Supplementary Information for:

**Experimental**

**General Procedures.** All manipulations were performed with rigorous exclusion of air and water in an argon-filled glovebox (MBraun MB150B-G; <1 ppm O₂, <1 ppm H₂O) or according to standard Schlenk techniques. The solvents were purified by using Grubbs columns (MBraun SPS-800, solvent purification system) and stored in a glovebox. Anhydrous cerium(III) chloride (99.9%), diisopropylamine (99.95%), HTMG (99%), hexachloroethane, and tritylchloride were purchased from Sigma-Aldrich and used as received. HTMG was freshly distilled and stored over molecular sieves 4 Å. Lithium diisopropylamide was synthesized according to standard procedures using amine and nBuLi. NMR spectra were recorded on a Bruker AVII+400 machine at 25 °C in deuterated and dry solvents from Eurisotop. Infrared spectra were recorded on a ThermoFisher Scientific NICOLET 6700 FTIR spectrometer using a DRIFT chamber with dry KBr/sample mixtures and KBr windows, collected data were converted using the Kubelka-Munk refinement. CHN elemental analyses were performed on an Elementar vario MICRO cube. Data collections for single crystal X-ray diffraction were done on a Bruker AXS Ultra TXS rotating anode CCD instrument using an Oxford Cryosystems series 700 N₂ cryostat. Data collection and reduction were done using the Bruker AXS APEX2 suite programs. Structure solution and refinement were done using the program SHELXL, respectively.² UV/Vis spectra of toluene solutions of compounds 1, 2, and 3 were measured with a Lambda 35 spectrophotometer from PerkinElmer. The spectra were collected from 700 nm to 283 nm with a scan speed of 720 nm/min. The effective magnetic moments (µ_{eff}) were determined by the Evans method³ on a Bruker AVII+500 at 298 K, using samples in benzene/deuterated benzene with hexamethyldisiloxane as reference.

**Synthesis of Ce(NiPr₃)₃Li(thf) (1).** CeCl₃(thf)₁.₀₄ (0.159 g, 0.490 mmol) was mixed with Li(NiPr₃) (0.2097 g, 1.96 mmol) and suspended in ~4 mL n-hexane. After 36 h of vigorous stirring, the suspension turned brown, was filtered and the volume reduced to about 1 ml. After cooling to -35 °C, orange crystals of 1 formed. The brown solution was removed via syringe and the product washed with cold n-pentane. Several recrystallization steps gave a clean product with a total yield of 85%. X-ray diffraction quality crystals were obtained from a concentrated n-hexane solution. Anal. calculated for CeC₂₈H₅₄N₄O₃Li: C, 54.25; H, 10.41; N, 9.04. Found: C, 54.45; H, 10.60; N, 9.35. ¹H NMR (CD₃OD): δ 13.94 (s, 4H, thf-OCH₂), 7.03 (s, 4H, NCH), 6.57 (s, 4H, thf-CH₂) 1.25 (s, 36 H, CH₃), -7.20 (s, 36 H, CH₃), -27.27 (s, 4H, NCH), the singlets at 7.03, 1.25, -7.20, and -27.27 originate from the isopropyl groups, which are starting to deconvolute at ambient temperature. DRIFT [cm⁻¹]: 2949 (s), 2916 (s), 2856 (s), 2821 (s), 2661 (m), 2598 (m), 2550 (m), 2165 (w), 1562 (w), 1460 (s), 1398 (s), 1379 (s), 1350 (s), 1327 (s), 1292 (m), 1267 (m), 1165 (s), 1109 (s), 1038 (s), 1002 (s), 1045 (w), 906 (s), 840 (m), 805 (m), 781 (m), 725 (m), 607 (m), 586 (w), 555 (m), 509 (s), 467 (m), 432 (s), 426 (m), 403 (s). UV/Vis: three weaker bands at 385 nm (ε_{385} =289 ± 17 L mol⁻¹ cm⁻¹), 453 nm (ε_{453} =356.0 ± 21 L mol⁻¹ cm⁻¹), and 561 nm (ε_{561} =115 ± 7 L mol⁻¹ cm⁻¹), and a strong band off-scale (~<283.5 nm). µ_{eff} = 2.06 ± 0.2 BM (c = 1.30 · 10⁻³ mol L⁻¹, Δ[Hz] = 58).
Synthesis of Ce(NiPr₂)₄ (2). Ce(NiPr₂)₄Li(thf) (0.79 g, 0.127 mmol) was dissolved in 3 ml of toluene. C₂Cl₂ (0.015 g, 0.0635 mmol) was dissolved in 4 ml of toluene and added dropwise which caused an immediate color change from orange to dark blue. After complete addition of the oxidant, the solution was dried under vacuum to remove C₂Cl₄ and dissolved in n-pentane. LiCl was filtered off and n-pentane was removed via vacuum distillation. 2 was isolated as a dark blue powder in almost quantitative yield (95%). X-ray diffraction quality crystals were collected from a concentrated n-hexane solution. X-ray data collection turned out to be difficult, since the single crystals started to decompose in paratone oil (polysobutylene). Finally, when using a perfluorinated polymer (Elf Atachem) we succeeded to obtain a data set for a twinned crystal. Anal. Calcd. for CeC₂H₆O₅N: C, 53.30; H, 10.44; N, 10.36; Found: C, 53.78; H, 10.64; N, 9.96. ¹H NMR (C₆D₆): δ 4.63 (sept., 8H, NCH₃) 1.36 (d, 48H, MeC). ¹³C NMR (C₆D₆): δ 46.52 (CH₃), 27.6 (Me). DRIFT [cm⁻¹]: 2968 (s), 2956 (s), 2921 (s), 2863 (s), 2684 (m), 2593 (m), 2524 (m), 1597 (w), 1462 (s), 1452 (s), 1371 (s), 1335 (s), 1317 (s), 1275 (m), 1178 (s), 1160 (s), 1114 (s), 1095 (s), 1045 (w), 999 (s), 908 (s), 845 (s), 700 (m), 592 (m), 511 (s), 474 (m), 413 (s), 406 (s). UV/Vis: two strong bands at 291 (w), 1462 (s), 1452 (s), 1371 (s), 1355 (s), 1335 (s), 1275 (m), 1178 (s), 1160 (s), 1114 (s), 1095 (s), 1045 (w), 999 (s), 908 (s), 845 (s), 700 (m), 592 (m), 511 (s), 474 (m), 413 (s), 406 (s). UV/Vis: two strong bands at 291 nm (ε₂₉₁ = 3536 ± 242 L mol⁻¹ cm⁻¹) and 570 nm (ε₅₇₀ = 4321 ± 297 L mol⁻¹ cm⁻¹) and a shoulder at around 426 nm. \( \mu_{\text{eff}} = 0.34 \pm 0.2 \text{ BM (c = 1.82} \times 10^{-5} \text{ molL}^{-1}, \Delta[\text{Hz}] = 15) \)

Synthesis of Ce₂(TMG)₆ (3). Ce(NiPr₂)₄ (0.0575 g, 0.106 mmol) was dissolved in toluene (3 ml). N,N,N’,N”-1,1,3,3-Tetramethylguanidine (0.0475 g, 0.413 mmol) in toluene was added and the solution was stirred for 2 h during which the color changed from dark blue to dark purple. The solvent and released amine were evaporated under vacuum to yield 3 (95%, 0.0601 g). Crystallization from HTMG yielded reddish brown needles suitable for X-ray crystallography. Anal. Calcd. for Ce₂C₂H₆O₅N₃: C, 40.25; H, 8.11; N 28.16. Found: C, 40.80; H, 7.70; N, 27.91. ¹H NMR (C₆D₆): δ 2.92 (s, NMe₂). ¹³C NMR (C₆D₆): δ 149.0 (N=C), 40.6 (NMe₂). DRIFT [cm⁻¹]: 2998 (m), 2924 (m), 2860 (m), 2787 (m), 1865 (w), 1790 (w), 1604 (s), 1560 (s), 1506 (s), 1475 (s), 1458 (s), 1414 (s), 1396 (s), 1348 (m), 1241 (m), 1219 (m), 1142 (s), 1118 (m), 1092 (s), 1054 (m), 1004 (m), 910 (s), 788 (m), 764 (m), 701 (m), 570 (s), 557 (m), 430 (m). UV/Vis: two strong bands at 342 nm (ε₃₄₂ = 17155 ± 1072 L mol⁻¹ cm⁻¹) and 442 nm (ε₄₄₂ = 12078 ± 755 L mol⁻¹ cm⁻¹). \( \mu_{\text{eff}} = 0.28 ± 0.2 \text{ BM (c = 8.67} \times 10^{-6} \text{ molL}^{-1}, \Delta[\text{Hz}] = 14) \)

**DRIFT spectra**

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**Fig. S1.** DRIFT spectrum of 1 in KBr.
Fig. S2. DRIFT spectrum of 2 in KBr.

Fig. S3. DRIFT spectrum of 3 in KBr.
UV/Vis Spectra

**Fig. S4.** UV/Vis spectra of compounds 1, 2, and 3 in toluene at ambient temperature, showing also the absorptivities of each band.
NMR Spectra

Fig. S5. $^1$H NMR spectrum of 1 in C$_6$D$_6$ at 25 °C.

Fig. S6. $^1$H NMR spectrum of 2 in C$_6$D$_6$ at 25 °C.
Fig. S7. $^{13}$C NMR spectrum of 2 in C$_6$D$_6$ at 25 °C.

Fig. S8. $^1$H NMR spectrum of 3 in C$_6$D$_6$ at 25 °C.
Fig. S9. $^{13}$C NMR spectrum of 3 in $\text{C}_6\text{D}_6$ at 25 °C.

Fig. S10. $pK_a$ measurement of HTMG with LiN(SiMe$_3$)$_2$ in thf-d8 at 25 °C.
References:

