Supporting Information For:

# Synthesis of a Terminal Ce(IV) Oxo Complex by Photolysis of a Ce(III) Nitrate

## Complex

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#### **Experimental**

**General Procedures:** All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions in the glovebox or on the Schlenk line, under an atmosphere of dinitrogen. Hexanes, diethyl ether (Et<sub>2</sub>O), and tetrahydrofuran (THF) were dried by passage over activated molecular sieves using a Vacuum Atmospheres solvent purification system. Isooctane was dried over activated 3Å molecular sieves for 24 h, degassed by bubbling dry N<sub>2</sub> into the solvent for 30 min, cannula transferred into a new vessel, and again dried over 3Å molecular sieves for 24 h prior to use. Pyridine-*d*<sub>5</sub> and toluene-*d*<sub>8</sub> were dried over activated 3 Å molecular sieves for 24 h prior to use. Ce(NO<sub>3</sub>)<sub>3</sub>(THF)<sub>4</sub> was prepared by the reported literature procedure.<sup>1</sup> Lumcrissy 12V flexible LED Lightstrips, emitting at 380 nm, were used for photolyses. All other reagents were purchased from commercial suppliers and used as received.

<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, and <sup>7</sup>Li{<sup>1</sup>H} NMR spectra were recorded on an Agilent Technologies 400 MHz 400-MR DD2 or Varian UNITY INOVA 500 spectrometer. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to external SiMe<sub>4</sub> using residual protio solvent resonances as internal standards. <sup>7</sup>Li{<sup>1</sup>H} NMR spectra were referenced indirectly to the <sup>1</sup>H chemical shift of SiMe<sub>4</sub> at 0 ppm, according to IUPAC standard.<sup>2,3</sup> IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. Electronic absorption spectra were recorded on a Shimadzu UV3600 UV-NIR Spectrometer. Elemental analyses were performed by the Microanalytical Laboratory at University of California (Berkeley, CA).

**Raman Spectroscopy.** Raman spectra were recorded on a LabRam Aramis microRaman system (Horiba Jobin Yvon) equipped with 1200 grooves/mm holographic gratings and a Peltier-cooled CCD camera. The 633 nm output of a Melles Griot He-Ne laser was used to excite the sample, and spectra were collected in a back scattering geometry using a confocal Raman Microscope

(high stability BX40) equipped with Olympus objectives (MPlan 50x). Sample preparation was performed inside the glovebox: Pure crystalline solid samples were placed between a glass microscope slide and coverslip, sealed with a bead of silicone grease, and removed from the glovebox for spectral acquisition.

**Cyclic Voltammetry Measurements.** CV experiments were performed with a CH Instruments 600c Potentiostat, and the data were processed using CHI software (version 6.29). All experiments were performed in a glove box using a 20 mL glass vial as the cell. The working electrode consisted of a platinum disk embedded in glass (2 mm diameter), the counter electrode and the reference electrode were both platinum wires. Solutions employed for CV studies were typically 1 mM in analyte, and 0.1 M in  $[NBu_4][PF_6]$ . All potentials are reported versus the  $[Cp_2Fe]^{0/+}$  couple.

X-ray Crystallography. Data for 1 - 4 were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromater with a Mo K $\alpha$  X-ray source ( $\alpha = 0.71073$  Å). The crystals of 1 - 4 were mounted on a cryoloop under Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream system. X-ray data for 1, 2, 3 and 4 were collected utilizing frame exposures of 5, 60, 10 and 5 seconds, respectively. Data collection and cell parameter determination were conducted using the SMART program.<sup>4</sup> Integration of the data frames and final cell parameter refinement were performed using SAINT software.<sup>5</sup> Absorption corrections of the data were carried out using the multi-scan method SADABS.<sup>6</sup> Subsequent calculations were carried out using SHELXTL.<sup>7</sup> Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed

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using SHELXTL.<sup>7</sup> Complexes 1 - 4 have been deposited in the Cambridge Structural Database (1: CCDC 1569781; 2: CCDC 1569782; 3: CCDC 1569783; 4: CCDC 1569784).

One 2,2,2-cryptand moiety in complex **3** exhibited positional disorder. Disordered carbon atoms were modelled over two positions with 50% occupancy. Hydrogen atoms were not assigned to disordered carbon atoms and disordered carbon atoms were refined isotropically.

Synthesis of LiOSiMe<sub>3</sub>: To a stirring, colorless solution of LiN(SiMe<sub>3</sub>)<sub>2</sub> (453.0 mg, 2.707 mmol) in hexanes (3 mL) was added dropwise a solution of HOSiMe<sub>3</sub> (0.30 mL, 240 mg, 2.7 mmol) in hexanes (1 mL). The resulting colorless reaction mixture was stirred for 30 min at room temperature. Subsequent concentration of this solution to ca. 1 mL and storage at -25 °C for 24 h resulted in deposition of white crystals of LiOSiMe<sub>3</sub>, which were isolated by decanting off the supernatant (172.5 mg, 66% yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 400 MHz):  $\delta$  0.19 (s, SiCH<sub>3</sub>). <sup>7</sup>Li{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 155 MHz):  $\delta$  0.65 (s). The <sup>1</sup>H NMR spectrum of this material is in good agreement with the previously reported spectrum for this compound.<sup>8</sup>

**Synthesis of Ce(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub>:** The synthesis of Ce(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub> was modified from a literature procedure.<sup>9</sup> To a stirring, colorless solution of Ce(NO<sub>3</sub>)<sub>3</sub>(THF)<sub>4</sub> (428.2 mg, 0.696 mmol) in THF (4 mL) was added a pale yellow solution of LiN(SiMe<sub>3</sub>)<sub>2</sub> (350.1 mg, 2.092 mmol) in hexanes (3 mL). Upon addition, the solution immediately turned yellow. The reaction mixture was stirred for 5 h at room temperature, which resulted in the deposition of a very fine white precipitate. The volatiles were then removed *in vacuo*, and the resulting solid was triturated with hexanes (1 mL) to yield a yellow powder. The solid was then extracted into hexanes (5 mL) and filtered through a Celite column supported on glass wool (0.5 cm × 2 cm). The pale orange filtrate was concentrated to ca. 2 mL, and subsequent storage of this solution at -25 °C for 24 h resulted in the deposition of a mixture of yellow needles and yellow-orange powder. The crude product was

collected by decanting off the supernatant. The solid was redissolved in hexanes (4 mL), and the resulting solution was filtered through a Celite column supported on glass wool (0.5 cm × 2 cm). The volume of the filtrate was then reduced to ca. 3 mL and the solution was stored at -25 °C for 24 h, resulting in deposition of bright yellow needles (110.7 mg). A second crop of crystals was obtained by further concentration of the supernatant, followed by storage of the concentrated solution at -25 °C for 24 h (Total: 182.4 mg, 42 % yield). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C, 400 MHz):  $\delta$  - 3.43 (br s, CH<sub>3</sub>). The <sup>1</sup>H NMR spectrum of this material is in good agreement with the previously reported spectrum for this complex.<sup>9</sup>

Synthesis of [Li(2.2,2-cryptand)][Ce( $\kappa^2$ -O<sub>2</sub>NO)(NR<sub>2</sub>)<sub>3</sub>] (1): To an orange solution of Ce(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub> (177.1 mg, 0.286 mmol) in THF (1 mL) was added LiNO<sub>3</sub> (20.0 mg, 0.289 mmol). This resulted in immediate formation of a yellow-orange solution. After stirring for 20 min, a colorless solution of 2,2,2-cryptand (102.0 mg, 0.270 mmol, 0.95 eq) in THF (1 mL) was added dropwise, which resulted in an immediate color change to yellow. The solution was stirred for a further 20 min. The volatiles were then removed in vacuo, which yielded a yellow oil. The oil was triturated with hexanes (1 mL) and the resulting yellow solid was then extracted into  $Et_2O(2 \text{ mL})$  and filtered through a Celite column supported on glass wool (0.5 cm  $\times$  2 cm). The filtrate was then concentrated to ca. 1 mL and layered with hexanes (1 mL). Storage of this solution at -25 °C for 24 h resulted in deposition of a mixture of yellow crystals and white powder. The crude solid was collected by decanting off the solvent and was then redissolved in Et<sub>2</sub>O (2 mL). The resulting yellow solution was filtered through a Celite column supported on glass wool ( $0.5 \text{ cm} \times 2 \text{ cm}$ ). The yellow filtrate was then concentrated to ca. 1 mL and layered with hexanes (1 mL). Storage of this solution at -25 °C for 24 h resulted in deposition of yellow plates, which were isolated by decanting off the supernatant (110.5 mg, 38 % yield). Anal. Calcd

for C<sub>36</sub>H<sub>90</sub>CeLiN<sub>6</sub>O<sub>9</sub>Si<sub>6</sub>: C, 40.53; H, 8.50; N, 7.88. Found: C, 40.37; H, 8.73; N, 8.00. <sup>1</sup>H NMR (py-*d*<sub>5</sub>, 25 °C, 400 MHz):  $\delta$  -1.32 (br s, 54H, NSiCH<sub>3</sub>), 2.48 (s, 12H, NCH<sub>2</sub>), 3.45 (s, 12H, OCH<sub>2</sub>CH<sub>2</sub>N), 3.51 (s, 12H, OCH<sub>2</sub>CH<sub>2</sub>O). <sup>7</sup>Li{<sup>1</sup>H} NMR (py-*d*<sub>5</sub>, 25 °C, 155 MHz):  $\delta$  -1.08 (s). UV-Vis/NIR (Et<sub>2</sub>O, 0.95 mM, 25 °C, L·mol<sup>-1</sup>·cm<sup>-1</sup>): 336 ( $\epsilon$  = 140), 380 ( $\epsilon$  = 200). IR (KBr pellet, cm<sup>-1</sup>): 2951 (s), 2889 (s), 2819 (m), 1919 (vw), 1637 (w), 1491 (s), 1446 (s), 1385 (m), 1356 (s), 1286 (s), 1242 (vs), 1184 (m), 1130 (m), 1093 (vs), 1009 (m), 985 (vs), 931 (s), 866 (s), 829 (vs), 769 (s), 754 (m), 685 (w), 665 (s), 598 (s), 563 (vw), 515 (vw). Raman (neat solid, cm<sup>-1</sup>): 1479 (m), 1441 (m), 1406 (m), 1294 (m), 1259 (m), 1168 (vw), 1132 (m), 1096 (w), 1072 (m), 1043 (s), 917 (br m), 855 (m), 825 (w), 742 (w), 678 (m), 571 (vs), 562 (s), 440 (br w), 347 (w).

Small Scale Synthesis of [Li(2,2,2-cryptand)][Ce(O)(NR<sub>2</sub>)<sub>3</sub>] (2): Yellow crystals of 1 (40.0 mg, 0.037 mmol) were dissolved in a 2:1 mixture of tol- $d_8$  and py- $d_5$  (1 mL total volume) resulting in formation of a clear yellow solution. This solution was transferred to an NMR tube equipped with a J-Young valve, brought out of the glovebox, cooled to -5 °C in a salt water/dry ice bath, and photolysed for 6 h using a flexible LED lightstrip that emitted at 380 nm. The temperature of the bath was kept at ca. -5 °C by periodically adding small pieces of dry ice. The color of the solution gradually changed from yellow to yellow-orange over the course of the photolysis. A <sup>1</sup>H NMR spectrum was then recorded. Integration of the SiMe<sub>3</sub> resonance assigned to complex 1, relative to the NCH<sub>2</sub> resonance of the 2,2,2-cryptand moiety, revealed approximately 80 % consumption of 1. <sup>1</sup>H NMR (2:1 tol- $d_8$ /py- $d_5$ , 25 °C, 400 MHz):  $\delta$  -1.18 (br s, 54H, NSiC $H_3$ , complex 1), -0.43 (s, 54H, NSiC $H_3$ , complex 4), -0.21 (s, 9H, OSiC $H_3$ , complex 4), 0.28 (br s, 108H, NSiC $H_3$ , complex 3), 0.80 (s, 54H, NSiC $H_3$ , complex 2), 2.28 (t, 12H,  $J_{HH} = 4$  Hz, NC $H_2$ ), 3.23 (t, 12H,  $J_{HH} = 4$  Hz, OC $H_2$ CH<sub>2</sub>N), 3.28 (s, 12H, OC $H_2$ CH<sub>2</sub>O). The sample

was then returned to glovebox and the volatiles were removed in vacuo. The resulting oil was triturated with  $Et_2O(2 \times 1 \text{ mL})$  to yield an orange-brown solid. The solid was then extracted into  $E_{12}O(2 \text{ mL})$  and filtered through a Celite column supported on glass wool (0.5 cm  $\times$  2 cm), resulting in generation of a yellow filtrate and leaving a plug of orange-brown solid on the Celite. The filtrate was transferred to a 4 mL scintillation vial, which was then placed inside a 20 mL scintillation vial. Isooctane (1 mL) was added to the outer vial. Storage of the two-vial system at -25 °C for 72 h resulted in the deposition of yellow plates, which were isolated by decanting off the supernatant (12.6 mg, 33 % yield). In one instance, storage of the two-vial system at -25 °C for 5 d resulted in deposition of 2, along with the deposition of small amounts of pale-yellow plates and colorless plates, which were subsequently identified as 3 and 4, respectively, by X-ray crystallography. Anal. Calcd for C<sub>36</sub>H<sub>90</sub>CeLiN<sub>5</sub>O<sub>7</sub>Si<sub>6</sub>: C, 42.36; H, 8.89; N, 6.86. Found: C, 42.12; H, 8.77; N, 6.86. <sup>1</sup>H NMR (py-*d*<sub>5</sub>, 25 °C, 500 MHz): δ 0.69 (s, 54H, NSiCH<sub>3</sub>), 2.56 (t, 12H,  $J_{HH} = 6$  Hz, NCH<sub>2</sub>), 3.52 (t, 12H,  $J_{HH} = 5$  Hz, OCH<sub>2</sub>CH<sub>2</sub>N), 3.59 (s, 12H, OCH<sub>2</sub>CH<sub>2</sub>O). <sup>13</sup>C NMR (py-d<sub>5</sub>, 25 °C, 125 MHz): δ 6.39 (SiCH<sub>3</sub>), 54.4 (NCH<sub>2</sub>), 69.3 (overlapping signals for OCH<sub>2</sub>CH<sub>2</sub>N and OCH<sub>2</sub>CH<sub>2</sub>O). <sup>7</sup>Li{<sup>1</sup>H} NMR (py-*d*<sub>5</sub>, 25 °C, 155 MHz): δ -1.00 (s). UV-Vis/NIR (Et<sub>2</sub>O, 0.79 mM, 25 °C, L·mol<sup>-1</sup>·cm<sup>-1</sup>): 306 (ε = 830). IR (KBr pellet, cm<sup>-1</sup>): 2943 (vs), 2885 (vs), 2821 (s), 2112 (vw), 1900 (vw), 1594 (vw), 1456 (m), 1358 (s), 1300 (m), 1238 (vs), 1157 (w), 1130 (s), 1095 (vs), 995 (vs), 933 (s), 866 (vs), 825 (vs), 768 (s), 752 (s), 685 (s), 663 (s), 594 (s), 561 (vw). Raman (neat solid, cm<sup>-1</sup>): 1479 (s), 1464 (s), 1445 (s), 1372 (w), 1294 (m), 1266 (m), 1176 (w), 1108 (s), 1068 (w), 1039 (m), 983 (vw), 917 (m), 888 (w), 830 (m), 737 (s), 418 (br vs), 312 (vw).

Larger Scale Synthesis of [Li(2,2,2-cryptand)][Ce(O)(NR<sub>2</sub>)<sub>3</sub>] (2): Yellow crystals of 1 (264.6 mg, 0.248 mmol) were dissolved in a 2:1 mixture of tol- $d_8$  and py- $d_5$  (5 mL total volume)

resulting in formation of a clear yellow solution. This solution was then divided into five portions and each portion was transferred to an NMR tube equipped with a J-Young valve. The samples were brought out of the glovebox, cooled to -5 °C in a salt water/dry ice bath, and photolysed for 7 h using a flexible LED lightstrip that emitted at 380 nm. The temperature of the bath was kept at ca. -5 °C by periodically adding small pieces of dry ice. The color of the solution gradually changed from yellow to yellow-orange over the course of the photolysis. A <sup>1</sup>H NMR spectrum of one of these samples was then recorded. Integration of the SiMe<sub>3</sub> resonance assigned to complex 1, relative to the NCH<sub>2</sub> resonance of the 2,2,2-cryptand moiety, reveals approximately 77 % consumption of 1.<sup>1</sup>H NMR (2:1 tol- $d_8$ /py- $d_5$ , 25 °C, 400 MHz):  $\delta$  -1.12 (br s, 54H, NSiCH<sub>3</sub>, complex 1), -0.42 (s, 54H, NSiCH<sub>3</sub>, complex 4), -0.12 (s, 9H, OSiCH<sub>3</sub>, complex 4), 0.29 (br s, 108H, NSiCH<sub>3</sub>, complex 3), 0.81 (s, 54H, NSiCH<sub>3</sub>, complex 2), 2.37 (t,  $12H, J_{HH} = 4$  Hz, NCH<sub>2</sub>), 3.32 (t,  $12H, J_{HH} = 4$  Hz, OCH<sub>2</sub>CH<sub>2</sub>N), 3.38 (s, 12H, OCH<sub>2</sub>CH<sub>2</sub>O). The five tubes were returned to the glovebox and combined into a single 20 mL scintillation vial. The volatiles were then removed under reduced pressure and the resulting oil was triturated with  $Et_2O$  (2 × 1 mL) to yield an orange-brown solid. The solid was extracted into  $Et_2O$  (4 mL) and filtered through a Celite column supported on glass wool ( $0.5 \text{ cm} \times 2 \text{ cm}$ ), resulting in generation of a yellow filtrate and leaving a plug of orange-brown solid on the Celite. The filtrate was concentrated to ca. 2 mL and transferred to a 4 mL scintillation vial, which was then placed inside a 20 mL scintillation vial. Isooctane (1 mL) was added to the outer vial. Storage of the two-vial system at -25 °C for 72 h resulted in the deposition of yellow plates, which were isolated by decanting off the supernatant (45.5 mg, 18 % yield). This material was identical to that prepared via the small scale synthesis (described above), according to <sup>1</sup>H NMR spectroscopy.

Synthesis of [Li(2,2,2-cryptand)] [Ce(OSiMe<sub>3</sub>)(NR<sub>2</sub>)<sub>3</sub>] (4): To a stirring, orange solution of Ce(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>3</sub> (100.1 mg, 0.161 mmol) in THF (3 mL) was added LiOSiMe<sub>3</sub> (15.0 mg, 0.156 mmol) as a solid, which resulted in an immediate color change to pale yellow. After stirring for 45 min, 2,2,2-cryptand (56.2 mg, 0.149 mmol) was added to the pale yellow solution. The solution was then stirred for a further 15 min. The volatiles were removed in vacuo and the resulting white solid was triturated with hexanes  $(2 \times 2 \text{ mL})$ . The solid was then extracted into  $Et_2O(3 mL)$  and filtered through a Celite column supported on glass wool (0.5 cm  $\times$  2 cm). The resulting pale yellow filtrate was concentrated to ca. 2 mL and layered with hexanes (1 mL). Storage of this solution at -25 °C for 24 h resulted in deposition of colorless crystals, which were isolated by decanting off the supernatant (76.8 mg, 47 % yield). Anal. Calcd for C<sub>39</sub>H<sub>99</sub>CeLiN<sub>5</sub>O<sub>7</sub>Si<sub>7</sub>: C, 42.82; H, 9.12; N, 6.40. Found: C, 42.69; H, 9.09; N, 6.44. <sup>1</sup>H NMR (pvd<sub>5</sub>, 25 °C, 400 MHz): δ -0.59 (br s, 54H, NSiCH<sub>3</sub>), -0.37 (s, 9H, OSiCH<sub>3</sub>), 2.56 (s, 12H, NCH<sub>2</sub>), 3.52 (s, 12H, OCH<sub>2</sub>CH<sub>2</sub>N), 3.60 (s, 12H, OCH<sub>2</sub>CH<sub>2</sub>O). <sup>7</sup>Li{<sup>1</sup>H} NMR (py-*d*<sub>5</sub>, 25 °C, 155 MHz): δ -0.97 (s). UV-Vis/NIR (Et<sub>2</sub>O, 0.68 mM, 25 °C, L·mol<sup>-1</sup>·cm<sup>-1</sup>): 276 (ε = 780), 330 (ε = 630), 347 ( $\epsilon$  = 740). IR (KBr pellet, cm<sup>-1</sup>): 2945 (s), 2889 (s), 2845 (m), 1917 (vw), 1618 (w), 1471 (w), 1456 (m), 1377 (w), 1358 (m), 1304 (m), 1238 (vs), 1182 (w), 1117 (w), 1097 (s), 1003 (vs), 964 (vs), 933 (m), 870 (s), 830 (vs), 768 (m), 750 (m), 687 (w), 663 (m), 609 (w), 592 (m), 517 (vw). Raman (neat solid, cm<sup>-1</sup>): 1481 (m), 1450 (m), 1408 (w), 1378 (vw), 1292 (w), 1265 (w), 1174 (vw), 1110 (m), 1070 (w), 1038 (w), 981 (vw), 915 (w), 887 (w), 833 (m), 741 (m), 673 (m), 622 (m), 566 (vs), 418 (br m) 347 (br m).



Figure S1: <sup>1</sup>H NMR spectrum of [Li(2,2,2-cryptand)][Ce( $\kappa^2$ -O<sub>2</sub>NO)(NR<sub>2</sub>)<sub>3</sub>] (1) in py-d<sub>5</sub>.



Figure S2: <sup>7</sup>Li{<sup>1</sup>H} NMR spectrum of [Li(2,2,2-cryptand)][Ce( $\kappa^2$ -O<sub>2</sub>NO)(NR<sub>2</sub>)<sub>3</sub>] (1) in py-d<sub>5</sub>.



**Figure S3:** <sup>1</sup>H NMR spectrum of the photolysis of **1** in 2:1 tol- $d_8$ /py- $d_5$ . \* indicates the presence of **1**. ^ indicates the presence of **2**. \$ indicates the presence of **3**. # indicates the presence of **4**.



**Figure S4**: <sup>1</sup>H NMR spectrum of the photolysis of **1** after 6 h in 2:1 tol- $d_8$ /py- $d_5$ . Integration of the SiMe<sub>3</sub> resonance assigned to complex **1**, relative to the NCH<sub>2</sub> resonance of the 2,2,2-cryptand moiety, reveals approximately 80 % consumption of **1**. \* indicates the presence of **1**. ^ indicates the presence of **2**. \$ indicates the presence of **3**. # indicates the presence of **4**. > indicates the presence of LiN(SiMe<sub>3</sub>)<sub>2</sub>. @ indicates a resonance tentatively assigned to HN(SiMe<sub>3</sub>)<sub>2</sub>. + indicates the presence of unidentified products.



Figure S5: <sup>1</sup>H NMR spectrum of [Li(2,2,2-cryptand)][Ce(O)(NR<sub>2</sub>)<sub>3</sub>] (2) in py- $d_5$ .



Figure S6:  ${}^{13}C{}^{1}H$  NMR spectrum of [Li(2,2,2-cryptand)][Ce(O)(NR<sub>2</sub>)<sub>3</sub>] (2) in py-d<sub>5</sub>.



Figure S7: <sup>7</sup>Li{<sup>1</sup>H} NMR spectrum of [Li(2,2,2-cryptand)][Ce(O)(NR<sub>2</sub>)<sub>3</sub>] (2) in py- $d_5$ .



Figure S8: <sup>1</sup>H NMR spectrum of [Li(2,2,2-cryptand)][Ce(OSiMe<sub>3</sub>)(NR<sub>2</sub>)<sub>3</sub>] (4) in py- $d_5$ .



Figure S9: <sup>7</sup>Li{<sup>1</sup>H} NMR spectrum of [Li(2,2,2-cryptand)][Ce(OSiMe<sub>3</sub>)(NR<sub>2</sub>)<sub>3</sub>] (4) in py- $d_5$ .



**Figure S10:** <sup>1</sup>H NMR spectrum of **1** in py- $d_5$  after standing at room temperature for 24 h. **Experimental details:** Yellow crystals of **1** (13.5 mg, 0.013 mmol) were dissolved in py- $d_5$  (0.75 mL), and the resulting yellow solution was transferred to an NMR tube equipped with a J-Young valve, and stored at room temperature in the absence of light for 24 h. Integration of the SiMe<sub>3</sub> resonance assigned to complex **1**, relative to the NCH<sub>2</sub> resonance of 2,2,2-cryptand moiety, suggests that approximately 80% of complex **1** remains unreacted. \* indicates the presence of **1**. ^ indicates the presence of **2**. \$ indicates the presence of **3**. # indicates the presence of **4**. + indicates presence of unidentified products.



**Figure S11**: <sup>1</sup>H NMR spectrum of **2** in py- $d_5$  after standing at room temperature for 4 d. **Experimental Details:** Yellow crystals of **2** (9.7 mg, 0.010 mmol) were dissolved in py- $d_5$  (0.75 mL) and the resulting yellow solution was transferred to an NMR tube equipped with a J-Young valve and stored at room temperature in the absence of light for 4 d. Integration of the SiMe<sub>3</sub> resonance assigned to complex **2**, relative to the NCH<sub>2</sub> resonance of the 2,2,2-cryptand moiety, reveals approximately 40% consumption of complex **2**. ^ indicates the presence of **2**. \$ indicates the presence of **3**. # indicates the presence of **4**.



**Figure S12**: <sup>1</sup>H NMR spectrum of **2** in 2:1 tol- $d_8$ /py- $d_5$  after standing at room temperature for 4d. **Experimental Details:** Yellow crystals of **2** (7.0 mg, 0.007 mmol) were dissolved in 2:1 tol- $d_8$ /py- $d_5$  (total volume: 0.75 mL) and the resulting yellow solution was transferred to an NMR tube equipped with a J-Young valve and stored at room temperature in the absence of light for 4 d. Integration of the SiMe<sub>3</sub> resonance assigned to complex **2**, relative to the CHD<sub>2</sub> resonance of tol- $d_8$ , reveals approximately 70% consumption of complex **2**. ^ indicates the presence of **2**. \$ indicates the presence of **3**. # indicates the presence of **4**. > indicates the presence of LiN(SiMe<sub>3</sub>)<sub>2</sub>. + indicates presence of unidentified products.



**Figure S13:** <sup>7</sup>Li{<sup>1</sup>H} NMR spectrum of **2** in 2:1 tol- $d_8$ /py- $d_5$  after standing at room temperature for 4d. > indicates the presence of LiN(SiMe<sub>3</sub>)<sub>2</sub>. % indicates overlapping resonances assignable to complexes **2**, **3** and **4**. **Experimental Details:** See Figure S12 caption.

	1	2	$3 \cdot \mathrm{Et}_2\mathrm{O}$	4
Formula	C <sub>36</sub> H <sub>90</sub> CeLiN <sub>6</sub> O <sub>9</sub> Si <sub>6</sub>	C <sub>36</sub> H <sub>90</sub> CeLiN <sub>5</sub> O <sub>7</sub> Si <sub>6</sub>	C <sub>76</sub> H <sub>172</sub> Ce <sub>3</sub> Li <sub>2</sub> N <sub>10</sub> O <sub>17</sub> Si <sub>12</sub>	C <sub>39</sub> H <sub>99</sub> CeLiN <sub>5</sub> O <sub>7</sub> Si <sub>7</sub>
Crystal Habit,	Plate, Yellow	Plate, Yellow	Plate, Yellow	Plate, Colorless
Color				
Crystal Size (mm)	$0.30 \times 0.25 \times 0.10$	0.10  imes 0.10  imes 0.05	$0.20 \times 0.10 \times 0.05$	$0.15 \times 0.15 \times 0.05$
MW (g/mol)	1066.73	1020.72	2269.55	1093.92
crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
space group	$P2_1/c$	$P2_1/c$	P-1	$P2_1/n$
a (Å)	11.3890(6)	16.2803(14)	15.060(2)	19.3389(7)
b (Å)	34.790(2)	15.8306(16)	15.339(3)	15.0467(5)
c (Å)	14.0047(8)	22.128(2)	25.158(4)	21.7679(8)
α(°)	90	90.00	89.555(5)	90.00
β(°)	92.144(3)	109.570(5)	89.167(5)	107.901(2)
γ (°)	90	90.00	84.713(5)	90.00
$V(Å^3)$	5545.0(5)	5373.7(9)	5786.2(16)	6027.5(4)
Z	4	4	2	4
T (K)	100(2)	100(2)	100(2)	100(2)
λÌÅ	0.71073	0.71073	0.71073	0.71073
GOF	1.107	0.981	0.983	1.076
Density (calcd)	1.278	1.262	1.303	1.205
$(Mg/m^3)$				
Absorption	0.999	1.024	1.340	0.936
coefficient (mm <sup>-1</sup> )				
F <sub>000</sub>	2260	2168	2364	2332
Total no	30623	20203	41741	33086
Reflections				
Unique Reflections	11256	8631	19719	10257
Final R indices*	$R_1 = 0.0391$	$R_1 = 0.0780$	$R_1 = 0.0733$	$R_1 = 0.0469$
	$wR_2 = 0.0768$	$wR_2 = 0.1493$	$wR_2 = 0.1434$	$wR_2 = 0.1176$
Largest Diff. peak and hole $(e^{-}A^{-3})$	1.383, -0.730	2.609, -0.922	1.887, -1.029	1.199, -0.607

Table S1.	Crystallog	raphic detai	ls for com	plexes $1 - 4$
	2 1			

\* For  $[I > 2\sigma(I)]$ 



Figure S14: UV-Vis spectrum of 1 in Et<sub>2</sub>O (0.95 mM).



Figure S15: UV-Vis spectrum of 2 in  $Et_2O$  (0.79 mM).



Figure S16: UV-Vis spectrum of 4 in Et<sub>2</sub>O (0.68 mM).



Figure S17: IR spectrum of 1 as a KBr pellet.



Figure S18: IR spectrum of 2 as a KBr pellet.



Figure S19: IR spectrum of 4 as a KBr pellet.



Figure S20: Partial Raman spectrum of 1.



Figure S21: Partial Raman spectrum of 2.



Figure S22: Partial Raman spectrum of 4.



**Figure S23:** Cyclic voltammogram of complex 4 (200 mV/s scan rate, vs.  $Fc/Fc^+$ ). Measured in THF with 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>] as the supporting electrolyte.



**Figure S24:** Partial cyclic voltammogram of the Ce(III)/Ce(IV) redox feature of complex 4 measured in THF with 0.1 M [NBu<sub>4</sub>][PF<sub>6</sub>] as the supporting electrolyte (vs.  $Fc/Fc^+$ ).

Oxidation	Scan Rate, V/s	E <sub>p,c</sub> , V	E <sub>p,a</sub> , V	$\Delta E_{p}$	$i_{\rm p,a}/i_{\rm p,c}$
Feature		•		-	
	0.010	-0.726	-0.412	0.314	2.5
	0.025	-0.769	-0.318	0.451	3.7
	0.050	-0.824	-0.276	0.548	4.2
	0.100	-0.860	-0.225	0.635	4.4
	0.200	-0.883	-0.166	0.717	3.9
	0.300	-0.914	-0.125	0.789	3.4
	0.500	-0.944	-0.083	0.861	3.3
	1.000	-0.995	-0.011	0.984	4.2

**Table S2.** Electrochemical parameters for  $[Li(2,2,2-cryptand)][Ce(OSiMe_3)(NR_2)_3]$  (4) in THF (vs. Fc/Fc<sup>+</sup>, [NBu<sub>4</sub>][PF<sub>6</sub>] as the supporting electrolyte).

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