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Rare-Earth Metal Tris(trimethylsilylmethyl) Anionic Complexes Bearing One 1-Phenyl-2,3,4,5-tetrapropylcyclopentadienyl Ligand: Synthesis, Structural Characterization, and Application

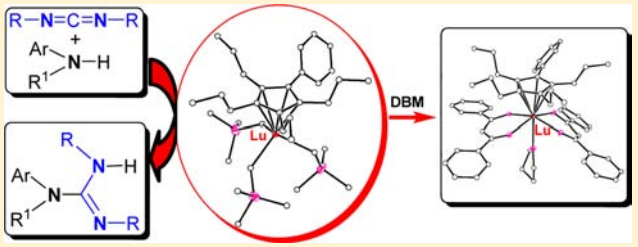
Ling Xu,[†] Zitao Wang,[†] Wen-Xiong Zhang,*[,†,‡] and Zhenfeng Xi*[,†]

[†]Beijing National Laboratory for Molecular Sciences, Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

[‡]State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, China

Supporting Information

ABSTRACT: Synthesis and structural characterization of half-sandwich rare-earth metal tris(trimethylsilylmethyl) anionic complexes bearing one 1-phenyl-2,3,4,5-tetrapropylcyclopentadienyl ligand are achieved. These soluble anionic compounds show good reactivity in the stoichiometric reaction with dibenzoylmethane (DBM) to give the salt-free half-sandwich complex bearing two chelate DBM ligands. More importantly, they can serve as excellent and general catalyst precursors for the addition of different types of amines including primary aromatic amines ($ArNH_2$), acyclic (RR′NH, ArRNH, and ArAr′NH; R, R′ = Alkyl group, Ar, Ar′ = Aromatic group), or cyclic secondary aliphatic amines to carbodiimides yielding efficiently guanidines. Acyclic secondary amines of the general formula ArAr′NH and ArRNH cannot be achieved efficiently by the previous rare-earth catalysts because of their weak nucleophilicity and steric hindrance. Our results show clearly the reactivities of anionic trialkyl precursors are comparable with the corresponding neutral alkyl complex in the stoichiometric reaction but exhibit better catalytic activity than the known catalysts.



INTRODUCTION

Recent years have witnessed a significant growth in the synthesis and catalytic application of neutral and cationic half-sandwich rare-earth alkyl complexes bearing only one cyclopentadienyl ancillary ligand.[1] This is because these complexes will provide a sterically and electronically more unsaturated metal center and be expected to show unique reactivities differing from those of the metallocenes.[1] However, anionic half-sandwich rare-earth alkyl complexes remain to be unexplored. This is mainly because it is generally known that anionic alkyl complexes have the decreased reactivity due to the additional electronic and steric saturation of the metal environment.[1c] In addition, their sparing solubility in common polar and nonpolar solvents hampers the isolation, purification, and characterization as well as further application. However, the formation of anionic rare-earth metal moieties is a commonly observed process in the salt metathesis reaction when alkali metal hydrocarbyl derivatives are utilized.[2] The production of anionic complexes is usually suppressed by carefully controlling the amount of alkali metal hydrocarbyl derivatives and reaction ratio. In some certain cases, it is an inevitable feature owing to the concomitant and competitive process between neutral and anionic complexes leading to the low-yield formation of the desirable neutral complexes. It will be a promising field if the reactivity of anionic half-sandwich rare-earth alkyl complexes is much closer to or better than that of neutral complexes. Therefore, it is of great interest and importance to explore the synthesis and application of the isolable and soluble anionic alkyl complexes having one cyclopentadienyl ligand.

The catalytic addition of amines to carbodiimides, also known as guanylation reaction of amines or hydroamination of carbodiimides, has received much current interest for the atom-economical preparation of guanidines.[3] Many catalysts including transition metal, main group, and rare-earth metal have been designed and tested for the guanylation reaction.[4−7] We have also reported the guanylation reaction between amines and carbodiimides by use of readily available $Zn(OTf)_2$ and $AlMe_3$ to provide trisubstituted guanidines.[4b,5d] The guanylation reaction of primary aromatic amines ($ArNH_2$), acyclic (RR′NH), or cyclic secondary aliphatic amines has been achieved by some catalysts.[4−6] In comparsion, because of their weak nucleophilicity and steric hindrance, the guanylation reaction of ArAr′NH cannot be accomplished by the reported rare-earth catalysts, but the guanylation reaction of secondary amines of the general formula ArRNH cannot be achieved by all reported catalysts. Thus, a general catalyst system performing the guanylation reaction of different types of amines is a great challenge and is of great importance in academy and pharmaceutical industry.

We report here the synthesis and characterization of rare-earth metal tris(trimethylsilylmethyl) anionic complexes

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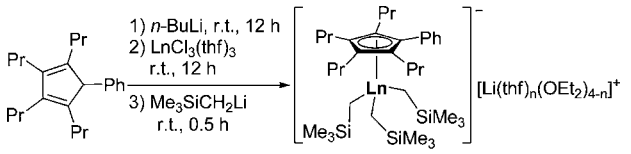
supported by one 1-phenyl-2,3,4,5-tetrapropylcyclopentadienyl ligand (Cp^{4PrPh} for short). The installation of four propyl groups on the Cp ring ensures trialkyl anionic complexes highly soluble in common solvents and makes them isolable. The reaction of trialkyl anionic complex with dibenzoylmethane (DBM) gave the salt-free half-sandwich complex. More importantly, these anionic complexes act as general and highly active catalysts for the guanylation reaction of various amines including primary aromatic amines ($ArNH_2$), acyclic (RR′NH, ArRNH, and ArAr′NH), or cyclic secondary aliphatic amines.

RESULTS AND DISCUSSION

Synthesis and Structure of Rare-Earth Metal Tris(trimethylsilylmethyl) Anionic Complexes Bearing One 1-Phenyl-2,3,4,5-tetrapropylcyclopentadienyl Ligand. HCp^{4PrPh} ligand was prepared by Lewis acid mediated reaction of tetrapropyl zirconacyclopentadiene with benzaldehyde.[8] Initially, we expected to synthesize salt-free rare-earth metal bis(trimethylsilylmethyl) complexes having one Cp^{4PrPh} ligand by acid−base reaction between the rare-earth tris(trimethylsilylmethyl) complexes $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln = Y, Ho, Er, Tm, and Lu) and a ligand HCp^{4PrPh}. The target dialkyl complexes were not observed at room temperature or even at higher temperatures because of the weak acidity of HCp^{4PrPh}. Then the salt metathesis reaction among $LiCp^{4PrPh}$, $LnCl_3(thf)_3$ and two Me_3SiCH_2Li was attempted; however, a mixture of neutral dialkyl and anionic trialkyl complexes was observed. So we turned our attention to the synthesis and isolation of anionic trialkyl complexes. Thus, after $LiCp^{4PrPh}$ which was generated from HCp^{4PrPh} and *n*-BuLi was first treated with $LuCl_3(thf)_3$ at room temperature for 12 h, then reacted with three equiv of Me_3SiCH_2Li at room temperature for 0.5 h in THF/OEt_2, the anionic trialkyl complex $[Cp^{4PrPh}Lu(CH_2SiMe_3)_3][Li(thf)_3(OEt_2)]$ (**1-Lu**) was obtained in 74% isolated yield. Similar to the synthesis of **1-Lu**, the analogous $[Cp^{4PrPh}Ln(CH_2SiMe_3)_3][Li(thf)_n(OEt_2)_{4-n}]$ **1-Ln** (Y, Er and Tm: n = 3, Ho: n = 4) were easily prepared in high yields. Rare-earth metal anionic complexes **1-Ln** (Ln = Y, Ho, Er, Tm, and Lu) are soluble in benzene, toluene, and many polar solvents (Scheme 1).

Scheme 1. Preparation of Half-Sandwich Rare-Earth Metal Tris(trimethylsilylmethyl) Anionic Complexes



1-Y: n = 3, 82%; **1-Ho**: n = 4, 77%; **1-Er**: n = 3, 82%; **1-Tm**: n = 3, 87%; **1-Lu**: n = 3, 74%

All of these anionic complexes **1-Ln** were structurally characterized by X-ray diffraction analyses. Their selected bond lengths and angles are summarized in Table 1, and only the ORTEP drawings of **1-Lu** and **1-Ho** are shown in Figures 1 and 2, respectively. X-ray analyses reveal that **1-Ln** (Ln = Y, Er, Tm, and Lu) are isostructural and isomorphous, which crystallize in the monoclinic $P2(1)/n$ space group. The solid state structure of **1-Lu** reveals a solvent separated ion pair. The lutetium atom in the anionic unit is surrounded by one Cp^{4PrPh} ligand and three tris(methylsilylmethyl) ligands. The lutetium anionic skeleton seems to be the three tripod piano. Each lithium cation in **1-Lu** is surrounded by three thf molecules and one ether, which form a distorted tetrahedral coordination sphere. The Li−O distances, which lie between 1.88(2) and 1.98(2) Å, agree with the range of 1.907(9) to 1.934(9) Å found in $[Li(thf)_4]^+[LuCl_2\{(C_{13}H_8)CPh_2(C_5H_4)\}]^-$.[9] X-ray analysis reveals that **1-Ho** crystallizes in the orthorhombic $Pna2(1)$ space group. The holmium anionic skeleton in **1-Ho** is analogous to that of **1-Lu**; however, lithium cation in **1-Ho** is surrounded by four thf molecules forming a distorted tetrahedral environment.

Reaction of 1-Lu with Dibenzoylmethane. The reaction of **1-Lu** with dibenzoylmethane (DBM) (see Scheme 2) gave rise to the salt-free half-sandwich lutetium complex $[Cp^{4PrPh}Lu(DBM)_2(thf)]$, showing the reactivity of half-sandwich rare-earth metal anionic trialkyl precursor is comparable with the corresponding neutral dialkyl complex. An X-ray analysis reveals that the space group of **2-Lu** is $P2(1)/c$. The central Lu atom was established as eight-coordinate and surrounded by one η^5-Cp^{4PrPh}, one thf and two η^2-dibenzoylmethane ligands. The distance of Lu1−Cp(centroid) 2.338(11) Å in this compound is slightly larger than that of the analogue $Cp^{4MeEt}Lu(acac)_2$ (acac = acetylacetonate, 2.276(2) Å),[10] whereas all of the four Li−O(DBM anion) bond lengths in **2-Lu** are consistent with those of $Cp^{4MeEt}Lu(acac)_2$. The centroid of Cp ring,Lu atom and the O atom of thf are almost collinear with the bond angle of 177.4(3)°. The bond angles of O1−Lu1−O2 and O3−Lu1−O4 are smaller than those of O1−Lu1−O4 and O2−Lu1−O3 probably owning to the strain of the six-membered $[LuO_2C_3]$ ring.

Catalytic Application in Addition of Amines to Carbodiimides. *a). Addition of Primary Aromatic Amines to Carbodiimides.* No reaction was observed when the mixture of aniline and *N*,*N*′-diisopropylcarbodiimide (^{i}PrN═C═N^{i}Pr) was heated to 140 °C for 24 h in C_6D_5Cl (Table 2, entry 1). In contrast, when 1 mol % **1-Y** was involved, the guanylation between aniline and *N*,*N*′-diisopropylcarbodiimide proceeded even at room temperature (Table 2, entries 2 and 3). Increased temperatures could accelerate this reaction, as it rose up to 50 or 80 °C, the yields of **3a** arrived up to 86% or 99%, respectively (Table 2, entries 4 and 5). This guanylation process also worked in toluene or THF, whereas the yields were slightly lower than in benzene (Table 2, entries 6 and 7). Other analogous complexes, **1-Ho, 1-Er, 1-Tm,** and **1-Lu**, also showed similar catalytic reactivity to **1-Y**. These slightly lower yields are possibly owing to the minor radii (Table 2, entries 8−11).

Complex **1-Y** was chosen as the catalyst for the guanylation process between various substituted anilines and carbodiimides. Representative results were shown in Table 3. For most anilines, the process could afford excellent yields whatever the position of functional group and whether electron-donating or electron-withdrawing substituents were installed on benzene ring. The reaction of an aniline with the bulkier *N*,*N*′-di-*tert*-butylcarbodiimide provided relatively low yield of guanidine **3d** probably owing to its steric hindrance. Aromatic C−F (**3e** and **3f**), C−Cl (**3g** and **3h**), C−Br (**3i**), and C−I (**3j**) bonds as well as CN group (**3n**) could tolerate the reaction conditions. In addition, 5-methylthiazol-2-amine was tested to be a good substrate in this reaction as a representative of heterocyclo-substituted amines (**3o**).

b). Addition of Secondary Amines to Carbodiimides. Generally, secondary amines are not as reactive as primary

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1-Ln (Ln: Y, Ho, Er, Tm, and Lu)

	1-Y	1-Ho	1-Er	1-Tm	1-Lu
Ln−C(CH_2TMS)	2.424(5)	2.392(10)	2.392(7)	2.373(7)	2.367(9)
	2.430(5)	2.427(10)	2.400(7)	2.375(7)	2.373(8)
	2.437(4)	2.428(10)	2.404(7)	2.411(7)	2.375(8)
Ln−Cp(centroid)	2.425(5)	2.396(10)	2.396(7)	2.403(7)	2.366(8)
Ln−Cp(av)	2.711(5)	2.685(10)	2.684(7)	2.690(7)	2.657(8)
Li−O(av)	1.91 (3)	1.90(4)	1.93 (3)	1.924(16)	1.93(2)
∠ C(CH_2TMS)−Ln−Cp(centroid)	112.5(2)	113.2(4)	112.9(2)	112.1(2)	112.8(3)
	113.0(2)	117.2(4)	113.2(2)	115.6(2)	113.6(3)
	114.5(2)	115.5(3)	113.6(3)	114.0(2)	114.4(3)
∠ C(CH_2TMS)−Ln−C(CH_2TMS)	104.53(18)	102.3(4)	104.4(3)	103.1(3)	104.5(4)
	106.30(17)	103.0(4)	105.6(3)	104.2(2)	104.6(4)
	106.33(18)	103.8(4)	106.4(3)	106.9(3)	105.9(3)

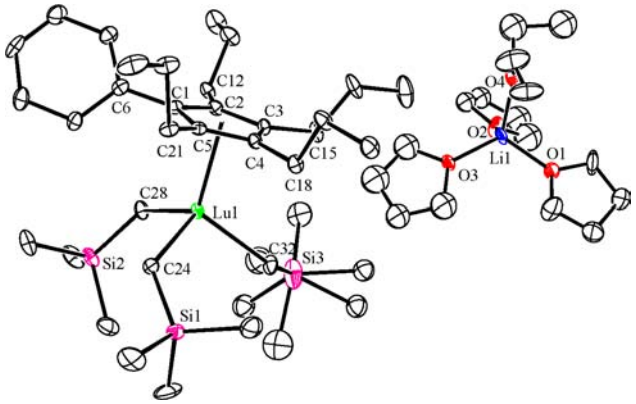


Figure 1. ORTEP drawing of **1-Lu** with 20% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

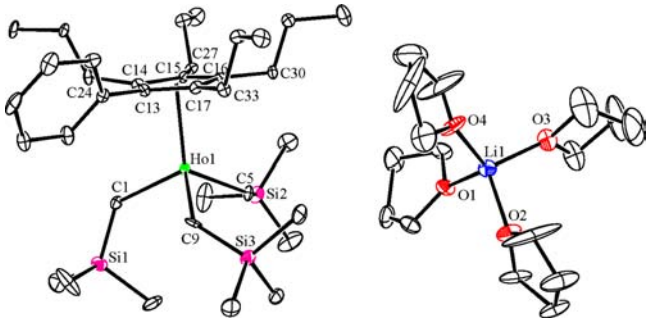
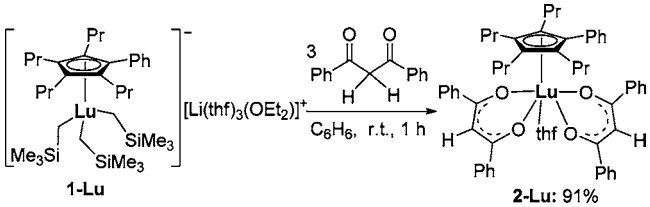


Figure 2. ORTEP drawing of **1-Ho** with 20% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Scheme 2. Reaction of 1-Lu with Dibenzoylmethane



amines in the addition reaction toward carbodiimides. However, **1-Y** could also catalyze various cyclic and acyclic secondary amines to furnish guanidines with the loading of 1 mol % in toluene at 130 °C (Table 4). Interestingly, in the presence of **1-Y**, the addition of *N*-methylaniline to a carbodiimide can smoothly provide the corresponding

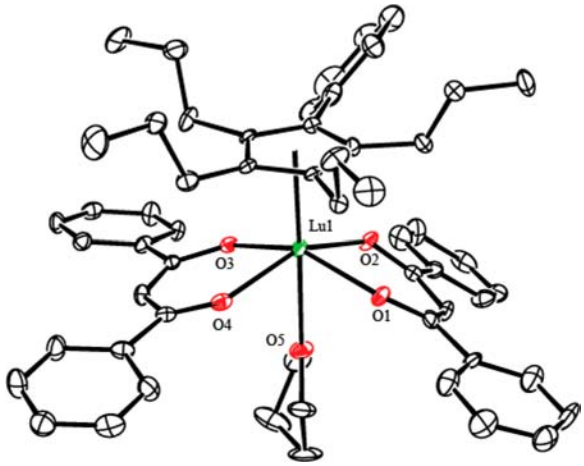
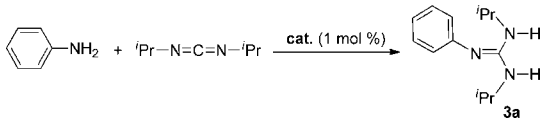


Figure 3. ORTEP drawing of **2-Lu** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Lu1−O1 2.188(6), Lu1−O2 2.186(7), Lu1−O3 2.207(7), Lu1−O4 2.214(8), Lu1−Cp(centroid) 2.338(11); O1−Lu1−O2 77.4(2), O3−Lu1−O4 78.6(3), O2−Lu1−O3 89.0(2), O1−Lu1−O4 99.7(3), O1−Lu1−Cp(centroid) 104.8(3), O2−Lu1−Cp-(centroid) 106.8 (3), O3−Lu1−Cp(centroid) 105.2(3), O4−Lu1−Cp(centroid) 103.1(3), O5−Lu1−Cp(centroid) 177.4(3).

Table 2. Rare-Earth Trialkyl Anionic Complexes Catalyzed Addition of an Aniline to *N,N′*-Diisopropylcarbodiimide[a]



entry	catalyst (mol %)	solvent	temp (°C)	time (h)	yield (%)[b]
1	0	C_6D_5Cl	140	24	0
2	**1-Y**	C_6D_6	r.t.	1	37
3	**1-Y**	C_6D_6	r.t.	24	81
4	**1-Y**	C_6D_6	50	1	86
5	**1-Y**	C_6D_6	80	1	>99
6	**1-Y**	[D_8]toluene	80	1	96
7	**1-Y**	[D_8]THF	80	1	93
8	**1-Ho**	C_6D_6	80	1	95
9	**1-Er**	C_6D_6	80	1	96
10	**1-Tm**	C_6D_6	80	1	95
11	**1-Lu**	C_6D_6	80	1	95

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

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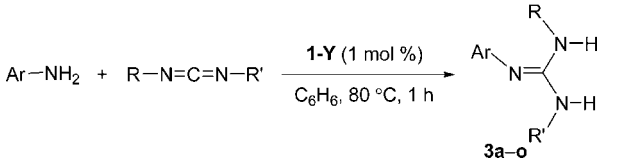
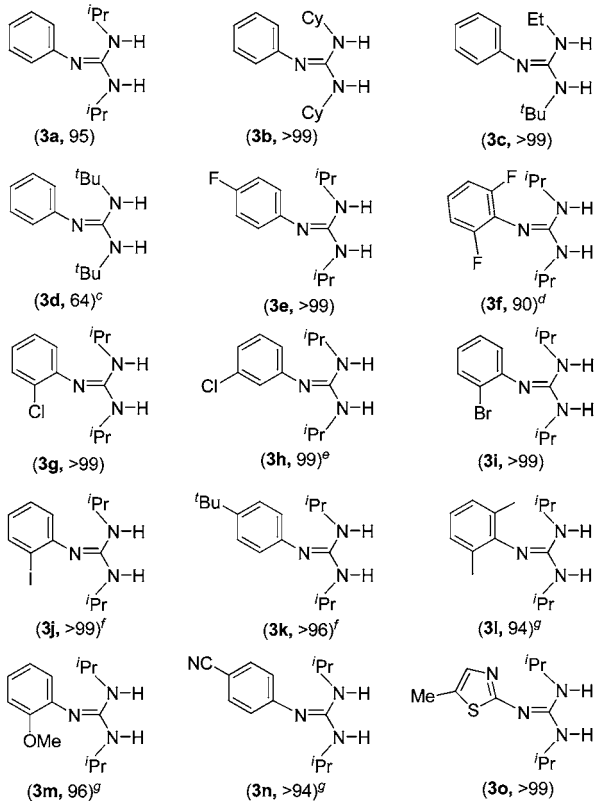
Table 3. Catalytic Addition of Various Primary Amines to Carbodiimides[a,b]



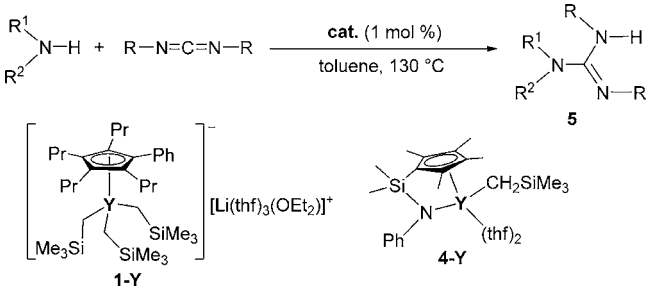


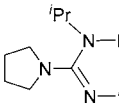
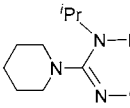
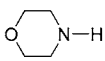
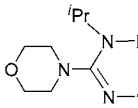
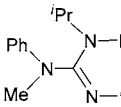
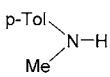
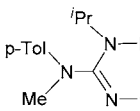
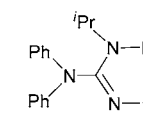
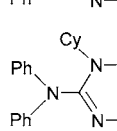
[a]Conditions: amines, 0.51 mmol; carbodiimides, 0.50 mmol; 1-Y, 0.005 mmol; benzene, 0.5 mL. [b]NMR yield (%). [c]Condition: 34 h. [d]Isolated yield. [e]Condition: 6 h. [f]Condition: 2 h. [g]Condition: 4 h.

guanidine **5d** in 81% yield. This result showed obviously better catalytic activity than the well-investigated **4-Y** compound (Table 4, entries 4−5). Similarly, the addition reaction of diphenylamine or *N*-methylaniline having a substituent on the phenyl ring also showed better catalytic activity using **1-Y** than **4-Y**(Table 4, entries 6−9). Although the guanylation reaction of acyclic (RR′NH) or cyclic secondary aliphatic amines have been achieved in good yields by those reported catalysts,[4−6] as far as we are aware, the complex **1-Y** is found to be the first catalyst to effect efficiently the guanylation reaction of secondary amines of the general formula ArRNH.

c). Mechanism. A possible mechanism of the catalytic cycle for the addition of amines into carbodiimides was proposed (Scheme 3). The precursor **1-Y** underwent an acid−base reaction with amine to give the active intermediate **A**. Then a nucleophilic addition of **A** to carbodiimide led to the formation of the guanidinate species **B**. The next step of the cycle was determined by the type of amines. If secondary amines were involved here, **B** would be protonated straightforwardly by another molecule of amine to give the final product **5** with the regeneration of **A**. However, when primary aromatic amines were involved, **B** could rearrange to the unsymmetrical guanidinate **C** as a more stable intermediate. The following

Table 4. Catalytic Addition of Secondary Amines to Carbodiimides[a]



entry	R^1R^2NH	R	cat.	time (h)	product (yield/%)
1		*i*Pr	**1-Y**	21	 (**5a**, 85[b])
2		*i*Pr	**1-Y**	24	 (**5b**, 92[b])
3		*i*Pr	**1-Y**	24	 (**5c**, 89[b])
4		*i*Pr	**1-Y**	1	 (**5d**, 81[c],75[d])
5			**4-Y**		(**5d**, 28[c])
6		*i*Pr	**1-Y**	1	 (**5e**, 65[c], 64[d])
7			**4-Y**		(**5e**, 25[c])
8		*i*Pr	**1-Y**	1	 (**5f**, 91[c], 88[d])
9			**4-Y**		(**5f**, 12[c])
10		Cy	**1-Y**	1	 (**5g**, 78[c], 66[d])
11			**4-Y**		(**5g**, 0[c])

[a]Conditions: amines, 0.51 mmol; carbodiimides, 0.50 mmol; **1-Y**, 0.005 mmol; toluene 0.5 mL. [b]NMR yield. [c]Determined by ^{13}C NMR (inverse gated decoupling). [d]Isolated yield.

steps were similar to that of secondary amines, **C** would react with another molecule of primary amine to give the guanidine **D** with the regeneration of species **A**. Intramolecular 1,3-hydrogen shift of **D** then afforded more stable guanidine **3** owing to the conjugation effect between the aromatic ring and C═N bond.

CONCLUSION

In summary, we report here the first synthesis of rare-earth metal tris(trimethylsilylmethyl) anionic complexes bearing one 1-phenyl-2,3,4,5-tetrapropylcyclopentadienyl ligand, whose structures are fully characterized. These soluble anionic compounds show similar reactivity to the neutral half-sandwich rare-earth metal dialkyl compounds in the stoichiometric reaction with dibenzoylmethane. For **1-Y**, it can catalyze the guanylation process between various amines and carbodiimides in good to excellent yields. For aromatic secondary amines, **1-Y** shows much better catalytic activity in the guanylation than the

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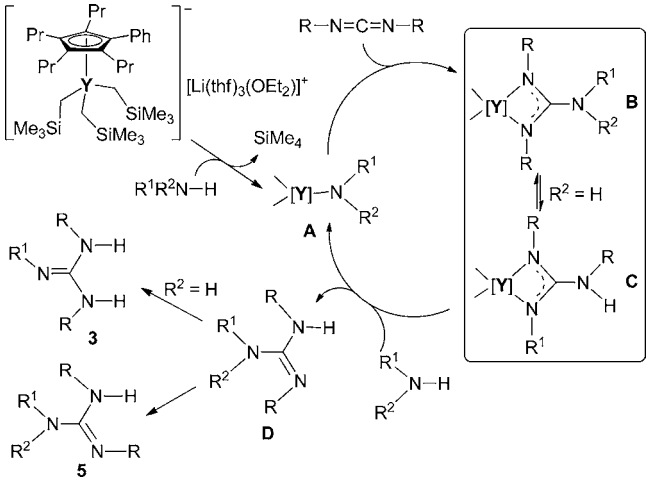
Scheme 3. Possible Mechanism of Catalytic Addition of Amines to Carbodiimides



corresponding well-investigated rare-earth alkyl compound bearing CGC (constrained geometry compound) ligand. These results on the application of half-sandwich rare-earth metal anionic trialkyl complexes show clearly the reactivity of anionic trialkyl precursor is comparable with the corresponding neutral dialkyl complex and, even in some cases, show better catalytic activity than the known catalysts.

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 Vigor (SG 1200/750TS-F) 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 an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. *n*-BuLi was obtained from J&K. Organometallic samples for NMR spectroscopic measurements were prepared in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-500 (FT, 500 MHz for ^{1}H; 125 MHz for ^{13}C), Bruker-400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C), or a JEOL-AL300 spectrometer (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C) at room temperature, unless otherwise noted. Infrared spectra (IR) were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker Apex IV FTMS mass spectrometer using ESI (electrospray ionization).

Preparation of [Cp^{4PrPh}Y(CH$_2$SiMe$_3$)$_3$][Li(thf)$_3$(OEt$_2$)] (1-Y). A solution of Cp^{4PrPh}Li (316 mg, 1.00 mmol) in THF (5 mL), which was prepared by reaction *n*-BuLi with one equivalent of Cp^{4PrPh}H in Et$_2$O/hexane (1:1 V/V), was added to suspension of YCl_3 (195 mg, 1.00 mmol) in THF (15 mL). The reaction mixture was stirred for 12 h at room temperature. Then a solution of Me_3SiCH_2Li (282 mg, 3.00 mmol) in THF (5 mL) was added to the reaction mixture at room temperature. After having been stirred for 0.5 h at room temperature, the solvent was removed under reduced pressure. The residue was extracted with toluene. Evaporation of toluene gave dark oil. The colorless powder of **1-Y** could be given by mixing the dark oil in the mixed solvents of Et$_2$O and hexane at −20 °C (784 mg, 0.82 mmol, 82% yield). Single crystals of **1-Y** suitable for X-ray analysis could be grown from Et$_2$O/hexane for 2 days at −20 °C. ^{1}H NMR (500 MHz, [D$_8$]THF, Me$_4$Si): δ = −1.19 (d, $J_{(Y,H)}$ = 3.0 Hz, 6H; C*H*$_2$SiMe$_3$), −0.13 (s, 27H; Me$_3$Si), 0.76 (t, *J* = 7.4 Hz, 6H; CH$_2$CH$_2$C*H*$_3$), 0.98 (t, *J* = 7.3 Hz, 6H; CH$_2$CH$_2$C*H*$_3$), 1.11 (t, *J* = 7.0 Hz, 6H; O(CH$_2$C*H*$_3$)$_2$), 1.26−1.42 (m, 4H; CH$_2$C*H*$_2$CH$_3$), 1.49−1.57 (m, 4H; CH$_2$C*H*$_2$CH$_3$), 1.75−1.79 (m, 12H; β-CH$_2$, THF), 2.37−2.47 (m, 4H; C*H*$_2$CH$_2$CH$_3$), 2.49−2.56 (m, 4H; C*H*$_2$CH$_2$CH$_3$), 3.38 (q, *J* = 7.0 Hz, 4H; O(C*H*$_2$CH$_3$)$_2$), 3.60−3.63 (m, 12H; α-CH$_2$, THF), 6.97−7.00 (m, 1H; *p*-C$_6$H$_5$), 7.13−7.16 (m, 2H; *m*-C$_6$H$_5$), 7.31−7.33 (m, 2H; *o*-C$_6$H$_5$) ppm; ^{13}C NMR (75 MHz, [D$_8$]THF, Me$_4$Si): δ = 5.3, 15.2, 15.5, 26.4, 26.9, 27.7, 31.0, 31.1, 38.1, 68.3, 119.3, 120.1, 122.7, 124.5, 127.7, 132.1, 141.7 ppm.

[Cp^{4PrPh}Ho(CH$_2$SiMe$_3$)$_3$][Li(thf)$_4$] (1-Ho). Starting from $HoCl_3$ (136 mg, 0.50 mmol), complex **1-Ho** was obtained as an orange powder (398 mg, 0.38 mmol, 77% yield) in a manner analogous to that described for the preparation of **1-Y**. Single crystals of **1-Ho** suitable for X-ray analysis could be grown from Et$_2$O/hexane for 2 days at −20 °C.

[Cp^{4PrPh}Er(CH$_2$SiMe$_3$)$_3$][Li(thf)$_3$(OEt$_2$)] (1-Er). Starting from $ErCl_3$ (137 mg, 0.50 mmol), complex **1-Er** was obtained as a pink powder (423 mg, 0.41 mmol, 82% yield) in a manner analogous to that described for the preparation of **1-Y**. Single crystals of **1-Er** suitable for X-ray analysis could be grown from Et$_2$O/hexane for 2 days at −20 °C. When **1-Er** was dried up under reduced pressure, the solvents coordinated to Li center were released to give pink powder. Anal. Calcd for $C_{35}H_{66}ErLiSi_3$: C, 56.40; H, 8.93; Found: C, 56.54; H, 8.91.

[Cp^{4PrPh}Tm(CH$_2$SiMe$_3$)$_3$][Li(thf)$_3$(OEt$_2$)] (1-Tm). Starting from $TmCl_3$ (138 mg, 0.50 mmol), complex **1-Tm** was obtained as a colorless powder (451 mg, 0.44 mmol, 87% yield) in a manner analogous to that described for the preparation of **1-Y**. Single crystals of **1-Tm** suitable for X-ray analysis could be grown from Et$_2$O/hexane for 2 days at −20 °C.

[Cp^{4PrPh}Lu(CH$_2$SiMe$_3$)$_3$][Li(thf)$_3$(OEt$_2$)] (1-Lu). Starting from $LuCl_3$ (281 mg, 1.00 mmol), complex **1-Lu** was obtained as a colorless powder (768 mg, 0.74 mmol, 74% yield) in a manner analogous to that described for the preparation of **1-Y**. Single crystals of **1-Lu** suitable for X-ray analysis could be grown from Et$_2$O/hexane for 2 days at −20 °C. ^{1}H NMR (500 MHz, [D$_8$]THF, Me$_4$Si): δ = −1.29 (s, 6H; C*H*$_2$SiMe$_3$), −0.05 (s, 27H; Me$_3$Si), 0.83 (t, *J* = 7.3 Hz, 6H; CH$_2$CH$_2$C*H*$_3$), 1.05 (t, *J* = 7.3 Hz, 6H; CH$_2$CH$_2$C*H*$_3$), 1.18 (t, *J* = 7.0 Hz, 6H; O(CH$_2$C*H*$_3$)$_2$), 1.32−1.47 (m, 4H; CH$_2$C*H*$_2$CH$_3$), 1.55−1.62 (m, 4H; CH$_2$C*H*$_2$CH$_3$), 1.82−1.87 (m, 12H; β-CH$_2$, THF), 2.42−2.63 (m, 8H; C*H*$_2$CH$_2$CH$_3$), 3.45 (q, *J* = 7.0 Hz, 4H; O(C*H*$_2$CH$_3$)$_2$), 3.67−3.70 (m, 12H; α-CH$_2$, THF), 7.05 (t, *J* = 7.3 Hz, 1H; *p*-C$_6$H$_5$), 7.20 (t, *J* = 7.5 Hz, 2H; *m*-C$_6$H$_5$), 7.39 (d, *J* = 7.8 Hz; 2H; *o*-C$_6$H$_5$) ppm; ^{13}C NMR (75 MHz, [D$_8$]THF, Me$_4$Si): δ = 5.3, 15.2, 15.5, 26.4, 26.9, 27.7, 31.0, 31.1, 38.1, 68.3, 119.3, 120.1, 122.7, 124.5, 127.7, 132.1, 141.7 ppm.

[Cp^{4PrPh}Lu(DBM)$_2$(thf)] (2-Lu). A solution of dibenzoylmethane (149 mg, 0.663 mmol) was added to the solution of **1-Lu** (230 mg, 0.221 mmol) in benzene (5 mL). The reaction mixture was stirred at room temperature for 1 h. After removal of the solvent under reduced pressure, the residue was extracted with hexane, and the insoluble light yellow powder was removed. After 24 h, **2-Lu** was given as orange crystals (202 mg, 0.201 mmol, 91% yield). Single crystals of **2-Lu** suitable for X-ray analysis could be grown from benzene/hexane for 2 days at room temperature. ^{1}H NMR (500 MHz, [D$_8$]THF, Me$_4$Si): δ = 0.61 (t, *J* = 7.3 Hz, 6H; CH$_2$CH$_2$C*H*$_3$), 0.89 (t, *J* = 7.3 Hz, 6H; CH$_2$CH$_2$C*H*$_3$), 1.26−1.34 (m, 4H; CH$_2$C*H*$_2$CH$_3$), 1.44−1.60 (m, 4H; CH$_2$C*H*$_2$CH$_3$), 1.72−1.78 (m, 4H; β-CH$_2$, THF), 2.27−2.61 (m, 8H; C*H*$_2$CH$_2$CH$_3$), 3.57−3.62 (m, 4H; α-CH$_2$, THF), 6.85 (s, 2H; C(O)C*H*C(O)), 7.16 (t, *J* = 7.4 Hz, 1H; *p*-C$_6$H$_5$, Cp), 7.32 (t, *J* = 7.6 Hz, 2H; *m*-C$_6$H$_5$, Cp), 7.38 (t, *J* = 7.3 Hz, 8H; *m*-C$_6$H$_5$, DBM), 7.43 (t, *J* = 7.3 Hz, 4H; *p*-C$_6$H$_5$, DBM), 7.73 (d, *J* = 7.5 Hz, 2H; *o*-C$_6$H$_5$, Cp), 7.98 (d, *J* = 7.3 Hz, 8H; *o*-C$_6$H$_5$, DBM) ppm; ^{13}C NMR (125 MHz, [D$_8$]THF, Me$_4$Si): δ = 15.0, 15.4, 26.1, 26.4, 26.9, 29.5, 30.7, 68.2, 95.3, 122.9, 130.10, 130.11, 124.8, 128.2, 128.3, 129.0, 131.5, 131.8, 140.9, 141.0, 185.3 ppm.

Typical Procedures for the Catalytic Reaction between Primary Aromatic Amines and Aarbodiimides. *i). NMR Tube Reaction.* In the glovebox, a J. Young valve NMR tube was charged with **1-Y** (4.8 mg, 0.005 mmol), C$_6$D$_6$ (0.5 mL), aniline (48 mg, 0.51 mmol), and *N*,*N*′-diisopropylcarbodiimide (63 mg, 0.50 mmol). The

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Table 5. Crystallographic Data and Structure Refinement Details for 1-Ln (Ln = Y, Ho, Er, Tm, and Lu) and 2-Lu

	1-Y	1-Ho	1-Er	1-Tm	1-Lu	2-Lu
formula	$C_{51}H_{100}YLiO_4Si_3$	$C_{51}H_{98}HoLiO_4Si_3$	$C_{51}H_{100}ErLiO_4Si_3$	$C_{51}H_{100}TmLiO_4Si_3$	$C_{51}H_{100}LuLiO_4Si_3$	$C_{57}H_{63}LuO_5$
M_w	957.43	1031.43	1035.78	1037.45	1043.49	1003.04
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
space group	P2(1)/n	Pna2(1)	P2(1)/n	P2(1)/n	P2(1)/n	P2(1)/c
a (Å)	13.149(3)	24.927(5)	13.102(3)	13.444(3)	13.362(3)	13.627(3)
b (Å)	22.409(5)	12.716(3)	22.346(5)	24.242(5)	21.979(5)	16.234(3)
c (Å)	20.587(4)	19.096(4)	20.541(4)	18.393(4)	20.520(5)	23.257(5)
β (°)	100.99(3)	90	101.08(3)	100.10(3)	99.219(3)	105.18(3)
V (Å^3)	5955(2)	6053(2)	5902(2)	5902(2)	5949(2)	4965.4(17)
Z	4	4	4	4	4	4
ρ_{calcd} (g cm^{-3})	1.068	1.132	1.166	1.168	1.165	1.342
μ (mm^{-1})	1.076	1.402	1.519	1.600	1.756	2.035
F(000)	2088	2192	2204	2208	2216	2064
θ range (°)	1.82 to 25.00	1.80 to 27.50	1.83 to 27.48	1.40 to 27.48	1.80 to 25.01	1.55 to 27.48
no of reflns collected	31742	40718	25947	25922	39299	11360
no of indep reflns	10168 [R(int) = 0.0828]	13276 [R(int) = 0.1463]	13395 [R(int) = 0.0612]	13482 [R(int) = 0.0580]	10379 [R(int) = 0.0570]	11360 [R(int) = 0.0955]
no of variables	717	507	638	557	469	573
GOF	1.155	0.871	1.144	1.004	1.180	1.001
R [$I > 2\sigma$ (I)]	0.0896	0.0691	0.0817	0.0428	0.0778	0.0406
Rw	0.1417	0.1579	0.1678	0.1024	0.1802	0.0918

tube was taken out of the glovebox and then heated at 80 °C in an oil bath for 1 h. Formation of **3** was monitored by ^{1}H NMR spectroscopy. The NMR data of **3a-e** and **3g-o** were consistent with those reported.[4b,5c,g,6l,j]

ii). Preparative Scale Reaction. In the glovebox, the mixture of benzene solution (1 mL) of **1-Y** (4.8 mg, 0.005 mmol) and benzene solution (2 mL) of 2,6-difluoroaniline (65 mg, 0.505 mmol) was added to a Schlenk tube. Then *N*,*N*′-diisopropylcarbodiimide (63 mg, 0.5 mmol) was added to the above reaction mixture. The Schlenk tube was taken outside the glovebox, and the mixture was stirred at 80 °C for 1 h. After the solvent and *N*,*N*′-diisopropylcarbodiimide were removed under vacuum, the white solid was extracted with Et_2O and then filtered to give colorless solution. After removal of Et_2O under reduced pressure, colorless solid (115 mg, 0.45 mmol) was given in 90% yield.

2-(2,6-Difluorophenyl)-1,3-diisopropylguanidine (3f). Colorless solid, 90% isolated yield. ^{1}H NMR (300 MHz, C_6D_6, Me_4Si): δ = 0.93 (d, J = 6.3 Hz, 12H; $CH(CH_3)_2$), 3.58 (br, 2H; NH), 3.65−3.73 (m, 2H; $CH(CH_3)_2$), 6.45−6.53 (m, 1H; *p*-C_6H_3), 6.71−6.77 (m, 2H; *m*-C_6H_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, Me_4Si): δ = 23.2, 43.4, 111.5 (dd, $J_{(C,CF)}$, $_{(C,CCCF)}$ = 17.0, 7.4 Hz), 120.8 (t, $J_{(C,CCF)}$ = 9.6 Hz), 127.0 (t, $J_{(C,CF)}$ = 16.6 Hz), 151.3, 156.9 (dd, $J_{(C,\ F)}$, $_{(C,CCF)}$ = 243.8, 6.8 Hz) ppm. IR (film): ν =1617 (C═N) cm^{-1}; HRMS: m/z calcd for $C_{13}H_{20}F_2N_3$: 256.1620 [M + H]$^+$; found: 256.1613.

Typical Procedures for the Catalytic Reaction between Secondary Amines and Carbodiimides. *i). NMR Tube Reaction.* In the glovebox, a J. Young valve NMR tube was charged with **1-Y** (4.8 mg, 0.005 mmol), [D_8]toluene (0.5 mL), tetrahydropyrrole (36 mg, 0.51 mmol), and *N*,*N*′-diisopropylcarbodiimide (63 mg, 0.50 mmol). The tube was taken out of the glovebox and then heated at 130 °C in an oil bath for 1 h. Formation of **3** was monitored by ^{1}H NMR and ^{13}C NMR spectroscopy. The NMR data of **5a-c** were consistent with those reported.[6j]

ii). Preparative Scale Reaction. In the glovebox, a mixture of toluene solution (2 mL) of **1-Y** (19.1 mg, 0.02 mmol) and toluene solution (4 mL) of *N*-methylaniline (217 mg, 2.02 mmol) was added to a Schlenk tube. Then *N*,*N*′-diisopropylcarbodiimide (252 mg, 2.00 mmol) was added to the above reaction mixture. The Schlenk tube was taken outside the glovebox, and the mixture was stirred at 130 °C for 1 h. After the solvent and *N*,*N*′-diisopropylcarbodiimide were removed under vacuum, the light yellow residue was purified by silica-gel column chromatography using CH_2Cl_2 and EtOAc as eluent to give a colorless oil (350 mg, 1.50 mmol) in 75% yield.

Broad peaks in ^{13}C NMR spectrum in **5d−g** are observed, and the integration of broad peaks is determined using inverse gated decoupling technique.

2,3-Diisopropyl-1-methyl-1-phenylguanidine (5d). Colorless oil, 75% isolated yield. ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.08 (br, 12H; $CH(CH_3)_2$), 2.70 (s, 3H; NCH_3), 3.02 (br, 1H; NH), 3.78 (br, 2H; $CH(CH_3)_2$), 6.71−6.81 (m, 3H; C_6H_5), 7.18−7.20 (m, 2H; C_6H_5) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 24.0 (br, 4C), 36.2, 44.0 (br), 47.3 (br), 112.7, 118.3, 129.4, 146.6, 148.3 ppm. IR (film): ν = 1650 (C═N) cm^{-1}; HRMS: m/z calcd for $C_{14}H_{24}N_3$: 234.1965 [M + H]$^+$; found: 234.1964.

2,3-Diisopropyl-1-methyl-1-(p-tolyl)guanidine (5e). Colorless oil, 64% yield. ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.10 (br, 12H; $CH(CH_3)_2$), 2.17 (s, 3H; *p*-C_6H_4−CH_3), 2.72 (s, 3H; NCH_3), 3.21 (br, 1H; NH), 3.84 (br, 2H; $CH(CH_3)_2$), 6.69 (br, 2H; C_6H_4), 7.01 (d, J = 7.3 Hz, 2H; C_6H_4) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 20.5, 23.9 (br, 4C), 36.3, 44.4 (br), 47.4 (br), 113.0, 127.2, 130.0, 144.6, 148.8 ppm. IR (film): ν =1649 (C═N) cm^{-1}; HRMS: m/z calcd for $C_{15}H_{26}N_3$: 248.2121 [M + H]$^+$; found: 248.2119.

2,3-Diisopropyl-1,1-diphenylguanidine (5f). Colorless oil, 88% isolated yield. ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 1.02 (br, 12H; $CH(CH_3)_2$), 3.31 (br, 1H; NH), 4.01 (br, 2H; $CH(CH_3)_2$), 6.84 (t, J = 7.3 Hz, 2H; *p*-C_6H_5), 7.04−7.12 (m, 4H; *m*-C_6H_5), 7.15−7.21 (m, 4H; *o*-C_6H_5) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 22.7 (br), 24.5 (br), 43.7 (br), 47.8 (br), 121.1, 123.7, 129.5, 145.0, 146.0 ppm. IR (film): ν = 1654 (C═N) cm^{-1}; HRMS: m/z calcd for $C_{19}H_{26}N_3$: 296.2121 [M + H]$^+$; found: 296.2121.

2,3-Dicyclohexyl-1,1-diphenylguanidine (5g). Colorless oil, 66% isolated yield. ^{1}H NMR (400 MHz, C_6D_6, Me_4Si): δ = 0.84−1.95 (m, 20H; CH_2, Cy), 3.42 (br, 1H; NH), 3.63−3.84 (m, 2H; CH, Cy), 6.84 (t, J = 7.3 Hz, 2H; *p*-C_6H_5), 7.10 (t, J = 7.9 Hz, 4H; *m*-C_6H_5), 7.21 (d, J = 7.7 Hz, 4H; *o*-C_6H_5) ppm; ^{13}C NMR (100 MHz, C_6D_6, Me_4Si): δ = 25.3 (4C), 26.3 (2C), 32.9, 35.1 (br), 50.6 (br), 56.5 (br), 121.2, 122.7, 129.5, 145.1, 146.0 ppm. IR (film): ν = 1653 (C═N) cm^{-1}; HRMS: m/z calcd for $C_{25}H_{34}N_3$: 376.2747 [M + H]$^+$; found: 376.2750.

X-ray Crystallographic Studies. The single crystals of **1-Y**, **1-Ho**, **1-Er**, **1-Tm**, **1-Lu**, and **2-Lu** suitable for X-ray analysis were grown as shown in the Experimental Section. The crystals of **1-Y**, **1-Ho**, **1-Er**, **1-Tm**, **1-Lu**, and **2-Lu** were manipulated under a nitrogen atmosphere

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and were sealed in a thin-walled glass capillary. Data collections for **1-Y**, **1-Lu**, and **1-Er** was performed at −100 °C on a RIGAKU CCD SATURN 724 diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). **1-Ho**, **1-Tm**, and **2-Lu** were performed at −150 °C on a Rigaku RAXIS RAPID IP diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the CrystalClear (Rigaku Inc., 2007) for **1-Y**, **1-Lu**, and **1-Er** or Rapid-AUTO (Rigaku 2000) program package for **1-Ho**, **1-Tm**, and **2-Lu**. The raw frame data were processed using Crystal Structure (Rigaku/MSC 2000) for **1-Ho**, **1-Tm**, and **2-Lu** or CrystalClear (Rigaku Inc., 2007) for **1-Y**, **1-Lu**, and **1-Er** to yield the reflection data file. The structures of **1-Y**, **1-Ho**, **1-Er**, **1-Tm**, **1-Lu**, and **2-Lu** were solved by use of the SHELXTL program.[11] Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the 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 **1-Y**, **1-Ho**, **1-Er**, **1-Tm**, **1-Lu**, and **2-Lu** are summarized in Table 5. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-886169 (**1-Y**), CCDC-886166 (**1-Ho**), CCDC-886165 (**1-Er**), CCDC-886168 (**1-Tm**), CCDC-886167 (**1-Lu**), and CCDC-886170 (**2-Lu**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Supporting Information

Additional NMR data, copies of ^{1}H NMR and ^{13}C NMR spectra of all new compounds, crystallographic tables, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wx_zhang@pku.edu.cn (W.-X.Z.), zfxi@pku.edu.cn (Z.X.).

Notes

The authors declare no competing financial interest.

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