Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Nitrile formation via dichlorocarbene insertion into the Si-N bond of Ln(III) bis(trimethylsilyl)amide complexes

Yangjuan Li, Yu Gong *

Department of Radiochemistry, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, 201800, China.

*E-mail: gongyu@sinap.ac.cn

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I. Experimental Procedures

General information

All reactions were carried out using modified Schlenk-line and Ar-atmosphere glove box (<1 ppm O_2/H_2O) techniques. n-Hexane and THF dried and degassed through a Vigor solvent purification system as well as $CDCl_3$ and $CHCl_3$ were stored over 4 Å sieves for 24 h under argon atmosphere before use. C_6D_6 were dried over Na and stored under argon atmosphere prior to use. n-Hexane-d_{14} and styrene (carbene trapping reagent) are used without purification. $Ln[N(SiMe_3)_2]_3$ (Ln=Eu, Sm, Yb) was synthesized according to the literature methods.[1] Elemental analyses (C, H, N) were performed on a Vario EL III elemental analyser. The powder X-ray diffraction patterns were collected on a Rigaku Synergy R (Cu Kα) diffractometer at 180 K. The powder wrapped in inert oil was cooled under a cold stream of nitrogen, and CrysAlisPro software was used for data collection and integration. All NMR spectra were recorded on a Zhongke-Niujin Quantum-I Plus 400 spectrometer (Zhongke-Niujin, Wuhan, China). ^1H and ^{13}C NMR chemical shifts (δ) are reported in ppm and were calibrated to residual solvent peaks (C_6D_6) or TMS (n-hexane-d_{14}). Due to the paramagnetic nature of trivalent europium, samarium and ytterbium, conclusive ^1H and ^{13}C NMR data of compounds **1**-**3** could not be obtained. The solution magnetic susceptibilities of **1-3** were determined by the Evans method in C_6D_6.[2] The FTIR samples were prepared as KBr pellets, and the spectra were obtained on a Nolay-50 spectrometer (Nuoleixinda, Tianjin, China). The UV−vis spectra were recorded on a Cary 6000i Agilent spectrophotometer.

X-ray Crystallography

The intensity data were collected on a Rigaku Synergy R (Mo Kα) diffractometer at 180 K. Absorption corrections were applied by using the program CrysAlisPro (multi-scan). The crystal structures were solved by SHELXT structure solution program using Intrinsic Phasing, and nonhydrogen atoms were refined anisotropically by least-squares techniques on F^2 by SHELXL with the graphical user interfaces of Olex2.[3] For all structures, H-atom parameters were constrained.

Synthesis of $[Eu\{N(SiMe_3)_2\}_2(\mu\text{-}Cl)(NCSiMe_3)]_2$ (1)

$CDCl_3$ (20 ul, 0.25 mmol) was added to a solution of $Eu[N(SiMe_3)_2]_3$ (158.3 mg, 0.25 mmol) in n-hexane (4 mL) at room temperature. The color of the mixture changed into red, and a purple precipitate was observed within 20 min. After filtration, solvent volatilized slowly at room temperature. The resulting dark red solid was washed three times by n-hexane and dried in vacuum. Yield: 36 mg, 47.4% based on $Eu[N(SiMe_3)_2]_3$. Anal. Calcd (%) for $C_{32}H_{90}Cl_2N_6Si_{10}Eu_2$: C, 31.64; H,7.47; N, 6.92. Found: C, 30.12; H, 7.24; N, 6.47. μ_{eff} = 4.99 μ_B (Evans method). FTIR (KBr, cm^{-1}): ν(C≡N), 2197 and 2129. Powder X-ray diffraction was used to confirm the purity of the bulk samples.

Synthesis of $[Sm\{N(SiMe_3)_2\}_2(\mu\text{-}Cl)(NCSiMe_3)]_2$ (2)

$CDCl_3$ (20 ul, 0.25 mmol) was added to a solution of $Sm[N(SiMe_3)_2]_3$ (158.1 mg, 0.25 mmol) in n-hexane (4 mL) at room temperature. A few white precipitate was observed within 20 min. After filtration, solvent volatilized slowly at room temperature. The resulting ivory solid was washed three times by n-hexane and dried in vacuum. Yield:

43 mg, 56.8% based on $Sm[N(SiMe_3)_2]_3$. Anal. Calcd (%) for $C_{32}H_{90}Cl_2N_6Si_{10}Sm_2$: C, 31.72; H,7.49; N, 6.94. Found: C, 31.83; H, 7.58; N, 6.90. μ_{eff} = 1.71 μ_B (Evans method). FTIR (KBr, cm^{-1}): ν(C≡N), 2197 and 2128. Powder X-ray diffraction was used to confirm the purity of the bulk samples.

Synthesis of $Yb[N(SiMe_3)_2]_3(NCSiMe_3)_2$ (3)

$CDCl_3$ (20 ul, 0.25 mmol) was added to a solution of $Yb[N(SiMe_3)_2]_3$ (163.8 mg, 0.25 mmol) in n-hexane (5 mL) at room temperature. The color of the mixture faded, and an earth-yellow precipitate was observed within 20 min. Filtrating the mixture, the filtrate was stored at -25 ^oC to afford colorless crystals. Yield: 36 mg, 33.8% based on $Yb[N(SiMe_3)_2]_3$. Anal. Calcd (%) for $C_{26}H_{72}N_5Si_8Yb$: C, 36.63; H, 8.51; N, 8.21. Found: C, 36.70; H, 8.53; N,7.38. μ_{eff} = 4.47 μ_B (Evans method). FTIR (KBr, cm^{-1}): ν(C≡N), 2136. Powder X-ray diffraction was used to confirm the purity of the bulk samples.

II. Characterization

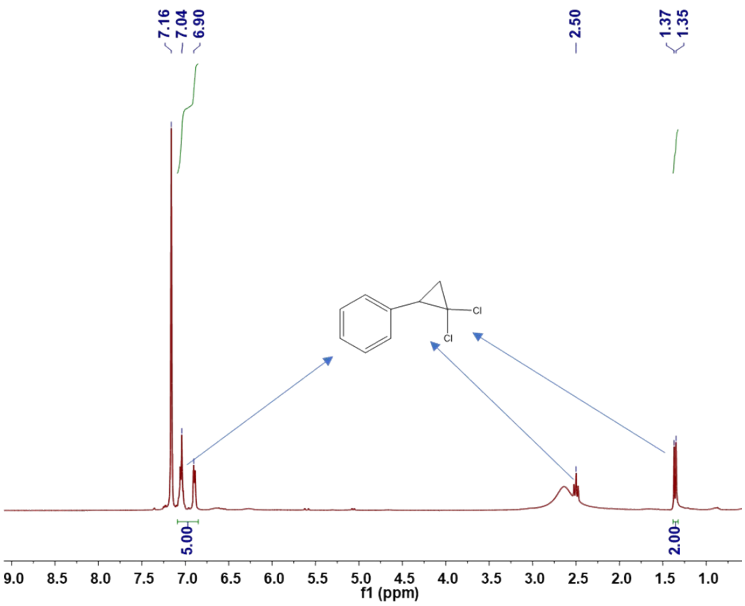

Fig. S1. ^{1}H NMR (C_6D_6) spectrum of the reaction products of $Eu[N(SiMe_3)_2]_3$ with styrene and $CDCl_3$ (1:1:1) at room temperature in n-hexane. The reaction mixture was filtered and the solvent was removed before the reaction proudcts were dissolved in C_6D_6.

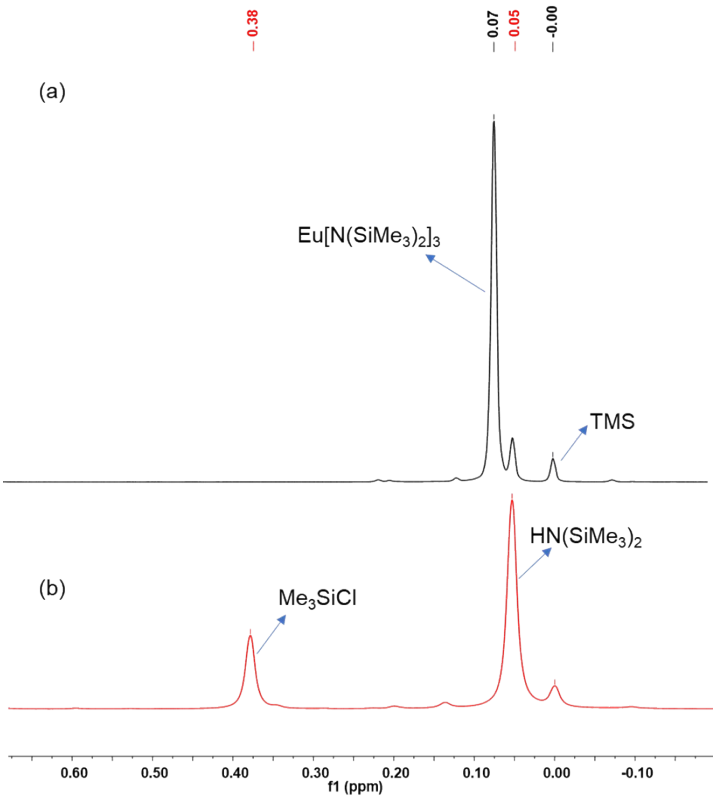

Fig. S2. (a) ^{1}H NMR spectrum of $Eu[N(SiMe_3)_2]_3$ in n-hexane-d_{14}. (b) ^{1}H NMR spectrum of the reaction of $Eu[N(SiMe_3)_2]_3$ with $CHCl_3$ (1:1) at room temperature in n-hexane-d_{14}.

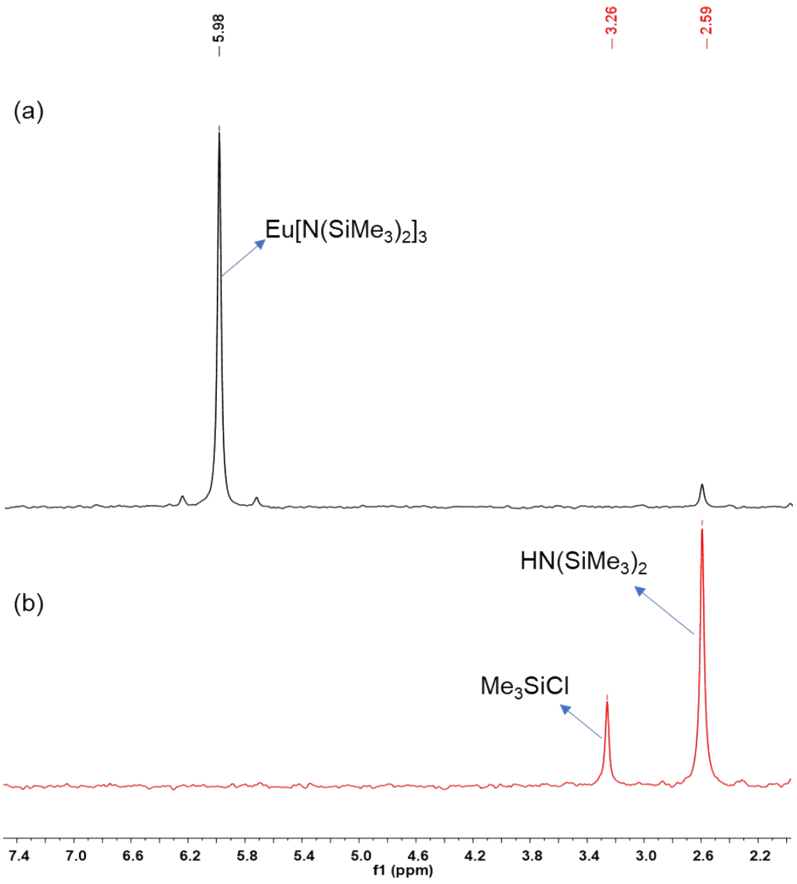

Fig. S3. (a) ^{13}C NMR spectrum of $Eu[N(SiMe_3)_2]_3$ in n-hexane-d_{14}. (b) ^{13}C NMR spectrum of the reaction of $Eu[N(SiMe_3)_2]_3$ with $CHCl_3$ (1:1) at room temperature in n-hexane-d_{14}.

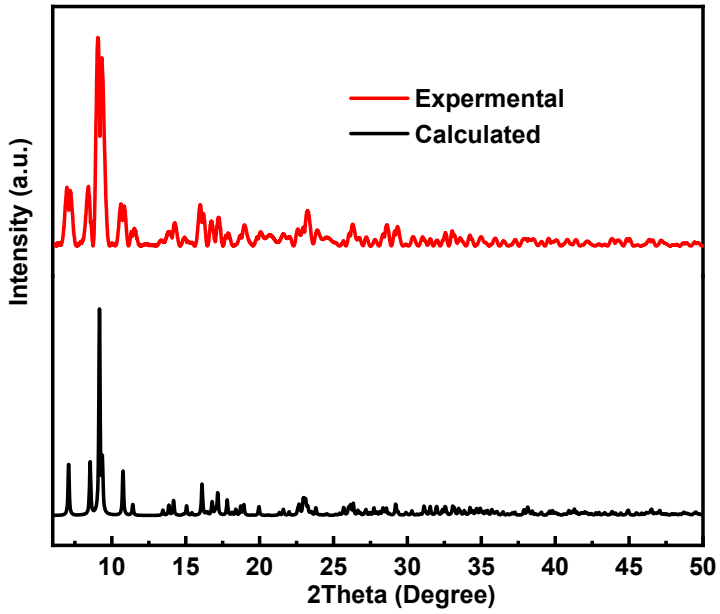

Fig. S4. Experimental and calculated PXRD patterns for $[Eu\{N(SiMe_3)_2\}_2(\mu\text{-}Cl)(NCSiMe_3)]_2$.

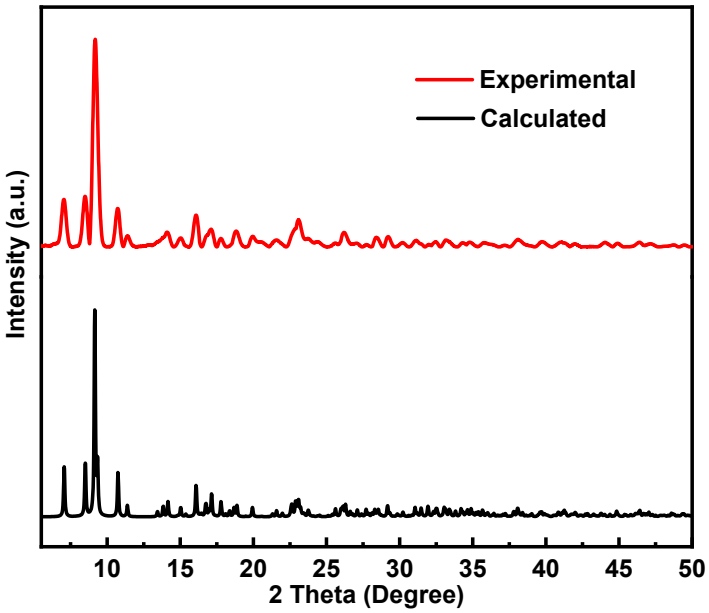

Fig. S5. Experimental and calculated PXRD patterns for $[Sm\{N(SiMe_3)_2\}_2(\mu\text{-}Cl)(NCSiMe_3)]_2$.

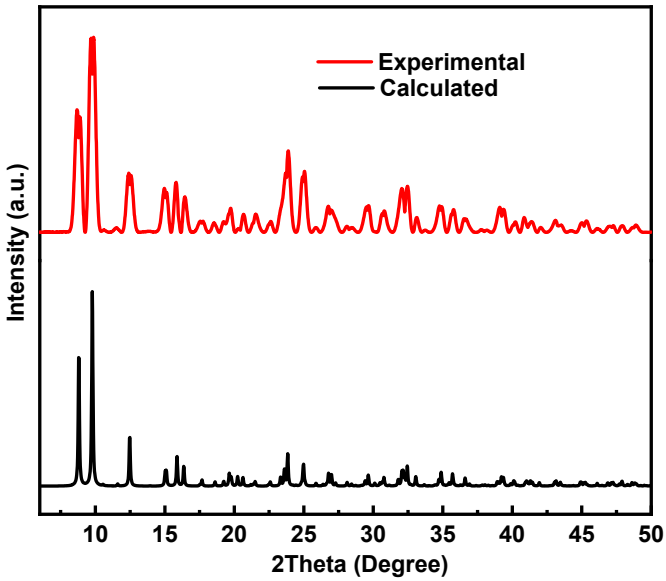

Fig. S6. Experimental and calculated PXRD patterns for $Yb[N(SiMe_3)_2]_3(NCSiMe_3)_2$.

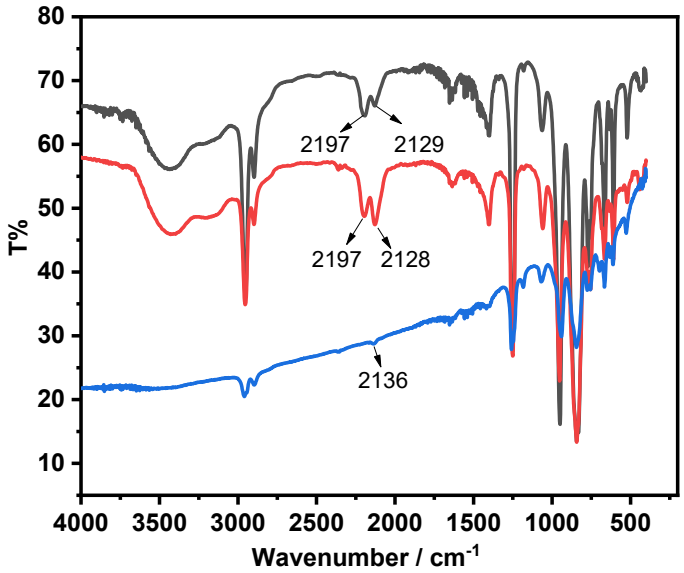

Fig. S7. FTIR spectra of complex **1** (black), **2** (red) and **3** (blue).

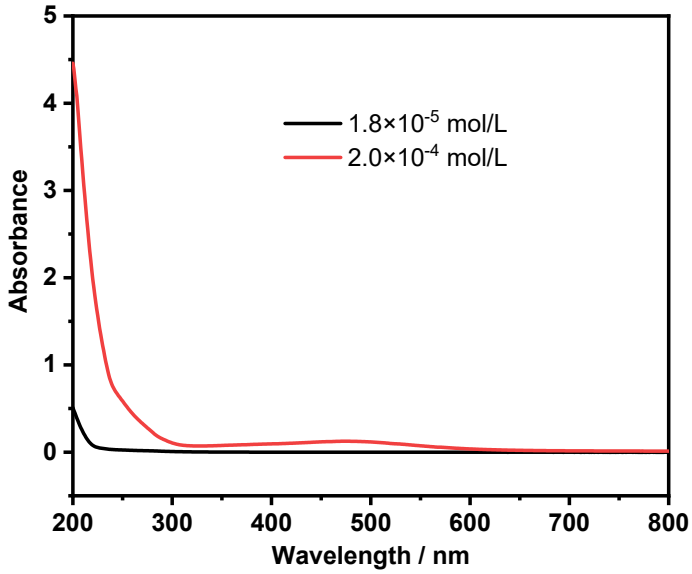

Fig. S8. UV-visible absorption spectra of complex **1** in n-hexane.

Table S1. Crystal data and structure refinements for complexes **1, 2** and **3**

Complex	**1**	**2**	**3**
CCDC	2144893	2189910	2144894
Empirical formula	$C_{32}H_{90}Cl_2N_6Si_{10}Eu_2$	$C_{32}H_{90}Cl_2N_6Si_{10}Sm_2$	$C_{26}H_{72}N_5Si_8Yb$
Formula weight	1214.81	1211.59	852.64
Temperature/K	180(2)	179.99(10)	180 (2)
Crystal system	monoclinic	monoclinic	tetragonal
Space group	C2/c	C2/c	$I4_1cd$
a /Å	20.7513(4)	20.8019(3)	20.0586(3)
b/Å	11.9059(2)	11.9155(2)	20.0586(3)
c/Å	25.0124(4)	25.0378(4)	23.4376(5)
α/°	90	90	90
β/°	93.4704(16)	93.368(2)	90
γ/°	90	90	90
Volume/Å^3	6168.30(19)	6195.28(17)	9430.1(3)
Z	4	4	8
ρ_{calc}g/cm^3	1.308	1.299	1.201
μ/mm^{-1}	2.321	2.182	2.208
F(000)	2496.0	2488.0	3560.0
2θ range/deg	3.932 to 56.564	3.922 to 62.204	4.062 to 52.738
Index ranges	-26 ≤ h ≤ 27 -15 ≤ k ≤ 15	-27 ≤ h ≤ 26 -16 ≤ k ≤ 13	-23 ≤ h ≤ 24 -24 ≤ k ≤ 24

	-31 ≤ l ≤ 33	-35 ≤ l ≤ 31	-29 ≤ l ≤ 29
Reflections collected	35817	37264	24214
	7328	8020	4540
Independent reflections	R_{int} = 0.0250	R_{int} = 0.0237	R_{int} = 0.0309
	R_{sigma} = 0.0187	R_{sigma} = 0.0185	R_{sigma} = 0.0236
Completeness	99.6%	100%	99.9%
Data/restraints/parameters	7328/0/250	8020/0/250	4540/1/194
Goodness-of-fit on F^2	1.035	1.054	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0187	R_1 = 0.0201	R_1 = 0.0225
	wR_2 = 0.0417	wR_2 = 0.0435	wR_2 = 0.0556
Final R indexes [all data]	R_1 = 0.0229	R_1 = 0.0238	R_1 = 0.0308
	wR_2 = 0.0429	wR_2 = 0.0445	wR_2 = 0.0611
Largest diff. peak/hole / e $Å^{-3}$	0.58/-0.30	0.37/-0.45	0.58/-0.53

III. References

1. D. C. Bradley, Ghotra,J. S. , Hart,F. A., *J. Chem. Soc., Dalton Trans.*, 1973, 1021.
2. (a) D. F. Evans, *J. Chem. Soc.*, 1959, 2003; (b) E. M. Schubert, *J. Chem. Educ.*, 1992, **69**, 62; (c) S. K. Sur, *J. Magn. Reson.*, 1989, **82**, 169−173.
3. (a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339; (b) G. Sheldrick, *Acta Crystallogr. Section A*, 2015, **71**, 3; (c) G. M. Sheldrick, *Acta Crystallogr. Section C*, 2015, **71**, 3.