

Supporting information for:

“Preparation of Lanthanide Corroles by Metathesis and Proton Exchange”

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A. General Considerations

All reactions were performed using standard Schlenk and N₂-atmosphere glovebox techniques. Glassware was stored in an oven at *ca.* 180 °C. Solvents were dried by passing through a column of activated alumina and degassed with nitrogen.^[1] *d*₈-Toluene was dried over Na/benzophenone, and vacuum transferred. NMR spectra were obtained in *d*₈-toluene at the specified temperature using a Bruker DRX 500 spectrometer. Temperature calibration was performed using changes in chemical shift separation of ethylene glycol at high temperature and methanol at low temperature. ¹H NMR chemical shifts (δ) were calibrated relative to residual solvent peak. UV-visible spectra were determined with a Varian Cary 50 UV-vis spectrophotometer using a 1 mm quartz cell. Mass spectral data (ESI-MS, positive mode) were obtained at the University of California, Berkeley Microanalytical Facility, using vacuum-dried samples dissolved in dry THF. X-ray crystal diffraction analyses were performed at the University of California, Berkeley CHEXRAY facility. Melting points were determined using sealed capillaries prepared under nitrogen and are uncorrected.

5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl)corrole (Mes₂(*p*-OMePh)corroleH₃) and trilithium 5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl)corrole hexakis(tetrahydrofuran) (Mes₂(*p*-OMePh)corroleLi₃·6THF) were prepared according to previously reported procedures.^[2] 1,4,7-trimethyl-1,4,7-triazacyclononane (TACNMe₃) was obtained from Sigma Aldrich and purified by vacuum distillation from calcium hydride. La((NSiMe₃)₂)₃ was obtained from Alfa Aesar, Tb((NSiMe₃)₂)₃ was obtained from Gelest, and GdCl₃ was obtained from Strem and used as received.

B. Synthesis and Characterization of Complexes 1-3

Lanthanum (III) 5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl)corrole tetrakis-dimethoxyethane (1·4.5DME). Mes₂(*p*-OMePh)corroleH₃ (100 mg, 0.16 mmol) La((NSiMe₃)₂)₃ (107 mg, 1.1 equiv, 0.17 mmol) and 10 mL THF were combined in a vial in the glovebox. The solution was stirred overnight. The solvent was removed under vacuum and the solid was dissolved in a minimum amount of dimethoxyethane (~2 mL) and filtered. Crystals suitable for X-ray diffraction were grown by vapor diffusion of hexane into a concentrated solution of dimethoxyethane at room temperature (102 mg, 58 %). ¹H NMR (*d*₈-toluene, room temperature, note some peaks are partially coalesced at this temperature, see VT studies in SI. Assignments are based upon VT experiments): 8.50 (broad s, 1H, C₆H₃HOMe), 8.32 (s, 4H), 8.26 (s, 2H, β-*H*), 8.17 (s, 2H, β-*H*), 7.96 (s, 2H, β-*H*), 7.68 (s, 2H, β-*H*), 7.48 (s with shoulder, 3H, C₆HMe₃H and C₆H₃HOMe), 7.06 (s, masked), 6.84 (s, 2H), 6.49 (s, 2H), 6.42 (s, 2H), 5.68, (s, 1H, C₆H₃HOMe), 3.50 (s, 6H), 3.26 (s, 6H), 2.17 (s, 6H), 1.82 (s, 6H), 1.29 (masked), 1.25-1.10 (broad, masked). UV-vis (nm): 438, 545, 585, 619. ESI-MS (+) Calcd: 766.2025 for C₄₄H₃₇N₄O₁La₁, Observed: 776.2013. Mp: decomposition above 350 °C.

Lanthanum (III) 5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl) corrole·1,4,7-trimethyl-1,4,7-triazacyclononane (1·TACNMe₃) was prepared *in situ* from Mes₂(*p*-OMePh)corroleH₃ (25 mg, 0.039 mmol), La((NSiMe₃)₂)₃ (27 mg, 1.1 equiv, 0.043 mmol) and TACNMe₃ (7.0 μL, 6.1 mg, 1.0 equiv, 0.043 mmol) in the same manner as **1·4DME** above for UV-visible characterization but was not isolated. UV-vis (nm): 423, 446, 588, 636.

Terbium (III) 5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxy phenyl) corrole-tetrakis-dimethoxyethane (2·4DME) was prepared from Mes₂(*p*-OMePh)corroleH₃ (50 mg, 0.078 mmol) and Tb((NSiMe₃)₂)₃ (55 mg, 1.1 equiv, 0.086 mmol) and crystals for X-ray diffraction grown in the same manner as **1·4DME** from (65 mg, 72 %). UV-vis (nm): 433, 541, 580, 611. ESI-MS (+) Calcd: 829.2192 for C₄₄H₃₈N₄O₃Tb₁ (corroleTbO₂H⁺), 901.2767 for C₄₈H₄₆N₄O₄Tb₁ (corroleTbO₂H⁺·THF), 973.3342 for C₅₂H₅₄N₄O₅Tb₁ (corroleTbO₂H⁺·2THF) Observed: 829.2198, 901.2771, 973.3342. Mp: decomposition above 350 °C.

Terbium (III) 5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl) corrole·1,4,7-trimethyl-1,4,7-triazacyclononane (2·TACNMe₃) was prepared *in situ* from Mes₂(*p*-OMePh)corroleH₃ (10 mg, 0.016 mmol), Tb((NSiMe₃)₂)₃ (11 mg, 1.1 equiv, 0.017 mmol) and TACNMe₃ (2.8 μL, 2.4 mg, 1.0 equiv, 0.016 mmol) in the same manner as **1·4DME** for UV-visible characterization but was not isolated. UV-vis (nm): 433, 541, 580, 611.

Gadolinium (III) 5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl) corrole·1,4,7-trimethyl-1,4,7-triazacyclononane (3·TACNMe₃). Mes₂(*p*-OMePh)corroleLi₃·6THF (75 mg, 0.069 mmol), gadolinium (III) trichloride (20 mg, 0.076 mmol), TACNMe₃ (12.2 μL, 10.8 mg, 0.069 mmol) and 10 mL THF were combined in a vial in the glovebox. The solution was stirred overnight. The solvent was removed under vacuum and the solid was dissolved in a minimum amount of toluene (~2 mL) and filtered. Crystals suitable for X-ray diffraction were grown by vapor diffusion of hexane into a concentrated solution of toluene at room temperature (53 mg, 73 %).

UV-vis (nm): 423, 445, 586, 634. ESI-MS (+) Calcd: 967.4017 for $C_{53}H_{59}O_1N_7Gd_1$ (corroleGdTACNMe₃H⁺) Observed: 967.4043. Mp: decomposition above 350 °C.

Gadolinium (III) 5,15-bis(2,4,6-trimethylphenyl)-10-(4-methoxyphenyl) corrole·nTHF (3·nTHF) was prepared *in situ* from Mes₂(*p*-OMePh)corroleLi₃·6THF (8 mg, 0.007 mmol), and gadolinium (III) trichloride (3 mg, 0.008 mmol) in the same manner as **1·4DME** for UV-visible characterization but was not isolated. UV-vis (nm): 422, 633.

B. Variable Temperature NMR experiments

A J-Young NMR tube containing ~20 mg **1·4.5DME** in *d*₈-toluene was prepared in the glove box. ¹H NMR spectra were obtained at temperatures from 203 K to 323 K. Spectra for the aromatic region at temperatures from 203 K to 293 K are shown in Figure S1. Above this temperature peaks were too broad to provide useful information.

To this same tube was added a slight excess (~3.5 μL) of TACNMe₃. ¹H NMR spectra of the resulting solution were obtained at temperatures from 253 K to 373 K. ¹H NMR (*d*₈-toluene, room temperature): δ 8.53 (d, *J* = 3.8 Hz, 2H, β-*H*), 8.49 (d, *J* = 4.1 Hz, 2H, β-*H*), 8.30 (d, *J* = 4.1 Hz, 2H, β-*H*), 8.21 – 8.10 (br s, 1H, *becomes sharp at high T*), 8.07 (d, *J* = 3.7 Hz, 2H, β-*H*), 7.38 (s, 2H, C₆HMe₃H), 6.94 (s, 2H, C₆HMe₃H), 3.47 (s, 3H, C₆H₄OCH₃), 3.37 (broad s, *becomes sharp at high T*), 3.00 (s, 6H), 2.63 (s, 9H, TACNCH₃), 2.48 (s, 6H), 2.27 (s, 6H), 0.66 (s, 6H), 0.20 (s, 12H), 0.08 (s, 6H), 0.05 – 0.10 (m, 12H, TACNMe₃). Figure S2 shows spectra for the aromatic region from 253 K to 373 K.

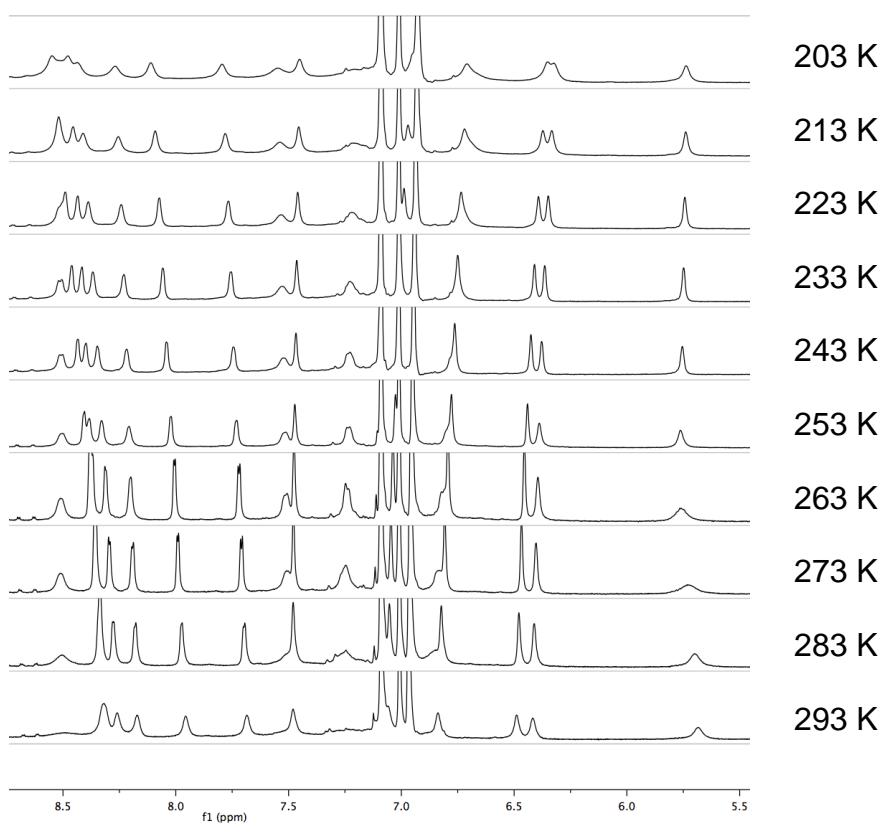


Figure S1. ¹H NMR spectra of **1·4.5DME** in *d*₈-toluene at variable temperatures

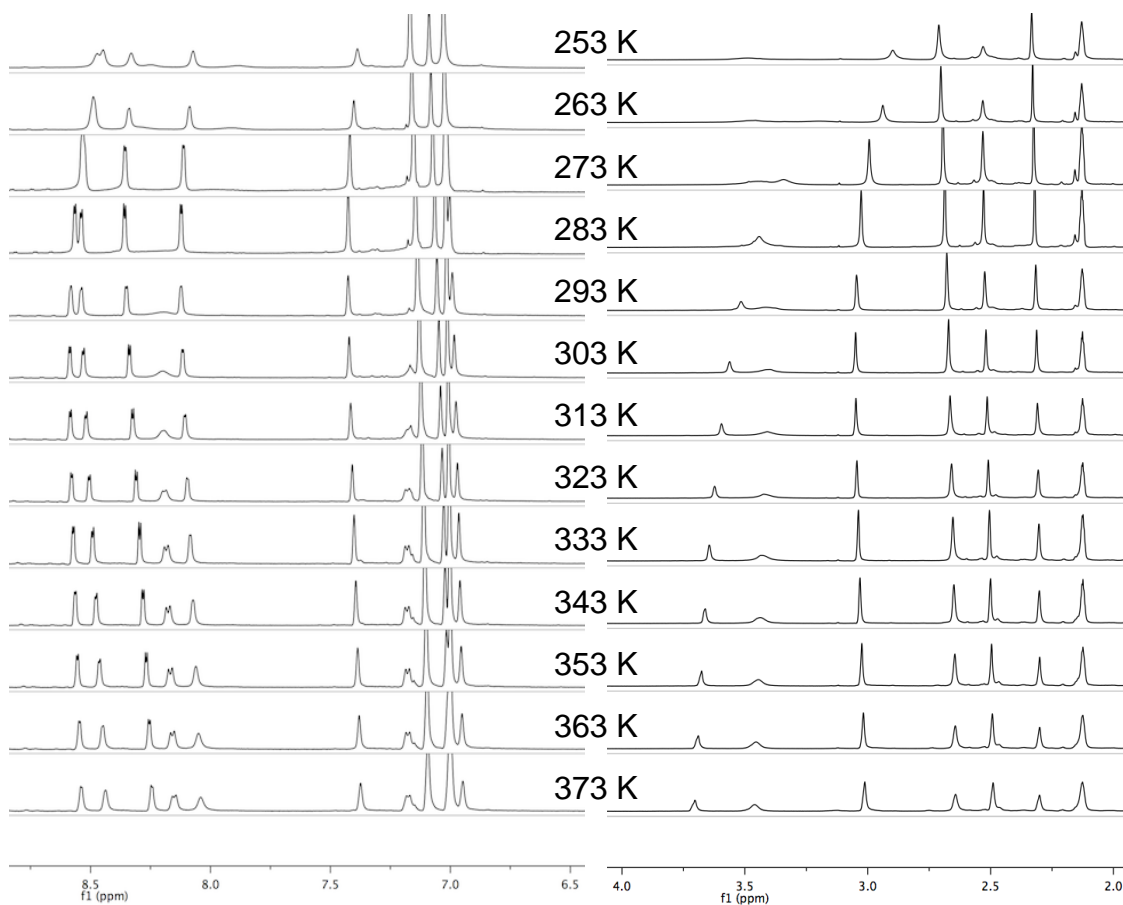


Figure S2. ¹H NMR spectra of 1·TACNMe₃ in d₈-toluene at variable temperatures (left and right spectra at different vertical scales to optimize peak visibility).

C. Determination of molecular structure by single-crystal X-ray diffraction

X-ray structural determinations were performed on a Bruker APEX II Quazar diffractometer. The instrument is Kappa Geometry with DX. And is a 3-circle diffractometer that couples a CCD detector^[3] with a sealed-tube source of monochromated Mo K α radiation. A crystal of appropriate size was coated in Paratone-N oil and mounted on a Kaptan® loop. The loop was transferred to the diffractometer, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. Preliminary orientation matrices and cell constants were determined by collection of 60 10 s frames, followed by spot integration and least-squares refinement. The reported cell dimensions were calculated from all reflections with $I > 10 \sigma$. The data were corrected for Lorentz and polarization effects; no correction for crystal decay was applied. An empirical absorption correction based on comparison of redundant and equivalent reflections was applied using SADABS.^[4] All software used for diffraction data processing and crystal-structure solution and refinement are contained in the APEX2 program suite (Bruker AXS, Madison, WI).^[5] Thermal parameters for all non-hydrogen atoms were refined anisotropically. For all structures, $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$. ORTEP diagrams were created using the ORTEP-3 software package and POV-ray.^[6]

Table S1 shows crystallographic data for corrole complexes **1·4.5DME**, **2·4DME**, and **3·TACNMe₃**. The formula given for **1·4.5DME** is in fact that of **1·3DME** because the residual 1.5 molecules of DME per formula unit were highly disordered and

were solved using Squeeze^[7] methodology in WinGX. **3·TACNMe₃** was solved as a twin.

Table S1. Crystallographic data for **1·4DME**, **2·4DME**, and **3·TACNMe₃**.

Compound	1·4DME	2·4DME	3·TACNMe₃
Formula	C ₅₆ H ₆₇ La ₁ N ₄ O ₇	C ₆₀ H ₅₇ N ₄ O ₉ Tb ₁	C ₆₀ H ₆₆ GdN ₇ O ₁
Form. wt. (amu)	1047.05	1137.02	1058.45
Wavelength (Å)	0.71073	0.71073	0.71073
Space Group	P-1	P-1	P2 ₁ /c
<i>a</i> (Å)	10.9588(9)	11.6378(8)	19.4694(10)
<i>b</i> (Å)	15.2867(13)	15.7546(10)	13.2999(7)
<i>c</i> (Å)	19.8423(15)	15.8507(11)	21.7953(12)
α (°)	68.450(3)	95.090(3)	90
β (°)	88.921(3)	101.785(3)	114.652(2)
γ (°)	83.803(3)	100.993(3)	90
<i>V</i> (Å ³)	3072.9(4)	2768.0(3)	5129.3(5)
<i>Z</i>	2	2	4
ρ_{calcd} (g/cm ³)	1.132	1.388	1.371
<i>F</i> ₀₀₀	1088	1204	2188
μ (mm ⁻¹)	0.741	1.337	1.341
<i>T</i> _{min} / <i>T</i> _{max}	1.46/25.46	1.33/25.52	1.84/25.37
Refl'ns collected	35604	10176	15792
Indep. refl'ns	11189	10139	9415
<i>R</i> _{int}	0.0673	0.0498	0.0676
<i>R</i> ₁ , <i>wR</i> ₂	0.0483/0.0982	0.0643/0.1520	0.0587/0.1322
<i>R</i> ₁ , (all data)	0.0715	0.0759	0.1067
GoF	1.015	1.072	1.099
Res. peak/hole (e ⁻ /Å ³)	1.132/-0.586	3.073/-2.057	2.159/-1.313

*Structure was solved as a twin

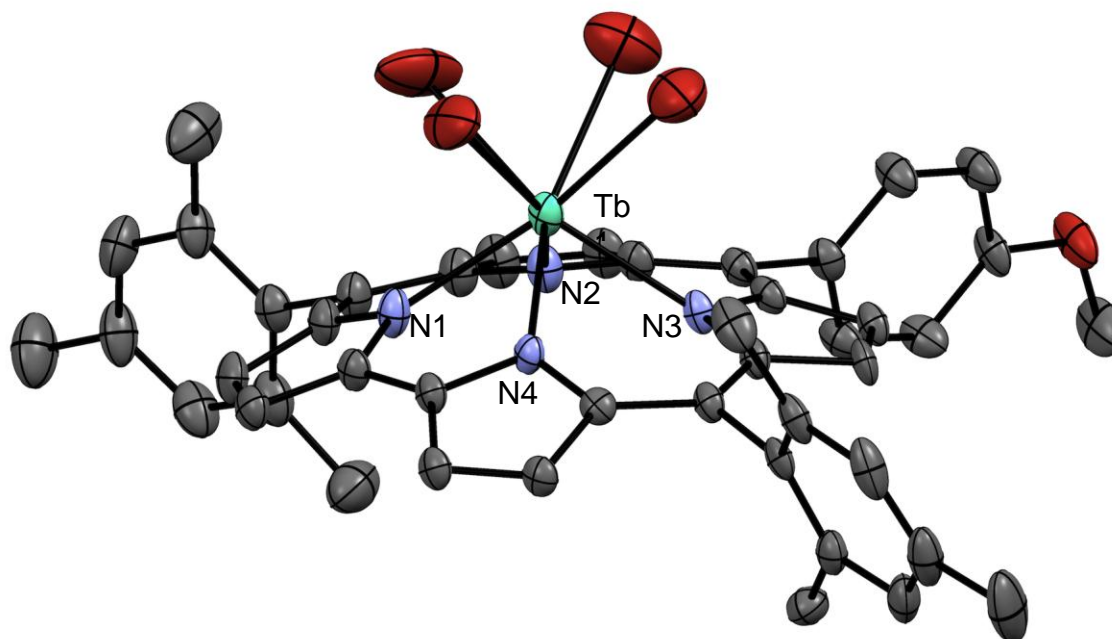


Figure S3. Molecular structure of terbium (III) corrole **2·4DME** determined by single-crystal X-ray diffraction. H atoms and solvent molecules except for coordinated O atoms have been omitted for clarity; thermal ellipsoids at 50 % probability level.

D. References

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