Supporting information for:

Synthesis and Characterization of Bis(amidate) Rare-Earth Metal Amides and the Application in Catalytic Addition of Amines to Carbodiimides

Hao Cheng,[†] Yang Xiao,[†] Chengrong Lu,[†] Bei Zhao,[*,†] Yaorong Wang,[†] Yingming Yao[*,†]

†Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou 215123, China

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General Methods

All manipulations and reactions were conducted under purified argon atmosphere by using vacuum line techniques or in a glovebox. Rare-earth metal precursors $RE[N(SiMe_3)_2]_3$ (RE = La, Nd, Sm, Yb, Y), and proligand N,N'-(cyclohexane-1,2-diyl)bis(4-tert-butylbenzamide) were prepared according to literature methods[1]. Solvents were distilled from sodium benzophenone ketyl under argon prior to use. Solid amines were degassed before use, and liquid amines were distilled from CaH_2 prior to use. The single crystal X-ray diffraction data were recorded on a Rigaku Mercury CCD X-ray diffractometer. ^1H and ^{13}C NMR spectra were obtained on a Bruker-400 spectrometer in $CDCl_3$. Metal analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. Melting points for the complexes were determined in sealed Ar-filled capillary tubes and are uncorrected.

*Synthesis of $\{LSm[N(SiMe_3)_2]\cdot THF\}_2$ (**4**)*

To a stirred tetrahydrofuran solution of $Sm[N(SiMe_3)_2]_3$ (1.50 mmol, 10 mL of THF), N,N'-(cyclohexane-1,2-diyl)bis(4-*tert*-butylbenzamide) (0.66 g, 1.50 mmol) in 10 mL THF was slowly added. After the mixture was stirred at 25 ^oC for 24 h, the solvent was pumped off, and the residue was recrystallized from THF at room temperature to give **4** as colourless crystals.

*Synthesis of $\{LYb[N(SiMe_3)_2]\cdot THF\}_2$ (**5**)*

Following the method described for complex **4**, reaction of N,N'-(cyclohexane-1,2-diyl)bis(4-tert-butylbenzamide) (0.62 g, 1.40 mmol) and $Yb[N(SiMe_3)_2]_3$ (1.40 mmol, 10 mL of THF), afforded colourless crystals **5** in THF.

*X-ray structure determination of complexes **4-5***

Owing to their air and moisture sensitivity, suitable single crystals of complexes **4-5** were each sealed in thin-walled glass capillaries. Intensity data were collected on a Rigaku Mercury CCD equipped with graphite-monochromatized Mo Kα (λ =

0.71075 Å) radiation. Details of the intensity data collection and crystal data are given in Tables 1 and 2. The crystal structures of these complexes were solved by direct methods and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by fullmatrix least-squares analysis on F^2. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically with assigned appropriate isotropic thermal parameters. The structures were solved and refined by using the SHELXL-97 program [2].

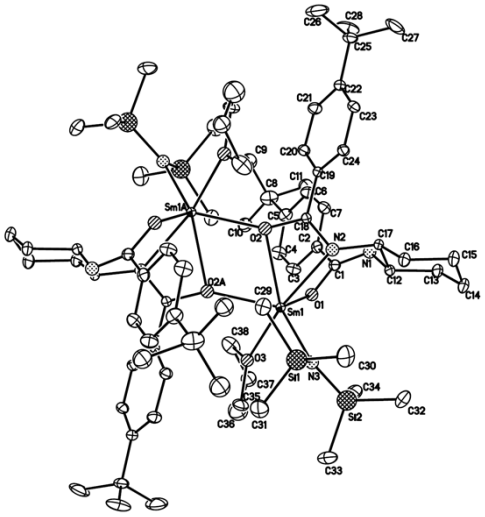

Figure 1. Structure of bridged bisamidate samarium amide **4·3THF**. Hydrogen atoms and the molecule of THF in the unit cell are omitted for clarity.

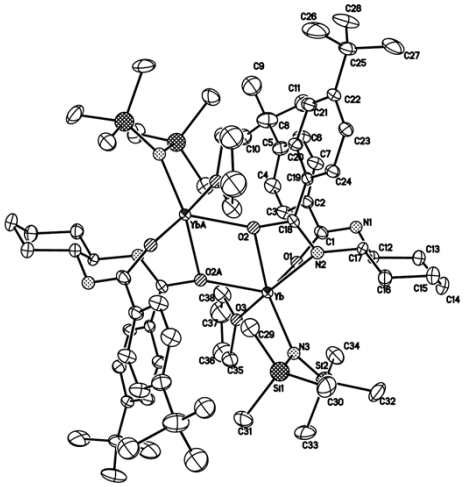

Figure 2. Structure of bridged bisamidate ytterbium amide **5·3THF**. Hydrogen atoms and the molecule of THF in the unit cell are omitted for clarity.

Table **1**. Crystallographic data and structure refinement details for complexes **4-5**.

	4•3C_4H_8O	**5•3C_4H_8O**
Empirical formula	$C_{88}H_{148}N_6O_9Si_4Sm_2$	$C_{88}H_{148}N_6O_9Si_4Yb_2$
Fw	1847.18	1892.56
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71075
Crystal system	Triclinic	Triclinic
Space group	P -1	P -1
Crystal size (mm)	0.75 × 0.4 × 0.2	0.8 × 0.4 × 0.2
a, b, c (Å)	13.7002(6) 13.9301(8) 15.2548(5)	13.700(16) 14.00(3) 15.31(2)
α, β, γ (deg)	108.997(4) 106.363(4) 97.835(4)	109.37(4) 105.895(8) 98.64(2)
Volume (Å^3)	2556.4(2)	2569(7)
Z	1	1
Calculated density (g/cm^3)	1.200	1.224
Absorption coefficient (mm^{-1})	1.234	1.906
F (000)	970	986
θ range (deg)	5.756-51	6.016-54.974
Limiting indices	-16 ≤ h ≤ 16, -16 ≤ k ≤ 15, -18 ≤ l ≤ 18	-17≤h≤17, -18≤k≤14, -19≤l≤19
Reflections collected	24937	23938
Unique	9499 [R(int) = 0.0313]	11585 [R(int) = 0.0379]
Max. and Min. transmission	1.000 and 0.704	0.473 and 0.319
Data/restraints/ parameters	9499/243/601	11585/341/619

GOF on F^2	1.128	1.085
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0349$, $wR_2 = 0.0979$	$R_1 = 0.0492$, $wR_2 = 0.1178$
R indices (all data)	$R_1 = 0.0432$, $wR_2 = 0.1012$	$R_1 = 0.0601$, $wR_2 = 0.1272$
Largest diff. Peak and hole ($e/Å^3$)	1.00 and -0.43	0.92and -1.3

Table 2 Selected bond lengths (Å) and bond angles (°) for complexes **4**-**5**.

	4•3C_4H_8O	**5•3C_4H_8O**
Ln(1)-O(1)	2.196(3)	2.113(4)
Ln(1)-N(3)	2.309(3)	2.219(5)
Ln(1)-O(2A)	2.363(3)	2.265(4)
Ln(1)-O(3)	2.494(3)	2.393(5)
Ln(1)-N(2)	2.501(3)	2.405(5)
Ln(1)-O(2)	2.551(3)	2.467(5)
O(1)-C(1)	1.327(4)	1.320(6)
O(2)-C(18)	1.332(4)	1.323(6)
N(1)-C(1)	1.274(5)	1.283(7)
N(2)-C(18)	1.282(5)	1.302(6)
O(1)- Ln(1)-O(3)	79.47(10)	78.52(18)
O(3)- Ln(1)-O(2A)	76.68(10)	77.00(18)
O(2A)- Ln(1)-N(2)	117.03(10)	117.85(17)
N(2)- Ln(1)-O(1)	77.51(10)	79.13(19)
N(3)- Ln(1)-O(2)	134.63(11)	135.98(16)
O(2A)- Ln(1)-O(2)	66.13(9)	65.68(15)

The characterization data of the guanidine products

1,3-diisopropyl-2-phenylguanidine (**7a**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.20 (m, 2H); 6.93 (t, J = 7.4 Hz, 1H); 6.86 (d, J = 7.4 Hz, 2H); 3.77 (s, 2H); 3.59 (s, 2H); 1.16 (d, J = 6.3 Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 150.4, 129.3, 123.6, 121.4, 43.3, 23.4 ppm.

1,3-dicyclohexyl-2-phenylguanidine (**7b**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.21 (m, 2H); 6.95-6.95-6.89 (m, 1H); 6.88-6.86 (m, 2H); 3.65 (s, 2H); 3.42 (s, 2H); 2.01-1.12 (m, 20H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.7, 150.7, 129.5, 123.9, 121.6, 50.5, 34.1, 26.0, 25.2 ppm.

1,3-diisopropyl-2-p-tolylguanidine (**7c**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (d, *J* = 7.6 Hz, 2 H); 6.74 (d, *J* = 7.6 Hz, 2 H); 3.76 (s, 2H); 3.56 (s, 2H); 2.28 (s, 3H); 1.16 (d, *J* = 7.6 Hz, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 147.6, 130.5, 129.9, 123.3, 43.2, 23.4, 20.8 ppm.

1,3-diisopropyl-2-o-tolylguanidine (**7d**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, *J* = 7.4 Hz, 1H); 7.09 (t, *J* = 7.5 Hz, 1H); 6.87 (t, *J* = 7.0 Hz, 1H); 6.76 (d, *J* = 7.7 Hz, 1H); 3.76 (s, 2H); 3.44 (s, 1H); 2.14 (s, 3H); 1.16 (d, J = 6.4 Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.9, 148.4, 130.5, 130.4, 126.6, 123.2, 121.8, 43.2, 23.5, 18.1 ppm.

1,3-dicyclohexyl-2-o-tolylguanidine (**7e**). ^{1}H NMR (400 MHz , $CDCl_3$): δ 6.93 (m, 2H); 6.78 (m, 2H); 3.62 (br, 2H); 3.40 (br, 2H); 2.00 (s, 3H); 1.97-1.03 (m, 20H) ppm. ^{13}CNMR (100 MHz , $CDCl_3$): δ 148.94, 148.70, 131.86, 130.60, 126.84, 123.48, 121.88, 50.40, 34.18, 25.94, 25.22, 18.41 ppm.

1,3-diisopropyl-2-(4-methoxyphenyl)guanidine (**7f**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.83-6.76 (m, 4H); 3.77 (s, 5H); 3.57 (s, 2H); 1.16-1.14 (m, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 150.9, 143.4, 124.5, 114.8, 55.6, 43.4, 23.6 ppm.

2-(2-chlorophenyl)-1,3-diisopropylguanidine (**7g**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.7 Hz, 1H); 7.14 (t, *J* = 7.3 Hz, 1H); 7.0-6.7 (m, 2H); 3.79 (dd, *J* = 12.3, 6.1 Hz, 2H); 3.47 (s, 2H); 1.16 (d, *J* = 6.3 Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 147.0, 130.0, 128.4, 127.5, 125.3, 122.5, 43.3, 23.5 ppm.

2-(2-chlorophenyl)-1,3-dicyclohexylguanidine (**7h**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.33 (m, 1H), 7.15-7.11 (m, 1H); 6.92-6.85 (m, 2H); 3.56 (s, 2H); 3.42 (s, 2H); 2.05-1.06 (m, 20H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 147.6, 130.1, 128.7, 127.8, 125.6, 122.6, 50.5, 34.1, 26.0, 25.2 ppm.

2-(4-chlorophenyl)-1,3-diisopropylguanidine (**7i**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.5 Hz, 2H); 6.77 (d, *J* = 8.5 Hz, 2H); 3.80-3.68 (m, 2H); 3.54 (s, 2H); 1.16 (d, *J* = 6.3 Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 148.9, 129.4, 126.3, 124.7, 43.2, 23.4 ppm.

2-(4-bromophenyl)-1,3-diisopropylguanidine (**7j**). ^{1}H NMR (400 MHz , $CDCl_3$): δ 7.33 (d, *J* = 8.4 Hz, 2 H); 6.73 (d, *J* = 8.4 Hz, 2 H); 3.82-3.67 (m, 2 H); 3.54 (s, 2H); 1.16 (d, *J* = 6.3 Hz, 12 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 149.6, 132.2, 125.4, 113.9, 43.2, 23.4 ppm.

2-(4-fluorophenyl)-1,3-diisopropylguanidine (**7k**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (t, *J* = 8.7 Hz, 2H); 6.82-6.73 (m, 2H); 3.75 (s, 2H); 3.52 (s, 2H); 1.16 (d, *J* = 6.3 Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 146.0, 141.8, 124.5, 124.4, 115.8, 115.6, 43.2, 23.4 ppm.

1,3-dicyclohexyl-2-(4-fluorophenyl)guanidine (**7l**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94-6.90 (m, 2 H); 6.77-6.73 (m, 2 H); 3.59 (s, 2 H); 3.38-3.36 (m, 2 H); 1.99-1.03 (m, 20 H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 150.6, 124.9, 124.8, 116.1, 115.9, 50.4, 34.1, 25.9, 25.2 ppm.

1,3-diisopropyl-2-(naphthalen-1-yl)guanidine (**7m**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J*＝8.0 Hz, 1H); 7.79 (d, *J*＝7.6 Hz, 1H); 7.35-7.47 (m, 4H); 6.92 (d, *J*＝7.2 Hz, 1H); 3.88 (brs, 2H); 3.63 (brs, 2H); 1.18 (d, *J*＝6.4 Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 147.1, 135.1, 129.9, 128.1, 126.8, 126.1, 124.9, 124.7, 121.7, 118.1, 43.6, 23.7 ppm.

1,3-diisopropyl-2-(4-nitrophenyl)guanidine (**7n**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.9 Hz, 2H); 6.89 (d, *J* = 8.9 Hz, 2H); 3.79 (s, 4H); 1.20 (s, 12H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 150.4, 140.9, 125.6, 122.8, 43.3, 23.2 ppm.

1,3-diisopropyl-2-(3-nitrophenyl)guanidine (**7o**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 -7.66 (m, 1H); 7.36 (t, *J* = 8.0 Hz, 1H); 7.17 (d, *J* = 7.7 Hz, 1H); 3.78 (dd, *J* = 12.9, 6.4 Hz, 2H); 3.60 (d, *J* = 6.0 Hz, 2H); 1.19 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 150.4, 149.3, 130.1, 129.7, 118.1, 115.8, 43.4, 23.4 ppm.

1,3-diisopropyl-2-(4-methyl-2-nitrophenyl)guanidine (**7p**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62(s, 1H); 7.21 (d, *J* = 9.6 Hz, 1H); 6.86 (d, *J* = 8.1 Hz, 1H); 3.75 (dd, *J* = 13.4, 6.7 Hz, 2H); 3.52 (d, *J* = 7.1 Hz, 2H); 2.32 (s, 3H); 1.17 (d, *J* = 6.4 Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.3, 143.5, 142.7, 134.4, 130.8, 126.8, 125.2, 43.4, 23.4, 20.4 ppm.

2-(3,5-bis(trifluoromethyl)phenyl)-1,3-diisopropylguanidine (**7q**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (s, 1H), 7.28 (s, 2H), 3.78 (dq, *J* = 12.8, 6.5 Hz, 2H), 3.61 (d, *J* = 7.4 Hz, 2H), 1.19 (d, *J* = 6.4 Hz, 12H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 150.6, 132.7, 132.4, 132.1, 131.7, 127.6, 124.9, 123.4, 122.2, 119.5, 113.9, 43.3, 23.2 ppm.

1,3-diisopropyl-2-(perfluorophenyl)guanidine (**7r**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (dq, *J* = 12.8, 6.4 Hz, 2H), 3.61 (d, *J* = 7.2 Hz, 2H), 1.20 (d, *J* = 6.4 Hz, 12H). ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 141.9, 139.6, 138.9, 136.4, 133.8, 126.2, 124.9, 124.5, 43.1, 22.6 ppm.

2-(2,6-diisopropylphenyl)-1,3-diisopropylguanidine (**7s**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07-7.03 (m, 2H); 6.96-6.90 (m, 1H); 4.13 (s, 2H); 3.44-3.10 (m, 2H); 3.10-3.05 (m, 2H); 1.25-1.04 (m, 24H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 144.3, 141.6, 123.2, 122.3, 43.5, 42.7, 28.0, 23.9 ppm.

1,3-diisopropyl-2-(pyridin-2-yl)guanidine (**7t**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (dd, *J* = 5.1, 1.4 Hz, 1H); 7.42 (ddd, *J* = 8.4, 7.1, 2.1 Hz, 1H); 6.83 (d, *J* = 8.3 Hz, 1H); 6.61 (ddd, *J* = 7.0, 5.1, 1.0 Hz, 1H); 3.93 (d, *J* = 4.5 Hz, 2H); 1.25 (d, *J* = 6.4 Hz, 12H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 153.8, 136.7, 120.3, 114.0, 42.6, 23.5 ppm.

(Z)-N,N'-diisopropylindoline-1-carboximidamide (**7u**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 7.5Hz, 1H); 7.13-7.02 (m, 2H); 6.75 (t, *J* = 7.2 Hz, 1H); 3.95-3.70 (m, 2H); 3.55-3.30 (m, 2H); 3.15-2.90 (m, 2H); 1.14 (d, *J* = 5.9 Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3, 146.0, 130.9, 126.5, 124.0, 119.0, 111.0, 50.0, 46.6, 45.1, 27.3, 24.3, 23.3 ppm.

(Z)-N,N'-diisopropylpyrrolidine-1-carboximidamide (**7v**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.39-3.28 (m, 2H); 3.26-3.16 (m, 4H); 1.80-1.71 (m, 4H); 1.06 (d, *J* = 6.4Hz, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 47.9, 46.6, 25.1, 24.6 ppm.

Reference:

[1] S. P. Anthony, K. Basavaiah, T. P. Radhakrishnan. *Crystal Growth & Design,* **2005**, 5, 1663–1665.

[2] G.M. Sheldrick, SHELXL-2013, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 2013.