Rare earth metal bis(trimethylsilyl)amido complexes bearing pyrrolyl-methylamide ligand. Synthesis, structure, and catalytic activity towards guanylation of amines†

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The *N*-arylaminomethyl substituted pyrrolyl ligand 2-[(2,4,6-$Me_3C_6H_2$)$NHCH_2$](C_4H_3NH) (**1**) was synthesized by reduction of 2-[(2,4,6-$Me_3C_6H_2$)N═CH](C_4H_3NH) using $NaBH_4$. Treatment of $[(Me_3Si)_2N]_3Ln(\mu\text{-Cl})Li(THF)_3$ with 1 equiv. of **1** in reflux toluene for 24 h, afforded the corresponding trivalent rare earth metal amides with formula $\{(\mu\text{-}\eta^5:\eta^1):\eta^1\text{-}2\text{-}[(2,4,6\text{-}Me_3C_6H_2)NCH_2]\text{-}C_4H_3N]LnN(SiMe_3)_2\}_2$ (Ln = Y(**2**), Nd(**3**), Sm(**4**), Dy(**5**), Er(**6**)). All compounds were fully characterised by spectroscopic methods and elemental analyses. The structures of complexes **2**, **4** and **6** were determined by single-crystal X-ray analyses. X-Ray analyses discovered that two rare-earth metal ions were bridged by dianion ligand with the pyrrolyl ring which coordinated to one rare earth metal in an η^5 mode, the tethered nitrogen anion and nitrogen atom of the pyrrolyl ring coordinated to another rare earth metal in η^1 modes forming the centrosymmetric dinuclear structures. The rare earth metal complexes as catalysts for the guanylation of aromatic amines were studied. Results showed all rare earth metal complexes exhibited a high catalytic activity on the guanylation of aromatic amines.

Introduction

Research and development of highly active, well-defined rare earth metallocene catalysts have stimulated the progress of organometallic chemistry, because of their well-known versatility in meeting the electronic and steric requirements to stabilize a wide variety of complexes.[1,2] In view of this progress, much work has been dedicated to finding new ligand systems similar to the Cp type ligands. Notably, nitrogen-based polydentate ligands such as the pyrrolyl derivatives are anticipated to be alternatives of cyclopentadienyl-based ligands in organolanthanide chemistry owing to their π-ligation ability.[3] On the other hand, they also offer the possibility of forming σ-bonds through the ring nitrogen donor atom, providing a variety of bonding modes necessary to accommodate diversified structures.

Group 4 transition metal complexes containing pyrrolyl-functionalized ligands have been greatly developed, which have exhibited high activities for olefin polymerization.[4] Gambarotta and co-workers have also demonstrated that the dipyrrolide ligand or macrocyclic tetrapyrrole polyanions could not only stabilize the divalent lanthanide complexes but also increase the reactivity of the metal centre such as reduction of N_2 and reversible fixation of ethylene.[3g,5] In contrast, the trivalent lanthanide complexes supported by dipyrrolide or porphyrinogen ligands usually aggregated to produce unexpected macrocyclic structures.[3b,6] Recently, Arnold and co-workers reported that the bis(pyrrolyimino)samarium alkyl complexes showed excellent stereocontrol of the polymerization of methyl methacrylate.[7] The rare earth metal complexes with the pyrrolide ligand have also been demonstrated to have high catalytic activities on the ROP of ε-caprolactone.[8] Cui and co-workers reported that the rare earth metal alkyl complexes bearing an η^5 or η^1-coordinated pyrrolide moiety exhibited high activities toward polymerisation of isoprene and lactide.[9] Hou *et al.* also reported that the coordination mode of the pyrrolyl ligands in the pyrrolyl rare earth metal aminobenzyl complexes had significant influence on the polymerisation of styrene.[10] The rare earth metal aminobenzyl complexes with η^5-coordinated pyrrolide showed a high catalytic activity and stereocontrol for the polymerisation of styrene, however, η^1-coordinated pyrrolyl rare earth metal aminobenzyl complexes had no catalytic activity. Very recently, Cui and co-workers synthesized the *ansa*-ytterbium(II) amide bearing $Me_2Si(Me_4C_5)(NC_4H_4)$ ligand, in which the Yb atom is η^5-coordinated to both the cyclopentadienyl ring and pyrrolyl ring, indicating pyrrolyl ligands to be alternatives of cyclopentadienyl ligands.[11] Though pyrrolyl ligands can bind to the metal atoms in either an η^1 or an η^5 fashion, only a few examples exist in which the pyrrolyl units bind to metal atoms in both ways simultaneously.[12] All the previous works on lanthanide chemistry incorporating pyrrolyl ligands were concentrated on the divalent complexes or trivalent alkyl complexes, the synthesis and catalytic activity of the rare-earth metal amides incorporating pyrrolyl units remains to be explored.

The catalytic addition of the N–H bond of the amines to carbodiimides (RN═C═NR) provides a direct and atom-efficient route to the multi-substituted guanidines, which are the important building blocks in many biologically relevant compounds[13] and also widely used as ligands for the construction

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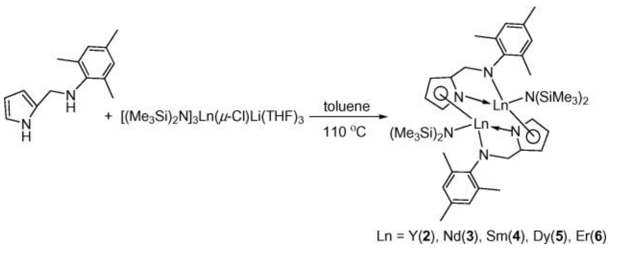
of a variety of organometallic catalysts containing early transition metals and lanthanides.[14] Only the primary aliphatic amines and cyclic secondary aliphatic amines can undergo direct guanylation with carbodiimides to yield the corresponding *N*,*N′*,*N″*trialkylguanidines under forcing conditions.[15] Recently, catalytic addition of N–H bond to carbodiimides has been developed using Ti[16] and V[17] imido complexes, half-sandwich yttrium alkyl,[18] lithium amide,[19] aluminium alkyl compound,[20] and titanacarborane amide complexes.[21]

In our previous study, we have demonstrated that the lanthanide amido complexes showed high catalytic activities for the guanylation of the aromatic and secondary amines.[22] As our continuous interest in developing lanthanide amido complexes as catalysts for the atom-economical process of the addition of the E–H bonds to the multiple bonds, we herein report that synthesis and structure of substituted pyrrolyl lanthanide amides with η^1 and η^5 bonding modes, and their catalytic activity towards guanylation of amines.

Results and discussion

Synthesis and characterisation of the rare earth metal amides with pyrrolyl–methylamide ligand

The reaction of $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$ with 1 equiv. of 2-$[(2,4,6\text{-}Me_3C_6H_2)NHCH_2](C_4H_3NH)$ (**1**) in toluene at 100 °C afforded the dinuclear rare earth metal amido complexes $\{(\mu\text{-}\eta^5{:}\eta^1){:}\eta^1\text{-}2\text{-}[(2,4,6\text{-}Me_3C_6H_2)NCH_2]C_4H_3N]LnN(SiMe_3)_2\}_2$ (Ln = Y (**2**), Nd (**3**), Sm (**4**), Dy(**5**), Er(**6**)] (Scheme 1). The complexes are sensitive to air and moisture, they have good solubility in either polar solvents or non-polar solvents. All complexes were fully characterised by IR and elemental analyses. Complex **2** was also characterised by ^1H NMR spectra analyses. ^1H NMR analyses of complex **2** displayed that the pyrrolyl protons resonated at 6.23, 6.52, and 7.62 ppm comparable with the pyrrolyl protons of $\{[2\text{-}(2,6\text{-}{}^iPr_2C_6H_3NC(H)(CH_2SiMe_3))C_4H_3N]Y(CH_2SiMe_3)(THF)\}_2$,[9a] suggesting that the pyrrolyl moiety coordinates to the yttrium atom in an η^5-fashion. The ^1H NMR spectra of complexes **3**–**6** were not informative due to lack of locking signal for the paramagnetic property of the complexes. Therefore, the structures of the complexes **2**, **4**, and **6** were determined by single-crystal X-ray analyses.



Scheme 1 Synthesis of the rare earth metal amides with pyrrolyl–methylamide ligand

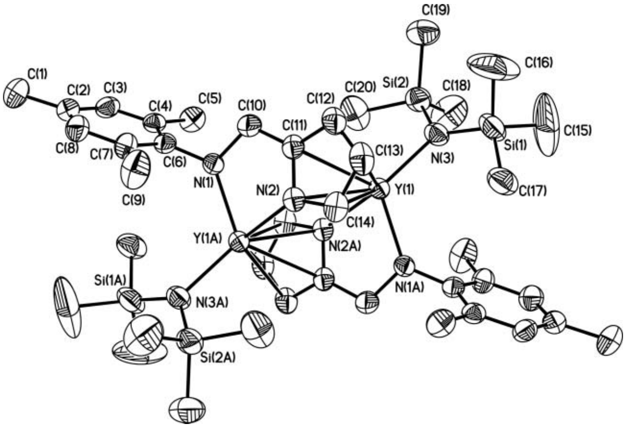


Fig. 1 Representative molecular structure of $\{(\mu\text{-}\eta^5{:}\eta^1){:}\eta^1\text{-}2\text{-}[(2,4,6\text{-}Me_3C_6H_2)NCH_2]C_4H_3N]LnN(SiMe_3)_2\}_2$ (**2**). Hydrogen atoms are omitted for clarity. The symmetry operation is $x + 1, -y, z + 1$.

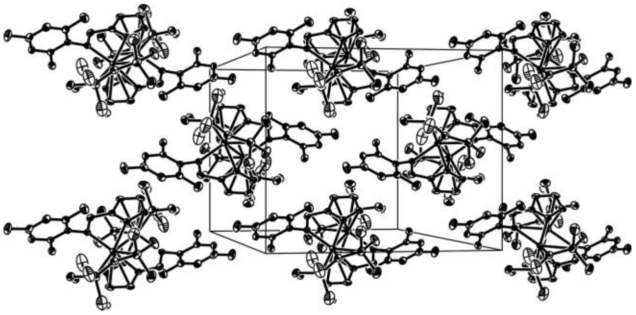


Fig. 2 Packing arrangement in the unit cell of representative $\{(\mu\text{-}\eta^5{:}\eta^1){:}\eta^1\text{-}2\text{-}[(2,4,6\text{-}Me_3C_6H_2)NCH_2]C_4H_3N]YN(SiMe_3)_2\}_2$ (**2**).

X-Ray analyses revealed that complexes **2**, **4** and **6** were isostructural with a centrosymmetric dinuclear structure. Representative structure diagrams are shown in Fig. 1 and Fig. 2. Each of the rare-earth metals adopted a distorted tetrahedral geometry, and the two metals in each complex were bridged by the dianion ligand with the pyrrolyl ring coordinated to one rare earth metal in an η^5 mode, the tethered nitrogen anion and nitrogen atom of the pyrrolyl ring coordinated to another rare earth metal in an η^1 mode. The bridged bonding mode of this type of pyrrolyl ligand is different to that of the so-called contained geometry ligand of the cyclopentadienyl type ligand in which the dianion ligand bonds to one metal.[18,23] To the best of our knowledge, these complexes represent the first example of rare earth metal amides incorporating the pyrrolyl ring coordinated to the rare-earth metal center in an η^5 and η^1-coordination mode. The selected bond lengths and angles are listed in Table 1. The bond distances between lanthanide ions and the pyrrolyl carbon in **2**, Y–η^5-C(pyr ring), ranging from 2.644(4) to 2.781(4) Å, are comparable to those in **6** (2.638(5) to 2.763(5) Å), $[2\text{-}(2\text{-}Ph_2PC_6H_3NC(H)(CH_2SiMe_3)C_4H_3N]_2Y_2(CH_2SiMe_3)_2(THF)$ (2.690(5) to 2.738(6) Å),[9a] and $[(2\text{-}(Me_2NCH_2)C_4H_3N)\text{-}Y(CH_2SiMe_3)_2]_2$ (2.725(3) to 2.743(3) Å).[9b] The Sm-η^5-C(pyr ring) in complex **4**, ranging from 2.710(4) to 2.852(4) Å, are slightly longer than those in **2** and **6**, indicating effects of lanthanide ionic radii. It is also noteworthy that the Ln-η^5-C(pyr ring) bond lengths are close to Ln-η^5-C(Cp ring), suggesting that the pyrrolyl ring can be an ideal alternative to the cyclopentadienyl ancillary ligand. The bond distance of Y(1)–N(2) (2.700(3) Å) and Y(1)–N(2A) (2.392(3) Å) in complex **2** is much longer than that of Y(1)–N(1A) (2.186(3) Å), well consistent with the $\eta^5/\eta^1{:}\eta^1$-coordination mode of the pyrrolide ligand, which is comparable to the Y–N bond distances in an $\eta^5/\eta^1{:}\eta^1$-pyrrolyl yttrium alkyl complex $[(2\text{-}(Me_2NCH_2)C_4H_3N)Y(CH_2SiMe_3)_2]_2$ (Y–N(1),

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

	2[a]	**4**[b]	**6**[c]
Ln(1)–N(1A)	2.186(3)	2.229(3)	2.164(3)
Ln(1)–N(2)	2.700(3)	2.762(3)	2.688(4)
Ln(1)–N(3)	2.204(3)	2.265(3)	2.189(4)
Ln(1)–N(2A)	2.392(3)	2.465(3)	2.368(3)
Ln(1)–C(11)	2.781(4)	2.847(3)	2.763(4)
Ln(1)–C(12)	2.777(4)	2.852(4)	2.756(5)
Ln(1)–C(13)	2.712(4)	2.776(4)	2.684(5)
Ln(1)–C(14)	2.644(4)	2.710(4)	2.638(5)
N(1A)–Ln(1)–N(3)	113.69(13)	115.56(11)	112.43(14)
N(1A)–Ln(1)–N(2A)	73.62(11)	71.35(10)	74.42(12)
N(3)–Ln(1)–N(2A)	128.82(12)	128.56(11)	127.72(15)

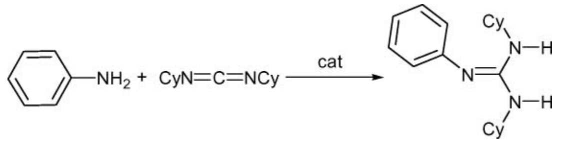
[a] The symmetry operation is $x + 1, -y, z + 1$. [b] The symmetry operation is $x + 2, -y, z + 1$. [c] The symmetry operation is $x + 1, -y, z$.

2.735(2) Å; Y–N(2A), 2.588(3) Å; and Y–N(1A), 2.446(2) Å).[9b] The bond distances in complex **4** (Sm(1)–N(2), 2.762(3) Å; Sm(1)–N(2A), 2.465(3) Å; and Sm(1)–N(1A), 2.229(3) Å) are slightly longer than those found in complex **6** (Er(1)–N(2), 2.688(4) Å; Er(1)–N(2A), 2.368(4) Å; and Er(1)–N(1A), 2.164(4) Å). The bond distances of Ln–N(3) in complex **2** (Y(1)–N(3), 2.204(3) Å), complex **4** (Sm(1)–N(3), 2.265(3) Å), and complex **6** (Er(1)–N(3), 2.189(3) Å), are compared with those in (EBI)YN$(SiMe_3)_2$ (Y(1)–N(1), 2.243(4) Å)[22a] and (EBI)SmN$(SiMe_3)_2$ (Sm(1)–N(1), 2.264(4) Å).[22a] The observed variations of bond distances may result from the combination effects of steric interactions, electronic effects and ionic radii difference.

Catalytic addition of the aromatic amines to carbodiimides

Although catalytic addition of the N–H bond to carbodiimides have been studied utilizing catalyst lanthanide alkyls, amides and other metal catalysts.[16–22] The lanthanide complexes with pyrrolyl ligands as catalysts for the corresponding reaction have not been reported. Thus, the above complexes as catalysts for the guanylation reaction were studied. The catalytic addition of aniline to *N*,*N*-dicyclohexylcarbodiimide were examined using the above rare-earth metal amides with substituted pyrrolyl ligands as catalysts, and the results are listed in Table 2. The reaction can work well producing the guanylation product by carrying out the reaction in THF at 60 °C for 6 h in the presence of 1 to 3 mol% of dinuclear complex **4** as the catalyst (Table 2, entries 1–3). The yield of the product decreased to 39% in the presence of 0.5 mol% catalyst **4** (Table 2, entry 4). Good to excellent yields of the products can also be isolated by carrying out the reaction in *n*-hexane, toluene and Et_2O in the presence of 2 mol% catalyst **4** (Table 2, entries 5–7), indicating the solvent compatibility of the catalysts. The catalytic activities of the other complexes **2**, **3**, **5**, **6** as catalysts for the guanylation reaction were surveyed (Table 2, entries 8–11). All complexes displayed high activities, indicating that the rare-earth metals have little influence on the catalytic activity of the catalysts. These results were comparable with those obtained by using the lanthanide amides (EBI)LnN$(TMS)_2$[22a] and $[(Me_3Si)_2N]_3Ln(\mu\text{-}Cl)Li(THF)_3$[22b] as catalysts. Therefore, complex **4** was selected as the catalyst for the following guanylation of the aromatic amines.

Table 2 Catalytic addition of an aniline to *N*,*N*-dicyclohexylcarbodiimide[a]



Entry	Catalyst	Catalyst loading (mol%)	Solvent	Yield (%)[b]
1	**4**	3	THF	95
2	**4**	2	THF	94
3	**4**	1	THF	87
4	**4**	0.5	THF	39
5	**4**	2	*n*-Hexane	89
6	**4**	2	Toluene	92
7	**4**	2	Et_2O	90
8	**2**	2	THF	94
9	**3**	2	THF	92
10	**5**	2	THF	92
11	**6**	2	THF	93

[a] Conditions: aniline, 2.00 mmol; *N*,*N*-dicyclohexylcarbodiimide, 2.00 mmol; time, 12 h; reaction temperature, 60 °C. [b] Isolated yield.

Under the optimized reactions, complex **4** as catalyst for the guanylation of selected aromatic amines (including amines having electron-donating or electron-withdrawing groups) and heterocyclic aromatic amines were studied, the results were listed in Table 3. From Table 3, we can also see that good to excellent yields of the products could be obtained by using the aromatic amines either having electron-donating group such as CH_3O– (Table 3, entries 3 and 4) or having strong electron-withdrawing group such as O_2N– (Table 3, entries 5 and 6). In case of the heteroaromatic amines, excellent yields of the products could also be isolated (Table 3, entries 9–12) in 12 h.

Conclusions

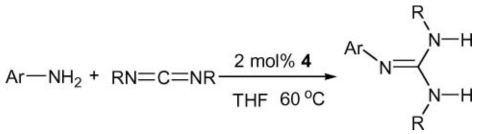
In summary, a series of dinuclear rare earth metal amido complexes with substituted pyrroly ligand $\{(\mu\text{-}\eta^5{:}\eta^1){:}\eta^1\text{-}2\text{-}[(2,4,6\text{-}Me_3C_6H_2)NCH_2]C_4H_3N]LnN(SiMe_3)_2\}_2$ [Ln = Y (**2**), Nd (**3**), Sm (**4**), Dy(**5**), Er(**6**)] were synthesized and characterised. The X-ray diffraction analyses of the complexes indicated that the complexes were centrosymmetric dinuclear structure and pyrrolyl ligands coordinated to one rare earth metal in an η^5 mode, the tethered nitrogen anion and nitrogen atom of the pyrrolyl ring coordinated to another rare earth metal in η^1 modes. This work also represents rare examples of the rare-earth metal amides supported by pyrrolide species in η^5- and η^1-coordination mode. All complexes displayed high catalytic activities for the guanylation of aryl amines, which represent the first example of the lanthanide amido complexes bearing pyrrolyl ligands as catalysts for the guanylation reaction. The results indicated that the catalysts have good compatibility for guanylation of various aryl amines in different solvents.

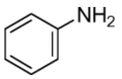
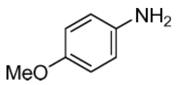
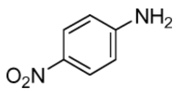
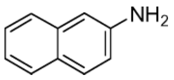
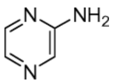
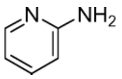
Experiments

General remarks

All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and oxygen-free

Table 3 Catalytic addition of aromatic amines to carbodiimides[a]



Entry	R	Ar–NH$_2$	Yield (%)[b]
1 2	Cy ^{i}Pr		94 91
3 4	Cy ^{i}Pr		95 93
5 6	Cy ^{i}Pr		87 83
7 8	Cy ^{i}Pr		91 92
9 10	Cy ^{i}Pr		88 89
11 12	Cy ^{i}Pr		93 91

[a] Conditions: aniline, 2.00 mmol; carbodiimide, 2.00 mmol; catalyst, 0.04 mol; THF, 5 mL; time, 12 h; reaction temperature, 60 °C. [b] Isolated yield.

atmosphere using standard Schlenk techniques or in a glovebox. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. All amines were sublimed, recrystallized or distilled before use. *N*,*N*′-dicyclohexylcarbodiimide and *N*,*N*′-diisopropylcarbodiimide were used without further purification. [(Me$_3$Si)$_2$N]$_3$Ln(μ-Cl)Li(THF)$_3$ were prepared according to literature methods.[24] IR spectra were recorded on SHIMADZU FTIR-8400S spectrometer. ^{1}H NMR and ^{13}C NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR spectrometer in C$_6$D$_6$ for lanthanide complexes and in CDCl$_3$ for organic compounds.

Synthesis of 2-[(2,4,6-Me$_3$C$_6$H$_2$)NHCH$_2$](C$_4$H$_3$NH) (1)

To a dried MeOH solution (20.0 mL) of pyrrole-2-carboxyaldehyde (5.74 g, 60.30 mmol) were added 2,4,6-trimethylaniline (10.0 mL, 60.30 mmol) and a catalytic amount of formic acid (2.0 mL) under stirring. The reaction mixture was stirred for 24 h at room temperature. Subsequently, the white precipitate was separated by filtration and then washed with cold methanol. Removal of the solvents afforded 2-[(2,4,6-Me$_3$C$_6$H$_2$)N═CH](C$_4$H$_3$NH) (3.75 g, 91% yield). mp 148–149 °C (from EtOH), δ_H (CDCl$_3$, ppm) 7.95 (s, 1 H, NCH), 6.90 (s, 2 H, ArH), 6.59–6.54 (m, 2 H, pyrrole H), 6.27 (s, 1 H, pyrrole H), 2.28 (s, 3 H, CH$_3$), 2.12 (s, 6 H, CH$_3$). δ_C (CDCl$_3$, ppm) 153.8, 148.3, 133.4, 130.1, 129.0, 128.4, 124.5, 117.0, 109.9, 21.0, 18.5. Found: C 79.33, H 7.32, N 13.27. Calcd for C$_{14}$H$_{16}$N$_2$: C 79.21, H 7.60, N 13.20%.

The compound 2-[(2,4,6-Me$_3$C$_6$H$_2$)N═CH](C$_4$H$_3$NH) (5.00 g, 23.36 mmol) in CH$_3$OH (30 mL) solution was reduced with NaBH$_4$ (1.76 g, 46.72 mmol) in 50 °C for another 5 h, then it was hydrolyzed. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The organic fractions were combined and dried with anhydrous MgSO$_4$, filtered, and evaporated to dryness. Recrystallization of crude product from hexane gave the product 2-[(2,4,6-Me$_3$C$_6$H$_2$)NHCH$_2$](C$_4$H$_3$NH) (**1**) (4.49 g, 89% yield). mp 65–66 °C. δ_H (CDCl$_3$, ppm) 8.34 (br, 1 H, NH), 6.85 (s, 2 H, ArH), 6.16 (s, 1 H, pyrrole H), 6.07 (s, 1 H, pyrrole H), 4.05 (s, 2 H, CH$_2$), 2.23 (s, 9 H, CH$_3$). δ_C (CDCl$_3$, ppm) 142.9, 132.3, 131.0, 130.6, 129.6, 117.4, 108.4, 106.0, 45.8, 20.7, 18.2. Found: C 78.59, H 8.64, N 13.04. Calcd for C$_{14}$H$_{18}$N$_2$: C 78.46, H 8.47, N 13.07%.

General procedures for synthesis of the rare earth metal amides with substituted pyrrolyl ligand

To a toluene (30.0 mL) solution of [(Me$_3$Si)$_2$N]$_3$Ln(μ-Cl)Li(THF)$_3$ (2.00 mmol) was added a toluene (10.0 mL) solution of ligand **1** (2.00 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was stirred for 24 h at 100 °C. The solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (20.0 mL). The extractions were combined and concentrated to about 10.0 mL. Products were obtained by recrystallization from the concentrated hexane solution at 0 °C for several days.

{(μ-η^5:η^1):η^1-2-[(2,4,6-Me$_3$C$_6$H$_2$)NCH$_2$]C$_4$H$_3$N]YN(SiMe$_3$)$_2$}$_2$ (2). Colourless crystals, 79% yield. mp 220–222 °C (from hexane); δ_H (C$_6$D$_6$, ppm) 7.62 (s, 2 H, pyrrole H), 7.04 (s, 4 H, Ar), 6.52 (s, 2 H, pyrrole H), 6.23 (s, 2 H, pyrrole H), 4.99 (s, 4 H, CH$_2$), 2.46 (s, 12 H, CH$_3$), 2.22 (s, 6 H, CH$_3$), 0.44–0.16 (m, 36 H, Si(CH$_3$)$_3$). ν_{max}(KBr)/cm^{-1}: 2887 m, 2855 m, 1481 s, 1435 s, 1224 m, 1198 m, 1130 w, 1063 w, 1030 s, 854 s, 793 m, 723 s, 610 w, 571 w. Found: C 51.87, H 7.18, N 8.95. Calcd for C$_{40}$H$_{68}$N$_6$Si$_4$Y$_2$: C 52.04, H 7.42, N 9.10%.

{(μ-η^5:η^1):η^1-2-[(2,4,6-Me$_3$C$_6$H$_2$)NCH$_2$]C$_4$H$_3$N]NdN(SiMe$_3$)$_2$}$_2$ (3). Green crystalline solid, 71% yield. mp 236–238 °C (from hexane); ν_{max}(KBr)/cm^{-1}: 2965 m, 2914 m, 2857 w, 1626 s, 1580 m, 1418 m, 1260 m, 1206 w, 1132 m, 1094 w, 1034 s, 856 m, 791 w, 743 m, 721 w. Found: C 46.05, H 6.70, N 8.13. Calcd for C$_{40}$H$_{68}$N$_6$Si$_4$Nd$_2$: C 46.47, H 6.63, N 8.13%.

{(μ-η^5:η^1):η^1-2-[(2,4,6-Me$_3$C$_6$H$_2$)NCH$_2$]C$_4$H$_3$N]SmN(SiMe$_3$)$_2$}$_2$ (4). Yellow crystals, 83% yield. mp 239–241 °C (from hexane); ν_{max}(KBr)/cm^{-1}: 2953 m, 2854 m, 1481 s, 1433 s, 1225 s, 1193 m, 1062 w, 1031 m, 932 s, 854 s, 793 w, 723 s, 610 w, 567 w. Found: C 45.81, H 6.59, N 8.16. Calcd for C$_{40}$H$_{68}$N$_6$Si$_4$Sm$_2$: C 45.93, H 6.55, N 8.03%.

{(μ-η^5:η^1):η^1-2-[(2,4,6-Me$_3$C$_6$H$_2$)NCH$_2$]C$_4$H$_3$N]DyN(SiMe$_3$)$_2$}$_2$ (5). Colourless crystalline solid, 81% yield. mp 238–240 °C (from hexane); ν_{max}(KBr)/cm^{-1}: 2912 m, 2855 m, 1570 w, 1481 s, 1431 m, 1225 s, 1194 m, 1130 m, 1062 w, 1031 m, 854 m, 793 m, 723 m, 610 w. Found: C 45.34, H 6.07, N 7.47. Calcd for C$_{40}$H$_{68}$N$_6$Si$_4$Dy$_2$: C 44.89, H 6.40, N 7.85%.

{(μ-η^5:η^1):η^1-2-[(2,4,6-Me$_3$C$_6$H$_2$)NCH$_2$]C$_4$H$_3$N]ErN(SiMe$_3$)$_2$}$_2$ (6). Pink crystals, 75% yield. mp 241–242 °C (from hexane). ν_{max}(KBr)/cm^{-1}: 2962 m, 2914 m, 1624 s, 1481 s, 1418 m, 1260 m,

Table 4 Crystallographic data for complexes **2**, **4** and **6**

	2	**4**	**6**
Empirical formula	$C_{40}H_{68}N_6Si_4Y_2$	$C_{40}H_{68}N_6Si_4Sm_2$	$C_{40}H_{68}N_6Si_4Er_2$
FW	923.18	1046.06	1079.88
T/K	293(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	*Pbca*	*Pbca*	*Pbca*
a/Å	12.4503(9)	12.5437(8)	12.4386(8)
b/Å	14.9010(11)	14.8642(9)	14.9104(10)
c/Å	26.724(2)	26.9042(17)	26.6642(17)
V/Å^3	4957.8(6)	5016.3(5)	4945.3(6)
Z	4	4	4
D_c/g cm^{-3}	1.237	1.385	1.450
μ/mm^{-1}	2.458	2.445	3.499
F(000)	1936	2120	2168
θ range/°	1.52 to 26.00	1.51 to 26.00	1.53 to 27.63
Reflections collected	36 612	36 826	40 636
Unique reflections	4873 (R_{int} = 0.0779)	4922 (R_{int} = 0.0313)	5739 (R_{int} = 0.0419)
Parameters	269	269	269
Goodness of fit	1.023	1.317	1.237
R_1 ($I > 2\sigma(I)$)	0.0420	0.0290	0.0353
wR_2 (all data)	0.1234	0.0833	0.0882
Min., max. residual density/e Å^{-3}	0.275 and −0.312	0.471 and −0.324	0.865 and −0.459

1204 w, 1128 m, 1093 w, 1031 s, 858 m, 799 m, 752 m, 721 m. Found: C 45.00, H 5.96, N 7.70. Calcd for $C_{40}H_{68}N_6Si_4Er_2$: C 44.49, H 6.35, N 7.78%.

General procedure for the catalytic addition of aromatic amines to carbodiimides

A 30.0 mL Schlenk tube under dried argon was charged with dinuclear rare earth metal bis(amido) complex **4** (0.05 mmol), aromatic amines (5.0 mmol), and THF (5.0 mL), then carbodiimides (5.0 mmol) was added to the mixture. The resulting mixture was stirred at 60 °C for a fixed interval. After the reaction was completed, the reaction mixture was hydrolyzed by water (3.0 mL), extracted with CH_2Cl_2 (3.0 × 10.0 mL), dried over anhydrous Na_2SO_4, and filtered. After the solvent was removed under reduced pressure, the final products were further purified by washing with diethyl ether or *n*-hexane.

Crystal structure determinations

Suitable crystal of complexes **2**, **4**, and **6** was each mounted in a sealed capillary. Diffraction was performed on a Burker SMART CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.[25] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.[26] See Table 4 for crystallographic data. All hydrogen atoms were refined using a riding model. It should be noted that disorders of the $SiMe_3$ groups in complexes **2**, **4**, and **6** were observed.

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