

Supporting Information

Rare-earth metal-mediated addition/cyclization of 2-cyanobenzoamino anion

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Experimental Section

General Procedure. All operations involving air- and moisture-sensitive compounds were carried out under an inert atmosphere of purified argon or nitrogen using standard Schlenk techniques. The solvents of THF, toluene, *n*-hexane were refluxed and distilled over sodium benzophenone ketyl under nitrogen immediately prior to use. $(C_5H_5)_2LnCl(THF)$ was prepared by the literature methods.¹ Anthranilonitrile and $HN(SiMe_3)_2$ were purchased from Aldrich and were used without purification. Elemental analyses for C, H and N were carried out on a Rapid CHN-O analyzer. Infrared spectra were obtained on a NICOLET FT-IR 360 spectrometer with samples prepared as Nujol mulls. ¹H NMR data were obtained on a Brüker DMX-400 NMR spectrometer.

Synthesis of $[2-NCC_6H_4NHLi(THF)]_n$ (1): A 30 mL THF solution of anthranilonitrile (0.688 g, 5.80 mmol) was added into the 30 mL THF solution of $LiN(SiMe_3)_2$ (0.970 g, 5.80 mmol) at room temperature. After stirring for 24 h, all volatile substances were removed under vacuum to give pale yellow powder. Yield: 1.09 g (96 %). Recrystallization of the powder from the mixture solvent of THF and *n*-hexane gave suited X-ray single crystal diffraction analysis crystals of **1**. C, H, N analysis (%) for $C_{11}H_{13}N_2OLi$: calcd: C 67.35, H 6.68, N 14.28; found: C 67.17, H 6.63, N 14.46; IR (Nujol): 3274 s, 2206 s, 1604 s, 1536 s, 1273 s, 1078 s, 1045 s, 910 m, 895 s, 741 s, 734s, 692 s cm^{-1} ; ¹H NMR (THF-*d*₈ 3.58, 1.72): δ 6.82, 6.72, 6.32,

5.73 (m, 4H NHC₆H₄CN), δ 3.90 (s, 1H NHC₆H₄CN), δ 3.54 (m, 4H O(CH₂CH₂)₂)
 δ 1.67 (m, 4H O(CH₂CH₂)₂). ¹³C NMR (THF-d₈ 67.21, 25.31): δ 167.28, 132.54,
132.47, 118.98, 107.60.

Synthesis of (C₅H₅)₂Er[κ^3 -(4-NH=(C₈N₂H₄)(2-NHC₆H₄)]Li(THF)₃ (2**):** A 15 mL THF solution of **1** (0.295 g, 1.50 mmol) was added into the 15 mL THF solution of (C₅H₅)₂ErCl(THF) (0.304 g, 0.75 mmol) at room temperature. After stirring for 24 h, the reaction solution was concentrated to ca. 5 mL by reduced pressure. Pink crystals of **2** were obtained at -20 °C for several days. Yield: 0.430 g (76 %). C, H, N analysis (%): calcd for C₃₆H₄₄N₄O₃ErLi: C 57.27, H 5.87, N 7.42; found: C 57.15, H 5.84, N 7.59; IR (Nujol): 3385 m, 3374 m, 1597 s, 1573 s, 1544 s, 1327 m, 1258 m, 1070 s, 1010 s, 962 s, 913 m, 888 m, 760 s, 704 w, 660 m.

Synthesis of (C₅H₅)₂Y[κ^3 -(4-NH=(C₈N₂H₄)(2-NHC₆H₄)]Li(THF)₃ (3**):** Following the procedure described for **2**, reaction of (C₅H₅)₂YCl(THF) (0.291 g, 0.89 mmol) with **1** (0.350 g, 1.78 mmol) gave **3** as colorless crystals. Yield: 0.486 g (81%). C, H, N analysis (%) for C₃₆H₄₄N₄O₃YLi: calcd: C 63.91, H 6.56, N 8.28; found: C 63.97, H 6.62, N, 8.11; IR (Nujol): 3388 m, 3376 m, 1596 s, 1571 s, 1541 s, 1323 m, 1256 m, 1074 s, 1011 s, 962 s, 910 m, 886 m, 761 s, 702 w, 661 m. cm⁻¹; ¹H NMR (C₆D₆ 7.16): δ 7.06, 7.02, 6.83, 6.13 (m, 8H C₈N₂H₄, C₆H₄), δ 6.33 (s, 10H C₅H₅), δ 4.86 (b, 2H NHC₆H₄, NH=C₈N₂H₄), δ 3.54 (m, 12H O(CH₂CH₂)₂), δ 1.45 (m, 4H O(CH₂CH₂)₂). ¹³C NMR (C₆D₆ 128.06): δ 110.21 (Cp ring), δ 165.02, 134.24, 131.91, 123.36, 119.27, 111.20, 108.81, 91.71.

X-ray Data Collection, Structure Determination and Refinement. Suitable single crystals of complexes **1-2** were sealed under argon in Lindemann glass capillaries for X-ray structural analysis. Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using graphite-monochromated MoK α (λ = 0.71073 Å) radiation. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption with SADABS program.² The structures were solved by the direct method using the SHELXL-97 program.³ All non-hydrogen atoms were found

from the difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms, but were not included in the refinement. All calculations were performed using the SHELXL program. A summary of the crystallographic data and selected experimental information are given in Table 1.

Table 1 Crystal and Data Collection Parameters of Complexes **1** and **2**

	1	2
Formula	C ₁₁ H ₁₃ N ₂ OLi	C ₃₆ H ₄₄ N ₄ O ₃ ErLi
Molecular weight	196.17	754.95
Crystal color	colorless	Pink
Crystal dimens (mm)	0.15 x 0.12 x 0.10	0.12 x 0.10 x 0.06
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2(1)/c</i>	<i>P2(1)/c</i>
Unit cell dimensions		
<i>a</i> (Å)	10.813(10)	13.067(4)
<i>b</i> (Å)	8.566(8)	20.093(6)
<i>c</i> (Å)	12.667(11)	14.494(5)
β (deg)	99.228(12)	115.783(4)
<i>V</i> (Å ³)	1158.0(18)	4592(2)
<i>Z</i>	4	4
<i>D_c</i> (g.cm ⁻³)	1.125	1.463
μ (mm ⁻¹)	0.072	2.489
<i>F</i> (000)	416	1532
Radiation ($\lambda = 0.71073$ Å)	Mo- <i>Kα</i>	Mo- <i>Kα</i>
Temperature (K)	293.2	293.2
Scan type	ω -2 θ	ω -2 θ
θ range (deg)	1.91 to 25.00	1.73 to 25.01
<i>h, k, l</i> range	-12 ≤ <i>h</i> ≤ 12, -10 ≤ <i>k</i> ≤ 10 -15 ≤ <i>l</i> ≤ 12	-15 ≤ <i>h</i> ≤ 15 -23 ≤ <i>k</i> ≤ 23 -17 ≤ <i>l</i> ≤ 8
No. of reflections measured	4634	14065
No. of unique reflections	2021 (<i>R</i> _{int} = 0.0521)	6043 (<i>R</i> _{int} = 0.0623)
Completeness to θ	99.1 % ($\theta = 25.00$)	100.0 % ($\theta = 25.01$)
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	2021/1/139	6043/2/412
Goodness-of-fit on <i>F</i> ²	0.994	0.780
Final R indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0835, <i>wR</i> ₂ = 0.2364	<i>R</i> ₁ = 0.0387, <i>wR</i> ₂ = 0.0380

R indices (all data)	$R_1 = 0.1231$, $wR_2 = 0.2638$	$R_1 = 0.1000$, $wR_2 = 0.0441$
Largest diff. peak and hole ($e \cdot \text{\AA}^{-3}$)	0.237 and -0.201	0.648 and -0.764

References:

1. W. J. Evans, M. S. Sollberger, J. L. Shreeve, J. M. Olofson, J. H. Hain and Ziller, J. *W. Inorg. Chem.* 1992, **31**, 2492.
2. G. M. Sheldrick, SADABS, *A Program for Empirical Absorption Correction*; Göttingen, Germany, 1998.
3. G. M. Sheldrick, SHELXL-97, Program for the refinement of the crystal structure; University of Göttingen: Germany, 1997.