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FULL PAPER

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Syntheses, structures and catalytic activities of low-coordinated rare-earth metal complexes containing 2,2′-pyridylpyrrolides

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Reactions of the ligand precursors 2-(2′-pyridyl)-3,5-Me$_2$-pyrrole (**L^1**H) and 2-(2-pyridyl)-3,4,5-Me$_3$-pyrrole (**L^2**H) with $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ in toluene afforded a series of low-coordinated rare-earth metal bis-amido complexes **L^1**RE$[N(SiMe_3)_2]_2$ [RE = Y (**1a**), Dy (**1b**), Er (**1c**), Yb (**1d**)] and **L^2**RE$[N(SiMe_3)_2]_2$ [RE = Y (**2a**), Dy (**2b**), Er (**2c**), Yb (**2d**)]. With the ionic radius of rare-earth metal increasing, the reaction of **L^1**H and $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ gave dinuclear complexes (**L^1**)$_2$RE(μ-Cl)(μ-η^5:η^1:η^1-**L^1**)RE(**L^1**)$[N(SiMe_3)_2]_2$ [RE = Sm (**1e**), Pr (**1f**)]; however, the reaction of **L^2**H and $[(Me_3Si)_2N]_3Sm(\mu\text{-}Cl)Li(THF)_3$ afforded (**L^2**)$_2$Sm$[N(SiMe_3)_2]_2$ (**2e**). Results indicated that the ionic radius of rare-earth metal and subtle change in the ligands have substantial effects on the structure and bonding mode of complexes. The complexes showed a high catalytic activity for the ring-opening reaction of cyclohexene oxide with amines to afford various β-aminoalcohols under mild solvent-free conditions.

KEYWORDS
2,2′-pyridylpyrrolide, catalysis, rare-earth metal complex, X-ray analysis

1 | INTRODUCTION

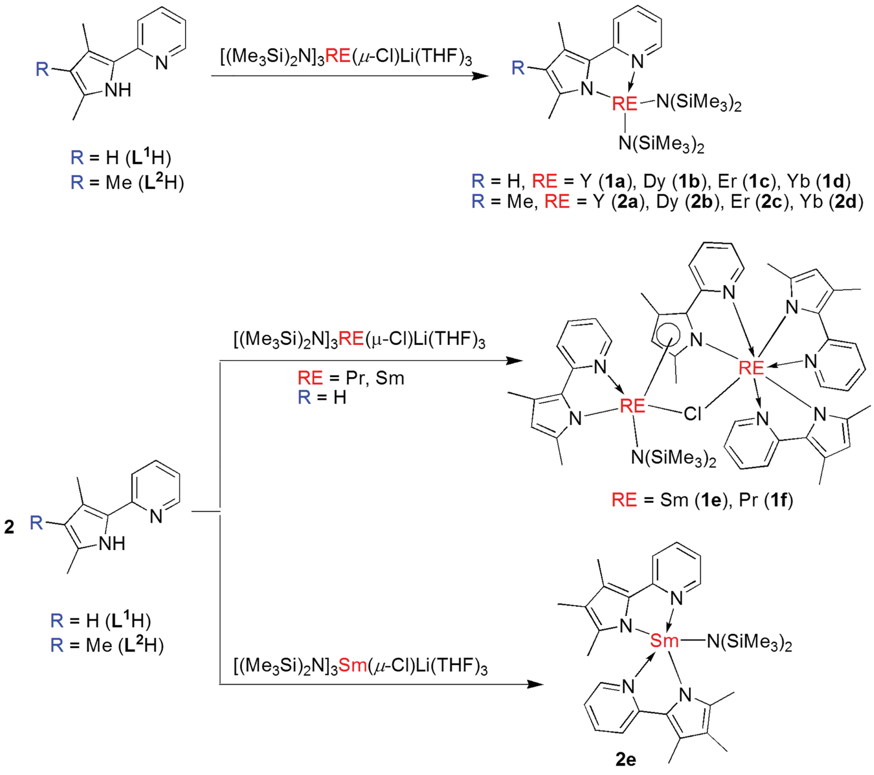
Pyrrole and its derivatives have been widely used in rare-earth organometallic chemistry, exhibiting increased reactivity toward electrophiles owing to their π-electron excessive properties.[1] However, pyridine is π-electron deficient but exhibits Lewis basicity because of its available lone-pair electrons. Owing to the complementary properties of pyridine and pyrrole, pyridylpyrrolide ligands can potentially generate push/pull interaction between the pyridyl and pyrrolide halves to exhibit the intramolecular excited-state proton transfer.[2] In particular, there has been significant interest in the metal-binding properties of 2-(2′-pyridyl)pyrroles in a 1,4-relationship,[3] which is similar to the α-diimine ligands, such as 2,2′-bipyridine. Additionally, 2-(2′-pyridyl)pyrroles can coordinate to metal, forming a five-membered chelate metallacycle, which is typical for many stable photoactive molecular materials.[4] Although various 2,2′-pyridylpyrrolide metal complexes for late transition metals have been reported to exhibit rich redox chemistry[5] and photoluminescent properties,[6] only a few reports are available for early transition metals.[7] It has been reported that the titanium complex bearing 2,2′-pyridylpyrrolyl ligand could highly catalyze the multicomponent coupling of alkynes, isonitriles and monosubstituted hydrazines to generate substituted pyrazoles.[7a] Recently, the group 4 metal complexes bearing 2,2′-pyridylpyrrolyl ligands were reported to exhibit photoluminescence in solution and facilitate photoredox processes as a photosensitizer.[7b–d] However, the rare-earth metal complexes containing 2,2′-pyridylpyrrolyl ligands remain unexplored. We herein report the syntheses and structural characterizations of a series of 2,2′-pyridylpyrrolyl ligand-supported rare-earth metal complexes. The resulting *bis*-amido complexes featured relatively low coordination number and the catalytic activities of all of the obtained complexes toward the ring-opening reaction of cyclohexene oxide with various amines were studied

2 | RESULTS AND DISCUSSION

2.1 | Syntheses and characterization of rare-earth metal complexes containing 2,2′-pyridylpyrrolyl ligands

The reaction of 2-(2′-pyridyl)-3,5-Me$_2$-pyrrole ($\mathbf{L}^1$H) and 2-(2′-pyridyl)-3,4,5-Me$_3$-pyrrole ($\mathbf{L}^2$H) with 1 equiv. of $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ in toluene afforded a series of low-coordinated rare-earth metal *bis*-amido complexes $\mathbf{L}^1$RE[N(SiMe$_3$)$_2$]$_2$ [RE = Y (**1a**), Dy (**1b**), Er (**1c**), Yb (**1d**)] and $\mathbf{L}^2$RE[N(SiMe$_3$)$_2$]$_2$ [RE = Y (**2a**), Dy (**2b**), Er (**2c**), Yb (**2d**)], respectively (Scheme 1). When the light rare-earth metals Sm and Pr were employed, the reaction of $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ with 2 equiv. of $\mathbf{L}^1$H afforded dinuclear complexes ($\mathbf{L}^1$)$_2$RE(μ-Cl)(μ-η^5:η^1:η^1-$\mathbf{L}^1$)RE($\mathbf{L}^1$)[N(SiMe$_3$)$_2$]$_2$ [RE = Sm (**1e**), Pr (**1f**)]; however, the reaction of $[(Me_3Si)_2N]_3Sm(\mu\text{-Cl})Li(THF)_3$ with 2 equiv. of $\mathbf{L}^2$H gave the mononuclear amido complex ($\mathbf{L}^2$)$_2$Sm[N(SiMe$_3$)$_2$] (**2e**) (Scheme 1). These results suggest that the structures and bonding modes of the complexes are largely affected by the ionic radius of rare-earth metal; however, a slight variation of the ligand by addition of a methyl group on the 4-position of the pyrrole backbone also subtly affects the resulting complexes, as in the case of **1e** and **2e**. These complexes are extremely sensitive to air and moisture, and they are soluble in THF, toluene and *n*-hexane. All of the complexes were fully characterized by NMR spectroscopic methods (for **1a** and **2a**), elemental analyses and X-ray crystallographic analyses.

X-ray diffraction analyses revealed that complexes **1a–1d** were isostructural tetra-coordinated rare-earth metal *bis*-amido complexes adopting distorted tetrahedral geometries, and a representative structure diagram of complex **1c** is shown in Figure 1. Compounds **1e** and **1f** were dinuclear complexes with two metal centers bridged by one μ-Cl ligand and one pyrrolide moiety in a μ-η^5:η^1:η^1 mode, and only one amido group coordinated to the metal center with the μ-η^5 bridged pyrrolide. The representative structure diagram of complex **1e** is shown in Figure 2. X-ray diffraction analyses revealed that



SCHEME 1 Syntheses of rare-earth metal complexes

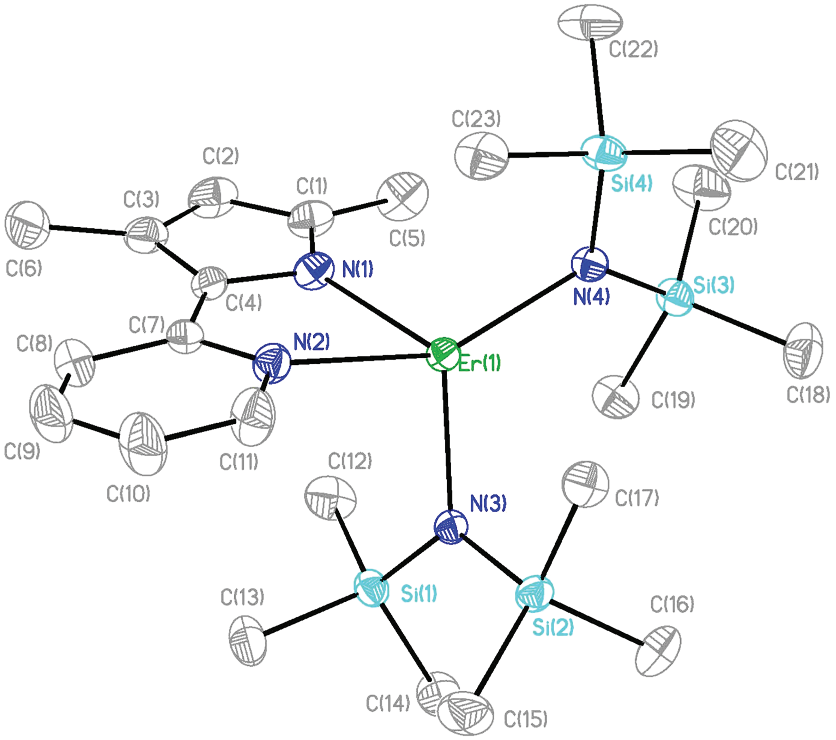


FIGURE 1 Representative molecular structure of complex **1c**. Hydrogen atoms are omitted for clarity.

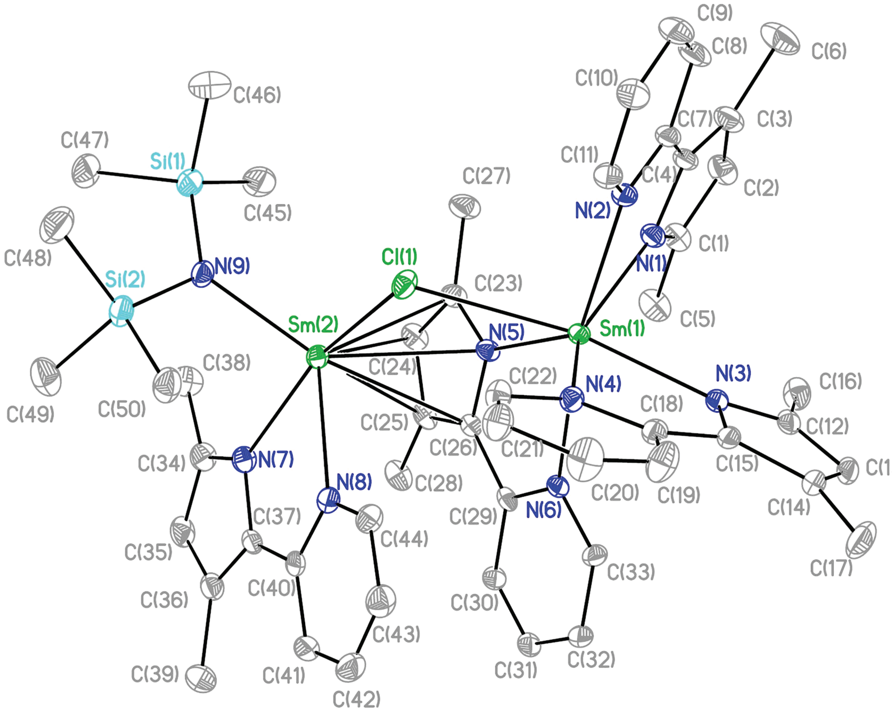


FIGURE 2 Representative molecular structure of complex **1e**. Hydrogen atoms are omitted for clarity.

complexes **2a–2d** were also isostructural with distorted tetrahedral geometries, and a representative structure diagram of complex **2c** is shown in Figure 3. The monoamido complex **2e** adopted a penta-coordinated square-based pyramidal configuration, and the structure diagram is shown in Figure 4. The selected bond distances and angles are listed in Tables 1–3.

As shown in Tables 1–3, the average RE(1)–N_{av} bond distances in complexes **1a–1d** are comparable with those in complexes **2a–2d**, and both series are also consistent with the trend in ionic radius of the corresponding rare-earth metals. The RE(1)–N(2) bond lengths in complexes **1a–1d** and **2a–2d** were slightly longer than those of RE(1)–N(1), N(3) and N(4), as expected, as the donation

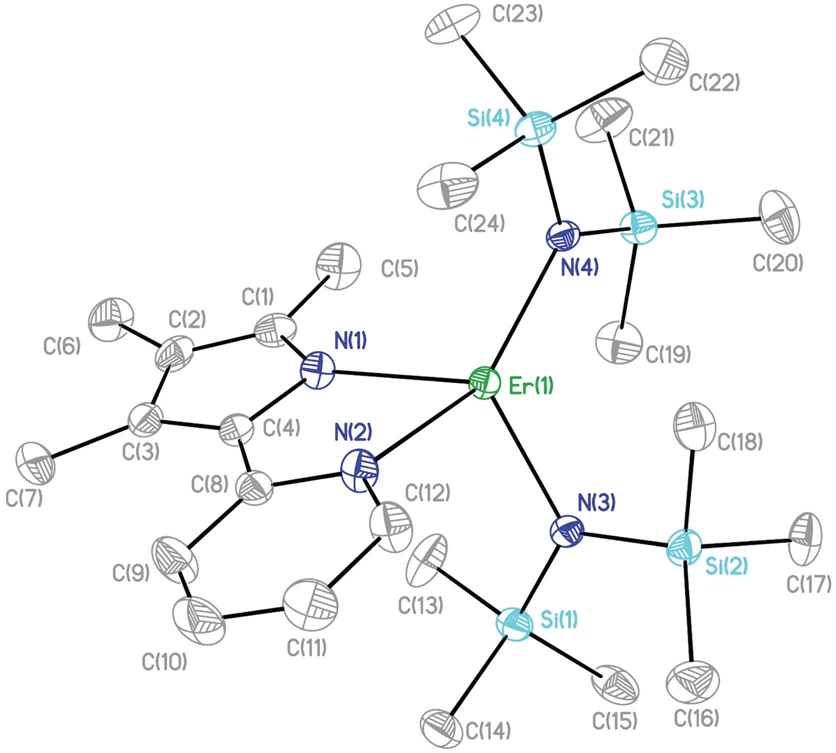


FIGURE 3 Representative molecular structure of complex **2c**. Hydrogen atoms are omitted for clarity.

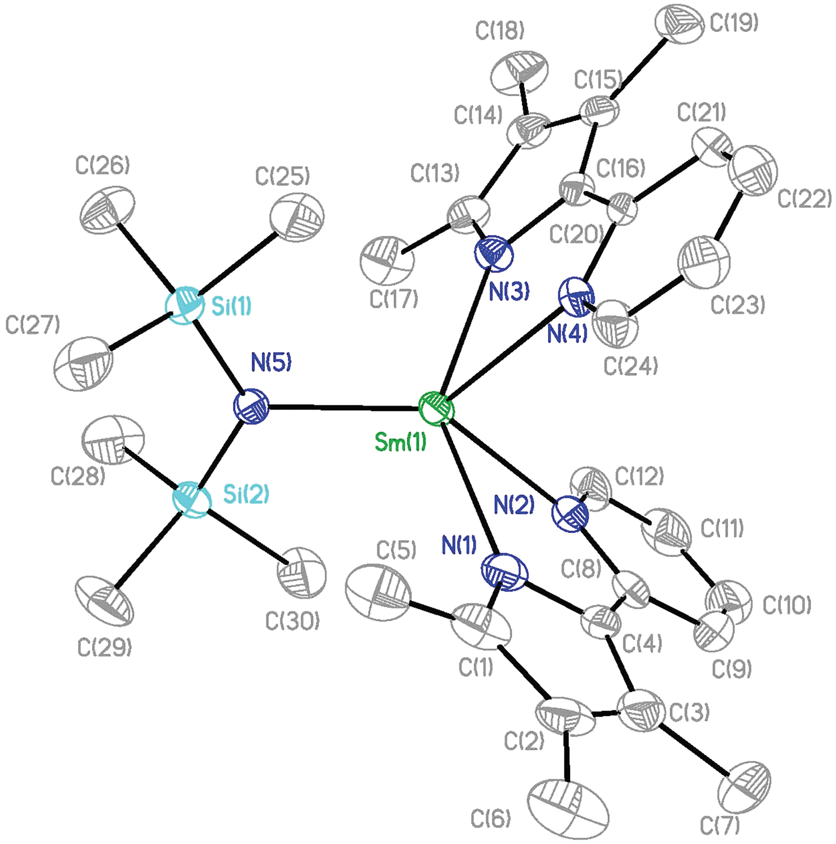


FIGURE 4 Molecular structure of complex **2e**. Hydrogen atoms are omitted for clarity.

from the neutral pyridine donor is weaker than those from the anionic pyrrolide and amido donors in the molecules. In the π coordinated pyrrolyl ring of **1e**, the bond distances between samarium ions with the five-membered pyrrolyl ring range from 2.760(5) to 2.967(5) Å, with the average value of 2.858(5) Å, comparable with

TABLE 1 Selected bond length (Å) and bond angle (deg) of complexes **1a–1d**

	1a (Y)	**1b (Dy)**	**1c (Er)**	**1d (Yb)**
RE(1)–N(1)	2.282(8)	2.278(6)	2.260(6)	2.233(4)
RE(1)–N(2)	2.422(7)	2.450(6)	2.442(6)	2.398(4)
RE(1)–N(3)	2.200(7)	2.222(9)	2.195(6)	2.165(4)
RE(1)–N(4)	2.204(7)	2.228(10)	2.204(6)	2.176(4)
RE(1)–N_{av}	2.277(8)	2.298(10)	2.275(6)	2.243(4)
N(1)–RE(1)–N(2)	70.4(3)	70.0(3)	70.9(2)	71.67(15)
N(2)–RE(1)–N(3)	93.8(2)	93.6(3)	95.0(2)	93.80(14)
N(3)–RE(1)–N(4)	116.8(2)	117.6(3)	115.9(2)	115.90(14)
N(4)–RE(1)–N(1)	106.4(3)	106.3(3)	106.1(2)	106.00(15)

TABLE 2 Selected bond length (Å) and bond angle (deg) of complexes **1e–1f**

	1e (Sm)	**1f (Pr)**
RE(1)–N(1)	2.384(4)	2.412(6)
RE(1)–N(2)	2.532(3)	2.573(8)
RE(1)–N(3)	2.415(3)	2.491(8)
RE(1)–N(4)	2.581(3)	2.641(8)
RE(1)–N(5)	2.487(3)	2.542(8)
RE(1)–N(6)	2.575(3)	2.672(8)
RE(2)–C(23)	2.760(5)	2.784(9)
RE(2)–C(24)	2.822(5)	2.876(9)
RE(2)–C(25)	2.967(5)	2.973(9)
RE(2)–C(26)	2.934(4)	2.878(9)
RE(2)–N(5)	2.806(3)	2.769(7)
RE(2)–Pyr_{av}	2.858(5)	2.874(9)
RE(2)–N(7)	2.376(4)	2.399(8)
RE(2)–N(8)	2.514(4)	2.602(8)
RE(2)–N(9)	2.279(3)	2.310(7)
RE(1)–Cl(1)	2.854(1)	2.913(2)
RE(2)–Cl(1)	2.804(1)	2.850(3)
N(1)–RE(1)–N(2)	67.45(13)	65.2(3)
N(3)–RE(1)–N(4)	67.19(11)	65.3(3)
N(5)–RE(1)–N(6)	64.36(11)	62.6(3)
N(7)–RE(2)–N(8)	66.90(13)	64.2(3)

that of 2.874(3) Å in calix[4]-pyrrolyl complex (η^5:η^1:η^5:η^1-Me_8-calix[4]-pyrrolyl){$SmN(SiMe_3)_2$}$_2$,[8] but slightly longer than those of 2.810 (3) and 2.796(4) Å in {2-[(2,6-$Me_2C_6H_3$)NCH_2](C_4H_3N)$SmN(SiMe_3)_2$}$_2$[11] and {2-[(2,4,6-$Me_3C_6H_2$)NCH_2](C_4H_3N)$SmN(SiMe_3)_2$}$_2$.[9]

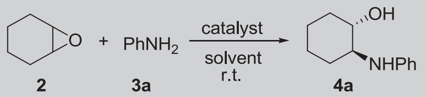
TABLE 3 Selected bond length (Å) and bond angle (deg) of complexes **2a–2e**

	2a (Y)	**2b (Dy)**	**2c (Er)**	**2d (Yb)**	**2e (Sm)**
RE(1)–N(1)	2.266(7)	2.299(7)	2.263(10)	2.236(2)	2.390(8)
RE(1)–N(2)	2.440(4)	2.454(7)	2.420(6)	2.396(2)	2.501(8)
RE(1)–N(3)	2.195(6)	2.216(7)	2.196(10)	2.166(2)	2.369(7)
RE(1)–N(4)	2.204(7)	2.224(7)	2.203(9)	2.182(2)	2.481(7)
RE(1)–N(5)					2.255(7)
RE(1)–N_{av}	2.276(7)	2.298(7)	2.271(10)	2.245(2)	2.399(8)
N(1)–RE(1)–N(2)	70.4(2)	70.1(2)	71.3(3)	71.85(8)	66.4(3)
N(2)–RE(1)–N(3)	93.3(2)	93.3(3)	94.3(3)	93.85(8)	89.3(3)
N(3)–RE(1)–N(4)	117.4(3)	117.5(2)	116.1(4)	115.98(8)	67.4(2)
N(1)–RE(1)–N(4)	106.1(3)	99.5(2)	105.6(4)	106.09(8)	
N(4)–RE(1)–N(5)					129.7(2)
N(1)–RE(1)–N(5)					109.4(3)

2.2 | Catalytic activity of rare-earth metal complexes containing 2,2′-pyridylpyrroly ligands.

The ring opening of epoxides with aromatic amines is an important and well-defined route for the synthesis of β-amino alcohols, which are versatile intermediates for the synthesis of natural products and bioactive molecules.[10] Various catalysts including metal triflates,[9,11] metal halides,[12] metal alkoxides,[13] metal amides[14] and other catalysts[15] are employed to achieve the products in high conversion and selectivity. However, these catalytic systems usually require elevated temperature, high pressure, stoichiometric amounts of catalyst and long reaction times. Recently, a green method for the synthesis of β-aminoalcohols was developed using a reusable catalyst or under solvent-free and mild reaction conditions.[16] Here, the rare-earth metal amido complexes containing 2,2′-pyridylpyrrolyl ligands as catalysts for the ring-opening reaction of cyclohexene oxide with amines were examined. The ring-opening reaction of cyclohexene oxide with aniline was initially investigated as the template reaction in the presence of 1 mol% of complex **1a** (entries 1–5, Table 4). Under solvent-free conditions at room temperature, the reaction afforded 2-phenylaminocyclohexanol **4a** in a 95% yield (entry 5, Table 4), which was identified as the *trans* isomer with characteristic ^{1}H NMR signals appearing at at 3.35 (ddd, $J = 10.0$, 9.5 and 4.5 Hz, 1H) for the C*H*OH and δ 3.14 (ddd, $J = 11.0$, 9.5 and 4.0 Hz, 1H) for the C*H*NH protons.[11c,12b] Further examination of the different complexes as catalysts showed that all of the complexes effectively catalyzed the reactions (entries 7–16, Table 4). Under optimized conditions, using 0.5 mol% of complex

TABLE 4 Optimization of the reaction condition[a]

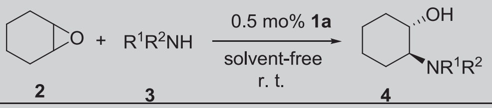


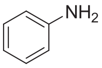
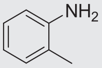
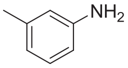
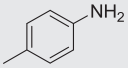
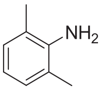
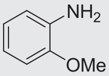
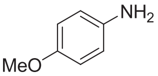
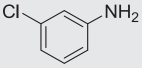
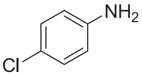
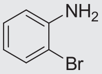
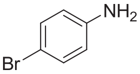
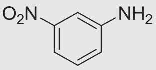
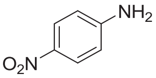
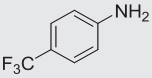
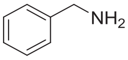
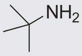
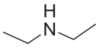
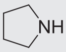
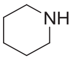
Entry	Catalyst	Loading (mol%)	Time (h)	Solvent	Yield (%)[b]
1	**1a**	1	10	Toluene	70
2	**1a**	1	10	THF	67
3	**1a**	1	10	Hexane	53
4	**1a**	1	10	PhCl	65
5	**1a**	1	10	Free	95
6	—	—	24	Free	Trace
7	**1b**	1	10	Free	91
8	**1c**	1	10	Free	90
9	**1d**	1	10	Free	92
10	**1e**	1	10	Free	94
11	**1f**	1	10	Free	93
12	**2a**	1	10	Free	89
13	**2b**	1	10	Free	91
14	**2c**	1	10	Free	87
15	**2d**	1	10	Free	90
16	**2e**	1	10	Free	87
17	**1a**	0.5	10	Free	90
18	**1a**	0.25	10	Free	78
19	**1a**	0.5	8	Free	92
20	**1a**	0.5	6	Free	92
21	**1a**	0.5	4	Free	91
22	**1a**	0.5	2	Free	79

[a] The reaction was performed by treating 1 equiv. of amines with 2 equiv. of epoxides under the given conditions.

[b] Isolated yield.

TABLE 5 Ring-opening reaction of cyclohexene oxide with different amines[a]



Entry	$R^1R^2NH_2$	Product	Yield (%)[b]
1		**4a**	91
2		**4b**	82
3		**4c**	91
4		**4d**	91
5		**4e**	70
6		**4f**	90
7		**4g**	88
8		**4h**	87
9		**4i**	89
10		**4j**	84
11		**4k**	91
12		**4l**	58[c]
13		**4m**	63[c]
14		**4n**	69[c]
15		**4o**	97
16		**4p**	98
17		**4q**	93
18		**4r**	91
19		**4s**	96

[a] Reaction conditions: complex **1a** (0.05 mol), amines (1.0 mmol), epoxides (2.0 mmol), solvent-free, room temperature.

[b] Isolated yields.

[c] Toluene as solvent, 70°C, 4 h.

1a under solvent-free conditions in 4 h, the reaction of cyclohexene oxide with aniline afforded the corresponding ring-opening product in a 91% yield (Entries 7–16, Table 4).

Complex **1a** was selected as the catalyst for the following experiments to examine the ring-opening reaction of cyclohexene oxide with various amines, and results are presented in Table 5. The results showed that high yields were achieved under mild reaction condition (0.5 mol% cat., solvent-free at r.t.) for a wide range of different amines. It was also found that both the electronic and the steric properties of the substrates affected the reactivity. In the case of *ortho*-substituted anilines, the ring-opened products were obtained in slightly lower yield (entries 2, 5 and 10, Table 5). For aryl amines bearing a strong electron-withdrawing substituent such as NO_2 or

CF_3, the ring-opened products **4l–4n** were also obtained in lower yields of 58–69%, even at 70°C (entries 12–14, Table 5). The ring-opened products **4o–4s** were obtained in satisfactory yields for the aliphatic primary and secondary amines (entries 15–19, Table 5). The probable reaction mechanism was that the complexes functioned as Lewis acid catalysts, the cyclohexene oxide was activated through the coordination of cyclohexene oxide oxygen atom to the rare-earth metal center, then amine as a nucleophile attacked to afford the desired product.[12c, 17] The low-coordinated *bis*-amido rare-earth complexes exhibited slightly high catalytic activity probably owing to the steric effect around the rare-earth metals.

3 | CONCLUSIONS

In summary, a series of the rare-earth metal complexes bearing 2,2′-pyridylpyrrolides have been synthesized and characterized. The X-ray diffraction studies showed that the structure of the resulted complexes were affected by the ionic radius of rare-earth metal, and a subtle change of ligand from $\mathbf{L^1}$H to $\mathbf{L^2}$H. The four coordinated *bis*-amido rare-earth complexes exhibited high catalytic activity for the ring-opening reaction of cyclohexene oxide with various aromatic and aliphatic amines, which provided a facile synthesis of the *β*-aminoalcohols under mild solvent-free conditions.

4 | EXPERIMENTAL

4.1 | General remarks

All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and oxygen-free atmosphere using standard Schlenk techniques or in a glovebox. Solvents were refluxed and distilled over sodium/benzophenone under argon prior to use. Compounds $\mathbf{L^1}$H and $\mathbf{L^2}$H,[18] $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$[19] were prepared according to literature methods. IR spectra were recorded on Shimadzu FTIR-8400S spectrometer. ^1H NMR and ^{13}C NMR spectra for analyses of compounds were recorded on a Bruker AV-400 or 500 NMR spectrometer in C_6D_6 for lanthanide complexes and in $CDCl_3$ for organic compounds.

4.2 | General synthesis of $\mathbf{L^1REN(SiMe_3)_2}$ and $\mathbf{L^2REN(SiMe_3)_2}$

Under an argon atmosphere, an oven-dried 50.0 ml Schlenk flask equipped with a magnetic stir bar was charged with the compound $\mathbf{L^1}$H (0.17 g, 1.00 mmol) or $\mathbf{L^2}$H (0.19 g, 1.00 mmol), $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (1.00 mmol) and toluene (30.0 ml) at room temperature. The reaction mixture was stirred at 100°C for 12 h, and the solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (15.0 ml), and the crystals were obtained by cooling the solution at 0°C for several days.

4.2.1 | Complex 1a

Yellow crystals (0.49 g, 85% yield). M.p.: 167–169°C. ^1H NMR (500 MHz, C_6D_6): δ 7.90 (d, J = 5.5 Hz, 1H, Ar*H*), 7.24 (d, J = 8.6 Hz, 1H, Ar*H*), 6.91–6.88 (m, 1H, Ar*H*), 6.18 (t, J = 6.5 Hz, 1H, Ar*H*), 6.02 (s, 1H, pyrrole-*H*), 2.57 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 0.26 (s, 36H, $SiCH_3$). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 157.0 (Ar*C*), 146.2 (Ar*C*), 141.7 (Ar*C*), 139.3 (Ar*C*), 131.5(Ar*C*), 127.4 (pyrrole-*C*), 119.9 (pyrrole-*C*), 115.9 (pyrrole-*C*), 115.7 (pyrrole-*C*), 17.6 (CH_3), 15.8 (CH_3), 4.4 ($SiCH_3$). Elemental analysis calcd (%) for $C_{23}H_{47}N_4Si_4Y\cdot0.3$ hexane: C 49.23, H 8.59, N 9.19; found: C 49.11, H 8.78, N 9.42.

4.2.2 | Complex 1b

Yellow crystals (0.58 g, 88% yield). M.p.: 154–156°C. IR (KBr pellets, cm^{-1}): ν 1586 (s), 1555 (s), 1502 (s), 1461 (m), 1277 (s), 1149 (m), 1093 (s), 838 (s). Elemental analysis calcd (%) for $C_{23}H_{47}N_4Si_4Dy\cdot0.5$ hexane: C 44.77, H 7.80, N 8.03; found: C 44.50, H 7.55, N 8.34.

4.2.3 | Complex 1c

Pink crystals (0.55 g, 83% yield). M.p.: 151–153°C. IR (KBr pellets, cm^{-1}): ν 1590 (s), 1559 (s), 1504 (s), 1456 (m), 1269 (s), 1183 (m), 1092 (s),846 (s). Elemental analysis calcd (%) for $C_{23}H_{47}N_4Si_4Er$: C 41.90, H 7.19, N 8.50; found: C 41.80, H 7.08, N 8.74.

4.2.4 | Complex 1d

Red crystals (0.59 g, 89% yield). M.p.: 156–158°C. IR (KBr pellets, cm^{-1}): ν 1589 (s), 1559 (s), 1504 (s), 1456 (m), 1269 (s), 1183 (m), 1092 (s), 846 (s). Elemental analysis calcd (%) for $C_{23}H_{47}N_4Si_4Yb\cdot0.5$ hexane: C 44.10, H 7.69, N 7.91; found: C 43.90, H 7.69, N 8.05.

4.2.5 | Complex 2a

Yellow crystals (0.48 g, 80% yield). M.p.: 142–144°C. ^1H NMR (500 MHz, C_6D_6): δ 7.87 (d, J = 5.5 Hz, 1H, Ar*H*), 7.29 (d, J = 8.5 Hz, 1H, Ar*H*), 6.92–6.88 (m, 1H, Ar*H*), 6.17–6.14 (m, 1H, Ar*H*), 2.53 (s, 3H, C*H₃*), 2.17 (s, 3H, C*H₃*), 2.02 (s, 3H, C*H₃*), 0.27 (s, 36H, SiC*H₃*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 156.9 (Ar*C*), 146.2 (Ar*C*), 139.4 (Ar*C*), 139.2 (Ar*C*), 130.8 (Ar*C*), 125.4 (pyrrole-*C*), 119.8 (pyrrole-*C*), 119.6 (pyrrole-*C*), 115.6 (pyrrole-*C*), 15.9 (CH_3), 13.6 (CH_3), 10.0 (CH_3), 4.4 ($SiCH_3$). IR (KBr pellets, cm^{-1}): ν 1591 (s), 1517 (s), 1466 (s), 1272 (s), 1152 (s), 976 (s), 779 (s), 746 (s). Elemental analysis calcd (%) for $C_{24}H_{49}N_4Si_4Y$·0.5 hexane: C 50.83, H 8.85, N 8.78; found: C 50.30, H 8.81, N 9.10.

4.2.6 | Complex 2b

Yellow crystals (0.58 g, 87% yield). M.p.: 137–139°C. IR (KBr pellets, cm^{-1}): 1589 (s), 1513 (s), 1460 (s), 1269 (s),1150 (s), 932 (m), 782 (s), 736 (s). Elemental analysis calcd (%) for $C_{24}H_{49}N_4Si_4Dy$: C 43.12, H 7.39, N 8.38; found: C 43.44, H 7.47, N 8.34.

4.2.7 | Complex 2c

Pink crystals (0.55 g, 82% yield). M.p.: 137–139°C. IR (KBr pellets, cm^{-1}): ν 1594 (s), 1514 (s), 1461 (s), 1274 (s), 1160 (s), 935 (s), 780 (s), 735 (s). Elemental analysis calcd (%) for $C_{24}H_{49}N_4Si_4Er$·0.5 hexane: C 45.27, H 8.88, N 7.82; found: C 45.02, H 8.02, N 7.90.

4.2.8 | Complex 2d

Red crystals (0.57 g, 84% yield). M.p.:139–141°C. IR (KBr pellets, cm^{-1}): ν 1591 (s), 1514 (s), 1463 (s), 1267 (s), 1154 (s), 932 (s), 774 (s), 734 (s). Elemental analysis calcd (%) for $C_{24}H_{49}N_4Si_4Yb$·0.5 hexane: C 44.91, H 7.82, N 7.76; found: C 44.63, H 7.78, N 8.05.

4.3 | General synthesis of 1e and 1f

Under an argon atmosphere, an oven-dried 50.0 ml Schlenk flask equipped with a magnetic stir bar was charged with the compound **L^1**H (0.17 g, 1.00 mmol), $[(Me_3Si)_2N]_3RE(\mu\text{-Cl})Li(THF)_3$ (0.50 mmol) and toluene (30.0 ml) at room temperature. The reaction mixture was stirred at 100°C for 12 h, and the solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (15.0 ml) and the crystals were obtained by cooling the solution at 0°C for several days.

4.3.1 | Complex 1e

Yellow crystals (0.36 g, 61% yield). M.p.: 164–166°C. IR (KBr pellets, cm^{-1}): ν 1591 (s), 1560 (s), 1504 (s), 1463 (m), 1262 (s), 1149 (m), 1093 (s), 797 (s). Elemental analysis calcd (%) for $C_{51}H_{65}ClN_9Si_2Sm_2$·hexane: C 53.38, H 6.21, N 9.83; found: C 53.19, H 5.51, N 10.18.

4.3.2 | Complex 1f

Yellow crystals (0.37 g, 63% yield). M.p.: 169–171°C. IR (KBr pellets, cm^{-1}): ν 1594 (s), 1558 (s), 1499 (s), 1466 (m), 1280 (s), 1154 (m), 1009 (s), 782 (s). Elemental analysis calcd (%) for $C_{51}H_{65}ClN_9Si_2Pr_2$: C 52.02, H 5.56, N 10.71; found: C 52.17, H 5.94, N 10.72.

4.4 | Synthesis of $L^2SmN(SiMe_3)_2$ (2e)

A similar method for preparation of complex **2e** was used for the treatment of **L^2**H (0.19 g, 1.00 mmol), $[(Me_3Si)_2N]_3Sm(\mu\text{-Cl})Li(THF)_3$ (0.50 mmol) and toluene (30.0 ml) at room temperature. Yellow crystals were obtained upon cooling the solution at 0°C for several days (0.22 g, 65% yield). M.p.: 137–139°C. IR (KBr pellets, cm^{-1}): 1594 (s), 1517 (s), 1468 (s), 1264 (s), 1149 (s), 930 (s), 785 (s), 739 (s). Elemental analysis calcd (%) for $C_{30}H_{44}N_5Si_2Sm$: C 52.89, H 6.51, N 10.28; found: C 53.48, H 6.73, N 10.12.

4.5 | X-ray crystallography

Suitable crystals of complexes **1a–1f** and **2a–2e** were 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. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package. All hydrogen atoms were refined using a riding model. See Supporting Information for crystallographic parameters and data collection and refinement information.

4.6 | General procedure for the ring opening reaction of cyclohexene oxide with amines

Under an argon atmosphere, an oven-dried 20.0 ml Schlenk flask equipped with a magnetic stir bar was charged with complex **1a** (3.0 mg, 0.005 mmol) and the amine (1.0 mmol). Cyclohexene oxide (0.202 ml, 2.0 mmol) was added and the resulting mixture was stirred under solvent-free conditions for 4 h. At completion, the crude product was purified by column chromatography on silica gel using ethyl acetate–petroleum ether (1:5, v/v) as the eluent to afford the final product.

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CONFLICTS OF INTEREST

There are no conflicts of interest to declare.

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