Supporting Information for:

Electrochemical Studies of Tris(cyclopentadienyl) Thorium and Uranium Complexes in the +2, +3, and +4 Oxidation States

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# Table of Contents

**Experimental Details**

| Description                                                                 | Page |
|----------------------------------------------------------------------------|------|
| UV-Visible spectra of [Li(crypt)][Cp''\text{Th}], [Na(crown)]_2[Cp''\text{Th}], [Rb(crypt)][Cp''\text{Th}], and [Cs(crypt)][Cp''\text{Th}] in THF | S10  |
| NMR Spectra of [Li(crypt)][Cp''\text{Th}], [Na(crown)]_2[Cp''\text{Th}], [Rb(crypt)][Cp''\text{Th}], and [Cs(crypt)][Cp''\text{Th}] | S11  |
| Electrochemical data for… (CsH_5)_2Fe and (CsMe_5)_2Fe under present conditions | S22  |
| Cp''\text{U}                                                                  | S23  |
| Cp'\text{U}                                                                   | S24  |
| Cp^{\text{tet}3}\text{U}                                                      | S26  |
| [K(crypt)][Cp'\text{U}]                                                      | S28  |
| [K(crown)(THF)]_2[Cp''\text{U}]                                               | S29  |
| [K(crypt)][Cp^{\text{tet}3}\text{U}]                                          | S31  |
| Cp''\text{ThBr}                                                              | S32  |
| Cp''\text{ThCl}                                                              | S34  |
| Cp'\text{ThCl}                                                               | S35  |
| Cp''\text{ThCl}                                                              | S35  |
| Cp'\text{Th}                                                                 | S37  |
| Cp^{\text{tet}3}\text{ThBr}                                                  | S39  |
| Cp^{\text{tet}5}\text{Th}                                                    | S41  |
| [K(crown)(THF)]_2[Cp''\text{Th}]                                              | S43  |
| [K(crypt)][Cp''\text{Th}]                                                    | S46  |
KCp\text{tet}, KCp, KCp', KCp'', [K(crown)][Cp''], [K(crypt)][Cp'']

Crystallographic Data for...

[K(crown)][Cp'']

[Na(crown)\textsubscript{2}][Cp''\textsubscript{3}Th]

[Rb(crypt)][Cp''\textsubscript{3}Th]

[Cs(crypt)][Cp''\textsubscript{3}Th]

References and Definitions
Experimental Details

Caution! $^{232}$Th and $^{238}$U are α emitters with half-lives of approximately $1.41 \times 10^{10}$ and $4.47 \times 10^9$ years, respectively. Samples should be prepared and handled only in laboratories appropriately equipped to handle radioactive materials.

All syntheses and manipulations were conducted under an Ar atmosphere with rigorous exclusion of air and water using standard glovebox and vacuum line techniques. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were dried over NaK alloy, degassed by three freeze-pump-thaw cycles, and vacuum transferred prior to use. NMR spectra were recorded on an AVANCE600 MHz spectrometer at 298 K and referenced to residual proteo-solvent resonances. Cp$'$3U,$^1$ [K(crypt)][Cp$'$3U],$^1$ Cp$''$3U,$^2$ [K(crown)(THF)$_2$][Cp$''$3U],$^2$ Cp$^{\text{tet}}$3U,$^3$ U(NR$_2$)$_3$,$^4$ Cp$''$3ThBr,$^5$ Cp$'$3ThCl,$^6$ Cp$^{\text{tet}}$3ThBr,$^7$ Cp$''$3Th,$^5$,$^8$ Cp$^{\text{tet}}$3Th,$^7$ [K(crown)(THF)$_2$][Cp$''$3Th],$^9$ [K(crypt)][Cp$''$3Th],$^9$ KCp$^{\text{tet}}$,$^3$ KCp$'$,$^10$ and KCp$''$,$^{10}$ were synthesized according to literature procedures. 18-crown-6 (Alfa Aesar) was sublimed at 30 °C at 10$^{-5}$ Torr before use. 2.2.2-cryptand (Aldrich) was dried under vacuum at 10$^{-5}$ Torr before use. Electrochemical grade (>99%) [$^n$Bu$_4$N][BPh$_4$] (Sigma) and electrochemical grade (>99.9%) [$^n$Bu$_4$N][PF$_6$] (Sigma) were recrystallized from acetone three times and dried at 80 °C and 10$^{-5}$ Torr overnight before use. (C$_5$Me$_5$)$_2$Fe was purified by sublimation before use.

All actinide compounds were purified by recrystallization and dried before data collection. Electrochemical measurements were collected with a freshly made THF solution of supporting electrolyte with a glassy carbon working electrode, platinum wire counter electrode, and silver wire pseudo-reference electrode with a Princeton Applied Research PARSTAT 2273 Advanced Electrochemical System and referenced with internal standard (C$_5$Me$_5$)$_2$Fe. Internal resistance was
measured for each solution and resistance was manually compensated by approximately 90% of the measured value. All scans were measured in the cathodic direction except for the isolated U(II) and Th(II) complexes and KC₅R₅ compounds which were measured in the anodic direction. UV-visible spectroelectrochemical measurements were made using a Pine Instruments UV-visible kit with a Pt working and counter electrode and Ag wire pseudo-reference and an Agilent Cary 60 UV-visible spectrophotometer fitted with an Agilent fiber optic coupler connected to an Ocean Optics CUV 1 cm cuvette holder inside the glovebox. UV-visible measurements were made using an Agilent Cary 60 spectrophotometer in THF in a 1 mm cuvette.

Although the highest purity of commercially available ["Bu₄N][BPh₄] was used, it reacted with some actinide compounds. The Th(IV) compounds Cp‴₃Th⁴Cl¹¹ and Cp‴₅Th⁴Br⁷ showed no noticeable decomposition while in the presence of this material, but purple Cp‴₅Th³⁻ showed immediate decomposition to a yellow solution and brown Cp‴₅U³⁻ turned orange when added to commercial ["Bu₄N][BPh₄] in THF. Hence, multiple recrystallizations of the commercial electrolyte were required until no reaction was observed with the actinide complexes and reproducible data were obtained. Fresh electrolyte solutions were made immediately before data collection, as small amounts of precipitate formed if the electrolyte solution sat for an extended period of time, even overnight. These samples caused decomposition with some actinide samples upon mixing. Small events were present in the voltammograms of Cp‴₃U and Cp‴₅U that are attributed to either decomposition or impurities in the sample, despite recrystallization immediately prior to data collection. These events were present across multiple runs with different batches of material. The solubility limit of ["Bu₄N][BPh₄] in THF was roughly 100 mM which is the concentration used for most experiments. Exceptions are Cp‴₃U³⁻ and [K(crypt)][Cp‴₃U²⁺] in which 50 mM concentrations were used since the compounds appeared to decompose in higher
concentration solutions. \[^{[n]Bu_4N}[PF_6]\] was used at a concentration of 200 mM to determine if peak separations would be smaller than 100–200 mV. They were not.

**General Electrochemistry Procedure.** Inside the glovebox, a stock electrolyte solution was freshly prepared in THF. Between 1–2 mL of this solution was transferred to a 20 mL scintillation vial and a voltammogram of this solution was collected to verify the electrolyte solution was free of impurities. Roughly 10–15 mg of actinide compound was dissolved in the same electrolyte solution to yield approximately a 5 mM solution. Electrodes were placed into the vial and the vial was left open to the box atmosphere during data collection. The internal resistance was measured and cyclic voltammetry experiments were recorded. Decamethylferrocene, \((C_5Me_5)_2Fe\) was added to the same solution following all data collection, and a single scan was recorded to measure the internal standard redox event.

**Synthesis of \([Li(crypt)][Cp''\_3Th]\).** \(Cp''_3Th\) (50 mg, 0.058 mmol) and crypt (23 mg, 0.061 mmol) were dissolved in THF (1 mL) and transferred to a vial containing a Li smear (~5 mg) and placed in the freezer at −35 °C overnight. The inky blue/green solution was filtered and dried under vacuum. The solids were dissolved in Et\(_2\)O (3 mL) and layered under hexane at −35 °C. Dark blue needles grew overnight (60 mg, 83%). \(^1\)H NMR (THF-d\(_8\)): \(\delta\ 5.10\ (s, 9H, C_5H_3R_2), 3.66\ (m, 11H, crypt), 3.57\ (m, 14H, crypt)\) (overlapping with THF), 2.68 \(m, 11H, crypt\), 0.60 ppm \(s, 42H, SiMe_3\). \(^{13}\)C (THF-d\(_8\)): \(\delta\ 119.5\ (C_5H_3R_2), 114.6\ (C_5H_3R_2), 113.0\ (C_5H_3R_2), 71.2\ (crypt), 69.2\ (crypt), 54.6\ (crypt), 1.5 ppm \(SiMe_3\). \(^7\)Li NMR (THF-d\(_8\)): \(\delta\ −1.19\ ppm\). IR: 2943 m, 2881 m, 1233 s, 1071 s, 910 s, 820 s, 743 s, 675 s cm\(^{-1}\). UV-visible (THF): 657 nm \((15,000 M^{-1} cm^{-1})\). Anal Calcd for \(C_{51}H_{99}N_2O_6Si_6ThLi\): C 49.25, H 8.02, N 2.25. Found: C 43.76, H 7.09, N 1.68. Low values were observed across multiple runs and suggests incomplete combustion.
which has been problematic for high silicon-containing actinide species.\textsuperscript{1,2,5,9,13} The calculated C:H:N ratio of C\textsubscript{51}H\textsubscript{98.5}N\textsubscript{1.5} is close to the expected value.

**Synthesis of [Na(crown)\textsubscript{2}][Cp"\textsubscript{3}Th].** Cp"\textsubscript{3}Th (48 mg, 0.056 mmol) and 18-crown-6 (28 mg, 0.11 mmol) were dissolved in THF (1 mL) and transferred into a vial containing a Na (22 mg, 0.96 mmol) smear along the wall. The vial was placed in the freezer at −35 °C overnight. The inky blue/green solution was filtered and dried under vacuum. The solids were dissolved in Et\textsubscript{2}O (3 mL) and layered under hexane at −35 °C. Dark blue crystals suitable for X-ray diffraction grew overnight (58 mg, 73%). \textsuperscript{1}H NMR (THF-d\textsubscript{8}): δ 4.42 (s, 9H, C\textsubscript{5}H\textsubscript{3}R\textsubscript{2}), 3.58 (s, 35H, OCH\textsubscript{2}CH\textsubscript{2}O) 0.18 ppm (s, 54H, SiMe\textsubscript{3}). \textsuperscript{13}C (THF-d\textsubscript{8}): δ 120.07 (C\textsubscript{5}H\textsubscript{3}R\textsubscript{2}), 115.33 (C\textsubscript{5}H\textsubscript{3}R\textsubscript{2}), 114.22 (C\textsubscript{5}H\textsubscript{3}R\textsubscript{2}), 70.64 (OCH\textsubscript{2}CH\textsubscript{2}O), 1.76 ppm (SiMe\textsubscript{3}). IR: 2943m, 2886m 1352m, 1233s, 1169s, 1105s, 965m, 910s, 822s, 783s, 742m, 673m cm\textsuperscript{−1}. UV-visible (THF): 658 nm (12,000 M\textsuperscript{−1}cm\textsuperscript{−1}). Anal Calcd for C\textsubscript{57}H\textsubscript{111}O\textsubscript{12}Si\textsubscript{6}ThNa: C 44.23, H 6.87. Found: C 44.23, H 6.87. Low values were observed across multiple runs and suggests incomplete combustion which has been problematic for high silicon-containing actinide species.\textsuperscript{1,2,5,9,13} The calculated C:H ratio was C\textsubscript{57}H\textsubscript{105.5}. The combustion values are suggestive of bulk formulation as [Na(crown)(THF)\textsubscript{3}][Cp"\textsubscript{3}Th] but crystallization repeatedly afforded single crystals of [Na(crown)\textsubscript{2}][Cp"\textsubscript{3}Th].

**Synthesis of [Rb(crypt)][Cp"\textsubscript{3}Th].** As above, Cp"\textsubscript{3}Th (50 mg, 0.058 mmol) and crypt (22 mg, 0.058 mmol) were reacted with a Rb (14 mg, 0.16 mmol) smear at −35 °C. Dark blue/red dichroic crystals were grown overnight from Et\textsubscript{2}O/hexane at −35 °C (47 mg, 61%). \textsuperscript{1}H NMR (THF-d\textsubscript{8}): δ 4.84 (s, 9H, C\textsubscript{5}H\textsubscript{3}R\textsubscript{2}), 3.54 (s, 14H, OCH\textsubscript{2}CH\textsubscript{2}O), 3.49 (m, 13H, crypt), 2.51 (m, 15H, crypt), 0.44 ppm (s, 53H, SiMe\textsubscript{3}). \textsuperscript{13}C (THF-d\textsubscript{8}): δ 120.4 (C\textsubscript{5}H\textsubscript{3}R\textsubscript{2}), 114.9 (C\textsubscript{5}H\textsubscript{3}R\textsubscript{2}), 111.9 (C\textsubscript{5}H\textsubscript{3}R\textsubscript{2}), 71.3 (crypt), 68.4 (crypt), 54.9 (crypt), 2.2 ppm (SiMe\textsubscript{3}). \textsuperscript{29}Si NMR (THF-d\textsubscript{8}): δ −15.69 ppm (SiMe\textsubscript{3}). UV-visible (THF): 656 nm (19,000 M\textsuperscript{−1}cm\textsuperscript{−1}). IR: 2944m, 2884m, 2810m,
1352m, 1296m, 1233s, 1171s, 1070s, 947s, 909s, 818s, 782m, 742s, 674s cm\(^{-1}\). Anal Calcd for C\(_{51}\)H\(_{99}\)N\(_2\)O\(_6\)Si\(_6\)ThRb: C 46.32, H 7.55, N 2.12. Found: C 43.80, H 7.20, N 2.53. Low C values were observed across multiple runs and suggests incomplete combustion or carbide formation which has been problematic for high silicon-containing actinide species.\(^{1,2,5,9,13}\) The calculated C:H:N ratio of C\(_{51}\)H\(_{99.9}\)N\(_{2.5}\) is close to the expected value.

**Synthesis of [Cs(crypt)][Cp"\(_3\)Th].** As above, Cp"\(_3\)Th (52 mg, 0.060 mmol) and crypt (22 mg, 0.058 mmol) were reacted with a Cs (10 mg, 0.075 mmol) smear at −35 °C. Dark blue/red dichroic crystals were grown overnight from Et\(_2\)O/hexane at −35 °C (43 mg, 54%). \(^1\)H NMR (THF-\(d_8\)): δ 5.51 (s, 9H, C\(_5\)H\(_3\)R\(_2\)), 3.57 (m, 18H, OCH\(_2\)CH\(_2\)O) (overlapping with THF), 3.50 (m, 7H, crypt), 2.54 (m, 9H, crypt), 0.87 ppm (s, 37H, SiMe\(_3\)). \(^{13}\)C (THF-\(d_8\)): δ 121.9 (C\(_5\)H\(_3\)R\(_2\)), 117.0 (C\(_5\)H\(_3\)R\(_2\)), 115.2 (C\(_5\)H\(_3\)R\(_2\)), 71.4 (OCH\(_2\)CH\(_2\)O), 68.3 (crypt), 54.6 (crypt), 1.5 ppm (SiMe\(_3\)). \(^{29}\)Si NMR (THF-\(d_8\)): δ −14.88 ppm (SiMe\(_3\)). \(^{133}\)Cs NMR (THF-\(d_8\)): δ 20 ppm (br, \(\nu_{1/2} = 3600\) Hz).

**Synthesis of [K(crown)(THF)]\(_2\)[Cp"\(_3\)ThCl.** Cp"\(_3\)ThCl (77 mg, 0.093 mmol) and 18-crown-6 (24 mg, 0.091 mmol) were dissolved in THF (3 mL). Pre-cooled KC\(_8\) (31 mg, 0.229 mmol) was added and the reaction was stirred for approximately 5 minutes. The initially colorless solution turned bright blue, followed by the change to inky blue/green. Black solids were removed via centrifugation and the solution was dried under vacuum. The product was extracted.
in Et₂O, filtered, and dried. The solids were washed with hexane to remove Cp"₃Th and dried. Dark blue crystals of [K(crown)(THF)₂][Cp"₃Th]⁹ were grown overnight from Et₂O/hexane at −35 °C (58 mg, 50%).

**Reaction of Cp"₃ThBr with Ba.** Cp"₃ThBr (47 mg, 0.054 mmol) was dissolved in THF (3 mL). Freshly shaved Ba powder (excess) was added and the solution was stirred vigorously. After approximately four hours of stirring, the solution began to turn blue. No further color changes were observed after an additional 5 hours of stirring. Cp"₃Th was identified by UV-visible spectroscopy.⁵,⁸

**Reaction of Cp"₃Th with Ba.** Cp"₃Th (26 mg, 0.030 mmol) was dissolved in THF (3 mL). Freshly shaved Ba powder (excess) was added and the solution was placed in the freezer overnight. The solution was stirred vigorously for approximately two hours of stirring at which point the solution began to turn dark blue/green. The solution was dried and the solids were washed with hexane to remove Cp"₃Th. The remaining solids were extracted into THF and the presence of [Cp"₃Th]¹⁻ was confirmed by UV-visible spectroscopy.

**Reaction of Cp"₃ThBr with Ba and crown.** Cp"₃ThBr (42 mg, 0.048 mmol) and crown (13 mg, 0.049 mmol) were dissolved in THF (3 mL). Freshly shaved Ba powder (excess) was added and the solution was stirred vigorously. After approximately 10 minutes of stirring, the solution began to turn blue. The solution was placed in the freezer overnight and maintained the dark blue color of Cp"₃Th. The solution was stirred again at which point a dark blue/green color developed. The solution was stirred for one hour and the presence of [Cp"₃Th]¹⁻ was confirmed by UV-Visible spectroscopy.

**Synthesis of [K(crown)][Cp"].** In a J-Young NMR tube, 18-crown-6 (8.7 mg, 0.033 mmol) was added to a solution of KCp" (8.2 mg, 0.033 mmol) in THF-d₈ (1 mL). The solution
was mixed by inversion multiple times before the spectrum was collected. $^1$H spectroscopy showed quantitative conversion to [K(crown)][Cp$''$]. $^1$H NMR (THF-$d_8$): $\delta$ 6.10 (s, 1H, $C_5H_3(SiMe_3)_2$), 5.95 (m, 2H, $C_5H_3(SiMe_3)_2$), 3.51 (s, 24H, O–$CH_2CH_2$–O), 0.06 ppm (s, 18H, SiMe$_3$). Cf. KCp$''$ $^1$H NMR (THF-$d_8$): $\delta$ 6.09 (s, 1H, $CsH_3(SiMe_3)_2$), 6.00 (m, 2H, $C_5H_3(SiMe_3)_2$), 0.07 ppm (s, 18H, SiMe$_3$).
Figure S1: UV-Visible spectra of [Li(crypt)][Cp‴3Th] (black), [Na(crown)2][Cp‴3Th] (red), [Rb(crypt)][Cp‴3Th] (blue), and [Cs(crypt)][Cp‴3Th] (green) in THF. The peak at 510 nm is due to Cp‴3Th.5,8
Figure S2: $^1$H NMR spectrum of [Li(crypt)][Cp‴Th] in THF-$d_8$. 
Figure S3: $^{13}$C NMR spectrum of [Li(crypt)][Cp"Th] in THF-$d_8$. 
Figure S4: $^7$Li NMR spectrum of [Li(crypt)][Cp''',Th] in THF-$d_8$.
Figure S5: $^1$H NMR spectrum of [Rb(crypt)][Cp$''$Th] in THF-$d_8$. 
Figure S6: $^{13}$C NMR spectrum of [Rb(crypt)][Cp''Th] in THF-$d_8$. 
Figure S7: \(^{29}\text{Si} \) NMR spectrum of \([\text{Rb(crypt)}][\text{Cp}''\text{Th}]\) in THF-\(d_8\).
Figure S8: $^1$H NMR spectrum of [Cs(crypt)][Cp"$\tau$"Th] in THF-$d_8$. 
Figure S9: $^{13}$C NMR spectrum of [Cs(crypt)][Cp$_3$Th] in THF-$d_8$. 
Figure S10: $^{29}$Si NMR spectrum of [Cs(crypt)][Cp"₃Th] in THF-$d_8$. 
Figure S11: $^{139}$Cs NMR spectrum of [Cs(crypt)][Cp"$^3$Th] in THF-$d_8$. 
Table S1: Reduction potentials of tris(cyclopentadienyl) thorium complexes with 200 mM [^Bu_4N][PF_6] supporting electrolyte

|                  | Th(IV)/Th(III) | Th(III)/Th(II) | ΔE_{pp} Fc (V) |
|------------------|----------------|----------------|----------------|
|                  | \( E_{PC} \) (V) | \( E_{PA} \) (V) | \( E_{1/2} \) (V) | \( E_{PC} \) (V) | \( E_{PA} \) (V) | \( E_{1/2} \) (V) |                |
| Cp^‴_3Th^IVBr    | -2.99          | -2.73          | -2.86          | 0.17           |
| Cp^‴_3Th^IVCl    | -3.39          | -2.70          | -3.04          | 0.14           |
| Cp^‴_3Th^IVBr    | -3.29          | -3.20          | -3.24          | 0.13           |
| Cp^‴_3Th^III     |               | -2.94          | -2.73          | -2.84          | 0.18           |
| Cp^‴_3Th^III     |               | -3.28          | -3.22          | -3.25          | 0.15           |
| [K(crown)(THF)₂][Cp^‴_3Th^{III}] | -2.89  | -2.73          | -2.81          | 0.13           |
| [K(crypt)][Cp^‴_3Th^{III}] | -2.88  | -2.75          | -2.82          | 0.06           |
Electrochemical Data

Figure S12: Voltammogram of (C₅Me₅)₂Fe and (C₅H₅)₂Fe (marked with asterisk) in the experimental cell at ν = 200 mV/s in 100 mM TBABPh₄/THF. Fc* has a potential of −0.495 V vs Fc⁺/Fc under these conditions. ΔEpp (Fc) = 0.20 V, ΔEpp (Fc*) = 0.10 V.

Figure S13: Voltammogram of (C₅Me₅)₂Fe and (C₅H₅)₂Fe (marked with asterisk) in the experimental cell at ν = 200 mV/s in 200 mM TBAPF₆/THF. Fc* has a potential of −0.47 V vs Fc⁺/Fc under these conditions. ΔEpp (Fc) = 0.24 V, ΔEpp (Fc*) = 0.18 V.
Figure S14: Voltammogram of 4.6 mM Cp''₃U at ν = 200 (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 100 mM TBABPh₄ / THF. The event centered at −0.495 V is due to internal standard (C₅Me₅)₂Fe⁺.

Figure S15: Scan rate dependence plot on the 3/2 couple of Cp''₃U.
Figure S16: Scan rate dependence plot on the 4/3 couple of Cp"₃U in 100 mM TBABPh₄ / THF.

Cp'₃U

Figure S17: Voltammogram of 11 mM Cp'₃U at ν = 200 (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 50 mM TBABPh₄ / THF. The event centered at -0.495 V is due to internal standard (C₅Me₅)₂Fe₆Iı.
Figure S18: Scan rate dependence plot on the 3/2 couple of Cp’₃U in 50 mM TBABPh₄/THF.

![Graph showing scan rate dependence plot](image)

Figure S19: Scan rate dependence plot on the 3/2 couple of Cp’₃U in 50 mM TBABPh₄/THF.

![Graph showing scan rate dependence plot](image)
Figure S20: Voltammogram of 7.2 mM Cp\textsuperscript{tet}_3U at $\nu = 200$ (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 100 mM TBABPh\textsubscript{4} / THF.

Figure S21: Scan rate dependence plot on the 3/2 couple of Cp\textsuperscript{tet}_3U in 100 mM TBABPh\textsubscript{4} / THF.
Figure S22: Scan rate dependence plot on the 4/3 couple of Cp_l3U in 100 mM TBABPh4 / THF.

Figure S23: Voltammogram of 7.2 mM Cp_l3U at ν = 200 mV/s over 5 cycles in 100 mM TBABPh4 / THF.
Figure S24: Voltammogram of 7.7 mM [K(crypt)][Cp′₃U] at ν = 200 (black), 400 (orange), 600 (grey), and 1000 (yellow) mV/s in 100 mM TBABPh₄ / THF. The peak centered at −0.495 V is due to internal standard (C₅Me₅)₂Fe.
[K(crown)(THF)₂][Cp‴U]

Figure S25: Voltammogram of 3.0 mM [K(crown)(THF)₂][Cp‴U] at ν = 200 (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 100 mM TBABPh₄ / THF.

Figure S26: Voltammogram of 3.0 mM [K(crown)(THF)₂][Cp‴U] at ν = 200 mV/s over 5 cycles in 100 mM TBABPh₄ / THF.
Figure S27: Scan rate dependence plot on the 3/2 couple of [K(crown)(THF)₂][Cp"₃U] in 100 mM TBABPh₄ / THF.

Figure S28: Scan rate dependence plot on the 4/3 couple of [K(crown)(THF)₂][Cp"₃U] in 100 mM TBABPh₄ / THF.
Figure S29: Voltammogram of $[\text{K(crypt)}][\text{Cp}^{\text{tet}}_3\text{U}]$ at $\nu = 200$ mV/s in 100 mM TBABPh$_4$ / THF.

The event centered at $-0.495$ V is due to internal standard $(\text{C}_5\text{Me}_5)_2\text{Fe}^\text{II}$. 
Figure S30: Voltammogram of 7.4 mM Cp''_3ThBr at \( \nu = 200 \) (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 100 mM TBABPh_4 / THF.

Figure S31: Scan rate dependence plot on the 4/3 couple of Cp''_3ThBr in 100 mM TBABPh_4 / THF.
Figure S32: Voltammogram of 8.0 mM Cp″₃ThBr at ν = 200 (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 200 mM TBAPF₆ / THF.

Figure S33: Scan rate dependence plot on the 4/3 couple of Cp″₃ThBr in 200 mM TBAPF₆ / THF.
Figure S34: Voltammogram of 12 mM Cp‴₃ThCl at \( v = 200 \) (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 100 mM TBABPh₄ / THF.

Figure S35: Scan rate dependence plot on the 4/3 couple of Cp‴₃ThCl in 100 mM TBABPh₄ / THF.
Figure S36: Voltammogram of 8.1 mM Cp′3ThCl at \( \nu = 200 \) (black), 400 (orange), 600 (grey), 800 (yellow), 1000 (blue), and 2000 (green) mV/s in 200 mM TBAPF₆ / THF.

Figure S37: Scan rate dependence plot on the \( E_{PC} \) value of Cp′3ThCl in 200 mM TBAPF₆ / THF.
Figure S38: Voltamogram of 14 mM Cp’3ThCl at $v = 200$ (black), 400 (orange), 600 (grey), 800 (yellow), 1000 (blue), and 2000 (green) mV/s in 100 mM TBABPh$_4$ / THF.

Figure S39: Scan rate dependence plot on the 4/3 couple of Cp’3ThCl in 100 mM TBABPh$_4$ / THF.
Figure S40: Voltammogram of 4.9 mM Cp”₃Th at ν = 200 (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 100 mM TBABPh₄ / THF.

Figure S41: Scan rate dependence plot on the 3/2 couple of Cp”₃Th in 100 mM TBABPh₄ / THF.
Figure S42: Voltammogram of 5.8 mM Cp‴₃Th at ν = 200 (black), 400 (orange), 600 (grey), 800 (yellow), 1000 (blue), and 1500 (green) mV/s in 200 mM TBAPF₆ / THF.

Figure S43: Scan rate dependence plot on the 3/2 couple of Cp‴₃Th in 200 mM TBAPF₆ / THF.
Figure S44: Voltammogram of 22 mM Cp\textsubscript{tet}3ThBr at \( v = 200 \) (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 100 mM TBABPh\textsubscript{4} / THF.

Figure S45: Scan rate dependence plot on the 4/3 couple of Cp\textsubscript{tet}3ThBr in 100 mM TBABPh\textsubscript{4} / THF.
Figure S46: Voltammogram of 6.7 mM Cp<sup>ext</sup><sub>3</sub>ThBr at \( \nu = 200 \) (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 200 mM TBAPF<sub>6</sub> / THF.

Figure S47: Scan rate dependence plot on the 4/3 couple of Cp<sup>ext</sup><sub>3</sub>ThBr in 200 mM TBAPF<sub>6</sub> / THF.
Figure S48: Voltammogram of 6.7 mM \textit{Cp}^{tet}_{3}Th at \( \nu = 200 \) (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 100 mM TBABPh$_4$ / THF.

Figure S49: Scan rate dependence plot on the 3/2 couple of \textit{Cp}^{tet}_{3}Th in 200 mM TBABPh$_4$ / THF.
Figure S50: Voltammogram of 10 mM Cp^{tet}Th at $v = 200$ (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 200 mM TBAPF$_6$ / THF.

Figure S51: Scan rate dependence plot on the 3/2 couple of Cp^{tet}Th in 200 mM TBAPF$_6$ / THF.
Figure S52: Voltammogram of 4.6 mM [K(crown)(THF)$_2$][Cp‴Th] at $\nu = 200$ (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 100 mM TBABPh$_4$ / THF.

Figure S53: Scan rate dependence plot on the 3/2 couple of [K(crown)(THF)$_2$][Cp‴Th] in 100 mM TBABPh$_4$ / THF.
Figure S54: Voltammogram of 4.6 mM [K(crown)(THF)]_2[[Cp''_3Th] at \( v = 200 \) mV/s over 5 cycles in 100 mM TBABPh_4 / THF.

Figure S55: Voltammogram of 4.3 mM [K(crown)(THF)]_2[[Cp''_3Th] at \( v = 200 \) (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 200 mM TBAPF_6 / THF.
Figure S56: Scan rate dependence plot on the 3/2 couple of [K(crown)(THF)₂][Cp″₃Th] in 200 mM TBAPF₆ / THF.

Figure S57: Voltammogram of 4.3 mM [K(crown)(THF)₂][Cp″₃Th] at \( \nu = 200 \) mV/s over 5 cycles in 200 mM TBAPF₆ / THF.
Figure S58: Voltammogram of 3.1 mM [K(crypt)][Cp"^3,Th] at \( \nu = 200 \) (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 200 mM TBAPF₆ / THF.

Figure S59: Scan rate dependence plot on the 3/2 couple of [K(crypt)][Cp"^3,Th] in 200 mM TBAPF₆ / THF.
Figure S60: Voltammogram of 3.1 mM [K(crypt)][Cp″₃Th] at $\nu = 200$ mV/s over 5 cycles in 200 mM TBAPF₆ / THF.

Figure S61: Voltammogram of 3.9 mM [K(crypt)][Cp″₃Th] at $\nu = 200$ (black), 400 (orange), 600 (grey), 800 (yellow) and 1000 (blue) mV/s in 100 mM TBABPh₄ / THF.
Figure S62: Scan rate dependence plot on the 3/2 couple of [K(crypt)][Cp‴Th] in 100 mM TBABPh₄ / THF.

Figure S63: Voltammogram of xx mM Cp‴Th⁴Br at ν = 200 (black), 400 (orange), 600 (grey), 800 (yellow), 1000 (blue) and 2000 (green) mV/s in 100 mM TBABPh₄ / THF.
Figure S64: Scan rate dependence plot on the cathodic event of \( \text{Cp}^{\prime} \text{Th}^{\text{IV}} \text{Br} \) in 100 mM TBABPh\(_4\) / THF.

Figure S65: Voltammogram of 15 mM \( \text{Cp}^{\prime} \text{Th}^{\text{IV}} \text{Br} \) and 14.6 mM \( \text{(C}_5\text{Me}_5\text{)}_2\text{Fe} \) in 100 mM TBABPh\(_4\) / THF. The ratio of current passed for \( \text{Cp}^{\prime} \text{Th}^{\text{IV}} \text{Br} \) to \( \text{(C}_5\text{Me}_5\text{)}_2\text{Fe} \) is 0.77, suggesting a one-electron process is occurring for \( \text{Cp}^{\prime} \text{Th}^{\text{IV}} \text{Br} \).
Potassium Cyclopentadienide Salts. To probe the ligand effects further and to help identify the events around −1.5 V in the voltammograms of the thorium complexes, the voltammograms for the ligands as potassium salts, KCp\textsuperscript{tet}, KCp, KCp', and KCp'', were examined with [\textsuperscript{t}Bu\textsubscript{4}N][PF\textsubscript{6}] as supporting electrolyte. Irreversible anodic processes were observed for each species, Table S2 and Figure S56. The irreversibility of these events is consistent with a chemical process occurring after oxidation such as dimerization of the \textit{in-situ} generated radical.\textsuperscript{18} This series of reduction potentials for simple potassium cyclopentadienyl salts does not match the trend observed in the thorium complexes above and in related zirconium systems.\textsuperscript{19} However, it was noted that trends in cyclopentadienyl donor strength are system dependent.

|        | $E_{PA}$ (V) |
|--------|--------------|
| KCp\textsuperscript{tet} | −1.17 |
| KCp    | −0.50 |
| KCp'   | −0.63 |
| KCp''  | −0.71 |
| [K(crown)][Cp''] | −0.76 |
| [K(crypt)][Cp''] | −0.77 |

Addition of one equivalent of crown to KCp'' shifts the event slightly negative, Figure S57, from −0.71 V to −0.76 V. The addition of crypt to KCp'' shifts the oxidation event in a similar fashion to −0.77 V. Although the structure of KCp'' in THF in the presence of the chelate and the supporting electrolyte is not known, information on the chelate-potassium interaction is known in the solid state. The X-ray crystal structure of [K(crypt)][Cp'] shows a distinct ion pair in the solid state with no K\textsuperscript{+}…[Cp']\textsuperscript{1−} interaction.\textsuperscript{20} However, the crystal structure of [K(crown)][Cp''] is reported as part of this study, Figure S58, and shows clear interaction of the K\textsuperscript{+} ion with the [Cp'']\textsuperscript{1−} anion in the solid state. The shifted potentials of the solutions containing chelate are consistent
with chelation of the potassium ion in solution diminishing the interaction with the
cyclopentadienyl ring, thus facilitating oxidation compared to KCp”. It would be expected, based
on the solid state structures, that crypt would have a greater effect than crown, but in solution, it is
possible that the crown system contains solvated [K(crown)(THF)]⁺ moieties and thus has less
interaction with the cyclopentadienyl than expected. The [K(crown)][Cp”]/ferrocene system
was also examined in THF-d₈ by ¹H NMR spectroscopy and no evidence for ligand exchange
between KCp” and ferrocene was observed.

The irreversible anodic events around −1.5 V observed in the thorium systems are thus
assigned as cyclopentadienide-based events. Interestingly, these types of irreversible anodic
events were not observed in the cyclopentadienyl-uranium systems. Previous electrochemical
studies of organoactinide complexes also observed irreversible anodic events in thorium
complexes and not the analogous uranium systems that were thus attributed to ligand-based
processes or ligand-distribution processes. Clearly, the Lewis acidity of the metal influences
the potential for these cyclopentadienide oxidations. There will be a shift in the observed oxidation
potential whether the cyclopentadienyl ring is bound to K⁺, [K(chelate)]⁺, or An”⁺.
Figure S66: Voltammogram of KCp\textsuperscript{tet} (solid, 15 mM), KCp\textsuperscript{''} (dashed, 17 mM), KCp\textsuperscript{'} (dotted, 14 mM), and KCp (dotted dash, 22 mM) at $\nu = 200$ mV/s in 200 mM ["Bu\textsubscript{4}N][PF\textsubscript{6}] / THF. The event centered at $-0.495$ V in the voltammogram of KCp\textsuperscript{tet} is due to internal standard ($C_5\text{Me}_5$)$_2$Fe\textsuperscript{II}.

Figure S67: Voltammogram of 17 mM KCp\textsuperscript{''} (solid), [K(crown)][Cp\textsuperscript{''}] (dashed), and [K(crypt)][Cp\textsuperscript{''}] (dotted) at 200 mV/s in 200 mM ["Bu\textsubscript{4}N][PF\textsubscript{6}] / THF. The event centered at $-0.495$ V is due to internal standard ($C_5\text{Me}_5$)$_2$Fe\textsuperscript{II}.
Crystallographic Details

X-ray Data Collection, Structure Solution and Refinement for [K(crown)][Cp”].

A blue crystal of approximate dimensions 0.129 x 0.144 x 0.191 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was used to determine the unit-cell parameters and for data collection (180 sec/frame scan time for a hemisphere of diffraction data). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space group P2_1/c that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. There were two molecules of the formula-unit present (Z = 8). C(41) and C(42) were disordered and included using multiple components with partial site-occupancy factors.

Least-squares analysis yielded wR2 = 0.0996 and Goof = 1.010 for 608 variables refined against 14783 data (0.73 Å), R1 = 0.0500 for those 10223 data with I > 2.0σ(I). The structure was refined as a two-component twin (BASF = 0.43).
Figure S68: Thermal ellipsoid plot of [K(crown)][Cp"] drawn at the 50% probability level. Hydrogen atoms have been removed for clarity.

Table S2. Crystal data and structure refinement for [K(crown)][Cp"]').

| Property                           | Value                          |
|------------------------------------|--------------------------------|
| Identification code                | rrl39                          |
| Empirical formula                  | C_{23} H_{45} K O_{6} Si_{2}    |
| Formula weight                     | 512.87                         |
| Temperature                        | 88(2) K                        |
| Wavelength                         | 0.71073 Å                      |
| Crystal system                     | Monoclinic                     |
| Space group                        | P2_1/c                         |
| Unit cell dimensions               | a = 18.737(4) Å                |
|                                   | b = 18.571(4) Å                |
|                                   | c = 16.803(3) Å                |
| Volume                             | 5847(2) Å^3                    |
| Z                                  | 8                              |
| Density (calculated)               | 1.165 Mg/m^3                   |
| Absorption coefficient             | 0.295 mm^{-1}                  |
F(000) 2224
Crystal color blue
Crystal size 0.191 x 0.144 x 0.129 mm³
Theta range for data collection 1.212 to 29.206°
Index ranges -25 ≤ h ≤ 25, -24 ≤ k ≤ 25, -22 ≤ l ≤ 23
Reflections collected 51430
Independent reflections 14783 [R(int) = 0.0719]
Completeness to theta = 25.500° 100.0 %
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 0.8016 and 0.7190
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 14783 / 0 / 608
Goodness-of-fit on F² 1.010
Final R indices [I>2sigma(I) = 10223 data] R1 = 0.0500, wR2 = 0.0872
R indices (all data, 0.73 Å) R1 = 0.0964, wR2 = 0.0996
Largest diff. peak and hole 0.442 and -0.493 e.Å⁻³

Table S3. Bond lengths [Å] and angles [°] for [K(crown)][Cp′′].

| Bond                  | Length [Å] | Angle [°] |
|-----------------------|------------|-----------|
| K(1)-Ct1              | 2.904      | Si(2)-C(9) | 1.862(3) |
| K(1)-O(3)             | 2.792(2)   | Si(2)-C(11)| 1.870(3) |
| K(1)-O(2)             | 2.857(2)   | Si(2)-C(10)| 1.874(3) |
| K(1)-O(6)             | 2.8574(19) | O(1)-C(12)| 1.425(3) |
| K(1)-O(5)             | 2.889(2)   | O(1)-C(23)| 1.432(3) |
| K(1)-O(1)             | 3.0122(18) | O(2)-C(13)| 1.428(3) |
| K(1)-O(4)             | 3.031(2)   | O(2)-C(14)| 1.429(3) |
| K(1)-C(4)             | 3.034(3)   | O(3)-C(15)| 1.422(3) |
| K(1)-C(3)             | 3.073(3)   | O(3)-C(16)| 1.431(3) |
| K(1)-C(5)             | 3.151(3)   | O(4)-C(17)| 1.414(4) |
| K(1)-C(2)             | 3.186(2)   | O(4)-C(18)| 1.430(3) |
| K(1)-C(1)             | 3.269(2)   | O(5)-C(20)| 1.422(3) |
| Si(1)-C(1)            | 1.848(3)   | O(5)-C(19)| 1.432(3) |
| Si(1)-C(8)            | 1.868(3)   | O(6)-C(21)| 1.416(3) |
| Si(1)-C(6)            | 1.880(3)   | O(6)-C(22)| 1.438(3) |
| Si(1)-C(7)            | 1.883(3)   | C(1)-C(5)  | 1.417(4) |
| Si(2)-C(3)            | 1.855(3)   | C(1)-C(2)  | 1.420(4) |
| Bond        | Length (Å) | Bond        | Length (Å) | Bond        | Length (Å) |
|-------------|------------|-------------|------------|-------------|------------|
| C(2)-C(3)   | 1.419(4)   | O(10)-C(41) | 1.429(7)   | C(3)-C(4)   | 1.425(4)   |
| C(3)-C(4)   | 1.425(4)   | O(10)-C(41B)| 1.517(8)   | C(4)-C(5)   | 1.394(4)   |
| C(4)-C(5)   | 1.394(4)   | O(11)-C(43) | 1.374(5)   | C(12)-C(13) | 1.489(4)   |
| C(12)-C(13) | 1.489(4)   | O(11)-C(42) | 1.452(6)   | C(14)-C(15) | 1.521(4)   |
| C(14)-C(15) | 1.521(4)   | O(11)-C(42B)| 1.570(8)   | C(16)-C(17) | 1.499(4)   |
| C(16)-C(17) | 1.499(4)   | O(12)-C(45) | 1.421(4)   | C(18)-C(19) | 1.492(4)   |
| C(18)-C(19) | 1.492(4)   | O(12)-C(44) | 1.438(4)   | C(20)-C(21) | 1.506(4)   |
| C(20)-C(21) | 1.506(4)   | C(24)-C(25) | 1.417(4)   | C(22)-C(23) | 1.487(4)   |
| C(22)-C(23) | 1.487(4)   | C(24)-C(28) | 1.423(4)   | K(2)-Cnt2   | 2.884      |
| K(2)-Cnt2   | 2.884      | C(25)-C(26) | 1.412(4)   | K(2)-O(11)  | 2.810(2)   |
| K(2)-O(11)  | 2.810(2)   | C(26)-C(27) | 1.435(4)   | K(2)-O(7)   | 2.820(2)   |
| K(2)-O(7)   | 2.820(2)   | C(27)-C(28) | 1.393(4)   | K(2)-O(8)   | 2.868(2)   |
| K(2)-O(8)   | 2.868(2)   | C(35)-C(36) | 1.499(4)   | K(2)-O(10)  | 2.903(2)   |
| K(2)-O(10)  | 2.903(2)   | C(37)-C(38) | 1.493(4)   | K(2)-O(9)   | 2.959(19)  |
| K(2)-O(9)   | 2.959(19)  | C(39)-C(40) | 1.486(4)   | K(2)-O(12)  | 2.981(2)   |
| K(2)-O(12)  | 2.981(2)   | C(41)-C(42) | 1.510(9)   | K(2)-C(24)  | 3.038(3)   |
| K(2)-C(24)  | 3.038(3)   | C(41B)-C(42B)| 1.455(10)  | K(2)-C(28)  | 3.039(3)   |
| K(2)-C(28)  | 3.039(3)   | C(43)-C(44) | 1.470(6)   | K(2)-C(25)  | 3.142(2)   |
| K(2)-C(25)  | 3.142(2)   | C(45)-C(46) | 1.506(5)   | K(2)-C(26)  | 3.249(2)   |
| K(2)-C(26)  | 3.249(2)   | Cnt1-K(1)-O(1)| 141.6     | Si(3)-C(24) | 1.826(3)   |
| Si(3)-C(24) | 1.826(3)   | Cnt1-K(1)-O(2)| 107.0     | Si(3)-C(29) | 1.870(3)   |
| Si(3)-C(29) | 1.870(3)   | Cnt1-K(1)-O(3)| 107.9     | Si(3)-C(30) | 1.872(3)   |
| Si(3)-C(30) | 1.872(3)   | Cnt1-K(1)-O(4)| 113.4     | Si(3)-C(31) | 1.881(3)   |
| Si(3)-C(31) | 1.881(3)   | Cnt1-K(1)-O(5)| 101.3     | Si(4)-C(26) | 1.835(3)   |
| Si(4)-C(26) | 1.835(3)   | Cnt1-K(1)-O(6)| 108.0     | Si(4)-C(32) | 1.876(3)   |
| Si(4)-C(32) | 1.876(3)   | O(3)-K(1)-O(2)| 60.23(6)  | Si(4)-C(33) | 1.876(3)   |
| Si(4)-C(33) | 1.876(3)   | O(3)-K(1)-O(6)| 144.13(6) | Si(4)-C(34) | 1.890(3)   |
| Si(4)-C(34) | 1.890(3)   | O(2)-K(1)-O(6)| 108.15(6) | O(7)-C(46)  | 1.416(4)   |
| O(7)-C(46)  | 1.416(4)   | O(3)-K(1)-O(5)| 113.78(6) | O(7)-C(35)  | 1.417(4)   |
| O(7)-C(35)  | 1.417(4)   | O(2)-K(1)-O(5)| 151.46(5) | O(8)-C(37)  | 1.426(3)   |
| O(8)-C(37)  | 1.426(3)   | O(6)-K(1)-O(5)| 58.69(6)  | O(8)-C(36)  | 1.427(3)   |
| O(8)-C(36)  | 1.427(3)   | O(3)-K(1)-O(1)| 93.30(6)  | O(9)-C(38)  | 1.419(3)   |
| O(9)-C(38)  | 1.419(3)   | O(2)-K(1)-O(1)| 56.40(5)  | O(9)-C(39)  | 1.443(3)   |
| O(9)-C(39)  | 1.443(3)   | O(6)-K(1)-O(1)| 57.10(5)  | O(10)-C(40) | 1.422(4)   |
| O(10)-C(40) | 1.422(4)   | O(5)-K(1)-O(1)| 98.53(5)  |
| Bond               | Distance (Å) | Bond               | Distance (Å) |
|--------------------|--------------|--------------------|--------------|
| O(3)-K(1)-O(4)     | 57.74(6)     | O(2)-K(1)-C(1)     | 101.82(6)    |
| O(2)-K(1)-O(4)     | 113.06(6)    | O(6)-K(1)-C(1)     | 128.94(6)    |
| O(6)-K(1)-O(4)     | 107.09(6)    | O(5)-K(1)-C(1)     | 105.73(6)    |
| O(5)-K(1)-O(4)     | 56.23(6)     | O(1)-K(1)-C(1)     | 153.46(6)    |
| O(1)-K(1)-O(4)     | 104.98(5)    | O(4)-K(1)-C(1)     | 97.46(6)     |
| O(3)-K(1)-C(4)     | 129.04(7)    | C(4)-K(1)-C(1)     | 42.50(7)     |
| O(2)-K(1)-C(4)     | 122.98(7)    | C(3)-K(1)-C(1)     | 43.19(7)     |
| O(6)-K(1)-C(4)     | 86.45(6)     | C(5)-K(1)-C(1)     | 25.43(7)     |
| O(5)-K(1)-C(4)     | 83.39(7)     | C(2)-K(1)-C(1)     | 25.37(7)     |
| O(1)-K(1)-C(4)     | 133.02(7)    | C(1)-Si(1)-C(8)    | 112.82(13)   |
| O(4)-K(1)-C(4)     | 114.20(7)    | C(1)-Si(1)-C(6)    | 110.65(14)   |
| O(3)-K(1)-C(3)     | 121.26(7)    | C(8)-Si(1)-C(6)    | 108.31(16)   |
| O(2)-K(1)-C(3)     | 96.15(7)     | C(1)-Si(1)-C(7)    | 111.77(13)   |
| O(6)-K(1)-C(3)     | 92.53(6)     | C(8)-Si(1)-C(7)    | 104.93(15)   |
| O(5)-K(1)-C(3)     | 108.95(7)    | C(6)-Si(1)-C(7)    | 108.07(13)   |
| O(1)-K(1)-C(3)     | 118.25(6)    | C(3)-Si(2)-C(9)    | 109.28(14)   |
| O(4)-K(1)-C(3)     | 136.41(6)    | C(3)-Si(2)-C(11)   | 112.24(13)   |
| C(4)-K(1)-C(3)     | 26.97(7)     | C(9)-Si(2)-C(11)   | 108.74(17)   |
| O(3)-K(1)-C(5)     | 105.60(6)    | C(3)-Si(2)-C(10)   | 112.99(13)   |
| O(2)-K(1)-C(5)     | 125.93(6)    | C(9)-Si(2)-C(10)   | 107.92(16)   |
| O(6)-K(1)-C(5)     | 107.65(6)    | C(11)-Si(2)-C(10)  | 105.48(15)   |
| O(5)-K(1)-C(5)     | 82.46(6)     | C(12)-O(1)-C(23)   | 112.1(2)     |
| O(1)-K(1)-C(5)     | 158.96(6)    | C(12)-O(1)-K(1)    | 115.48(14)   |
| O(4)-K(1)-C(5)     | 93.11(6)     | C(23)-O(1)-K(1)    | 116.11(15)   |
| C(4)-K(1)-C(5)     | 25.97(7)     | C(13)-O(2)-C(14)   | 113.0(2)     |
| C(3)-K(1)-C(5)     | 43.40(7)     | C(13)-O(2)-K(1)    | 120.00(15)   |
| O(3)-K(1)-C(2)     | 95.33(7)     | C(14)-O(2)-K(1)    | 106.44(15)   |
| O(2)-K(1)-C(2)     | 85.48(6)     | C(15)-O(3)-C(16)   | 112.2(2)     |
| O(6)-K(1)-C(2)     | 118.54(6)    | C(15)-O(3)-K(1)    | 121.14(16)   |
| O(5)-K(1)-C(2)     | 122.97(6)    | C(16)-O(3)-K(1)    | 122.78(16)   |
| O(1)-K(1)-C(2)     | 128.84(6)    | C(17)-O(4)-C(18)   | 111.1(2)     |
| O(4)-K(1)-C(2)     | 122.04(6)    | C(17)-O(4)-K(1)    | 105.57(15)   |
| C(4)-K(1)-C(2)     | 42.38(7)     | C(18)-O(4)-K(1)    | 106.08(16)   |
| C(3)-K(1)-C(2)     | 26.12(7)     | C(20)-O(5)-C(19)   | 113.5(2)     |
| C(5)-K(1)-C(2)     | 41.65(7)     | C(20)-O(5)-K(1)    | 120.24(16)   |
| O(3)-K(1)-C(1)     | 86.75(7)     | C(19)-O(5)-K(1)    | 122.48(16)   |
C(21)-O(6)-C(22)  113.8(2)  O(6)-C(22)-C(23)  108.2(2)
C(21)-O(6)-K(1)  109.56(15)  O(1)-C(23)-C(22)  107.3(2)
C(22)-O(6)-K(1)  111.09(15)  Cnt2-K(2)-O(7)  107.1
C(5)-C(1)-C(2)  105.2(2)  Cnt2-K(2)-O(8)  103.7
C(5)-C(1)-Si(1)  126.1(2)  Cnt2-K(2)-O(9)  138.6
C(2)-C(1)-Si(1)  128.1(2)  Cnt2-K(2)-O(10)  109.8
C(5)-C(1)-K(1)  72.64(13)  Cnt2-K(2)-O(11)  98.8
C(2)-C(1)-K(1)  74.07(13)  Cnt2-K(2)-O(12)  117.0
Si(1)-C(1)-K(1)  124.91(12)  O(11)-K(2)-O(7)  115.95(8)
C(3)-C(2)-C(1)  111.1(2)  O(11)-K(2)-O(8)  157.39(8)
C(3)-C(2)-K(1)  72.48(14)  O(11)-K(2)-O(9)  59.24(6)
C(1)-C(2)-K(1)  80.56(14)  O(11)-K(2)-O(10)  57.72(7)
C(2)-C(3)-C(4)  104.8(2)  O(7)-K(2)-O(10)  143.08(6)
C(2)-C(3)-Si(2)  128.0(2)  O(8)-K(2)-O(10)  111.21(6)
C(4)-C(3)-Si(2)  127.2(2)  O(11)-K(2)-O(9)  102.87(7)
C(2)-C(3)-K(1)  81.40(15)  O(7)-K(2)-O(9)  94.44(6)
C(4)-C(3)-K(1)  74.98(14)  O(8)-K(2)-O(9)  57.90(5)
Si(2)-C(3)-K(1)  108.01(10)  O(10)-K(2)-O(9)  57.12(6)
C(5)-C(4)-C(3)  109.5(2)  O(11)-K(2)-O(12)  57.67(8)
C(5)-C(4)-K(1)  81.71(15)  O(7)-K(2)-O(12)  58.32(7)
C(3)-C(4)-K(1)  78.05(15)  O(8)-K(2)-O(12)  112.29(6)
C(4)-C(5)-C(1)  109.4(2)  O(10)-K(2)-O(12)  103.00(7)
C(4)-C(5)-K(1)  72.33(14)  O(9)-K(2)-O(12)  104.37(6)
C(1)-C(5)-K(1)  81.94(14)  O(11)-K(2)-C(24)  110.65(9)
O(1)-C(12)-C(13)  108.7(2)  O(7)-K(2)-C(24)  116.28(7)
O(2)-C(13)-C(12)  108.3(2)  O(8)-K(2)-C(24)  89.70(7)
O(2)-C(14)-C(15)  113.1(2)  O(10)-K(2)-C(24)  98.22(7)
O(2)-C(14)-K(1)  50.76(12)  O(9)-K(2)-C(24)  114.98(7)
C(15)-C(14)-K(1)  85.19(16)  O(12)-K(2)-C(24)  140.65(6)
O(3)-C(15)-C(14)  107.7(2)  O(11)-K(2)-C(28)  83.80(9)
O(3)-C(16)-C(17)  108.0(2)  O(7)-K(2)-C(28)  129.89(7)
O(4)-C(17)-C(16)  109.3(2)  O(8)-K(2)-C(28)  116.76(7)
O(4)-C(18)-C(19)  108.7(2)  O(10)-K(2)-C(28)  86.91(7)
O(5)-C(19)-C(18)  108.5(2)  O(9)-K(2)-C(28)  127.25(7)
O(5)-C(20)-C(21)  108.9(2)  O(12)-K(2)-C(28)  121.81(7)
O(6)-C(21)-C(20)  113.9(2)  C(24)-K(2)-C(28)  27.08(7)
| Bond                  | Angle (deg) | Bond                  | Angle (deg) |
|----------------------|-------------|----------------------|-------------|
| O(11)-K(2)-C(25)    | 120.18(8)   | C(26)-Si(4)-C(34)    | 113.26(13)  |
| O(7)-K(2)-C(25)     | 91.00(7)    | C(32)-Si(4)-C(34)    | 104.78(15)  |
| O(8)-K(2)-C(25)     | 82.43(6)    | C(33)-Si(4)-C(34)    | 106.04(13)  |
| O(10)-K(2)-C(25)    | 124.55(7)   | C(46)-O(7)-C(35)     | 112.3(2)    |
| O(9)-K(2)-C(25)     | 128.53(7)   | C(46)-O(7)-K(2)      | 121.5(2)    |
| O(12)-K(2)-C(25)    | 121.46(7)   | C(35)-O(7)-K(2)      | 121.42(18)  |
| C(24)-K(2)-C(25)    | 26.44(7)    | C(37)-O(8)-C(36)     | 113.5(2)    |
| C(28)-K(2)-C(25)    | 42.98(7)    | C(37)-O(8)-K(2)      | 116.03(16)  |
| O(11)-K(2)-C(27)    | 78.09(8)    | C(36)-O(8)-K(2)      | 107.87(17)  |
| O(7)-K(2)-C(27)     | 109.47(7)   | C(38)-O(9)-C(39)     | 111.2(2)    |
| O(8)-K(2)-C(27)     | 124.50(6)   | C(38)-O(9)-K(2)      | 115.37(14)  |
| O(10)-K(2)-C(27)    | 104.53(7)   | C(39)-O(9)-K(2)      | 117.34(15)  |
| O(9)-K(2)-C(27)     | 153.11(7)   | C(40)-O(10)-C(41)    | 125.6(3)    |
| O(12)-K(2)-C(27)    | 98.75(7)    | C(40)-O(10)-C(41B)   | 97.1(4)     |
| C(24)-K(2)-C(27)    | 43.39(7)    | C(40)-O(10)-K(2)     | 115.55(17)  |
| C(28)-K(2)-C(27)    | 25.92(7)    | C(41)-O(10)-K(2)     | 106.4(3)    |
| C(25)-K(2)-C(27)    | 42.13(7)    | C(41B)-O(10)-K(2)    | 119.3(3)    |
| O(11)-K(2)-C(26)    | 99.64(8)    | C(43)-O(11)-C(42)    | 98.4(3)     |
| O(7)-K(2)-C(26)     | 87.28(7)    | C(43)-O(11)-C(42B)   | 129.1(4)    |
| O(8)-K(2)-C(26)     | 102.07(6)   | C(43)-O(11)-K(2)     | 122.6(2)    |
| O(10)-K(2)-C(26)    | 128.89(7)   | C(42)-O(11)-K(2)     | 122.7(3)    |
| O(9)-K(2)-C(26)     | 153.97(6)   | C(42B)-O(11)-K(2)    | 106.9(3)    |
| O(12)-K(2)-C(26)    | 98.61(6)    | C(45)-O(12)-C(44)    | 112.7(3)    |
| C(24)-K(2)-C(26)    | 43.29(7)    | C(45)-O(12)-K(2)     | 107.62(18)  |
| C(28)-K(2)-C(26)    | 42.86(7)    | C(44)-O(12)-K(2)     | 106.87(19)  |
| C(25)-K(2)-C(26)    | 25.46(7)    | C(25)-C(24)-C(28)    | 105.9(2)    |
| C(27)-K(2)-C(26)    | 25.84(7)    | C(25)-C(24)-Si(3)    | 127.3(2)    |
| C(24)-Si(3)-C(29)   | 109.60(13)  | C(28)-C(24)-Si(3)    | 126.8(2)    |
| C(24)-Si(3)-C(30)   | 112.17(13)  | C(25)-C(24)-K(2)     | 80.88(15)   |
| C(29)-Si(3)-C(30)   | 106.46(15)  | C(28)-C(24)-K(2)     | 76.48(15)   |
| C(24)-Si(3)-C(31)   | 110.25(14)  | Si(3)-C(24)-K(2)     | 110.86(10)  |
| C(29)-Si(3)-C(31)   | 110.24(16)  | C(26)-C(25)-C(24)    | 110.7(2)    |
| C(30)-Si(3)-C(31)   | 108.05(15)  | C(26)-C(25)-K(2)     | 81.49(15)   |
| C(26)-Si(4)-C(32)   | 112.56(13)  | C(24)-C(25)-K(2)     | 72.68(14)   |
| C(26)-Si(4)-C(33)   | 109.32(14)  | C(25)-C(26)-C(27)    | 105.3(2)    |
| C(32)-Si(4)-C(33)   | 110.63(15)  | C(25)-C(26)-Si(4)    | 128.1(2)    |
X-ray Data Collection, Structure Solution and Refinement for [Na(crown)$_2$][Cp‴$_3$Th].

A red crystal of approximate dimensions 0.153 x 0.258 x 0.289 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2$^{32}$ program package was used to determine the unit-cell parameters and for data collection (30 sec/frame scan time). The raw frame data was processed using SAINT$^{33}$ and SADABS$^{34}$ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL$^{35}$ program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\overline{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors$^{36}$ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Disordered atoms were included using multiple components, partial site-occupancy-factors, thermal (EADP) and geometric restraints (DFIX)$^{35}$.

Least-squares analysis yielded $wR^2 = 0.1218$ and $Goof = 1.044$ for 598 variables refined against 12873 data (0.80 Å), $R1 = 0.0479$ for those 10989 data with $I > 2.0\sigma(I)$. 
**Table S4. Crystal data and structure refinement for [Na(crown)₂][Cp''₃Th].**

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Identification code                           | jcw35 (Justin Wedal)                       |
| Empirical formula                             | C₅₇H₁₁₁ Na O₁₂ Si₆ Th                      |
| Formula weight                                 | 1412.02                                    |
| Temperature                                   | 133(2) K                                   |
| Wavelength                                    | 0.71073 Å                                  |
| Crystal system                                | Triclinic                                  |
| Space group                                   | $P\bar{1}$                                 |
| Unit cell dimensions                          | $a = 13.8938(13)$ Å                        |
|                                              | $b = 14.4588(13)$ Å                        |
|                                              | $c = 18.3420(17)$ Å                       |
|                                              | $\alpha = 74.4602(14)^\circ$              |
|                                              | $\beta = 84.1350(14)^\circ$               |
|                                              | $\gamma = 83.5214(14)^\circ$              |
| Volume                                        | 3517.3(6) Å                               |
| Density (calculated)                          | 1.333 Mg/m$^3$                            |
| Absorption coefficient                        | 2.280 mm$^{-1}$                           |
| F(000)                                        | 1468                                       |
| Crystal color                                 | red                                        |
| Crystal size                                  | 0.289 x 0.258 x 0.153 mm$^3$               |
| Theta range for data collection               | 1.156 to 25.350°                          |
| Index ranges                                  | -16 ≤ $h$ ≤ 16, -17 ≤ $k$ ≤ 17, -22 ≤ $l$ ≤ 22 |
| Reflections collected                         | 39152                                      |
| Independent reflections                       | 12873 [R(int) = 0.0464]                    |
| Completeness to theta = 25.242°               | 100.0 %                                    |
| Absorption correction                         | Semi-empirical from equivalents            |
| Max. and min. transmission                    | 0.6465 and 0.5424                         |
| Refinement method                             | Full-matrix least-squares on F$^2$         |
| Data / restraints / parameters                 | 12873 / 36 / 598                          |
| Goodness-of-fit on F$^2$                       | 1.044                                      |
| Final R indices [I>2sigma(I) = 10989 data]     | R1 = 0.0479, wR2 = 0.1153                  |
| R indices (all data, 0.80 Å)                  | R1 = 0.0608, wR2 = 0.1218                  |
| Largest diff. peak and hole                   | 2.464 and -2.311 e.Å$^{-3}$                |

**Table S5. Bond lengths [Å] and angles [°] for [Na(crown)₂][Cp''₃Th].**

| Bond                  | Length [Å] | Bond                  | Length [Å] |
|-----------------------|------------|-----------------------|------------|
| Th(1)-Cnt1            | 2.527      | Th(1)-C(13)           | 2.754(6)   |
| Th(1)-Cnt2            | 2.521      | Th(1)-C(2)            | 2.757(6)   |
| Th(1)-Cnt3            | 2.531      | Th(1)-C(24)           | 2.761(6)   |

S62
| Bond                        | Distance (Å) | Bond                        | Distance (Å) | Bond                        | Distance (Å) |
|-----------------------------|--------------|-----------------------------|--------------|-----------------------------|--------------|
| Th(1)-C(25)                 | 2.785(6)     | C(1)-C(2)                   | 1.419(9)     | Th(1)-C(12)                 | 2.796(6)     |
| Th(1)-C(12)                 | 2.796(6)     | C(1)-C(5)                   | 1.431(9)     | Th(1)-C(14)                 | 2.798(6)     |
| Th(1)-C(14)                 | 2.798(6)     | C(2)-C(3)                   | 1.438(9)     | Th(1)-C(3)                  | 2.800(6)     |
| Th(1)-C(3)                  | 2.800(6)     | C(3)-C(4)                   | 1.434(9)     | Th(1)-C(4)                  | 2.807(6)     |
| Th(1)-C(4)                  | 2.807(6)     | C(4)-C(5)                   | 1.383(9)     | Th(1)-C(16)                 | 2.813(6)     |
| Th(1)-C(16)                 | 2.813(6)     | C(12)-C(16)                 | 1.423(9)     | Th(1)-C(15)                 | 2.816(6)     |
| Th(1)-C(15)                 | 2.816(6)     | C(12)-C(13)                 | 1.433(8)     | Th(1)-C(1)                  | 2.818(6)     |
| Th(1)-C(1)                  | 2.818(6)     | C(13)-C(14)                 | 1.426(9)     | Th(1)-C(26)                 | 2.818(6)     |
| Th(1)-C(26)                 | 2.818(6)     | C(14)-C(15)                 | 1.423(9)     | Th(1)-C(23)                 | 2.826(6)     |
| Th(1)-C(23)                 | 2.826(6)     | C(15)-C(16)                 | 1.390(9)     | Th(1)-C(5)                  | 2.826(6)     |
| Th(1)-C(5)                  | 2.826(6)     | C(23)-C(24)                 | 1.421(9)     | Th(1)-C(27)                 | 2.832(5)     |
| Th(1)-C(27)                 | 2.832(5)     | C(23)-C(27)                 | 1.426(8)     | Si(1)-C(1)                  | 1.849(7)     |
| Si(1)-C(1)                  | 1.849(7)     | C(24)-C(25)                 | 1.447(8)     | Si(1)-C(7)                  | 1.866(9)     |
| Si(1)-C(7)                  | 1.866(9)     | C(25)-C(26)                 | 1.424(8)     | Si(1)-C(6)                  | 1.881(8)     |
| Si(1)-C(6)                  | 1.881(8)     | C(26)-C(27)                 | 1.388(9)     | Si(1)-C(8)                  | 1.882(8)     |
| Si(1)-C(8)                  | 1.882(8)     | Na(1)-O(12)                 | 2.429(13)    | Si(2)-C(3)                  | 1.837(7)     |
| Si(2)-C(3)                  | 1.837(7)     | Na(1)-O(6)                  | 2.519(5)     | Si(2)-C(11)                 | 1.861(7)     |
| Si(2)-C(11)                 | 1.861(7)     | Na(1)-O(2)                  | 2.520(5)     | Si(2)-C(9)                  | 1.863(9)     |
| Si(2)-C(9)                  | 1.863(9)     | Na(1)-O(7B)                 | 2.541(19)    | Si(2)-C(10)                 | 1.877(8)     |
| Si(2)-C(10)                 | 1.877(8)     | Na(1)-O(7)                  | 2.579(13)    | Si(3)-C(12)                 | 1.847(7)     |
| Si(3)-C(12)                 | 1.847(7)     | Na(1)-O(4)                  | 2.583(5)     | Si(3)-C(17)                 | 1.865(9)     |
| Si(3)-C(17)                 | 1.865(9)     | Na(1)-O(1)                  | 2.589(5)     | Si(3)-C(19)                 | 1.866(8)     |
| Si(3)-C(19)                 | 1.866(8)     | Na(1)-O(12B)                | 2.593(19)    | Si(3)-C(18)                 | 1.875(8)     |
| Si(3)-C(18)                 | 1.875(8)     | Na(1)-O(3)                  | 2.617(6)     | Si(4)-C(14)                 | 1.839(6)     |
| Si(4)-C(14)                 | 1.839(6)     | Na(1)-O(5)                  | 2.652(6)     | Si(4)-C(20)                 | 1.861(8)     |
| Si(4)-C(20)                 | 1.861(8)     | O(1)-C(34)                  | 1.414(8)     | Si(4)-C(22)                 | 1.879(7)     |
| Si(4)-C(22)                 | 1.879(7)     | O(1)-C(45)                  | 1.421(8)     | Si(4)-C(21)                 | 1.882(9)     |
| Si(4)-C(21)                 | 1.882(9)     | O(2)-C(35)                  | 1.410(8)     | Si(5)-C(23)                 | 1.846(6)     |
| Si(5)-C(23)                 | 1.846(6)     | O(2)-C(36)                  | 1.412(8)     | Si(5)-C(28)                 | 1.871(7)     |
| Si(5)-C(28)                 | 1.871(7)     | O(3)-C(38)                  | 1.344(11)    | Si(5)-C(30)                 | 1.872(7)     |
| Si(5)-C(30)                 | 1.872(7)     | O(3)-C(37)                  | 1.415(14)    | Si(5)-C(29)                 | 1.879(7)     |
| Si(5)-C(29)                 | 1.879(7)     | O(4)-C(39)                  | 1.403(11)    | Si(6)-C(25)                 | 1.848(6)     |
| Si(6)-C(25)                 | 1.848(6)     | O(4)-C(40)                  | 1.410(9)     | Si(6)-C(33)                 | 1.861(7)     |
| Si(6)-C(33)                 | 1.861(7)     | O(5)-C(42)                  | 1.398(9)     | Si(6)-C(32)                 | 1.869(7)     |
| Si(6)-C(32)                 | 1.869(7)     | O(5)-C(41)                  | 1.427(10)    | Si(6)-C(31)                 | 1.883(8)     |
| Si(6)-C(31)                 | 1.883(8)     | O(6)-C(44)                  | 1.414(8)     |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|-----------------------|--------------|-----------------------|--------------|
| C(12)-Th(1)-C(4)     | 84.08(19)    | C(3)-Th(1)-C(26)     | 96.87(18)    |
| C(14)-Th(1)-C(4)     | 95.60(19)    | C(4)-Th(1)-C(26)     | 121.46(17)   |
| C(3)-Th(1)-C(4)      | 29.63(18)    | C(16)-Th(1)-C(26)    | 123.27(18)   |
| C(13)-Th(1)-C(16)    | 47.83(18)    | C(15)-Th(1)-C(26)    | 115.73(18)   |
| C(2)-Th(1)-C(16)     | 158.3(2)     | C(1)-Th(1)-C(26)     | 82.68(17)    |
| C(24)-Th(1)-C(16)    | 75.38(18)    | C(13)-Th(1)-C(23)    | 130.38(17)   |
| C(25)-Th(1)-C(16)    | 99.76(18)    | C(2)-Th(1)-C(23)     | 103.93(18)   |
| C(12)-Th(1)-C(16)    | 29.39(19)    | C(24)-Th(1)-C(23)    | 29.43(18)    |
| C(14)-Th(1)-C(16)    | 48.49(17)    | C(25)-Th(1)-C(23)    | 49.76(17)    |
| C(3)-Th(1)-C(16)     | 128.39(19)   | C(12)-Th(1)-C(23)    | 103.23(17)   |
| C(4)-Th(1)-C(16)     | 113.43(19)   | C(14)-Th(1)-C(23)    | 122.89(18)   |
| C(13)-Th(1)-C(15)    | 47.7(2)      | C(3)-Th(1)-C(23)     | 107.53(18)   |
| C(2)-Th(1)-C(15)     | 161.57(18)   | C(4)-Th(1)-C(23)     | 135.54(19)   |
| C(24)-Th(1)-C(15)    | 73.37(18)    | C(16)-Th(1)-C(23)    | 83.00(17)    |
| C(25)-Th(1)-C(15)    | 86.64(18)    | C(15)-Th(1)-C(23)    | 93.61(18)    |
| C(12)-Th(1)-C(15)    | 48.4(2)      | C(1)-Th(1)-C(23)     | 125.93(17)   |
| C(14)-Th(1)-C(15)    | 29.36(18)    | C(26)-Th(1)-C(23)    | 48.13(17)    |
| C(3)-Th(1)-C(15)     | 147.32(19)   | C(13)-Th(1)-C(5)     | 75.48(18)    |
| C(4)-Th(1)-C(15)     | 120.96(19)   | C(2)-Th(1)-C(5)      | 47.42(18)    |
| C(16)-Th(1)-C(15)    | 28.59(18)    | C(24)-Th(1)-C(5)     | 156.24(18)   |
| C(13)-Th(1)-C(1)     | 103.48(18)   | C(25)-Th(1)-C(5)     | 125.99(17)   |
| C(2)-Th(1)-C(1)      | 29.48(18)    | C(12)-Th(1)-C(5)     | 97.81(18)    |
| C(24)-Th(1)-C(1)     | 128.61(18)   | C(14)-Th(1)-C(5)     | 85.61(18)    |
| C(25)-Th(1)-C(1)     | 99.60(18)    | C(3)-Th(1)-C(5)      | 48.52(18)    |
| C(12)-Th(1)-C(1)     | 127.16(18)   | C(4)-Th(1)-C(5)      | 28.42(18)    |
| C(14)-Th(1)-C(1)     | 105.69(18)   | C(16)-Th(1)-C(5)     | 123.16(18)   |
| C(3)-Th(1)-C(1)      | 49.97(19)    | C(15)-Th(1)-C(5)     | 114.96(18)   |
| C(4)-Th(1)-C(1)      | 48.42(19)    | C(1)-Th(1)-C(5)      | 29.38(18)    |
| C(16)-Th(1)-C(1)     | 151.05(18)   | C(26)-Th(1)-C(5)     | 112.05(17)   |
| C(15)-Th(1)-C(1)     | 132.80(18)   | C(23)-Th(1)-C(5)     | 151.34(18)   |
| C(13)-Th(1)-C(26)    | 161.63(19)   | C(13)-Th(1)-C(27)    | 158.50(17)   |
| C(2)-Th(1)-C(26)     | 73.76(18)    | C(2)-Th(1)-C(27)     | 76.00(17)    |
| C(24)-Th(1)-C(26)    | 47.90(17)    | C(24)-Th(1)-C(27)    | 47.63(17)    |
| C(25)-Th(1)-C(26)    | 29.44(17)    | C(25)-Th(1)-C(27)    | 48.46(18)    |
| C(12)-Th(1)-C(26)    | 150.04(18)   | C(12)-Th(1)-C(27)    | 129.01(17)   |
| C(14)-Th(1)-C(26)    | 132.04(19)   | C(14)-Th(1)-C(27)    | 147.58(18)   |
| Bond                        | Bond Angle    | Bond Angle   |
|-----------------------------|---------------|--------------|
| C(3)-Th(1)-C(27)            | 87.30(18)     | C(28)-Si(5)-C(29) | 108.3(4)   |
| C(4)-Th(1)-C(27)            | 116.82(18)    | C(30)-Si(5)-C(29) | 105.0(3)   |
| C(16)-Th(1)-C(27)           | 112.13(17)    | C(25)-Si(6)-C(33) | 117.5(3)   |
| C(15)-Th(1)-C(27)           | 120.21(17)    | C(25)-Si(6)-C(32) | 108.7(3)   |
| C(1)-Th(1)-C(27)            | 96.81(17)     | C(33)-Si(6)-C(32) | 109.5(3)   |
| C(26)-Th(1)-C(27)           | 28.43(17)     | C(25)-Si(6)-C(31) | 108.1(3)   |
| C(23)-Th(1)-C(27)           | 29.19(16)     | C(33)-Si(6)-C(31) | 105.3(4)   |
| C(5)-Th(1)-C(27)            | 123.00(17)    | C(32)-Si(6)-C(31) | 107.3(4)   |
| C(1)-Si(1)-C(7)             | 111.8(3)      | C(2)-C(1)-C(5)   | 104.0(5)   |
| C(1)-Si(1)-C(6)             | 108.5(4)      | C(2)-C(1)-Si(1)  | 126.1(5)   |
| C(7)-Si(1)-C(6)             | 108.5(4)      | C(5)-C(1)-Si(1)  | 127.1(5)   |
| C(1)-Si(1)-C(8)             | 111.9(3)      | C(2)-C(1)-Th(1)  | 72.9(3)    |
| C(7)-Si(1)-C(8)             | 111.3(4)      | C(5)-C(1)-Th(1)  | 75.6(3)    |
| C(6)-Si(1)-C(8)             | 104.4(4)      | Si(1)-C(1)-Th(1) | 130.6(3)   |
| C(3)-Si(2)-C(11)            | 110.4(3)      | C(1)-C(2)-C(3)   | 112.3(5)   |
| C(3)-Si(2)-C(9)             | 115.2(3)      | C(1)-C(2)-Th(1)  | 77.6(3)    |
| C(11)-Si(2)-C(9)            | 108.6(4)      | C(3)-C(2)-Th(1)  | 76.7(3)    |
| C(3)-Si(2)-C(10)            | 108.2(3)      | C(4)-C(3)-C(2)   | 103.3(6)   |
| C(11)-Si(2)-C(10)           | 105.8(4)      | C(4)-C(3)-Si(2)  | 129.0(5)   |
| C(9)-Si(2)-C(10)            | 108.2(5)      | C(2)-C(3)-Si(2)  | 124.3(5)   |
| C(12)-Si(3)-C(17)           | 107.8(4)      | C(4)-C(3)-Th(1)  | 75.5(4)    |
| C(12)-Si(3)-C(19)           | 112.1(3)      | C(2)-C(3)-Th(1)  | 73.4(3)    |
| C(17)-Si(3)-C(19)           | 106.2(4)      | Si(2)-C(3)-Th(1) | 131.4(3)   |
| C(12)-Si(3)-C(18)           | 112.6(3)      | C(5)-C(4)-C(3)   | 110.3(6)   |
| C(17)-Si(3)-C(18)           | 106.9(4)      | C(5)-C(4)-Th(1)  | 76.5(4)    |
| C(19)-Si(3)-C(18)           | 110.9(4)      | C(3)-C(4)-Th(1)  | 74.9(3)    |
| C(14)-Si(4)-C(20)           | 112.7(3)      | C(4)-C(5)-C(1)   | 110.1(6)   |
| C(14)-Si(4)-C(22)           | 106.5(3)      | C(4)-C(5)-Th(1)  | 75.0(3)    |
| C(20)-Si(4)-C(22)           | 107.0(4)      | C(1)-C(5)-Th(1)  | 75.0(3)    |
| C(14)-Si(4)-C(21)           | 112.6(3)      | C(16)-C(12)-C(13)| 104.5(6)   |
| C(20)-Si(4)-C(21)           | 110.6(5)      | C(16)-C(12)-Si(3)| 125.4(5)   |
| C(22)-Si(4)-C(21)           | 106.9(4)      | C(13)-C(12)-Si(3)| 125.4(5)   |
| C(23)-Si(5)-C(28)           | 110.9(3)      | C(16)-C(12)-Th(1)| 76.0(3)    |
| C(23)-Si(5)-C(30)           | 113.2(3)      | C(13)-C(12)-Th(1)| 73.4(3)    |
| C(28)-Si(5)-C(30)           | 111.0(3)      | Si(3)-C(12)-Th(1)| 134.4(3)   |
| C(23)-Si(5)-C(29)           | 108.2(3)      | C(14)-C(13)-C(12)| 111.2(6)   |
| Bond                        | Length (Å) | Angle (°)   |
|-----------------------------|------------|------------|
| C(14)-C(13)-Th(1)          | 76.8(3)    | O(12)-Na(1)-O(2) | 83.8(3) |
| C(12)-C(13)-Th(1)          | 76.7(3)    | O(6)-Na(1)-O(2)  | 99.38(17) |
| C(15)-C(14)-C(13)          | 104.5(5)   | O(6)-Na(1)-O(7B) | 99.9(3)  |
| C(15)-C(14)-Si(4)          | 125.9(5)   | O(2)-Na(1)-O(7B) | 135.8(4) |
| C(13)-C(14)-Si(4)          | 124.5(5)   | O(12)-Na(1)-O(7) | 65.6(3)  |
| C(15)-C(14)-Th(1)          | 76.0(3)    | O(6)-Na(1)-O(7)  | 92.7(3)  |
| C(13)-C(14)-Th(1)          | 73.4(3)    | O(2)-Na(1)-O(7)  | 135.1(3) |
| Si(4)-C(14)-Th(1)          | 135.0(3)   | O(12)-Na(1)-O(4) | 79.8(3)  |
| C(16)-C(15)-C(14)          | 110.0(6)   | O(6)-Na(1)-O(4)  | 123.22(19) |
| C(16)-C(15)-Th(1)          | 75.6(3)    | O(2)-Na(1)-O(4)  | 118.0(2) |
| C(14)-C(15)-Th(1)          | 74.6(3)    | O(7B)-Na(1)-O(4) | 82.5(4)  |
| C(15)-C(16)-C(12)          | 109.8(6)   | O(7)-Na(1)-O(4)  | 89.2(3)  |
| C(15)-C(16)-Th(1)          | 75.8(3)    | O(12)-Na(1)-O(1) | 90.4(3)  |
| C(12)-C(16)-Th(1)          | 74.6(3)    | O(6)-Na(1)-O(1)  | 64.70(16) |
| C(24)-C(23)-C(27)          | 105.1(5)   | O(2)-Na(1)-O(1)  | 63.96(16) |
| C(24)-C(23)-Si(5)          | 125.2(4)   | O(7B)-Na(1)-O(1) | 89.6(4)  |
| C(27)-C(23)-Si(5)          | 125.7(5)   | O(7)-Na(1)-O(1)  | 83.4(3)  |
| C(24)-C(23)-Th(1)          | 72.8(3)    | O(4)-Na(1)-O(1)  | 169.57(19) |
| C(27)-C(23)-Th(1)          | 75.6(3)    | O(6)-Na(1)-O(12B)| 148.1(4) |
| Si(5)-C(23)-Th(1)          | 133.9(3)   | O(2)-Na(1)-O(12B)| 76.8(3)  |
| C(23)-C(24)-C(25)          | 110.8(5)   | O(7B)-Na(1)-O(12B)| 66.0(5)  |
| C(23)-C(24)-Th(1)          | 77.8(3)    | O(4)-Na(1)-O(12B)| 84.7(4)  |
| C(25)-C(24)-Th(1)          | 75.8(3)    | O(1)-Na(1)-O(12B)| 85.9(4)  |
| C(26)-C(25)-C(24)          | 104.2(5)   | O(12)-Na(1)-O(3) | 101.7(3) |
| C(26)-C(25)-Si(6)          | 129.3(4)   | O(6)-Na(1)-O(3)  | 106.8(2) |
| C(24)-C(25)-Si(6)          | 122.2(4)   | O(2)-Na(1)-O(3)  | 62.85(17) |
| C(26)-C(25)-Th(1)          | 76.6(3)    | O(7B)-Na(1)-O(3) | 144.0(4) |
| C(24)-C(25)-Th(1)          | 74.0(3)    | O(7)-Na(1)-O(3)  | 151.6(3) |
| Si(6)-C(25)-Th(1)          | 132.2(3)   | O(4)-Na(1)-O(3)  | 62.88(18) |
| C(27)-C(26)-C(25)          | 110.1(5)   | O(1)-Na(1)-O(3)  | 123.42(18) |
| C(27)-C(26)-Th(1)          | 76.3(3)    | O(12B)-Na(1)-O(3)| 99.5(4)  |
| C(25)-C(26)-Th(1)          | 74.0(3)    | O(12)-Na(1)-O(5) | 124.0(3) |
| C(26)-C(27)-C(23)          | 109.8(5)   | O(6)-Na(1)-O(5)  | 62.89(16) |
| C(26)-C(27)-Th(1)          | 75.2(3)    | O(2)-Na(1)-O(5)  | 150.22(18) |
| C(23)-C(27)-Th(1)          | 75.2(3)    | O(7B)-Na(1)-O(5) | 73.3(4)  |
| O(12)-Na(1)-O(6)           | 149.4(3)   | O(7)-Na(1)-O(5)  | 72.5(3)  |
O(4)-Na(1)-O(5)  63.88(18)  C(46)-O(7)-Na(1)  125.6(10)
O(1)-Na(1)-O(5)  120.20(18)  C(47)-O(8)-C(48)  107.4(10)
O(12B)-Na(1)-O(5)  131.2(4)  C(50)-O(9)-C(49)  111.3(10)
O(3)-Na(1)-O(5)  97.9(2)  C(52)-O(10)-C(51)  116.8(10)
C(34)-O(1)-C(45)  113.1(5)  C(54)-O(11)-C(53)  132.5(10)
C(34)-O(1)-Na(1)  106.6(4)  C(56)-O(12)-C(55)  111.4(11)
C(45)-O(1)-Na(1)  109.7(4)  C(56)-O(12)-Na(1)  114.9(9)
C(35)-O(2)-C(36)  114.6(5)  C(55)-O(12)-Na(1)  115.2(9)
C(35)-O(2)-Na(1)  121.8(4)  O(7)-C(46)-C(47)  114.2(12)
C(36)-O(2)-Na(1)  120.6(4)  O(8)-C(47)-C(46)  109.0(11)
C(38)-O(3)-C(37)  106.2(9)  O(8)-C(48)-C(49)  106.0(11)
C(38)-O(3)-Na(1)  116.0(5)  O(9)-C(49)-C(48)  128.5(11)
C(37)-O(3)-Na(1)  118.4(7)  O(9)-C(50)-C(51)  113.1(10)
C(39)-O(4)-C(40)  112.1(7)  O(10)-C(51)-C(50)  105.8(9)
C(39)-O(4)-Na(1)  113.9(5)  O(10)-C(52)-C(53)  126.0(11)
C(40)-O(4)-Na(1)  110.4(5)  O(11)-C(53)-C(52)  117.0(11)
C(42)-O(5)-C(41)  113.7(6)  O(11)-C(54)-C(55)  119.8(11)
C(42)-O(5)-Na(1)  110.3(4)  O(12)-C(55)-C(54)  120.9(12)
C(41)-O(5)-Na(1)  117.7(5)  O(12)-C(56)-C(57)  107.9(13)
C(44)-O(6)-C(43)  112.1(5)  O(7)-C(57)-C(56)  109.0(12)
C(44)-O(6)-Na(1)  118.0(4)  C(57B)-O(7B)-C(46B)  113.3(17)
C(43)-O(6)-Na(1)  121.3(4)  C(57B)-O(7B)-Na(1)  115.3(15)
O(1)-C(34)-C(35)  113.1(6)  C(46B)-O(7B)-Na(1)  123.4(14)
O(2)-C(35)-C(34)  107.6(6)  C(47B)-O(8B)-C(48B)  120.4(15)
O(2)-C(36)-C(37)  112.3(8)  C(50B)-O(9B)-C(49B)  104.8(13)
O(3)-C(37)-C(36)  111.2(10)  C(52B)-O(10B)-C(51B)  137.1(15)
O(3)-C(38)-C(39)  112.5(9)  C(54B)-O(11B)-C(53B)  111.5(15)
O(4)-C(39)-C(38)  111.8(9)  C(56B)-O(12B)-C(55B)  108.2(16)
O(4)-C(40)-C(41)  113.0(7)  C(56B)-O(12B)-Na(1)  107.4(14)
O(5)-C(41)-C(40)  108.2(7)  C(55B)-O(12B)-Na(1)  115.5(14)
O(5)-C(42)-C(43)  108.9(6)  O(7B)-C(46B)-C(47B)  113.3(17)
O(6)-C(43)-C(42)  108.6(6)  O(8B)-C(47B)-C(46B)  109.7(16)
O(6)-C(44)-C(45)  108.8(6)  O(8B)-C(48B)-C(49B)  123.3(17)
O(1)-C(45)-C(44)  107.2(5)  O(9B)-C(49B)-C(48B)  119.1(16)
C(57)-O(7)-C(46)  116.2(12)  O(9B)-C(50B)-C(51B)  104.4(12)
C(57)-O(7)-Na(1)  114.2(10)  O(10B)-C(51B)-C(50B)  109.7(13)
X-ray Data Collection, Structure Solution and Refinement for [Rb(crypt)][Cp″Th].

A blue crystal of approximate dimensions 0.296 x 0.316 x 0.435 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was used to determine the unit-cell parameters and for data collection (10 sec/frame scan time). The raw frame data was processed using SAINT and SADABS to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct.

The structure was solved by direct methods and refined on $F^2$ by full-matrix least-squares techniques. The analytical scattering factors for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

Least-squares analysis yielded $wR^2 = 0.0475$ and $Goof = 1.019$ for 622 variables refined against 15844 data (0.73 Å), $R1 = 0.0212$ for those 14524 data with $I > 2.0\sigma(I)$. 
Figure S69: Thermal ellipsoid plot of [Rb(crypt)][Cp”sThII] drawn at the 50% probability level.
Hydrogen atoms have been removed for clarity.

Table S6. Crystal data and structure refinement for [Rb(crypt)][Cp”sTh].

| Identification code   | nrr6 (Nick Rightmire)                        |
|-----------------------|----------------------------------------------|
| Empirical formula     | C₅₁H₉₉N₂O₆RbSi₆Th                          |
| Formula weight        | 1322.37                                      |
| Temperature           | 88(2) K                                      |
| Wavelength            | 0.71073 Å                                    |
| Crystal system        | Triclinic                                    |
| Space group           | \(P\overline{1}\)                             |
| Unit cell dimensions  | \(a = 12.1971(13) \text{ Å} \quad \alpha = 100.6648(13)^\circ.
\(b = 12.7473(13) \text{ Å} \quad \beta = 104.4725(13)^\circ.
\(c = 22.242(2) \text{ Å} \quad \gamma = 95.7340(13)^\circ.\) |
| Volume                | \(3251.6(6) \text{ Å}^3\)                   |
| \(Z\)                | 2                                            |
Density (calculated) 1.351 Mg/m³
Absorption coefficient 3.189 mm⁻¹
F(000) 1356
Crystal color blue
Crystal size 0.435 x 0.316 x 0.296 mm³
Theta range for data collection 1.645 to 29.044°
Index ranges -16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -30 ≤ l ≤ 30
Reflections collected 40057
Independent reflections 15844 [R(int) = 0.0213]
Completeness to theta = 25.242° 99.9 %
Absorption correction Numerical
Max. and min. transmission 0.4085 and 0.2845
Refinement method Full-matrix least-squares on F²
Data / restraints / parameters 15844 / 0 / 622
Goodness-of-fit on F² 1.019
Final R indices [I>2sigma(I) = 14524 data] R1 = 0.0212, wR2 = 0.0462
R indices (all data, R) Th(1) = 0.0256, wR2 = 0.0475
Largest diff. peak and hole 1.117 and -0.690 e.Å⁻³

Table S7. Bond lengths [Å] and angles [°] for [Rb(crypt)][Cp‴Th].

| Bond             | Length [Å] | Bond             | Length [Å] |
|------------------|------------|------------------|------------|
| Th(1)-Cnt1       | 2.536      | Th(1)-C(27)      | 2.853(2)   |
| Th(1)-Cnt2       | 2.509      | Th(1)-C(4)       | 2.8567(19) |
| Th(1)-Cnt3       | 2.522      | Th(1)-C(23)      | 2.860(2)   |
| Th(1)-C(13)      | 2.739(2)   | Si(1)-C(1)       | 1.848(2)   |
| Th(1)-C(25)      | 2.7453(19) | Si(1)-C(8)       | 1.868(2)   |
| Th(1)-C(24)      | 2.7556(19) | Si(1)-C(7)       | 1.873(2)   |
| Th(1)-C(2)       | 2.7607(19) | Si(1)-C(6)       | 1.886(2)   |
| Th(1)-C(12)      | 2.770(2)   | Si(2)-C(3)       | 1.849(2)   |
| Th(1)-C(1)       | 2.7774(19) | Si(2)-C(9)       | 1.868(2)   |
| Th(1)-C(26)      | 2.7825(19) | Si(2)-C(11)      | 1.877(2)   |
| Th(1)-C(16)      | 2.8029(19) | Si(2)-C(10)      | 1.885(2)   |
| Th(1)-C(14)      | 2.8087(19) | Si(3)-C(12)      | 1.842(2)   |
| Th(1)-C(5)       | 2.8139(19) | Si(3)-C(19)      | 1.873(2)   |
| Th(1)-C(15)      | 2.8208(19) | Si(3)-C(18)      | 1.874(2)   |
| Th(1)-C(3)       | 2.8502(19) | Si(3)-C(17)      | 1.880(2)   |
| Bond                  | Distance | Bond                  | Distance |
|-----------------------|----------|-----------------------|----------|
| Si(4)-C(14)           | 1.850(2) | O(1)-C(36)            | 1.434(3) |
| Si(4)-C(20)           | 1.869(2) | O(2)-C(38)            | 1.425(3) |
| Si(4)-C(21)           | 1.870(2) | O(2)-C(37)            | 1.428(3) |
| Si(4)-C(22)           | 1.880(2) | O(3)-C(41)            | 1.421(3) |
| Si(5)-C(23)           | 1.852(2) | O(3)-C(42)            | 1.430(3) |
| Si(5)-C(30)           | 1.867(2) | O(4)-C(43)            | 1.423(3) |
| Si(5)-C(29)           | 1.870(2) | O(4)-C(44)            | 1.430(3) |
| Si(5)-C(28)           | 1.882(2) | O(5)-C(47)            | 1.427(2) |
| Si(6)-C(25)           | 1.848(2) | O(5)-C(48)            | 1.428(2) |
| Si(6)-C(32)           | 1.869(2) | O(6)-C(50)            | 1.423(3) |
| Si(6)-C(33)           | 1.875(2) | O(6)-C(49)            | 1.432(3) |
| Si(6)-C(31)           | 1.878(2) | N(1)-C(34)            | 1.469(3) |
| C(1)-C(5)             | 1.439(3) | N(1)-C(40)            | 1.473(3) |
| C(1)-C(2)             | 1.440(3) | N(1)-C(46)            | 1.479(3) |
| C(2)-C(3)             | 1.432(3) | N(2)-C(51)            | 1.468(3) |
| C(3)-C(4)             | 1.426(3) | N(2)-C(39)            | 1.475(3) |
| C(4)-C(5)             | 1.401(3) | N(2)-C(45)            | 1.480(3) |
| C(12)-C(16)           | 1.437(3) | C(34)-C(35)           | 1.505(3) |
| C(12)-C(13)           | 1.447(3) | C(36)-C(37)           | 1.496(3) |
| C(13)-C(14)           | 1.434(3) | C(38)-C(39)           | 1.490(4) |
| C(14)-C(15)           | 1.430(3) | C(40)-C(41)           | 1.511(3) |
| C(15)-C(16)           | 1.401(3) | C(42)-C(43)           | 1.506(3) |
| C(23)-C(27)           | 1.426(3) | C(44)-C(45)           | 1.506(3) |
| C(23)-C(24)           | 1.431(3) | C(46)-C(47)           | 1.505(3) |
| C(24)-C(25)           | 1.439(3) | C(48)-C(49)           | 1.497(3) |
| C(25)-C(26)           | 1.443(3) | C(50)-C(51)           | 1.514(3) |
| C(26)-C(27)           | 1.401(3) |                       |          |
| Rb(1)-O(1)            | 2.8662(15)| Cnt1-Th(1)-Cnt2       | 122.7    |
| Rb(1)-O(2)            | 2.8717(15)| Cnt1-Th(1)-Cnt3       | 119.7    |
| Rb(1)-O(5)            | 2.8743(14)| Cnt2-Th(1)-Cnt3       | 117.6    |
| Rb(1)-O(6)            | 2.8822(15)| C(13)-Th(1)-C(25)    | 132.68(6) |
| Rb(1)-O(3)            | 2.8890(15)| C(13)-Th(1)-C(24)    | 118.07(6) |
| Rb(1)-O(4)            | 2.8918(15)| C(25)-Th(1)-C(24)    | 30.32(6)  |
| Rb(1)-N(1)            | 3.0535(17)| C(13)-Th(1)-C(2)     | 121.78(6) |
| Rb(1)-N(2)            | 3.0564(19)| C(25)-Th(1)-C(2)     | 100.74(6) |
| O(1)-C(35)            | 1.424(3) | C(24)-Th(1)-C(2)     | 120.05(6) |
| Bond                     | Distance (Å) | Bond                     | Distance (Å) |
|-------------------------|--------------|-------------------------|--------------|
| C(13)-Th(1)-C(12)      | 30.46(6)     | C(26)-Th(1)-C(5)        | 121.20(6)    |
| C(25)-Th(1)-C(12)      | 125.95(6)    | C(16)-Th(1)-C(5)        | 117.63(6)    |
| C(24)-Th(1)-C(12)      | 99.49(6)     | C(14)-Th(1)-C(5)        | 93.26(6)     |
| C(2)-Th(1)-C(12)       | 131.61(6)    | C(13)-Th(1)-C(15)       | 48.20(6)     |
| C(13)-Th(1)-C(1)       | 98.38(6)     | C(25)-Th(1)-C(15)       | 85.26(6)     |
| C(25)-Th(1)-C(1)       | 128.26(6)    | C(24)-Th(1)-C(15)       | 72.33(6)     |
| C(24)-Th(1)-C(1)       | 136.88(6)    | C(2)-Th(1)-C(15)        | 163.26(6)    |
| C(2)-Th(1)-C(1)        | 30.13(6)     | C(12)-Th(1)-C(15)       | 49.05(6)     |
| C(12)-Th(1)-C(1)       | 101.64(6)    | C(1)-Th(1)-C(15)        | 146.42(6)    |
| C(13)-Th(1)-C(26)      | 162.92(6)    | C(26)-Th(1)-C(15)       | 115.13(6)    |
| C(25)-Th(1)-C(26)      | 30.24(6)     | C(16)-Th(1)-C(15)       | 28.86(6)     |
| C(24)-Th(1)-C(26)      | 48.36(6)     | C(14)-Th(1)-C(15)       | 29.42(6)     |
| C(2)-Th(1)-C(26)       | 73.21(6)     | C(5)-Th(1)-C(15)        | 120.65(6)    |
| C(12)-Th(1)-C(26)      | 145.89(6)    | C(13)-Th(1)-C(3)        | 109.19(6)    |
| C(1)-Th(1)-C(26)       | 98.43(6)     | C(25)-Th(1)-C(3)        | 97.55(6)     |
| C(13)-Th(1)-C(16)      | 48.53(6)     | C(24)-Th(1)-C(3)        | 126.30(6)    |
| C(25)-Th(1)-C(16)      | 96.17(6)     | C(2)-Th(1)-C(3)         | 29.52(5)     |
| C(24)-Th(1)-C(16)      | 71.67(6)     | C(12)-Th(1)-C(3)        | 133.89(6)    |
| C(2)-Th(1)-C(16)       | 159.86(6)    | C(1)-Th(1)-C(3)         | 49.73(6)     |
| C(12)-Th(1)-C(16)      | 29.87(6)     | C(26)-Th(1)-C(3)        | 79.79(6)     |
| C(1)-Th(1)-C(16)       | 129.99(6)    | C(16)-Th(1)-C(3)        | 156.80(6)    |
| C(26)-Th(1)-C(16)      | 120.00(6)    | C(14)-Th(1)-C(3)        | 109.28(6)    |
| C(13)-Th(1)-C(14)      | 29.92(6)     | C(5)-Th(1)-C(3)         | 48.17(6)     |
| C(25)-Th(1)-C(14)      | 104.82(6)    | C(15)-Th(1)-C(3)        | 134.68(6)    |
| C(24)-Th(1)-C(14)      | 100.12(6)    | C(13)-Th(1)-C(27)       | 154.35(6)    |
| C(2)-Th(1)-C(14)       | 134.53(6)    | C(25)-Th(1)-C(27)       | 49.12(6)     |
| C(12)-Th(1)-C(14)      | 50.36(6)     | C(24)-Th(1)-C(27)       | 47.64(6)     |
| C(1)-Th(1)-C(14)       | 122.26(6)    | C(2)-Th(1)-C(27)        | 75.44(6)     |
| C(26)-Th(1)-C(14)      | 134.01(6)    | C(12)-Th(1)-C(27)       | 124.05(6)    |
| C(16)-Th(1)-C(14)      | 48.79(6)     | C(1)-Th(1)-C(27)        | 89.64(6)     |
| C(13)-Th(1)-C(5)       | 73.75(6)     | C(26)-Th(1)-C(27)       | 28.76(6)     |
| C(25)-Th(1)-C(5)       | 145.41(6)    | C(16)-Th(1)-C(27)       | 108.51(6)    |
| C(24)-Th(1)-C(5)       | 165.59(6)    | C(14)-Th(1)-C(27)       | 147.75(6)    |
| C(2)-Th(1)-C(5)        | 48.14(6)     | C(5)-Th(1)-C(27)        | 118.97(6)    |
| C(12)-Th(1)-C(5)       | 88.29(6)     | C(15)-Th(1)-C(27)       | 119.18(6)    |
| C(1)-Th(1)-C(5)        | 29.82(6)     | C(3)-Th(1)-C(27)        | 94.61(6)     |
| Bond                  | Angle (°)     | Bond                  | Angle (°)     |
|----------------------|--------------|----------------------|--------------|
| C(13)-Th(1)-C(4)     | 80.63(6)     | C(3)-Si(2)-C(10)     | 106.88(10)   |
| C(25)-Th(1)-C(4)     | 122.02(6)    | C(9)-Si(2)-C(10)     | 108.62(12)   |
| C(24)-Th(1)-C(4)     | 152.34(6)    | C(11)-Si(2)-C(10)    | 103.03(11)   |
| C(2)-Th(1)-C(4)      | 47.63(6)     | C(12)-Si(3)-C(19)    | 107.34(10)   |
| C(12)-Th(1)-C(4)     | 105.39(6)    | C(12)-Si(3)-C(18)    | 114.96(10)   |
| C(1)-Th(1)-C(4)      | 48.65(6)     | C(19)-Si(3)-C(18)    | 111.38(10)   |
| C(26)-Th(1)-C(4)     | 108.58(6)    | C(12)-Si(3)-C(17)    | 109.78(10)   |
| C(16)-Th(1)-C(4)     | 129.09(6)    | C(19)-Si(3)-C(17)    | 106.66(12)   |
| C(14)-Th(1)-C(4)     | 86.90(6)     | C(18)-Si(3)-C(17)    | 106.43(11)   |
| C(5)-Th(1)-C(4)      | 28.60(6)     | C(14)-Si(4)-C(20)    | 110.80(10)   |
| C(15)-Th(1)-C(4)     | 116.04(6)    | C(14)-Si(4)-C(21)    | 114.44(9)    |
| C(3)-Th(1)-C(4)      | 28.93(6)     | C(20)-Si(4)-C(21)    | 108.68(11)   |
| C(27)-Th(1)-C(4)     | 121.70(6)    | C(14)-Si(4)-C(22)    | 107.51(9)    |
| C(13)-Th(1)-C(23)    | 127.02(6)    | C(20)-Si(4)-C(22)    | 107.34(11)   |
| C(25)-Th(1)-C(23)    | 50.02(6)     | C(21)-Si(4)-C(22)    | 107.80(10)   |
| C(24)-Th(1)-C(23)    | 29.44(5)     | C(23)-Si(5)-C(30)    | 112.94(10)   |
| C(2)-Th(1)-C(23)     | 103.04(6)    | C(23)-Si(5)-C(29)    | 113.14(10)   |
| C(12)-Th(1)-C(23)    | 98.57(6)     | C(30)-Si(5)-C(29)    | 110.06(11)   |
| C(1)-Th(1)-C(23)     | 109.80(6)    | C(23)-Si(5)-C(28)    | 106.83(10)   |
| C(26)-Th(1)-C(23)    | 48.32(6)     | C(30)-Si(5)-C(28)    | 105.97(11)   |
| C(16)-Th(1)-C(23)    | 79.64(6)     | C(29)-Si(5)-C(28)    | 107.44(11)   |
| C(14)-Th(1)-C(23)    | 122.22(6)    | C(25)-Si(6)-C(32)    | 117.87(10)   |
| C(5)-Th(1)-C(23)     | 138.83(6)    | C(25)-Si(6)-C(33)    | 109.48(10)   |
| C(15)-Th(1)-C(23)    | 92.81(6)     | C(32)-Si(6)-C(33)    | 106.61(10)   |
| C(3)-Th(1)-C(23)     | 123.39(6)    | C(25)-Si(6)-C(31)    | 106.99(10)   |
| C(27)-Th(1)-C(23)    | 28.91(5)     | C(32)-Si(6)-C(31)    | 107.11(11)   |
| C(4)-Th(1)-C(23)     | 150.35(6)    | C(33)-Si(6)-C(31)    | 108.47(10)   |
| C(1)-Si(1)-C(8)      | 110.90(10)   | C(5)-C(1)-C(2)       | 104.38(17)   |
| C(1)-Si(1)-C(7)      | 112.46(10)   | C(5)-C(1)-Si(1)      | 127.10(15)   |
| C(8)-Si(1)-C(7)      | 112.23(11)   | C(2)-C(1)-Si(1)      | 124.23(15)   |
| C(1)-Si(1)-C(6)      | 108.11(10)   | C(5)-C(1)-Th(1)      | 76.50(11)    |
| C(8)-Si(1)-C(6)      | 106.35(11)   | C(2)-C(1)-Th(1)      | 74.29(10)    |
| C(7)-Si(1)-C(6)      | 106.42(10)   | Si(1)-C(1)-Th(1)     | 132.21(9)    |
| C(3)-Si(2)-C(9)      | 111.74(10)   | C(3)-C(2)-C(1)       | 111.03(17)   |
| C(3)-Si(2)-C(11)     | 114.91(9)    | C(3)-C(2)-Th(1)      | 78.71(11)    |
| C(9)-Si(2)-C(11)     | 111.04(10)   | C(1)-C(2)-Th(1)      | 75.58(11)    |
| Bond                  | Bond Length (Å) | Angle (°)       |
|----------------------|-----------------|-----------------|
| O(6)-Rb(1)-N(1)      | 120.02(5)       | C(39)-N(2)-C(45) | 109.86(19) |
| O(3)-Rb(1)-N(1)      | 59.96(4)        | C(51)-N(2)-Rb(1) | 108.43(13) |
| O(4)-Rb(1)-N(1)      | 119.09(4)       | C(39)-N(2)-Rb(1) | 108.67(13) |
| O(1)-Rb(1)-N(2)      | 120.45(5)       | C(45)-N(2)-Rb(1) | 108.40(13) |
| O(2)-Rb(1)-N(2)      | 60.17(5)        | N(1)-C(34)-C(35) | 113.95(18) |
| O(5)-Rb(1)-N(2)      | 119.91(5)       | O(1)-C(35)-C(34) | 108.94(18) |
| O(6)-Rb(1)-N(2)      | 60.19(5)        | O(1)-C(35)-Rb(1) | 44.03(9)   |
| O(3)-Rb(1)-N(2)      | 119.48(5)       | C(34)-C(35)-Rb(1) | 81.67(12)  |
| O(4)-Rb(1)-N(2)      | 60.36(5)        | O(1)-C(36)-C(37) | 108.68(18) |
| N(1)-Rb(1)-N(2)      | 179.43(5)       | O(1)-C(36)-Rb(1) | 46.58(9)   |
| C(35)-O(1)-C(36)     | 112.31(17)      | C(37)-C(36)-Rb(1) | 76.80(12)  |
| C(35)-O(1)-Rb(1)     | 115.76(12)      | O(2)-C(37)-C(36) | 109.94(17) |
| C(36)-O(1)-Rb(1)     | 112.11(12)      | O(2)-C(37)-Rb(1) | 48.15(9)   |
| C(38)-O(2)-C(37)     | 111.11(17)      | C(36)-C(37)-Rb(1) | 79.47(12)  |
| C(38)-O(2)-Rb(1)     | 114.71(13)      | O(2)-C(38)-C(39) | 109.77(19) |
| C(37)-O(2)-Rb(1)     | 110.12(12)      | O(2)-C(38)-Rb(1) | 44.81(10)  |
| C(41)-O(3)-C(42)     | 111.21(16)      | C(39)-C(38)-Rb(1) | 82.10(13)  |
| C(41)-O(3)-Rb(1)     | 115.91(12)      | N(2)-C(39)-C(38) | 114.5(2)   |
| C(42)-O(3)-Rb(1)     | 112.69(12)      | N(1)-C(40)-C(41) | 114.17(18) |
| C(43)-O(4)-C(44)     | 111.87(17)      | O(3)-C(41)-C(40) | 109.26(17) |
| C(43)-O(4)-Rb(1)     | 113.56(12)      | O(3)-C(41)-Rb(1) | 44.07(9)   |
| C(44)-O(4)-Rb(1)     | 114.19(12)      | C(40)-C(41)-Rb(1) | 80.80(11)  |
| C(47)-O(5)-C(48)     | 111.66(16)      | O(3)-C(42)-C(43) | 109.13(17) |
| C(47)-O(5)-Rb(1)     | 112.71(11)      | O(3)-C(42)-Rb(1) | 46.33(9)   |
| C(48)-O(5)-Rb(1)     | 113.69(11)      | C(43)-C(42)-Rb(1) | 78.73(12)  |
| C(50)-O(6)-C(49)     | 111.15(17)      | O(4)-C(43)-C(42) | 109.05(18) |
| C(50)-O(6)-Rb(1)     | 115.59(13)      | O(4)-C(43)-Rb(1) | 45.79(9)   |
| C(49)-O(6)-Rb(1)     | 110.58(12)      | C(42)-C(43)-Rb(1) | 77.73(12)  |
| C(34)-N(1)-C(40)     | 110.42(17)      | O(4)-C(44)-C(45) | 108.91(19) |
| C(34)-N(1)-C(46)     | 110.20(17)      | O(4)-C(44)-Rb(1) | 45.25(9)   |
| C(40)-N(1)-C(46)     | 109.25(17)      | C(45)-C(44)-Rb(1) | 81.38(12)  |
| C(34)-N(1)-Rb(1)     | 109.23(12)      | N(2)-C(45)-C(44) | 114.33(19) |
| C(40)-N(1)-Rb(1)     | 109.09(12)      | N(1)-C(46)-C(47) | 113.85(17) |
| C(46)-N(1)-Rb(1)     | 108.61(12)      | O(5)-C(47)-C(46) | 108.76(16) |
| C(51)-N(2)-C(39)     | 110.90(19)      | O(5)-C(47)-Rb(1) | 46.26(9)   |
| C(51)-N(2)-C(45)     | 110.51(19)      | C(46)-C(47)-Rb(1) | 83.05(11)  |
O(5)-C(48)-C(49) 109.25(18)  C(48)-C(49)-Rb(1) 79.96(12)
O(5)-C(48)-Rb(1)  45.54(9)  O(6)-C(50)-C(51) 109.36(18)
C(49)-C(48)-Rb(1)  76.49(12)  O(6)-C(50)-Rb(1)  44.25(10)
O(6)-C(49)-C(48) 109.76(18)  C(51)-C(50)-Rb(1)  80.64(12)
O(6)-C(49)-Rb(1)  47.82(9)  N(2)-C(51)-C(50) 113.90(19)

Figure S70: Thermal ellipsoid plot of [Cs(crypt)][Cp"₃Th] plotted at the 50% probability level. Hydrogen atoms have been removed for clarity.

X-ray Data Collection, Structure Solution and Refinement for [Cs(crypt)][Cp"₃Th].

A blue crystal of approximate dimensions 0.082 x 0.110 x 0.182 mm was mounted in a cryoloop and transferred to a Bruker SMART APEX II diffractometer. The APEX2 program package was used to determine the unit-cell parameters and for data collection (120 sec/frame scan time). The raw frame data was processed using SAINT and SADABS to yield the reflection
data file. Subsequent calculations were carried out using the SHELXTL \textsuperscript{35} program package. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group \( P\bar{T} \) was assigned and later determined to be correct.

The structure was solved by direct methods and refined on \( F^2 \) by full-matrix least-squares techniques. The analytical scattering factors\textsuperscript{36} for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

Least-squares analysis yielded \( wR^2 = 0.0866 \) and Goof = 1.024 for 622 variables refined against 16125 data (0.75 Å), \( R1 = 0.0382 \) for those 13147 data with \( I > 2.0\sigma(I) \).

**Table S. Crystal data and structure refinement for [Cs(crypt)][Cp″:Th].**

| Identification code   | jcw48 (Justin Wedal) |
|-----------------------|-----------------------|
| Empirical formula     | \( C_{51}H_{99}CsN_{2}O_{6}Si_{6}Th \) |
| Formula weight        | 1369.81               |
| Temperature           | 133(2) K              |
| Wavelength            | 0.71073 Å             |
| Crystal system        | Triclinic             |
| Space group           | \( P\bar{T} \)       |
| Unit cell dimensions  | \( a = 12.1953(8) \) Å \( \alpha = 100.6711(10)^\circ \). |
|                       | \( b = 12.7501(8) \) Å \( \beta = 104.3758(9)^\circ \). |
|                       | \( c = 22.2212(14) \) Å \( \gamma = 95.7421(10)^\circ \). |
| Volume                | 3250.2(4) Å\(^3\)    |
| \( Z \)               | 2                     |
| Density (calculated)  | 1.400 Mg/m\(^3\)     |
| Absorption coefficient| 2.998 mm\(^-1\)       |
| \( F(000) \)           | 1392                  |
| Crystal color         | blue                  |
| Crystal size          | 0.182 x 0.110 x 0.082 mm\(^3\) |
| Theta range for data collection | 1.645 to 28.322\(^\circ\) |
| Index ranges          | \(-16 \leq h \leq 16, -17 \leq k \leq 17, -29 \leq l \leq 29\) |
| Reflections collected | 43962                 |
| Independent reflections| 16125 [R(int) = 0.0464] |
| Completeness to theta = 25.242\(^\circ\) | 100.0 % |

S78
Absorption correction  
Semi-empirical from equivalents  
Max. and min. transmission  
0.6471 and 0.5186  
Refinement method  
Full-matrix least-squares on F^2  
Data / restraints / parameters  
16125 / 0 / 622  
Goodness-of-fit on F^2  
1.024  
Final R indices [I>2sigma(I) = 13147 data]  
R1 = 0.0382, wR2 = 0.0809  
R indices (all data, 0.75 Å)  
R1 = 0.0556, wR2 = 0.0866  
Largest diff. peak and hole  
1.613 and -2.543 e.Å^-3

### Table S9. Bond lengths [Å] and angles [°] for [Cs(crypt)][Cp″:Th].

| Bond                        | Th(1)-Cnt1 | Si(2)-C(11) | Si(3)-C(12) | Si(3)-C(19) | Si(3)-C(17) | Si(3)-C(18) | Si(4)-C(14) | Si(4)-C(14) | Si(4)-C(22) | Si(5)-C(23) | Si(5)-C(28) | Si(5)-C(29) | Si(5)-C(30) | Si(5)-C(23) | Si(5)-C(31) | Si(6)-C(25) | Si(6)-C(33) | Si(6)-C(32) | Si(6)-C(30) | Si(6)-C(31) | C(1)-C(5) | C(1)-C(2) | C(2)-C(3) | C(3)-C(4) | C(4)-C(5) | C(12)-C(16) | C(12)-C(13) | C(13)-C(14) |
|-----------------------------|------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Th(1)-Cnt1                  | 2.534      |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-Cnt2                  | 2.522      |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-Cnt3                  | 2.507      |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-C(24)                 | 2.731(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-C(12)                 | 2.749(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-C(13)                 | 2.756(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-C(2)                  | 2.759(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-C(25)                 | 2.769(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-C(26)                 | 2.795(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-C(23)                 | 2.804(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-C(27)                 | 2.816(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-C(15)                 | 2.843(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-C(16)                 | 2.854(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-C(5)                  | 2.853(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Th(1)-C(14)                 | 2.854(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Si(1)-C(1)                  | 1.844(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Si(1)-C(8)                  | 1.867(5)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Si(1)-C(7)                  | 1.872(5)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Si(1)-C(6)                  | 1.887(5)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Si(2)-C(3)                  | 1.843(4)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Si(2)-C(9)                  | 1.860(5)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
| Si(2)-C(10)                 | 1.866(5)   |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |             |
C(14)-C(15)  1.423(6)  C(23)-C(27)  1.418(6)  C(24)-C(25)  1.435(6)  C(25)-C(26)  1.433(6)  C(26)-C(27)  1.392(6)
C(15)-C(16)  1.389(6)  C(23)-C(24)  1.432(6)  C(24)-C(25)  1.435(6)  C(25)-C(26)  1.433(6)
C(23)-C(27)  1.418(6)  C(23)-C(24)  1.432(6)  C(24)-C(25)  1.435(6)  C(25)-C(26)  1.433(6)
C(24)-C(25)  1.435(6)  C(23)-C(27)  1.418(6)  C(24)-C(25)  1.435(6)  C(25)-C(26)  1.433(6)
C(25)-C(26)  1.433(6)  C(23)-C(27)  1.418(6)  C(24)-C(25)  1.435(6)  C(25)-C(26)  1.433(6)
Cs(1)-O(6)  2.931(3)  Cnt1-Th(1)-Cnt2  119.7
Cs(1)-O(5)  2.933(3)  Cnt1-Th(1)-Cnt3  122.7
Cs(1)-O(1)  2.933(3)  Cnt2-Th(1)-Cnt3  117.6
Cs(1)-O(2)  2.941(3)  C(24)-Th(1)-C(12)  132.66(12)
Cs(1)-O(3)  2.942(3)  C(24)-Th(1)-C(13)  117.94(12)
Cs(1)-O(4)  2.947(3)  C(12)-Th(1)-C(13)  30.33(12)
Cs(1)-N(2)  3.073(4)  C(24)-Th(1)-C(2)  121.81(13)
Cs(1)-N(1)  3.073(4)  C(12)-Th(1)-C(2)  100.86(13)
O(1)-C(35)  1.414(5)  C(13)-Th(1)-C(2)  120.14(13)
O(1)-C(36)  1.426(5)  C(24)-Th(1)-C(25)  30.24(13)
O(2)-C(37)  1.426(6)  C(12)-Th(1)-C(25)  126.02(13)
O(2)-C(38)  1.429(6)  C(13)-Th(1)-C(25)  99.55(13)
O(3)-C(42)  1.420(5)  C(2)-Th(1)-C(25)  131.41(13)
O(3)-C(41)  1.421(6)  C(24)-Th(1)-C(3)  98.37(12)
O(4)-C(44)  1.418(6)  C(12)-Th(1)-C(3)  128.34(13)
O(4)-C(43)  1.427(6)  C(13)-Th(1)-C(3)  136.89(12)
O(5)-C(47)  1.421(6)  C(2)-Th(1)-C(3)  30.11(13)
O(5)-C(48)  1.431(6)  C(25)-Th(1)-C(3)  101.48(13)
O(6)-C(49)  1.425(6)  C(24)-Th(1)-C(16)  162.80(12)
O(6)-C(50)  1.426(6)  C(12)-Th(1)-C(16)  30.15(12)
N(1)-C(34)  1.469(6)  C(13)-Th(1)-C(16)  48.30(12)
N(1)-C(46)  1.471(6)  C(2)-Th(1)-C(16)  73.40(12)
N(1)-C(40)  1.474(6)  C(25)-Th(1)-C(16)  145.92(13)
N(2)-C(39)  1.473(7)  C(3)-Th(1)-C(16)  98.59(12)
N(2)-C(51)  1.475(7)  C(24)-Th(1)-C(26)  48.13(13)
N(2)-C(45)  1.476(6)  C(12)-Th(1)-C(26)  96.27(13)
C(34)-C(35)  1.515(7)  C(13)-Th(1)-C(26)  71.84(13)
C(36)-C(37)  1.501(7)  C(2)-Th(1)-C(26)  159.78(13)
C(38)-C(39)  1.514(7)  C(25)-Th(1)-C(26)  29.85(12)
| Bond                  | Distance (Å) |
|----------------------|--------------|
| C(3)-Th(1)-C(26)    | 129.90(13)   |
| C(16)-Th(1)-C(26)   | 120.12(12)   |
| C(24)-Th(1)-C(23)   | 29.96(12)    |
| C(12)-Th(1)-C(23)   | 104.84(12)   |
| C(13)-Th(1)-C(23)   | 100.12(12)   |
| C(2)-Th(1)-C(23)    | 134.52(12)   |
| C(25)-Th(1)-C(23)   | 50.35(12)    |
| C(3)-Th(1)-C(23)    | 122.23(12)   |
| C(16)-Th(1)-C(23)   | 133.93(12)   |
| C(26)-Th(1)-C(23)   | 48.49(12)    |
| C(24)-Th(1)-C(4)    | 73.85(12)    |
| C(12)-Th(1)-C(4)    | 145.38(12)   |
| C(13)-Th(1)-C(4)    | 166.64(12)   |
| C(2)-Th(1)-C(4)     | 48.05(12)    |
| C(25)-Th(1)-C(4)    | 88.25(13)    |
| C(3)-Th(1)-C(4)     | 29.87(12)    |
| C(16)-Th(1)-C(4)    | 121.28(12)   |
| C(26)-Th(1)-C(4)    | 117.51(13)   |
| C(23)-Th(1)-C(4)    | 93.21(12)    |
| C(24)-Th(1)-C(27)   | 47.97(12)    |
| C(12)-Th(1)-C(27)   | 85.41(12)    |
| C(13)-Th(1)-C(27)   | 72.52(12)    |
| C(2)-Th(1)-C(27)    | 163.09(12)   |
| C(25)-Th(1)-C(27)   | 49.06(12)    |
| C(3)-Th(1)-C(27)    | 146.21(12)   |
| C(16)-Th(1)-C(27)   | 115.19(12)   |
| C(26)-Th(1)-C(27)   | 28.73(12)    |
| C(23)-Th(1)-C(27)   | 29.22(12)    |
| C(4)-Th(1)-C(27)    | 120.43(12)   |
| C(24)-Th(1)-C(27)   | 154.28(13)   |
| C(12)-Th(1)-C(27)   | 48.83(12)    |
| C(13)-Th(1)-C(27)   | 47.46(12)    |
| C(2)-Th(1)-C(27)    | 75.59(12)    |
| C(25)-Th(1)-C(27)   | 124.23(13)   |
| C(3)-Th(1)-C(27)    | 89.87(12)    |
| C(16)-Th(1)-C(27)   | 28.57(12)    |
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| C(26)-Th(1)-C(14)    | 79.88(12)    | C(29)-Si(5)-C(30)    | 106.8(2)     |
| C(23)-Th(1)-C(14)    | 122.13(12)   | C(25)-Si(6)-C(33)    | 115.2(2)     |
| C(4)-Th(1)-C(14)     | 139.06(12)   | C(25)-Si(6)-C(32)    | 107.3(2)     |
| C(27)-Th(1)-C(14)    | 92.92(12)    | C(33)-Si(6)-C(32)    | 111.0(2)     |
| C(15)-Th(1)-C(14)    | 28.92(12)    | C(25)-Si(6)-C(31)    | 109.9(2)     |
| C(1)-Th(1)-C(14)     | 123.25(12)   | C(33)-Si(6)-C(31)    | 106.4(2)     |
| C(5)-Th(1)-C(14)     | 150.32(12)   | C(32)-Si(6)-C(31)    | 106.7(3)     |
| C(1)-Si(1)-C(8)      | 115.2(2)     | C(5)-C(1)-C(2)       | 105.2(4)     |
| C(1)-Si(1)-C(7)      | 111.6(2)     | C(5)-C(1)-Si(1)      | 125.8(3)     |
| C(8)-Si(1)-C(7)      | 110.8(2)     | C(2)-C(1)-Si(1)      | 124.9(3)     |
| C(1)-Si(1)-C(6)      | 106.6(2)     | C(5)-C(1)-Th(1)      | 75.7(2)      |
| C(8)-Si(1)-C(6)      | 102.7(2)     | C(2)-C(1)-Th(1)      | 71.8(2)      |
| C(7)-Si(1)-C(6)      | 109.3(2)     | Si(1)-C(1)-Th(1)     | 134.8(2)     |
| C(3)-Si(2)-C(9)      | 112.4(2)     | C(1)-C(2)-C(3)       | 111.4(4)     |
| C(3)-Si(2)-C(10)     | 110.8(2)     | C(1)-C(2)-Th(1)      | 78.8(2)      |
| C(9)-Si(2)-C(10)     | 112.7(2)     | C(3)-C(2)-Th(1)      | 75.6(2)      |
| C(3)-Si(2)-C(11)     | 108.2(2)     | C(2)-C(3)-C(4)       | 104.0(4)     |
| C(9)-Si(2)-C(11)     | 105.8(2)     | C(2)-C(3)-Si(2)      | 124.2(3)     |
| C(10)-Si(2)-C(11)    | 106.6(2)     | C(4)-C(3)-Si(2)      | 127.4(3)     |
| C(12)-Si(3)-C(19)    | 117.8(2)     | C(2)-C(3)-Th(1)      | 74.3(2)      |
| C(12)-Si(3)-C(17)    | 106.6(2)     | C(4)-C(3)-Th(1)      | 76.3(2)      |
| C(19)-Si(3)-C(17)    | 107.2(2)     | Si(2)-C(3)-Th(1)     | 132.5(2)     |
| C(12)-Si(3)-C(18)    | 109.5(2)     | C(5)-C(4)-C(3)       | 109.9(4)     |
| C(19)-Si(3)-C(18)    | 106.8(2)     | C(5)-C(4)-Th(1)      | 77.5(2)      |
| C(17)-Si(3)-C(18)    | 108.7(2)     | C(3)-C(4)-Th(1)      | 73.9(2)      |
| C(14)-Si(4)-C(22)    | 113.0(2)     | C(4)-C(5)-C(1)       | 109.5(4)     |
| C(14)-Si(4)-C(20)    | 113.2(2)     | C(4)-C(5)-Th(1)      | 73.9(2)      |
| C(22)-Si(4)-C(20)    | 110.0(3)     | C(1)-C(5)-Th(1)      | 75.3(2)      |
| C(14)-Si(4)-C(21)    | 106.7(2)     | C(16)-C(12)-C(13)    | 103.8(4)     |
| C(22)-Si(4)-C(21)    | 106.0(2)     | C(16)-C(12)-Si(3)    | 129.6(3)     |
| C(20)-Si(4)-C(21)    | 107.5(3)     | C(13)-C(12)-Si(3)    | 122.6(3)     |
| C(23)-Si(5)-C(28)    | 114.9(2)     | C(16)-C(12)-Th(1)    | 76.2(2)      |
| C(23)-Si(5)-C(29)    | 110.7(2)     | C(13)-C(12)-Th(1)    | 75.1(2)      |
| C(28)-Si(5)-C(29)    | 109.1(2)     | Si(3)-C(12)-Th(1)    | 130.75(19)   |
| C(23)-Si(5)-C(30)    | 107.5(2)     | C(14)-C(13)-C(12)    | 111.4(4)     |
| C(28)-Si(5)-C(30)    | 107.4(2)     | C(14)-C(13)-Th(1)    | 79.2(2)      |
| Bond                                      | Distance | Bond Angle                  | Angle            |
|-------------------------------------------|----------|-----------------------------|------------------|
| C(12)-C(13)-Th(1)                        | 74.5(2)  | O(5)-Cs(1)-O(1)             | 95.39(9)         |
| C(13)-C(14)-C(15)                        | 104.9(4) | O(6)-Cs(1)-O(2)             | 95.79(9)         |
| C(13)-C(14)-Si(4)                        | 123.3(3) | O(5)-Cs(1)-O(2)             | 135.79(9)        |
| C(15)-C(14)-Si(4)                        | 126.2(3) | O(1)-Cs(1)-O(2)             | 60.38(9)         |
| C(13)-C(14)-Th(1)                        | 71.6(2)  | O(6)-Cs(1)-O(3)             | 137.09(9)        |
| C(15)-C(14)-Th(1)                        | 75.1(2)  | O(5)-Cs(1)-O(3)             | 96.65(9)         |
| Si(4)-C(14)-Th(1)                        | 138.6(2) | O(1)-Cs(1)-O(3)             | 100.03(9)        |
| C(16)-C(15)-C(14)                        | 110.1(4) | O(2)-Cs(1)-O(3)             | 122.23(9)        |
| C(16)-C(15)-Th(1)                        | 73.3(2)  | O(6)-Cs(1)-O(4)             | 97.59(9)         |
| C(14)-C(15)-Th(1)                        | 76.0(2)  | O(5)-Cs(1)-O(4)             | 119.05(9)        |
| C(15)-C(16)-C(12)                        | 109.8(4) | O(1)-Cs(1)-O(4)             | 140.46(9)        |
| C(15)-C(16)-Th(1)                        | 78.2(2)  | O(2)-Cs(1)-O(4)             | 99.77(9)         |
| C(12)-C(16)-Th(1)                        | 73.7(2)  | O(3)-Cs(1)-O(4)             | 59.79(9)         |
| C(27)-C(23)-C(24)                        | 104.7(4) | O(6)-Cs(1)-N(2)             | 60.24(11)        |
| C(27)-C(23)-Si(5)                        | 125.6(3) | O(5)-Cs(1)-N(2)             | 120.16(11)       |
| C(24)-C(23)-Si(5)                        | 126.4(3) | O(1)-Cs(1)-N(2)             | 119.84(10)       |
| C(27)-C(23)-Th(1)                        | 75.9(2)  | O(2)-Cs(1)-N(2)             | 60.42(11)        |
| C(24)-C(23)-Th(1)                        | 72.2(2)  | O(3)-Cs(1)-N(2)             | 119.56(10)       |
| Si(5)-C(23)-Th(1)                        | 132.6(2) | O(4)-Cs(1)-N(2)             | 60.60(10)        |
| C(23)-C(24)-C(25)                        | 111.6(4) | O(6)-Cs(1)-N(1)             | 119.77(10)       |
| C(23)-C(24)-Th(1)                        | 77.8(2)  | O(5)-Cs(1)-N(1)             | 59.81(10)        |
| C(25)-C(24)-Th(1)                        | 76.3(2)  | O(1)-Cs(1)-N(1)             | 60.35(9)         |
| C(26)-C(25)-C(24)                        | 103.6(4) | O(2)-Cs(1)-N(1)             | 119.75(10)       |
| C(26)-C(25)-Si(6)                        | 127.4(3) | O(3)-Cs(1)-N(1)             | 60.28(9)         |
| C(24)-C(25)-Si(6)                        | 126.8(3) | O(4)-Cs(1)-N(1)             | 119.22(9)        |
| C(26)-C(25)-Th(1)                        | 76.1(2)  | N(2)-Cs(1)-N(1)             | 179.80(11)       |
| C(24)-C(25)-Th(1)                        | 73.4(2)  | C(35)-O(1)-C(36)            | 112.5(3)         |
| Si(6)-C(25)-Th(1)                        | 127.8(2) | C(35)-O(1)-Cs(1)            | 110.0(2)         |
| C(27)-C(26)-C(25)                        | 110.3(4) | C(36)-O(1)-Cs(1)            | 111.6(3)         |
| C(27)-C(26)-Th(1)                        | 76.5(2)  | C(37)-O(2)-C(38)            | 111.7(4)         |
| C(25)-C(26)-Th(1)                        | 74.1(2)  | C(37)-O(2)-Cs(1)            | 108.7(3)         |
| C(26)-C(27)-C(23)                        | 109.8(4) | C(38)-O(2)-Cs(1)            | 112.3(3)         |
| C(26)-C(27)-Th(1)                        | 74.8(2)  | C(42)-O(3)-C(41)            | 112.3(4)         |
| C(23)-C(27)-Th(1)                        | 74.9(2)  | C(42)-O(3)-Cs(1)            | 110.8(3)         |
| O(6)-Cs(1)-O(5)                           | 60.88(10) | C(41)-O(3)-Cs(1)            | 112.9(3)         |
| O(6)-Cs(1)-O(1)                           | 117.03(9) | C(44)-O(4)-C(43)            | 112.8(4)         |
| Bond                  | Distance     | Bond                  | Distance     |
|----------------------|--------------|----------------------|--------------|
| C(44)-O(4)-Cs(1)     | 110.5(3)     | N(2)-C(39)-Cs(1)     | 50.1(2)      |
| C(43)-O(4)-Cs(1)     | 111.3(3)     | C(38)-C(39)-Cs(1)    | 75.5(3)      |
| C(47)-O(5)-C(48)     | 113.1(4)     | N(1)-C(40)-C(41)     | 114.8(4)     |
| C(47)-O(5)-Cs(1)     | 113.1(3)     | N(1)-C(40)-Cs(1)     | 50.1(2)      |
| C(48)-O(5)-Cs(1)     | 110.0(3)     | C(41)-C(40)-Cs(1)    | 75.8(3)      |
| C(49)-O(6)-C(50)     | 111.6(4)     | O(3)-C(41)-C(40)     | 109.9(4)     |
| C(49)-O(6)-Cs(1)     | 108.2(3)     | O(3)-C(41)-Cs(1)     | 46.6(2)      |
| C(50)-O(6)-Cs(1)     | 112.0(3)     | C(40)-C(41)-Cs(1)    | 81.1(3)      |
| C(34)-N(1)-C(46)     | 110.3(4)     | O(3)-C(42)-C(43)     | 109.7(4)     |
| C(34)-N(1)-C(40)     | 110.0(4)     | O(3)-C(42)-Cs(1)     | 48.2(2)      |
| C(46)-N(1)-C(40)     | 110.5(4)     | C(43)-C(42)-Cs(1)    | 79.0(2)      |
| C(34)-N(1)-Cs(1)     | 108.5(3)     | O(4)-C(43)-C(42)     | 109.3(4)     |
| C(46)-N(1)-Cs(1)     | 109.1(3)     | O(4)-C(43)-Cs(1)     | 47.7(2)      |
| C(40)-N(1)-Cs(1)     | 108.3(3)     | C(42)-C(43)-Cs(1)    | 77.6(2)      |
| C(39)-N(2)-C(51)     | 111.0(4)     | O(4)-C(44)-C(45)     | 109.7(4)     |
| C(39)-N(2)-C(45)     | 110.6(4)     | O(4)-C(44)-Cs(1)     | 48.4(2)      |
| C(51)-N(2)-C(45)     | 110.6(4)     | C(45)-C(44)-Cs(1)    | 82.2(3)      |
| C(39)-N(2)-Cs(1)     | 108.3(3)     | N(2)-C(45)-C(44)     | 114.9(4)     |
| C(51)-N(2)-Cs(1)     | 108.6(3)     | N(2)-C(45)-Cs(1)     | 50.6(2)      |
| C(45)-N(2)-Cs(1)     | 107.6(3)     | C(44)-C(45)-Cs(1)    | 74.7(3)      |
| N(1)-C(34)-C(35)     | 114.0(4)     | N(1)-C(46)-C(47)     | 114.2(4)     |
| N(1)-C(34)-Cs(1)     | 50.0(2)      | N(1)-C(46)-Cs(1)     | 49.6(2)      |
| C(35)-C(34)-Cs(1)    | 73.3(2)      | C(47)-C(46)-Cs(1)    | 75.1(3)      |
| O(1)-C(35)-C(34)     | 109.5(4)     | O(5)-C(47)-C(46)     | 109.3(4)     |
| O(1)-C(35)-Cs(1)     | 48.72(19)    | O(5)-C(47)-Cs(1)     | 46.4(2)      |
| C(34)-C(35)-Cs(1)    | 83.4(3)      | C(46)-C(47)-Cs(1)    | 81.8(3)      |
| O(1)-C(36)-C(37)     | 109.6(4)     | O(5)-C(48)-C(49)     | 109.1(4)     |
| O(1)-C(36)-Cs(1)     | 47.4(2)      | O(5)-C(48)-Cs(1)     | 48.6(2)      |
| C(37)-C(36)-Cs(1)    | 76.6(3)      | C(49)-C(48)-Cs(1)    | 76.8(3)      |
| O(2)-C(37)-C(36)     | 109.9(4)     | O(6)-C(49)-C(48)     | 110.5(4)     |
| O(2)-C(37)-Cs(1)     | 49.6(2)      | O(6)-C(49)-Cs(1)     | 50.0(2)      |
| C(36)-C(37)-Cs(1)    | 79.9(3)      | C(48)-C(49)-Cs(1)    | 79.7(3)      |
| O(2)-C(38)-C(39)     | 110.0(4)     | O(6)-C(50)-C(51)     | 110.0(4)     |
| O(2)-C(38)-Cs(1)     | 46.9(2)      | O(6)-C(50)-Cs(1)     | 47.2(2)      |
| C(39)-C(38)-Cs(1)    | 81.3(3)      | C(51)-C(50)-Cs(1)    | 82.3(3)      |
| N(2)-C(39)-C(38)     | 113.8(4)     | N(2)-C(51)-C(50)     | 114.8(4)     |
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**Definitions:**

\[ wR^2 = \left( \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right)^{1/2} \]

\[ R1 = \frac{\sum |F_o|-|F_c|}{\sum |F_o|} \]

\[ \text{Goof} = S = \left( \frac{\sum w(F_o^2 - F_c^2)^2}{(n-p)} \right)^{1/2} \]

where \( n \) is the number of reflections and \( p \) is the total number of parameters refined.