparable with that of catalysts reported previously, including [{Me$_2$Si(C$_5$Me$_4$)(NPh)}Y(CH$_2$SiMe$_3$)(thf)],[8m] [Cp^{4PrPh}Y(CH$_2$SiMe$_3$)$_3$][Li(thf)$_3$],[8b] and Zn(OTf)$_2$.[6b]

Substrate Scope. Complex **3** was chosen as the catalyst precursor for the guanylation process between various substituted amines and carbodiimides. Representative results are shown in Table 3. For most anilines, the processes could afford excellent yields, whatever the position of the functional group and whether electron-donating or electron-withdrawing substituents were installed on the benzene ring. The reaction of an aniline with the bulkier *N*,*N*′-di-*tert*-butylcarbodiimide provided a relatively low yield of guanidine **8d**, probably owing to its steric hindrance. 5-Methylthiazol-2-amine was tested to be a good substrate in this reaction as a representative of heterocycle-substituted amines (**8g**). In addition, complex **3**

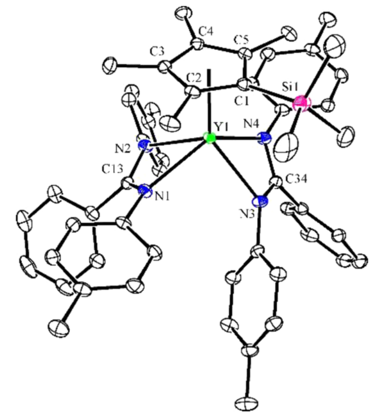


Figure 1. ORTEP drawing of **3** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

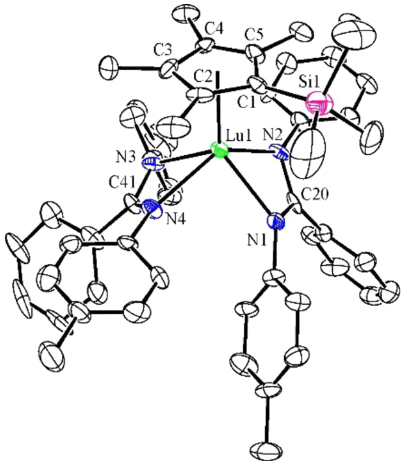
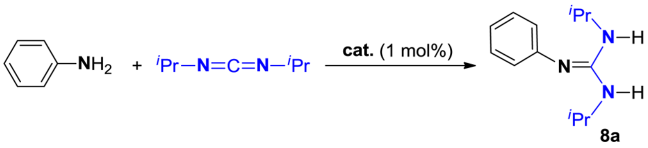


Figure 2. ORTEP drawing of **7** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 2–7 and 10

	2	3	4	5	6	7	10
Ln–N1	2.352(3)	2.380(3)	2.366(2)	2.337(4)	2.307(3)	2.321(7)	2.273(7)
Ln–N2	2.357(3)	2.339(3)	2.356(2)	2.341(4)	2.293(3)	2.312(7)	2.340(7)
Ln–N3	2.364(3)	2.351(3)	2.361(2)	2.324(4)	2.309(3)	2.272(8)	2.346(6)
Ln–N4	2.342(3)	2.341(3)	2.361(2)	2.339(4)	2.302(3)	2.304(7)	2.267(7)
Ln–N5							2.339(8)
N1–C(NCN)	1.332(4)	1.336(5)	1.333(3)	1.341(6)	1.342(5)	1.337(10)	1.342(9)
N2–C(NCN)	1.338(4)	1.349(5)	1.342(3)	1.334(6)	1.353(5)	1.388(11)	1.340(11)
N3–C(NCN)	1.334(4)	1.341(5)	1.339(3)	1.349(6)	1.335(5)	1.325(11)	1.346(11)
N4–C(NCN)	1.348(4)	1.340(5)	1.334(3)	1.328(6)	1.339(5)	1.334(10)	1.345(10)
Ln–Cp(centroid)	2.372(30)	2.336(4)	2.293(10)	2.311(5)	2.276(4)	2.286(9)	
Ln–Cp(av)	2.664(30)	2.631(4)	2.595(10)	2.606(5)	2.584(4)	2.581(9)	
∠N1–Ln–N2	56.87(10)	57.06(11)	56.82(6)	57.21(13)	58.36(11)	58.5(3)	57.8(2)
∠N3–Ln–N4	56.82(10)	57.16(11)	56.54(6)	57.60(14)	57.93(11)	57.7(3)	58.2(2)
∠N1–C–N2	114.3(3)	114.2(3)	114.2(2)	113.7(4)	112.6(3)	112.3(8)	112.5(8)
∠N3–C–N4	113.3(3)	113.6(3)	113.6(2)	114.1(4)	113.2(3)	112.2(8)	113.1(7)

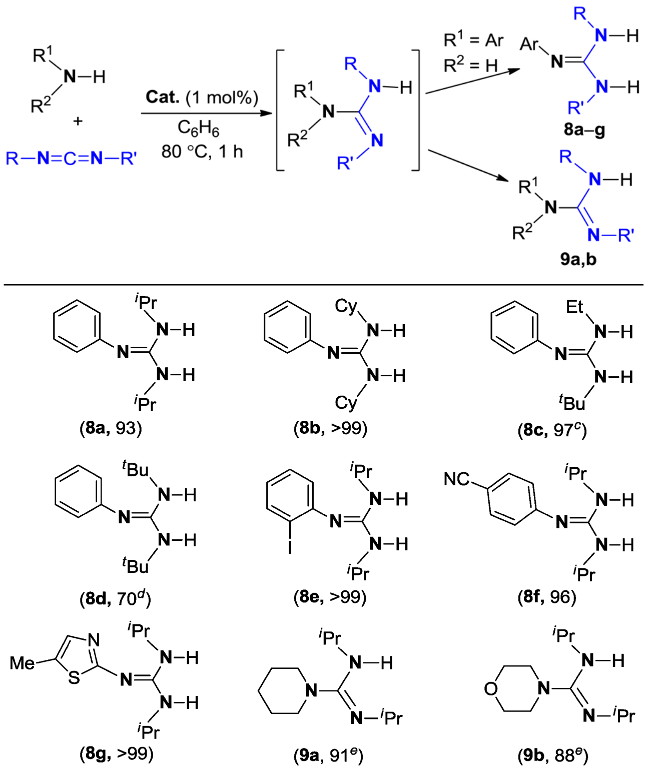
Table 2. Addition Reaction of an Aniline to *N*,*N*′-Diisopropylcarbodiimide Catalyzed by the Mixed Cp′/Bis(amidinato) Lanthanide Complexes[a]



entry	amt of catalyst (mol %)	solvent	temp (°C)	time (h)	yield (%)[b]
1	0	C_6D_5Cl	140	24	0
2	2	C_6D_6	80	2	85
3	3	C_6D_6	80	2	98
4	4	C_6D_6	80	2	83
5	5	C_6D_6	80	2	91
6	6	C_6D_6	80	2	76
7	7	C_6D_6	80	2	95

[a]Conditions: aniline, 0.51 mmol; *N*,*N*′-diisopropylcarbodiimide, 0.50 mmol. [b]Yields were determined by ^{1}H NMR.

Table 3. Catalytic Addition of Amines to Carbodiimides[a,b]

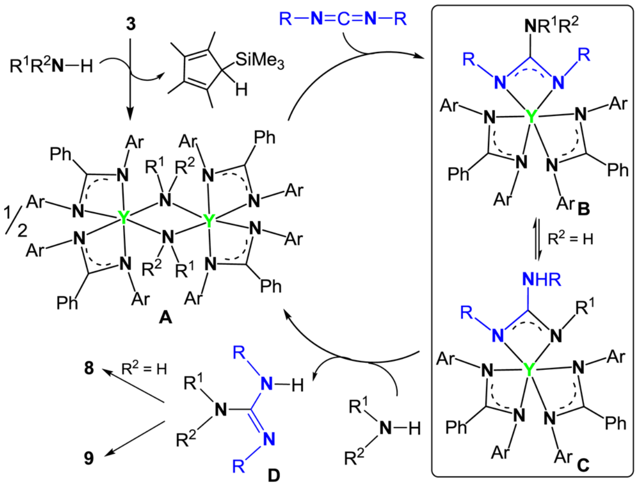


[a]Conditions unless otherwise specified: amines, 0.51 mmol; carbodiimides, 0.50 mmol; **3**, 0.005 mmol; benzene, 0.5 mL. [b]NMR yield. [c]Condition: 3 h. [d]Condition: 12 h. [e]Conditions: toluene, 24 h.

was found to be a good catalyst to effect efficiently the guanylation reaction of secondary amines (**9a**,**b**).

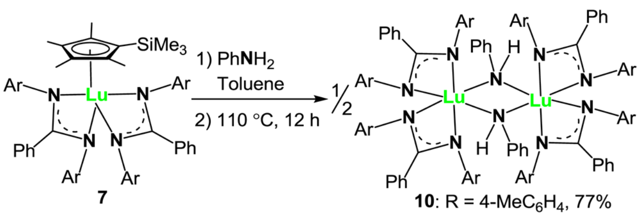
Mechanistic Aspects. A catalytic cycle for the addition of amines to carbodiimides is shown in Scheme 2. The precursor **3** is thought to react with an amine to yield in situ the binuclear yttrium amido species **A**. The active species **A**, having Y−N bonds, brings about the catalytic cycle by two continuous steps: the insertion of the carbodiimide into the Y−N bond and the protonation of a guanidinate unit by an amine. In this process, when primary aromatic amines were involved, **B** could rearrange to the unsymmetrical guanidinate **C** as a more stable intermediate.

Scheme 2. Possible Mechanism of Catalytic Addition of Amines to Carbodiimides



On the basis of the above catalytic cycle, the formation of the amido species **A** should be the key point for the present reaction. Thus, the isolation and structural characterization of the intermediate **A** are of critical importance to elucidate the initiation of the catalytic cycle. The reaction of **3** with aniline was monitored by ^{1}H NMR spectroscopy in [D$_6$]benzene to indicate the occurrence of the amination of **3** by the release of Cp′. However, attempts to obtain suitable single crystals have not yet been successful. Therefore, the analogous lutetium complex **7** was chosen to react with aniline. The reaction of **7** with 1 equiv of aniline in [D$_6$]benzene at 80 °C for 2 h yielded the corresponding binuclear lutetium amido complex **10** in 70% NMR yield. To make the transformation complete, we chose toluene as the solvent. When the reaction was conducted at 110 °C for 12 h, complex **10** could be isolated in 77% yield (Scheme 3). The complex **10** was structurally characterized by X-ray diffraction analyses. Its selected bond lengths and angles are summarized in Table 1, and an ORTEP drawing of **10** is shown in Figure 3. Furthermore, the reaction of aniline with DIC in the presence of 1 mol % of **10** in [D$_6$]benzene at 80 °C for 2 h yielded the corresponding guanidine **8a** in more than 95% NMR yield. This result shows clearly that the catalytic cycle is initiated by the dissociation of Cp′ to yield the active bis(amidinato) amido complexes.

Scheme 3. Isolation of Binuclear Lutetium Amido Complex **10**



CONCLUSIONS

We have reported the synthesis of a series of mixed Cp′/bis(amidinato) lanthanide complexes by the 1:2 acid−base reaction between half-sandwich dialkyl complexes Cp′Ln-

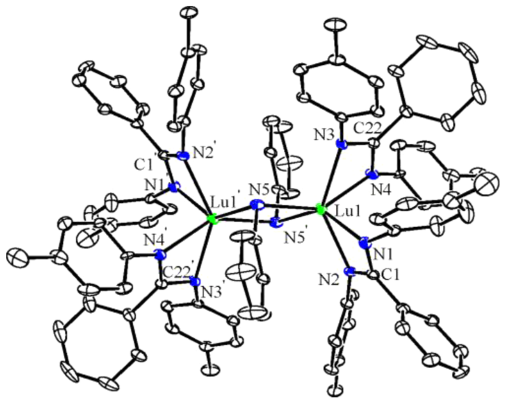


Figure 3. ORTEP drawing of **10** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

$(CH_2SiMe_3)_2$(THF) (Ln = Y, Dy, Er, Lu) and amidines. All Cp′/bis(amidinato) complexes have been characterized unambiguously by single-crystal X-ray diffraction analyses. Excellent catalytic activity of these complexes was observed for the addition of amines to carbodiimides, yielding the corresponding guanidines. A mechanistic study showed that the catalytic cycle was initiated by the dissociation of Cp′ to yield the active bis(amidinato) amido complexes. These results demonstrated that these half-sandwich bis(amidinato) rare-earth-metal complexes served as the first example of an η^5-cyclopentadienyl-like ligand acting as a reactive site to yield the active Ln−N species. A comparison between Cp′ and amidinate in the reaction with amine suggested that the coordinative ability of the chelate amidinate was stronger than that of η^5-Cp′, which will be useful for ligand design and mechanistic elucidation in related stoichiometric and catalytic processes.

■ EXPERIMENTAL SECTION

General Methods. All reactions were conducted under a slightly positive pressure of dry nitrogen using standard Schlenk line techniques or under a nitrogen atmosphere in a glovebox. The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer to ensure both were always below 1 ppm. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Solvents were purified by a Solvent Purification System and dried over fresh Na chips in the glovebox. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes. ^{1}H and ^{13}C NMR spectra were recorded on a 400 M spectrometer (FT, 400 MHz for ^{1}H, 100 MHz for ^{13}C) at room temperature, unless otherwise noted.

Preparation of 2. A solution of PhNHCPh(=NPh) (163.4 mg, 0.600 mmol) in toluene (ca. 3 mL) was added to a solution of Cp′Y$(CH_2SiMe_3)_2$(thf) (158.6 mg, 0.300 mmol) in toluene (ca. 3 mL). The reaction mixture was stirred for 12 h at room temperature. Evaporation of toluene gave a yellow powder. When this powder was washed with hexane (ca. 2 mL), **2** could be obtained as a pale yellow solid (233 mg, 0.282 mmol, 94% yield). ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ 0.56 (s, 9H; Si*Me*$_3$), 2.16 (s, 6H; *Me*Cp), 2.26 (s, 6H; *Me*Cp), 6.62−6.64 (m, 8H; C_6H_5) 6.70 (br, 6H; C_6H_5), 6.73−6.77 (m, 4H; C_6H_5), 6.96−7.00 (m, 12H; C_6H_5). ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ 2.7, 11.6, 14.0, 115.6 (d, *J* = 2.3 Hz), 122.4, 124.9 (d, *J* = 0.7 Hz), 125.3, 128.7, 128.9, 129.0 (d, *J* = 1.0 Hz), 129.3, 130.5, 132.7 (d, *J* = 2.7 Hz), 148.5, 173.7 (d, *J* = 2.8 Hz). Anal. Calcd for $C_{50}H_{51}N_4SiY$: C, 72.80; H, 6.23; N, 6.79. Found: C, 72.78; H, 6.19; N, 6.75. Single crystals of **2** suitable for X-ray analysis could be grown from toluene/hexane at room temperature.

Preparation of 3. With 4-MeC_6H_4NHCPh(=NC_6H_4Me-4) (180.2 mg, 0.600 mmol) and Cp′Y$(CH_2SiMe_3)_2$(thf) (158.6 mg, 0.300 mmol) as starting materials, **3** was obtained as a pale yellow solid (214 mg, 0.243 mmol, 81% yield) in a manner analogous to that described for the preparation of **2**. Single crystals suitable for X-ray analysis could be grown from toluene/hexane at room temperature. ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ 0.60 (s, 9H, Si*Me*$_3$), 2.02 (s, 12H, C*H*$_3C_6H_4$), 2.23 (s, 6H, *Me*Cp), 2.32 (s, 6H, *Me*Cp), 6.58 (d, *J* = 7.6 Hz, 8H, *Ar*), 6.73 (br, 6H, *Ar*), 6.83 (d, *J* = 8.0 Hz, 8H, *Ar*), 7.08 (br, 4H, *Ar*). ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ 2.8, 11.7, 14.2, 20.8, 115.4 (d, *J* = 2.3 Hz), 124.7, 125.2, 128.71, 128.74, 129.3, 130.5, 131.3, 133.1 (d, *J* = 2.7 Hz), 146.1, 173.6 (d, *J* = 2.8 Hz). Anal. Calcd for $C_{54}H_{59}N_4SiY$: C, 73.61; H, 6.75; N, 6.36. Found: C, 73.33; H, 6.78; N, 6.23. Single crystals of **3**·0.5(hexane) suitable for X-ray analysis could be grown from toluene/hexane at room temperature.

Preparation of 4. With PhNHCPh(=NPh) (163.4 mg, 0.600 mmol) and Cp′Dy$(CH_2SiMe_3)_2$(thf) (180.7 mg, 0.300 mmol) as starting materials, **4** was obtained as a pale yellow solid (216 mg, 0.240 mmol, 80% yield) in a manner analogous to that described for the preparation of **2**. Single crystals suitable for X-ray analysis could be grown from toluene/hexane at room temperature. Anal. Calcd for $C_{50}H_{51}N_4SiDy$: C, 66.83; H, 5.72; N, 6.24. Found: C, 66.73; H, 5.62; N, 6.21.

Preparation of 5. With PhNHCPh(=NPh) (163.4 mg, 0.600 mmol) and Cp′Er$(CH_2SiMe_3)_2$(thf) (182.2 mg, 0.300 mmol) as starting materials, **5** was obtained as a pink solid (222 mg, 0.246 mmol, 82% yield) in a manner analogous to that described for the preparation of **2**. Single crystals suitable for X-ray analysis could be grown from toluene/hexane at room temperature. Anal. Calcd for $C_{50}H_{51}ErN_4Si$: C, 66.48; H, 5.69; N, 6.20; Found: C, 66.32; H, 5.66; N, 6.13.

Preparation of 6. With PhNHCPh(=NPh) (163.4 mg, 0.600 mmol) and Cp′Lu$(CH_2SiMe_3)_2$(thf) (184.5 mg, 0.300 mmol) as starting materials, **6** was obtained as a pale yellow solid (235 mg, 0.258 mmol, 86% yield) in a manner analogous to that described for the preparation of **2**. ^{1}H NMR (400 MHz, [D_8]THF): δ 0.36 (s, 9H; Si*Me*$_3$), 1.87 (s, 6H; *Me*Cp), 2.12 (s, 6H; *Me*Cp), 6.40 (d, *J* = 7.4 Hz, 8H; C_6H_5) 6.73 (t, *J* = 7.4 Hz, 4H; C_6H_5), 6.85−7.01 (m, 18H; C_6H_5). ^{13}C NMR (100 MHz, [D_8]THF): δ 2.8, 11.7, 14.2, 114.4, 122.8, 124.0, 126.1, 128.4, 128.7, 128.8, 129.4, 131.0, 133.3, 149.0, 173.6. Anal. Calcd for $C_{50}H_{51}LuN_4Si$: C, 65.92; H, 5.64; N, 6.15. Found: C, 65.78; H, 5.53; N, 6.02. Single crystals of **6** suitable for X-ray analysis could be grown from toluene/hexane at room temperature.

Preparation of 7. With 4-MeC_6H_4NHCPh(=NC_6H_4Me-4) (180.2 mg, 0.600 mmol) and Cp′Lu$(CH_2SiMe_3)_2$(thf) (184.5 mg, 0.300 mmol) as starting materials, **7** was obtained as a pale yellow solid (226 mg, 0.233 mmol, 78% yield) in a manner analogous to that described for the preparation of **2**. Single crystals of **7**·0.5(hexane) suitable for X-ray analysis could be grown from toluene/hexane/Et_2O at room temperature. The NMR data for **7**·0.5(hexane) are as follows. ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ 0.63 (s, 9H, Si*Me*$_3$), 0.89 (t, *J* = 6.9 Hz, 3H; *Me*, hexane), 1.17−1.33 (m, 4H; C*H*$_2$, hexane), 2.02 (s, 12H, C*H*$_3C_6H_4$), 2.21 (s, 6H, *Me*Cp), 2.35 (s, 6H, *Me*Cp), 6.58 (s, 4H, *Ar*), 6.60 (s, 4H, *Ar*), 6.73 (br, 5H, *Ar*), 6.82 (s, 4H, *Ar*), 6.84 (s, 4H, *Ar*), 7.00−7.13 (m, 5H, *Ar*). ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ 2.9, 11.8, 14.30 (hexane), 14.32, 20.8, 23.0 (hexane), 31.9 (hexane), 114.2, 123.8, 125.6, 128.5, 128.8, 129.2, 129.3, 130.6, 131.6, 133.2, 146.1, 173.0. It is noted that there is a residual ether peak in **7**·0.5(hexane). Anal. Calcd for $C_{54}H_{59}LuN_4Si$: C, 67.06; H, 6.15; N, 5.79. Found: C, 67.29; H, 6.27; N, 5.55.

Preparation of 10. In a glovebox, a solution of $PhNH_2$ (17.7 mg, 0.180 mmol) in toluene (ca. 1 mL) and a solution of **7** (164 mg, 0.170 mmol) in toluene (ca. 2 mL) were placed in a Schlenk tube. Then the Schlenk tube was taken outside the glovebox, and the mixture was stirred at 110 °C for 12 h. Then the Schlenk tube was moved inside the glovebox after cooling to room temperature. After the solvent was removed under reduced pressure, the solid was washed with hexane (2 × 1 mL). **10** was obtained as a colorless solid (113 mg, 0.0653 mmol, 77% yield). ^{1}H NMR (400 MHz, [D_8]THF): δ 2.13 (s, 24H; *Me*), 4.14 (2H, N*H*C_6H_5), 6.12 (t, *J* = 7.1 Hz, 2H; NHC_6H_5), 6.43 (d, *J* = 8.1 Hz, 16H; $C_6H_4CH_3$), 6.65 (d, *J* = 8.0 Hz, 4H; *Ar*), 6.72 (d, *J* = 8.1

Hz, 16H; C_6H_4Me), 6.83−6.87 (m, 4H; *Ar*), 6.99−7.01 (m, 8H; *Ar*), 7.05−7.10 (m, 12H; *Ar*). ^{13}C NMR (100 MHz, $[D_8]$THF): δ 20.8, 111.7, 116.6, 125.5, 128.4, 128.8, 129.2, 129.3, 130.41, 130.44, 135.2, 147.5, 160.3, 172.7. Anal. Calcd for $C_{96}H_{88}N_{10}Lu_2$: C, 66.58; H, 5.12; N, 8.09. Found: C, 66.35; H, 4.98; N, 7.93. Single crystals of **10** suitable for X-ray analysis could be grown from toluene/hexane at room temperature.

Typical Procedures for the Catalytic Reaction between Amines and Carbodiimides: NMR Tube Reaction. In the glovebox, a J. Young valve NMR tube was charged with **3** (4.4 mg, 0.005 mmol), C_6D_6 (0.5 mL), aniline (48 mg, 0.51 mmol), and *N*,*N′*-diisopropylcarbodiimide (63 mg, 0.50 mmol). The tube was taken out of the glovebox and then heated to 80 °C in an oil bath for 1 h. Formation of **8a−g** and **9a,b** was monitored by ^1H NMR spectroscopy. The NMR data of **8a−g** and **9a,b** were consistent with those reported.[8b]

X-ray Crystallographic Studies. Single crystals of **2**−**7** and **10** suitable for X-ray analysis were grown as shown in the Experimental Section. The crystals of **7** were manipulated under a nitrogen atmosphere and were sealed in a thin-walled glass capillary. Data collection for **2**, **3**, and **6** was performed at −100 °C on a Rigaku CCD SATURN 724 diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). **7** was performed at 20 °C on a Rigaku RAXIS RAPID IP diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data collection for **4** and **10** was performed at −173 °C and for **5** was performed at 20 °C on an Agilent SuperNova Dual Atlas CCD diffractometer (CCD-2) using graphite-monochromated Mo Kα radiation (α = 0.71073 Å).[11] The determination of crystal class and unit cell parameters was carried out by the CrystalClear (Rigaku Inc., 2007) for **2**, **3**, and **6** or Rapid-AUTO (Rigaku 2000) program package for **7**. The raw frame data were processed using Crystal Structure (Rigaku/MSC 2000) for **7** or CrystalClear (Rigaku Inc., 2007) for **2**, **3**, and **6** to yield the reflection data file. The structures of **2**, **3**, **6**, and **7** were solved by use of the SHELXTL program.[12] Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. Using Olex2, the structure of **4** was solved with XS using direct methods and refined with the ShelXL refinement package using least-squares minimization.[13] The structure of **5** was solved with Superflip and refined with the XL refinement package using least-squares minimization. The structure of **10** was solved with the Superflip structure solution program using Charge Flipping and refined with the XL refinement package using least-squares minimization. The hydrogen atoms were placed at calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection, and processing parameters for the rare-earth complexes **2**−**7** and **10** are summarized in the Supporting Information. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-972190 (**2**), CCDC-972191 (**3**·0.5(hexane)), CCDC-972192 (**4**), CCDC-972194 (**5**), CCDC-972195 (**6**), CCDC-972196 (**7**·0.5(hexane)), and CCDC-972197 (**10**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre viawww.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving additional NMR data, ^1H NMR and ^{13}C NMR spectra of all new compounds, crystallographic tables, and X-ray crystallographic data for **2**−**7** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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