Supporting Information

Formation of N,N,N',N'-Tetramethylethylenediamine via Coupling of the Two Charge Reversed C-N Bonds of Me_3NO in the Presence of Eu(II) Bis(trimethylsilyl)amide Complex

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

Contents

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. Solvents were dried and degassed through a Vigor solvent purification system and stored over 4 Å sieves for 24 h before use. C_6D_6 were dried over Na and stored under argon atmosphere prior to use. 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. 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 the CrysAlisPro software was used for data collection and integration. The X-ray photoelectron spectra (XPS) were recorded on a ThermoFisher Scientific ESCALAB Xi^+ spectrometer. The charging effect and corresponding binding energy shift for all the elements have been calibrated by the carbon 1s peak at 284.8 eV. $Ln[N(SiMe_3)_2]_2(THF)_2$ (Ln=Eu, Yb, Sm) was synthesized according to slightly modified literature methods.[1] Me_3NO was obtained from Tokyo Chemical Industry Co., Ltd. (TCI) and used as purchased.

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.[2] For all structures, H-atom parameters were constrained.

Synthesis of $Eu[N(SiMe_3)_2]_2(TMEDA)$ (1)

Me_3NO (19 mg, 0.25 mmol) was added to a solution of $Eu[N(SiMe_3)_2]_2(THF)_2$ (154.1 mg, 0.25 mmol) in n-hexane (6 mL) at room temperature. The mixture was stirred for 20 min, and there is no significant change in color. After filtration, solvent was removed under reduced pressure. The resulting orange-yellow solid was washed three times by n-hexane and dried in vacuum. Yield: 22 mg, 45%. ^1H NMR signals of complex **1** in C_6D_6 were not located in the range of +600 to -600 ppm, and the elemental analysis and powder X-ray diffraction were used to confirm the purity of the bulk

samples. Anal. Calcd (%) for $C_{18}H_{52}EuN_4Si_4$: C, 36.71; H, 8.90; N, 9.51. Found: C, 36.34; H, 8.84; N, 9.14.

Synthesis of $[Yb(NR_2)_2(ONMe_3)]_2(\mu\text{-}O)$ (R=$SiMe_3$) (2)

Me_3NO (18.9 mg, 0.25 mmol) was added to a solution of $Yb[N(SiMe_3)_2]_2(THF)_2$ (159.8 mg, 0.25 mmol) in n-hexane (15 mL) at room temperature. The mixture changed from red to colorless, and white precipitates appeared within 20 min. After the white precipitates was separated, solvent was removed under reduced pressure. The resulting white solid was washed three times by n-hexane and dried in vacuum. Yield: 20 mg, 21%. Anal. Calcd (%) for $C_{30}H_{90}Yb_2N_6O_3Si_8$: C, 31.23; H, 7.86; N, 7.28. Found: C, 31.50; H, 7.63; N,5.78. The low nitrogen content is presumably due to the high sensitivity of this compound toward moisture. ^{1}H NMR signals of complex **2** in C_6D_6 were not located in the range of +250 to -250 ppm. Powder X-ray diffraction were used to confirm the purity of the bulk samples.

Synthesis of $[Sm(NR_2)_2(THF)]_2(\mu\text{-}O)$ (R=$SiMe_3$) (3)

Me_3NO (18.7 mg, 0.25 mmol) was added to a solution of $Sm[N(SiMe_3)_2]_2(THF)_2$ (154.2 mg, 0.25 mmol) in n-hexane (6 mL) at room temperature. The mixture changed from dark brown to pale brown, and white precipitates appeared within 20 min. The white precipitate was isolated by centrifugation and the solvent of supernatant was removed under reduced pressure. The resulting two batches of white solid was washed by n-hexane and dried in vacuum. Yield: 34 mg, 25%. X-ray quality crystals of **3** were grown as colorless blocks by slow evaporation of n-hexane at temperature, which matched the unit cell of $[Sm(NR_2)_2(THF)]_2(\mu\text{-}O)$ (R=$SiMe_3$).[3]

II. Characterization

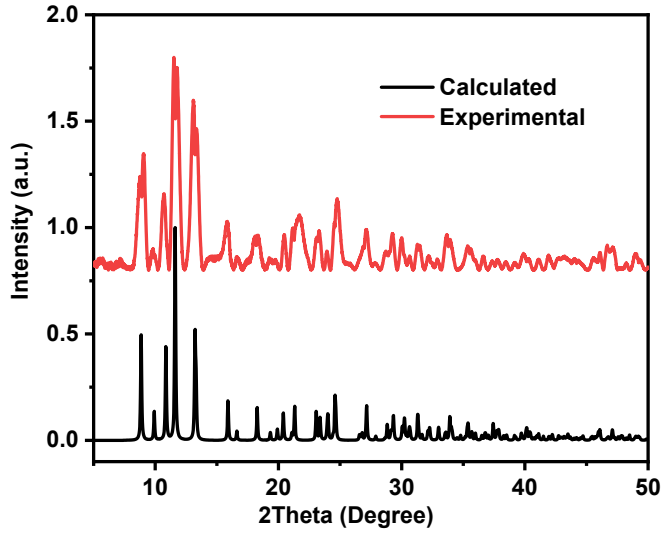

Fig. S1. Experimental and calculated PXRD patterns for $Eu[N(SiMe_3)_2]_2(TMEDA)$.

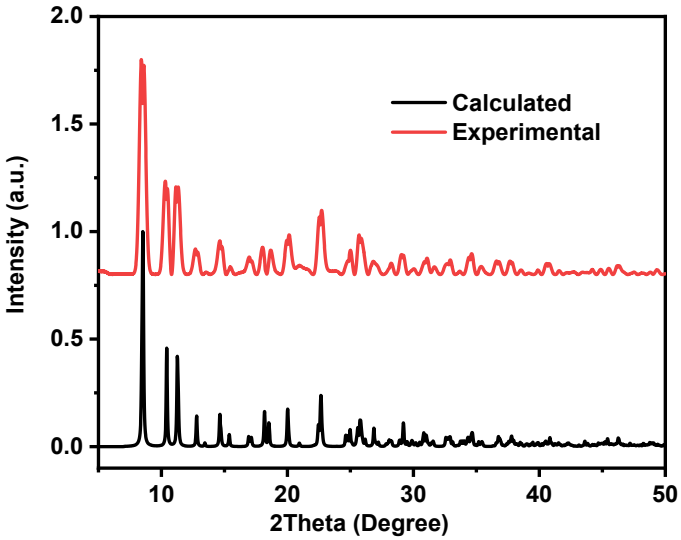

Fig. S2. Experimental and calculated PXRD patterns for $[Yb(NR_2)_2(ONMe_3)]_2(\mu\text{-}O)$ ($R=SiMe_3$) .

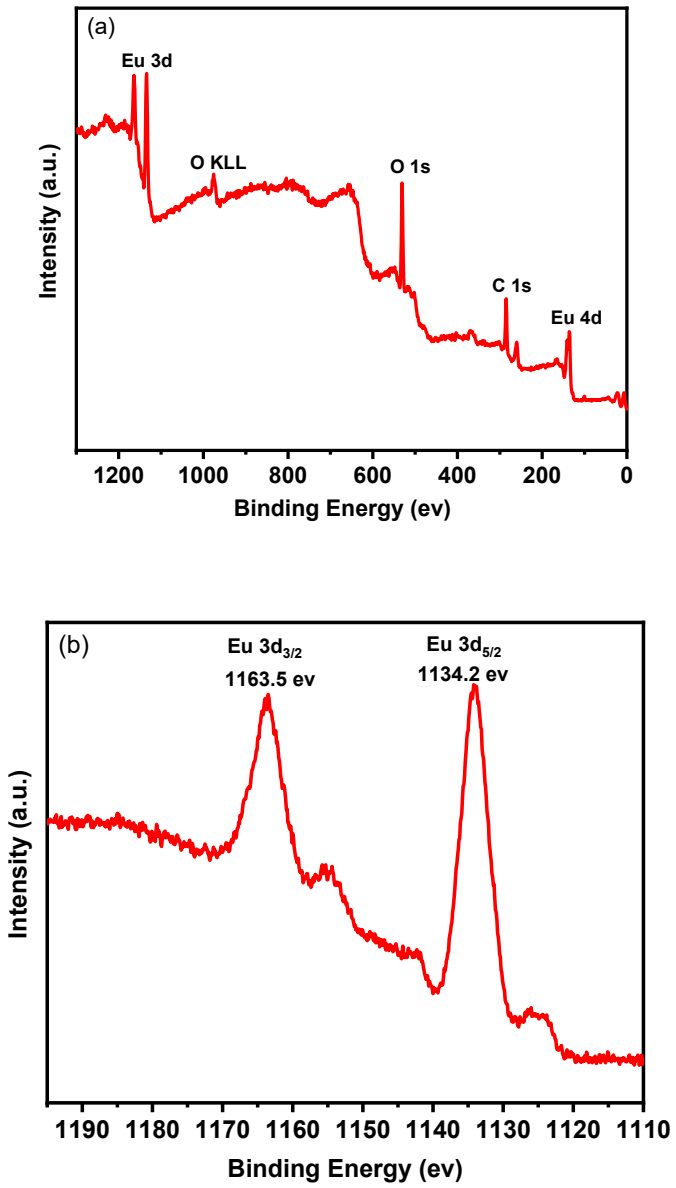

Fig. S3. XPS survey spectrum (a) and Eu 3d spectrum (b) of the yellow precipitates from the reaction of $Eu[N(SiMe_3)_2]_2(THF)_2$ with Me_3NO (1:1).

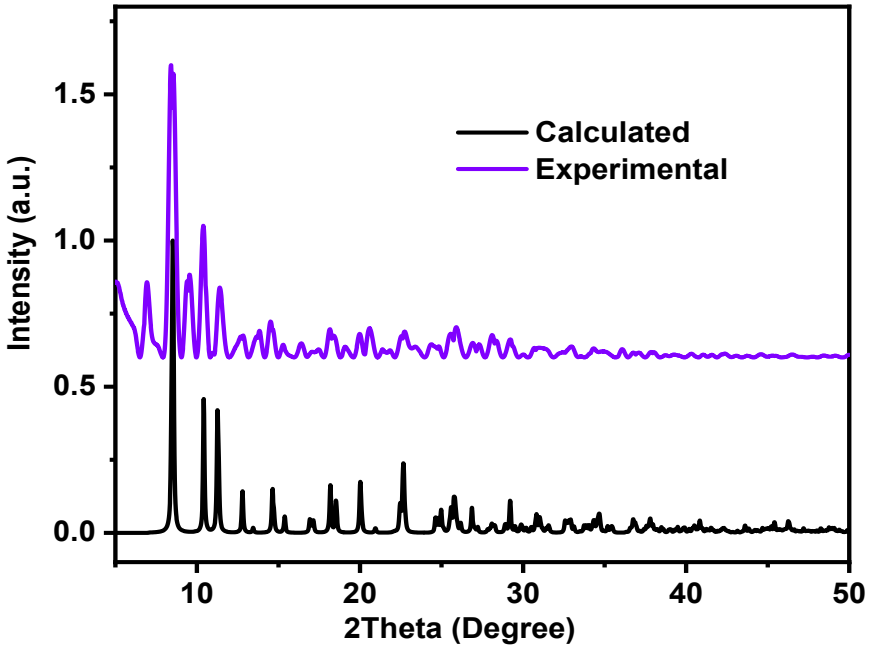

Fig. S4. PXRD pattern of the white precipitates from the reaction of $Yb[N(SiMe_3)_2]_2(THF)_2$ with Me_3NO and calculated PXRD pattern of $[Yb(NR_2)_2(ONMe_3)]_2(\mu\text{-}O)$ (R=$SiMe_3$).

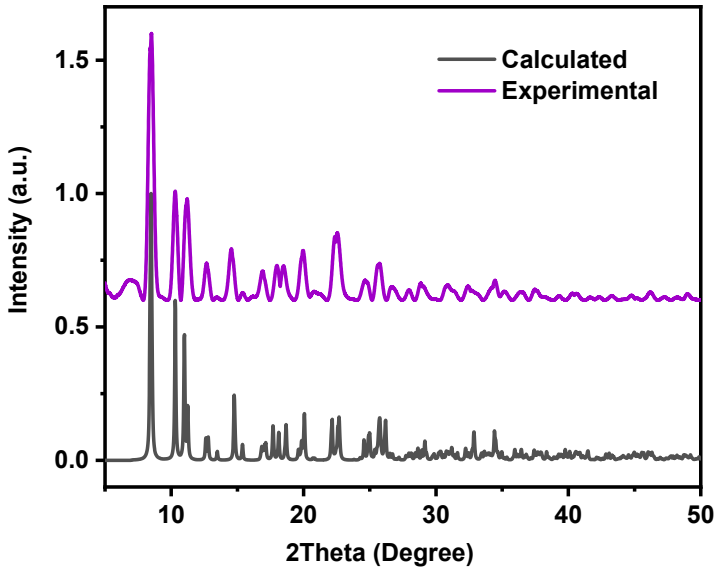

Fig. S5. PXRD pattern of the white precipitates from the reaction of $Sm[N(SiMe_3)_2]_2(THF)_2$ with Me_3NO and calculated PXRD pattern of $[Sm(NR_2)_2(THF)]_2(\mu\text{-}O)$ (R=$SiMe_3$).

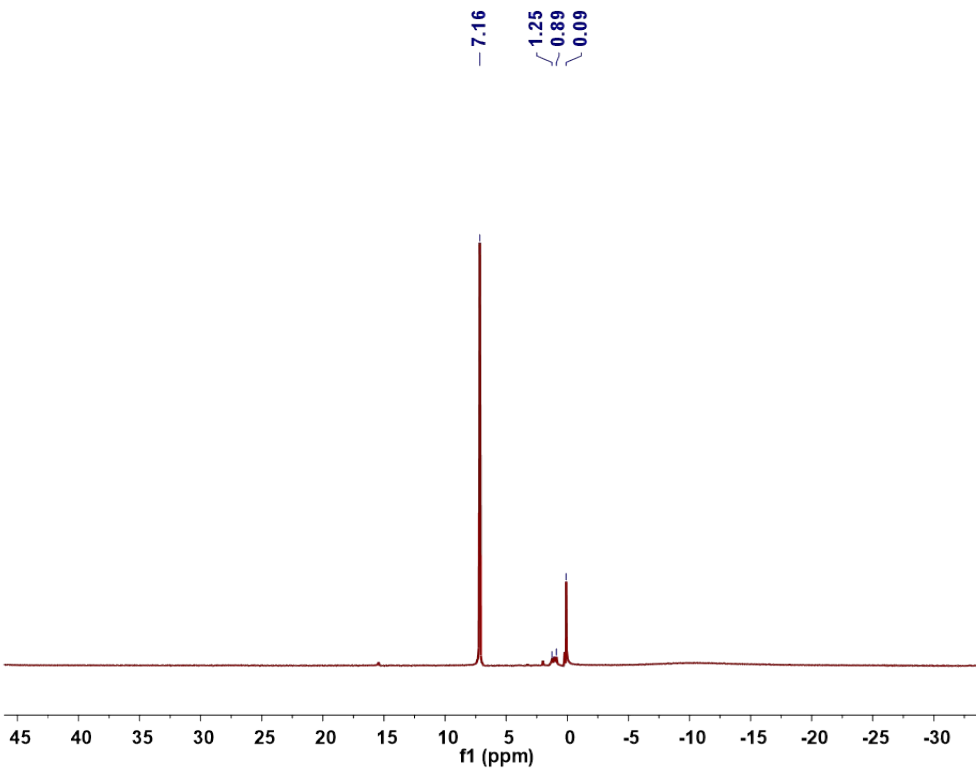

Fig. S6. ^{1}H NMR spectrum of complex **1** in C_6D_6. The resonance at 0.09 is assignable to $HN(SiMe_3)_2$. The resonances at 0.89 and 1.25 ppm are assignable to n-hexane.

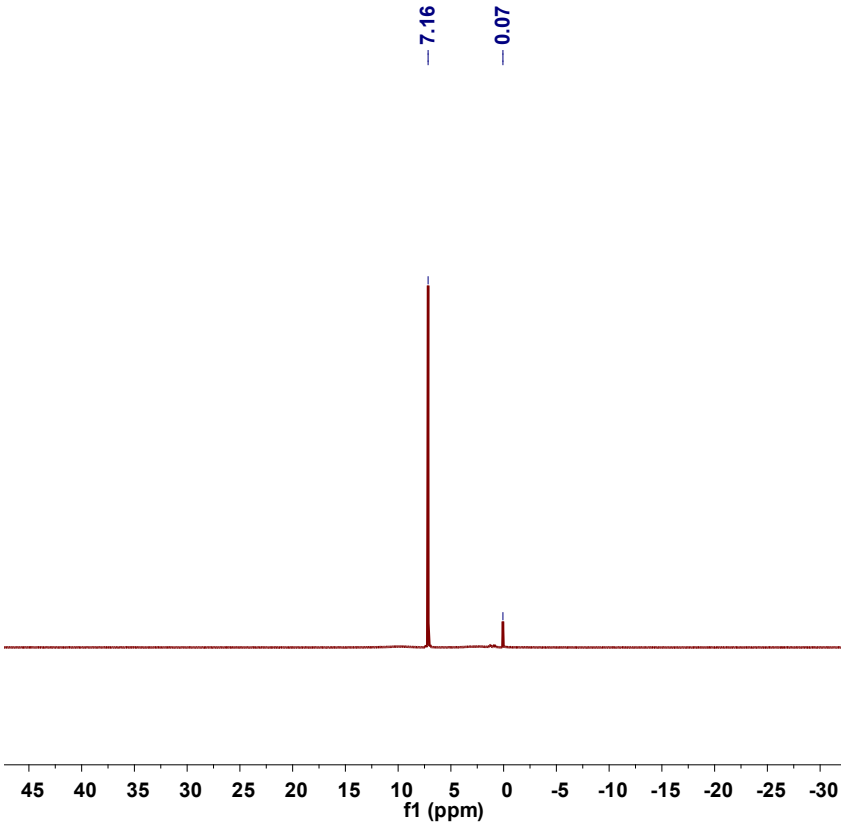

Fig. S7. ^{1}H NMR spectrum of complex **2** in C_6D_6. The resonance at 0.07 is assignable to $HN(SiMe_3)_2$.

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

Complex	**1**	**2**	**3**
CCDC	2120652	2120653	2299402
Empirical formula	$C_{18}H_{52}EuN_4Si_4$	$C_{30}H_{90}Yb_2N_6O_3Si_8$	$C_{32}H_{88}N_4O_3Si_8Sm_2$
Formula weight	588.95	1153.87	1102.48
Temperature/K	180(2)	180.00(10)	179.99(10)
Crystal system	monoclinic	triclinic	triclinic
Space group	C2/c	P-1	P-1
a /Å	8.6046(2)	10.6610(4)	10.8990(3)
b/Å	17.8193(4)	11.9772(5)	12.0887(3)
c/Å	20.3916(4)	12.3171(6)	12.2407(3)
α/°	90	118.634(5)	119.001(3)
β/°	101.988(2)	102.460(4)	102.554(2)
γ/°	90	90.275(4)	91.310(2)
Volume/Å^3	3058.41(12)	1337.11(12)	1361.20(7)
Z	4	1	1
ρ_{calc}g/cm^3	1.279	1.433	1.345
μ/mm^{-1}	2.218	3.687	2.342
F(000)	1228.0	588.0	568.0
2θ range/deg	4.084 to 56.562	3.93 to 52.742	3.872 to 52.73

	$-11 \leq h \leq 11$	$-13 \leq h \leq 13$	$-13 \leq h \leq 13$
Index ranges	$-23 \leq k \leq 23$	$-14 \leq k \leq 14$	$-15 \leq k \leq 15$
	$-26 \leq l \leq 27$	$-15 \leq l \leq 15$	$-15 \leq l \leq 15$
Reflections collected	18076	14154	
	3685	5340	5560
Independent reflections	$R_{int} = 0.0295$	$R_{int} = 0.0353$	$R_{int} = 0.0321$
	$R_{sigma} = 0.0229$	$R_{sigma} = 0.0372$	$R_{sigma} = 0.0231$
Completeness	99.7%	97.8%	100%
Data/restraints/parameters	3685/0/131	5340/2/232	5560/99/235
Goodness-of-fit on F^2	1.069	1.055	1.042
Final R indexes [I>=2σ (I)]	$R_1 = 0.0180$	$R_1 = 0.0334$	$R_1 = 0.0276$
	$wR_2 = 0.0424$	$wR_2 = 0.0889$	$wR_2 = 0.0738$
Final R indexes [all data]	$R_1 = 0.0216$	$R_1 = 0.0372$	$R_1 = 0.0308$
	$wR_2 = 0.0447$	$wR_2 = 0.0906$	$wR_2 = 0.0753$
Largest diff. peak/hole / e $Å^{-3}$	0.38/-0.37	1.43/-0.91	1.67/-1.06

III. References

1. W. J. Evans, D. K. Drummond, H. Zhang and J. L. Atwood, *Inorg. Chem.*, 1988, **27**, 575.

2. (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.

3. E. D. Brady, D. L. Clark, D. W. Keogh, B. L. Scott and J. G. Watkin, *J. Am. Chem. Soc.*, 2002, **124**, 7007.