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In Search of Tris(Trimethylsilylcyclopentadienyl) Thorium

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Abstract. Reduction of $\text{Cp}'_3\text{ThCl}$, $\text{Cp}'_3\text{ThBr}$, and $\text{Cp}'_3\text{ThI}$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$) with potassium graphite generates dark blue solutions with reactivity and spectroscopic properties consistent with the formation of $\text{Cp}'_3\text{Th}$. The EPR and UV-visible spectra of the solutions are similar to those of crystallographically-characterized tris(cyclopentadienyl) Th(III) complexes: $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{Th}$, $(\text{C}_5\text{Me}_4\text{H})_3\text{Th}$, $(\text{C}_5^t\text{Bu}_2\text{H}_3)_3\text{Th}$, and $(\text{C}_5\text{Me}_5)_3\text{Th}$. Density functional theory (DFT) analysis indicates that the UV-visible spectrum is consistent with $\text{Cp}'_3\text{Th}$ and not $[\text{Cp}'_3\text{ThBr}]^{1-}$. Although single crystals of $\text{Cp}'_3\text{Th}$ have not been isolated, the blue solution reacts with Me_3SiCl , I_2 , and $\text{HC}\equiv\text{CPh}$ to afford products expected from $\text{Cp}'_3\text{Th}$, namely, $\text{Cp}'_3\text{ThCl}$, $\text{Cp}'_3\text{ThI}$, and $\text{Cp}'_3\text{Th}(\text{C}\equiv\text{CPh})$, respectively. Reactions with MeI give mixtures of $\text{Cp}'_3\text{ThI}$ and $\text{Cp}'_3\text{ThMe}$. Evidence for further reduction of the blue solutions to a Cp' -ligated Th(II) complex has not been observed. The crystal structures of $\text{Cp}'_3\text{ThMe}$ and $(\text{Cp}'_3\text{Th})_2(\mu\text{-O})$ were also determined as part of these studies.

Introduction

Complexes of Th(III) ions are difficult to synthesize due to the extremely negative reduction potential of Th(IV)/Th(III), which was originally estimated to be between -3.0 and -3.82 V vs NHE.¹⁻³ A recent electrochemical study by Inman and Cloke determined four

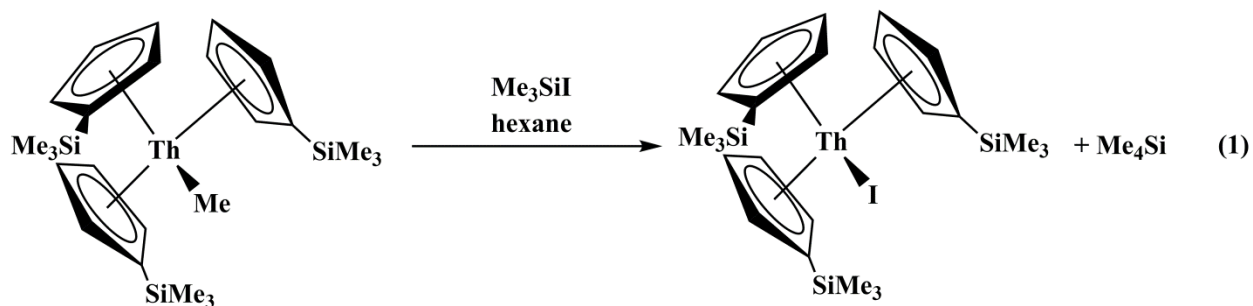
Th(IV)/Th(III) redox couples to range between -2.96 to -3.32 V vs Fc⁺/Fc [Fc = (C₅H₅)₂Fe].⁴ Although careful choice of ligand environment and synthetic procedures can allow isolation of Th(III) complexes, to our knowledge, there are currently only twelve crystallographically-characterized Th(III) complexes.⁵⁻¹⁴ There are also synthetic reports of (C₅H₅)₃Th, (C₅MeH₄)₃Th, and (indenyl)₃Th from β -hydride elimination¹⁵ and [(Cp*₂ThH₂)₂]⁻ from reduction of (Cp*₂ThH₂)₂ [Cp* = C₅Me₅],¹⁰ but these compounds have not been characterized by X-ray diffraction. A review of these complexes and the difficulties associated with their syntheses has been published recently.¹⁶

Th(III) complexes are of interest not only as strong reductants, but also as precursors to Th(II) compounds. The first molecular example of Th(II) was isolated as [K(chelate)][Cp''₃Th] via reduction of Cp''₃Th [Cp'' = C₅H₃(SiMe₃)₂, chelate = 2.2.2-cryptand or (18-crown-6)(THF)₂]¹⁷ despite an estimated Th(III)/Th(II) reduction potential as negative as -4.9 V vs SHE.¹ Previously, the first example of U(II) was isolated with Cp' [Cp' = C₅H₄(SiMe₃)] ligands via reduction of Cp'₃U,¹⁸ but this route could not be applied to thorium since Cp'₃Th is not known. In efforts to find additional coordination environments suitable for the synthesis of other Th(II) complexes, we have pursued isolation of Cp'₃Th. Spectroscopic and reactivity evidence for Cp'₃Th is presented. To support these studies, the syntheses of Cp'₃ThI and Cp'₃Th(C≡CPh) were developed and X-ray crystal structures of Cp'₃ThMe^{19,20} and (Cp'₃Th)₂(μ -O) were obtained.

Results

A variety of Cp'₃ThX precursors (X = Cl, Br, I) were synthesized to examine their reduction chemistry. Cp'₃ThCl and Cp'₃ThBr were prepared according to the literature from ThCl₄(DME)₂ or ThBr₄(THF)₄ and KCp', respectively.²¹ Cp'₃ThI was synthesized for the first time by reaction of Me₃SiI with Cp'₃ThMe^{19,20} in a metathesis reaction which generated Me₄Si as

a product, eqn (1). The $\text{Cp}'_3\text{ThMe}$ precursor in eqn (1) was prepared from $\text{Cp}'_3\text{ThBr}$ and MeLi and was crystallographically characterized (*vide infra*, Fig. 5).



Reaction of $\text{Cp}'_3\text{ThBr}$ with KC_8 in THF at -35°C generates a dark blue solution, **A**, and a black precipitate, presumably graphite, eqn (2). The solution displays an axial EPR signal at 77 K with $g_{\parallel} = 1.98$ and $g_{\perp} = 1.89$, and an isotropic signal at room temperature with $g_{\text{iso}} = 1.90$, Fig. 1. The g values are consistent with all other crystallographically-characterized tris(cyclopentadienyl) Th(III) compounds as shown in Table 1.

The UV-visible absorption spectrum of **A** in THF is very similar to previously characterized $\text{Cp}'_3\text{Th}^7$ and has three main features between 490 and 650 nm, Fig. 2. The measured $100\text{--}200 \text{ M}^{-1}\text{cm}^{-1}$ extinction coefficients are significantly lower than all other crystallographically-characterized tris(cyclopentadienyl) Th(III) species, which have extinction coefficients in the thousands.^{7,9,12} The measured values assume complete conversion of $\text{Cp}'_3\text{ThBr}$ to $\text{Cp}'_3\text{Th}$ with no decomposition and hence the minimum values. Since further studies (*vide infra*, ESI, Fig. S10) show that $\text{Cp}'_3\text{Th}$ decomposes rapidly, the measured extinction coefficients are not likely to be accurate.

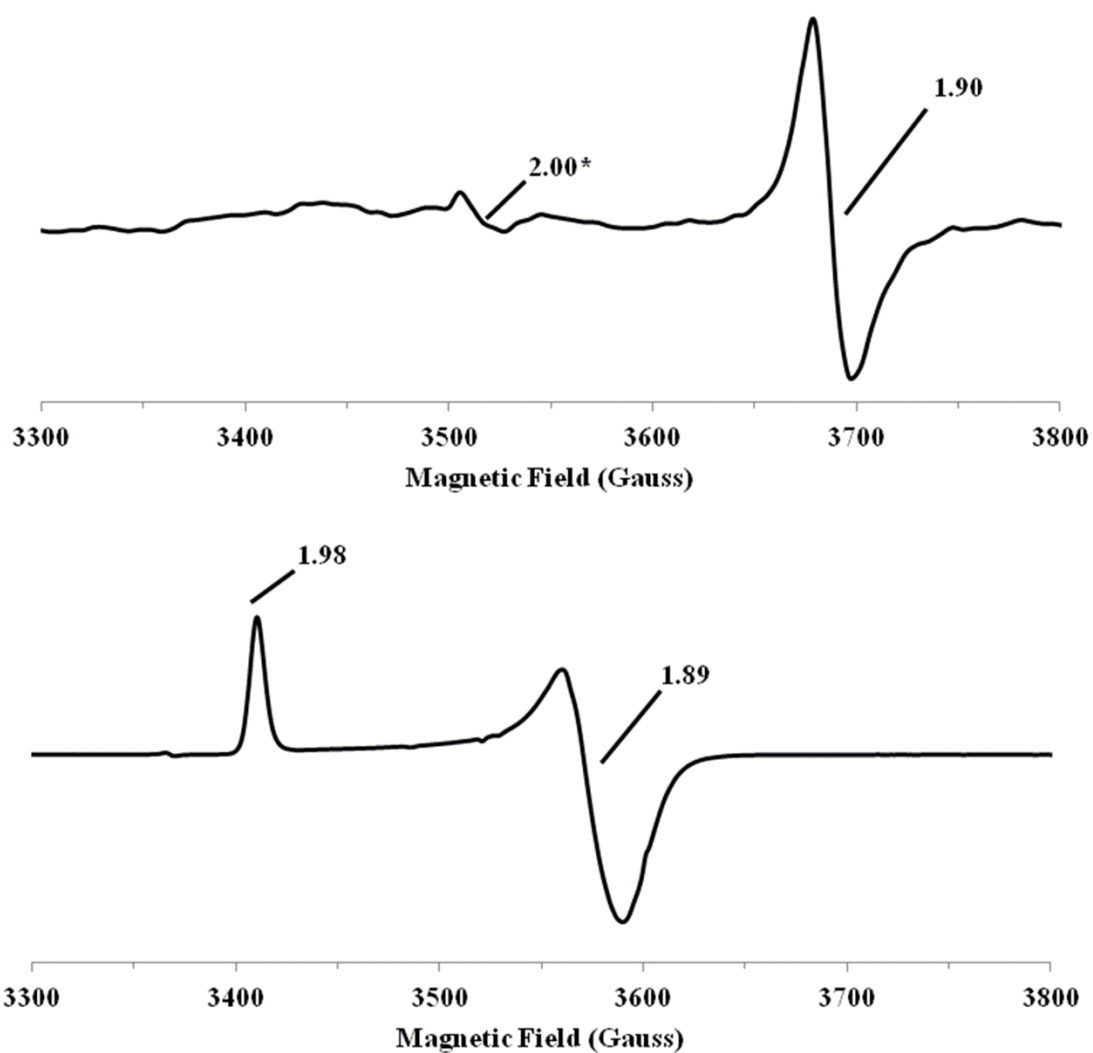


Fig. 1. X-band EPR of **A** in THF at room temperature (top; mode: perpendicular, $\nu = 9.816566$ GHz, $P = 2.021$, modulation amplitude = 2 mT) and at 77 K (bottom; mode: perpendicular, $\nu = 9.45551$ GHz, $P = 2.138$; modulation amplitude = 2 mT). *The feature at $g = 2.00$ is attributed to electride.²²

Table 1. Room temperature and 77 K EPR g values of $(C_5R_5)_3Th$ compounds.

	Room temperature g_{iso}	77 K g_{\parallel}, g_{\perp}
$[C_5H_3(SiMe_2^tBu)_2]_3Th^7$	1.91	1.98, 1.89 ^a
$[C_5H_3(SiMe_3)_2]_3Th^7$	1.91	1.97, 1.88 ^a
$(C_5Me_4H)_3Th^9$	1.92	1.98, 1.86
$(C_5Me_5)_3Th^{12}$	1.88	1.97, 1.85 ^b
$(C_5^tBu_2H_3)_3Th^{11}$	Not reported	1.97, 1.88 ^a
A	1.90	1.98, 1.89

^a Taken at 100 K ^b See Figure S7

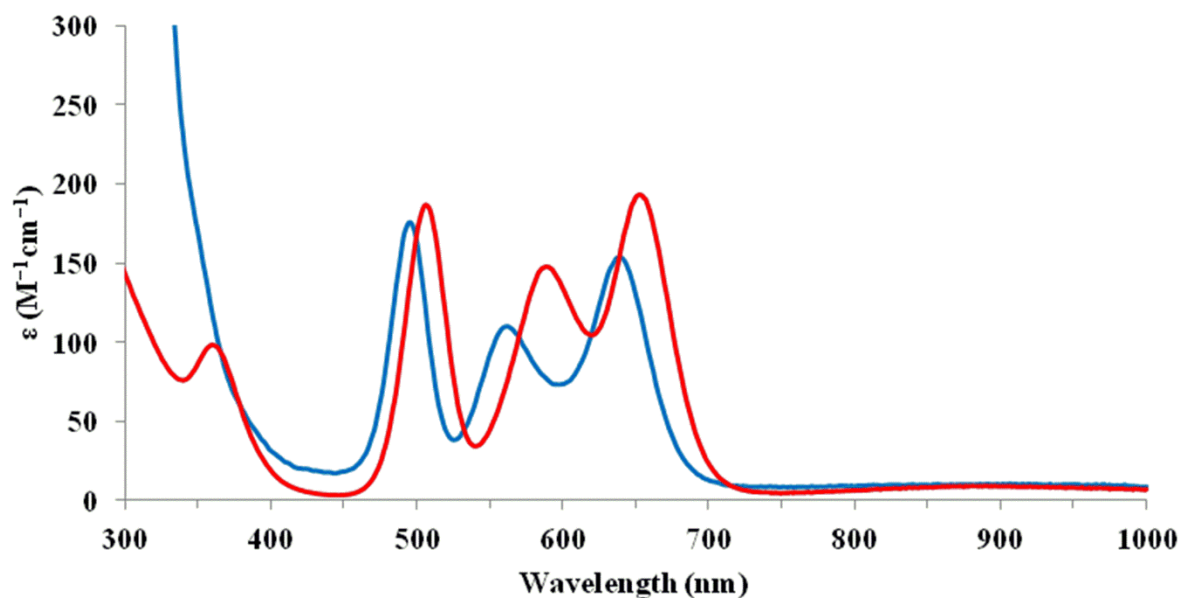
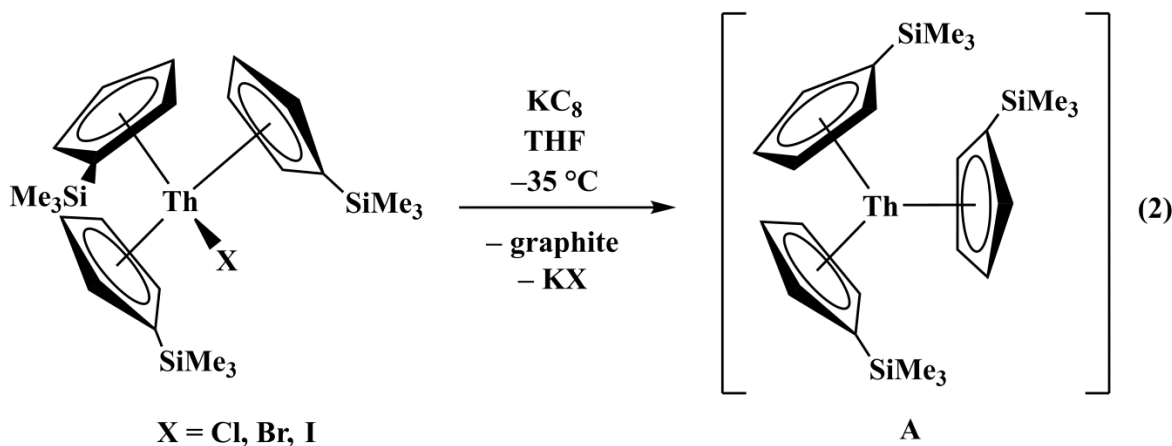


Fig. 2: UV-visible spectrum of **A** (blue) in THF and $Cp^*_3Th,^7$ (red) scaled down by a factor of 30, in THF.

Reduction of $\text{Cp}'_3\text{ThCl}^{17}$ and $\text{Cp}'_3\text{ThI}$ with KC_8 in THF also yields dark blue solutions. The EPR spectra at 77 K, as well as the UV-visible spectrum at room temperature, are indistinguishable from the reduction of $\text{Cp}'_3\text{ThBr}$, which indicates that this reaction scheme is independent of the halide ligand, eqn (2). The reduction of $\text{Cp}'_3\text{ThBr}$ can also be done in Et_2O and toluene with KC_8 . However, crystallization attempts at $-35\text{ }^\circ\text{C}$ immediately following synthesis yield intractable solids and colorless solutions within approximately two hours regardless of the crystallization technique or the toluene, Et_2O , or THF solvent used. When solution **A** in THF was placed under vacuum immediately after synthesis in attempts to isolate solids, the blue color faded to grey within 15 minutes as the mixture was warmed to room temperature from $-35\text{ }^\circ\text{C}$. Decomposition of **A** could be monitored by the decrease in absorbance at 496 nm in THF (ESI Fig. S10), and a half-life of 5.5 min was estimated for **A** in THF at room temperature.



The first electrochemical redox couples of thorium complexes have been published recently by Inman and Cloke.⁴ Common electrolytes, such as $[\text{nBu}_4][\text{PF}_6]$ are decomposed by Th(III) complexes, but Inman and Cloke were able to use $[\text{nBu}_4][\text{BPh}_4]$ as an electrolyte to examine both Th(IV) and Th(III) complexes. Using this electrolyte, we were able to study the

electrochemical behavior of the Cp' system. The cyclic voltammogram of Cp'₃ThCl exhibits a quasi-reversible redox process at -3.17 V vs Fc⁺/Fc, Fig. 3. The process occurs at an identical potential at a scan rate of 200 mV/s, 500 mV/s, and 1 V/s, but reversibility is not improved at higher scan rates. Full details of the data can be found in the ESI. The irreversibility of this redox couple might suggest some chemical process occurring once the reduced species is formed, highlighting the highly reactive nature of Th(III) compounds.

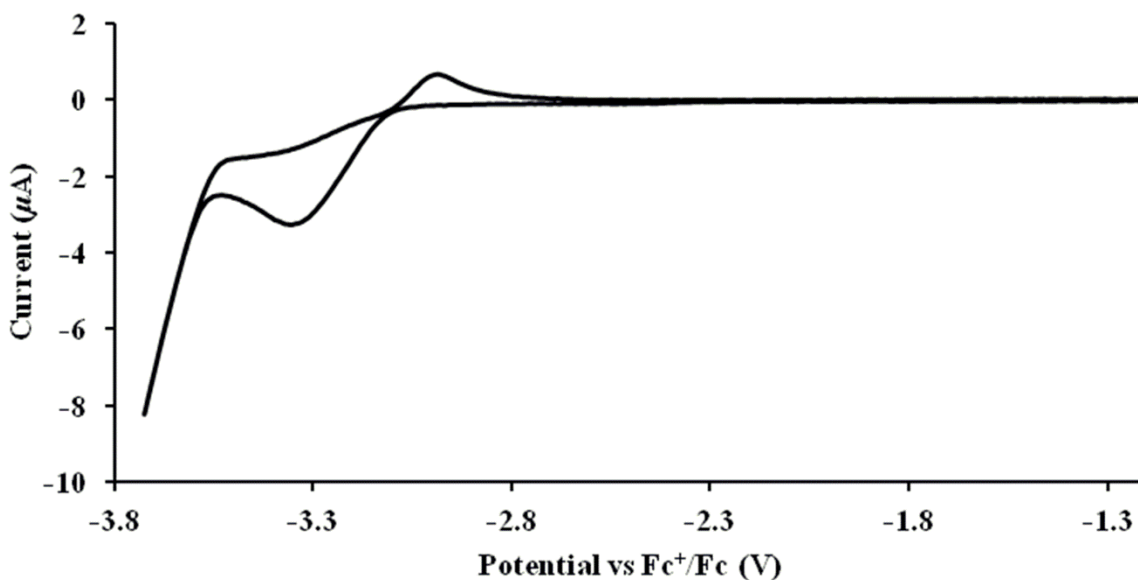


Fig. 3: Cyclic voltammogram of Cp'₃ThCl in 0.50 mM [ⁿBu₄][BPh₄]/THF with a scan rate of 200 mV/s. Details can be found in the ESI.

A common product observed in the reactions with **A** is Cp'₃ThH.²⁰ Stirring **A** in THF for 90 min at room temperature leads to complete decomposition to a grey solution. The ¹H NMR spectrum of this mixture in C₆D₆ displays peaks consistent with Cp'₃ThH as well as at least five other sets of Cp' resonances suggestive of multiple Cp' environments. When the same reaction was done in THF-*d*₈, Cp'₃ThH was still observed in the ¹H NMR spectrum and no Th-D

resonance was observed in the ^2H NMR spectrum. This suggests the hydride does not come from the solvent. $\text{Cp}'_3\text{ThH}$ also appears as a byproduct in reactions with **A** as described below.

Geometry optimization calculations on $\text{Cp}'_3\text{Th}$, $\text{Cp}'_3\text{ThBr}$, and its possible reduction product, $(\text{Cp}'_3\text{ThBr})^{1-}$, were carried out at the density functional level of theory using the TPSSh38 functional.²³ Scalar relativistic effective core potentials (ECPs)³⁹²⁴ with the def-TZVP40²⁵ basis set were used for thorium and polarized split-valence basis sets with diffuse functions def2-SVPD41²⁶ were used for the other atoms. DFT calculations on $\text{Cp}'_3\text{ThBr}$ matched the known structure within 0.009 Å in bond distances and within degrees in angles. The calculations yielded a $\text{Cp}'_3\text{Th}$ minimum structure that has a trigonal planar arrangement of the cyclopentadienyl rings as found in crystallographically characterized $\text{Cp}''_3\text{Th}$.^{5,6} Two SiMe_3 substituents point the direction opposite the third, which is consistent with structure of other $\text{Cp}'_3\text{M}$ complexes ($\text{M} = \text{Y}$,²⁷ La-Nd ,^{28,29} Sm-Lu ,²⁸⁻³⁰ U ,¹⁸ Np ³¹). In order to directly compare the geometry of $\text{Cp}'_3\text{Th}$ with previously analyzed $\text{Cp}''_3\text{Th}$,¹⁰ $\text{Cp}'_3\text{Th}$ was also optimized with the def2-SV(P) basis set.²⁶ The average optimized Th–Cp' ring centroid distance was 0.04 Å shorter than the 2.520 Å distance in $\text{Cp}''_3\text{Th}$, as expected for a smaller ligand. For comparison, the average U-ring centroid distances are 2.508 and 2.542 Å in the structures of $\text{Cp}'_3\text{U}$ ³² and $\text{Cp}''_3\text{U}$,³³ respectively.

The HOMO calculated for $\text{Cp}'_3\text{Th}$ had significant $6d_{z^2}$ character, Fig. 4, which is consistent with the EPR spectra of all other crystallographically-characterized tris(cyclopentadienyl) Th(III) compounds.^{7,9,11,12} Time dependent DFT calculations predicted a UV-visible spectrum for $\text{Cp}'_3\text{Th}$ in good agreement with the experimental spectrum, Fig. 5. In contrast, the predicted spectrum of the possible reduction product, $[\text{Cp}'_3\text{ThBr}]^{1-}$, has only a single excitation between 300–800 nm, and an excitation between 900–1000 nm (ESI Fig. S8),

neither of which are observed in the experimental spectrum. The electronic transitions of $\text{Cp}'_3\text{Th}$ between 400–1000 nm are predominantly d-f in character, in agreement with analyses of previous Th(III) complexes.^{8,11–14,34}

The optimized structure of $(\text{Cp}'_3\text{ThBr})^{1-}$ shows that it is less stable than $\text{Cp}'_3\text{Th}$ by 2.2 kcal/mol. Further thermochemical calculations indicate that $[\text{Cp}'_3\text{ThBr}]^{1-}$ is unstable with respect to $\text{Cp}'_3\text{Th}$ and a bromide ion. Hence, these calculations are consistent with $\text{Cp}'_3\text{Th}$ being the product of the reduction of $\text{Cp}'_3\text{ThBr}$.

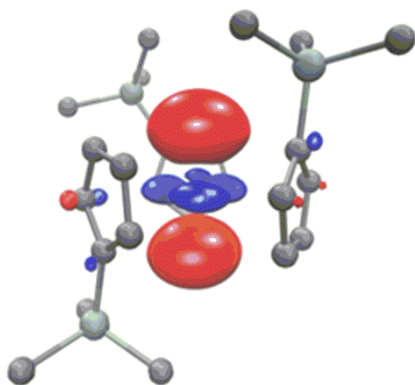


Fig. 4. Calculated dz^2 -like HOMO of $\text{Cp}'_3\text{Th}$ obtained using DFT with the TPPSSh38 functional, plotted with a contour value of 0.06.

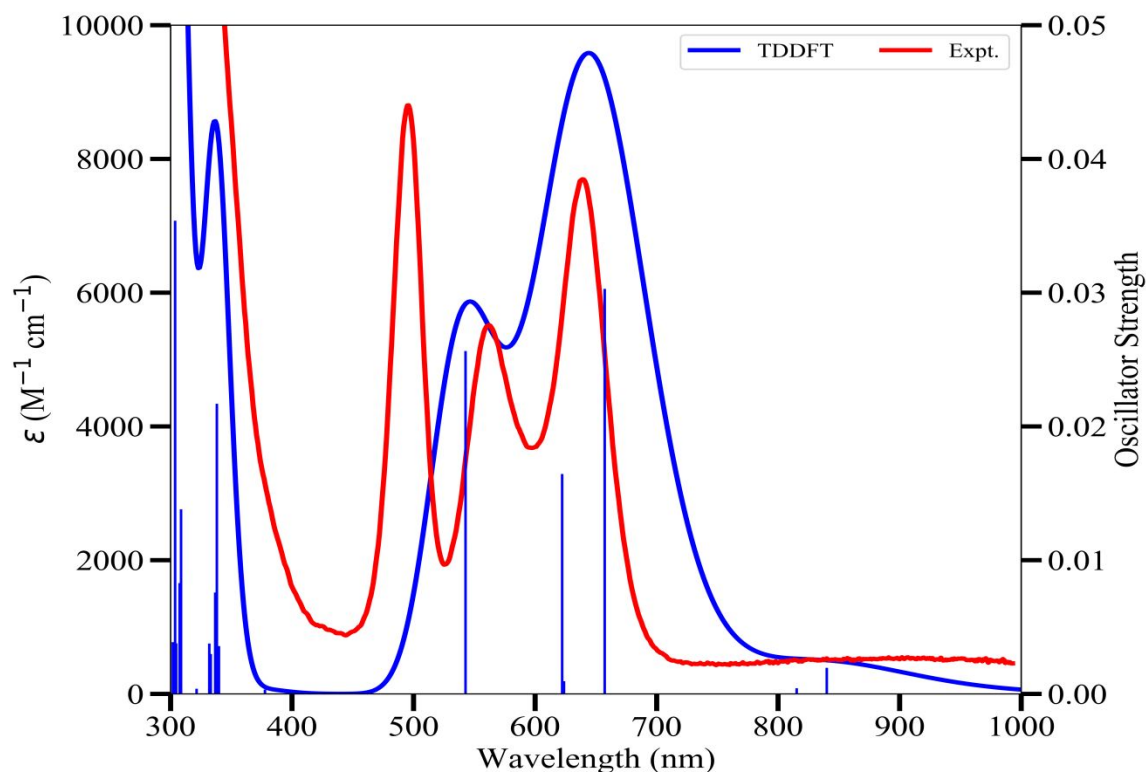


Fig. 5. Experimental UV-visible spectrum of **A** in THF (red) scaled by a factor of 50 compared to the simulated TDDFT spectrum of $\text{Cp}'_3\text{Th}$ (blue). The computed electronic excitation spectrum was empirically blue-shifted by 0.4 eV and broadened using Gaussians with root mean squared width of 0.12 eV, see the ESI for details.

Further reduction of **A** to Th(II) was attempted to determine if a color transformation from blue to green would occur as happens when the blue Th(III) complex $\text{Cp}''_3\text{Th}$ is reduced to the green Th(II) complex, $[\text{Cp}''_3\text{Th}]^{1-}$.^{7,17} However, no green color was observed in reactions of $\text{Cp}'_3\text{ThBr}$ with excess KC_8 or K in THF or toluene, or with **A** and another equivalent of KC_8 in THF.

Addition of Me_3SiCl to the dark blue solution **A** formed by KC_8 reduction of $\text{Cp}'_3\text{ThBr}$ gave $\text{Cp}'_3\text{ThCl}$ as the major product, along with $\text{Cp}'_3\text{ThH}$ in an 8:1 ratio and at least three other sets of unique Cp' resonances.

Reaction of **A** with excess I_2 ¹² gave a color change to orange from which $\text{Cp}'_3\text{ThI}$ and $\text{Cp}'_3\text{ThBr}$ were identified by ^1H NMR spectroscopy in a 10:1 ratio, along with at least two other Cp' environments. No $\text{Cp}'_3\text{ThH}$ was observed in this reaction.

Addition of $\text{HC}\equiv\text{CPh}$ to the dark blue solution **A** gave an immediate color change to orange. $\text{Cp}'_3\text{Th}(\text{C}\equiv\text{CPh})$, $\text{Cp}'_3\text{ThBr}$, and $\text{Cp}'_3\text{ThH}$ were identified in approximately 9:8:1 ratio by ^1H NMR spectroscopy. Small signals consistent with other Cp' environments were also observed. $\text{Cp}'_3\text{Th}(\text{C}\equiv\text{CPh})$ was synthesized independently from $\text{Cp}'_3\text{ThBr}$ and $\text{LiC}\equiv\text{CPh}$ to allow this characterization.

Addition of 1 drop of neat MeI to **A** immediately formed a colorless solution. The ^1H NMR spectrum contained numerous Cp' resonances. $\text{Cp}'_3\text{ThMe}$, $\text{Cp}'_3\text{ThI}$, $\text{Cp}'_3\text{ThH}$, and $\text{Cp}'_3\text{ThBr}$ could be identified in approximately a 4 : 1.5 : 1 : 9 ratio. This differs from the reactivity of $(\text{C}_5\text{Me}_5)_3\text{Th}$ with MeI , which cleanly affords a 2:3 mixture of $(\text{C}_5\text{Me}_5)_3\text{ThMe}$ and $(\text{C}_5\text{Me}_5)_3\text{ThI}$ in an overall yield of 75%.¹² Further experimental details on the reactivity of **A** with substrates and ^1H NMR spectra for the reaction of **A** with MeI can be found in the ESI.

Although $\text{Cp}'_3\text{ThMe}$ was reported in the literature in 1987,¹⁸ it had not been characterized by X-ray crystallography. The structure was determined as part of this study, Fig. 6. $\text{Cp}'_3\text{ThMe}$ crystallizes in the $P\bar{3}$ space group and is only the third example of a tris(cyclopentadienyl)thorium methyl structure after $\text{Cp}''_3\text{ThMe}$ ³⁵ and $(\text{C}_5\text{Me}_5)_3\text{ThMe}$.¹² $\text{Cp}'_3\text{ThMe}$ is isomorphous with $\text{Cp}'_3\text{ThBr}$ ²¹ just as $\text{Cp}''_3\text{ThMe}$ is isomorphous with $\text{Cp}''_3\text{ThCl}$.³⁶ Interestingly, $\text{Cp}'_3\text{ThCl}$ does not readily crystallize in our hands. In the course of these studies,

$\text{Cp}'_3\text{ThBr}$ was crystallized in the space group $P2_1/c$, a different unit cell from the $P\bar{3}$ space group of the literature.²¹

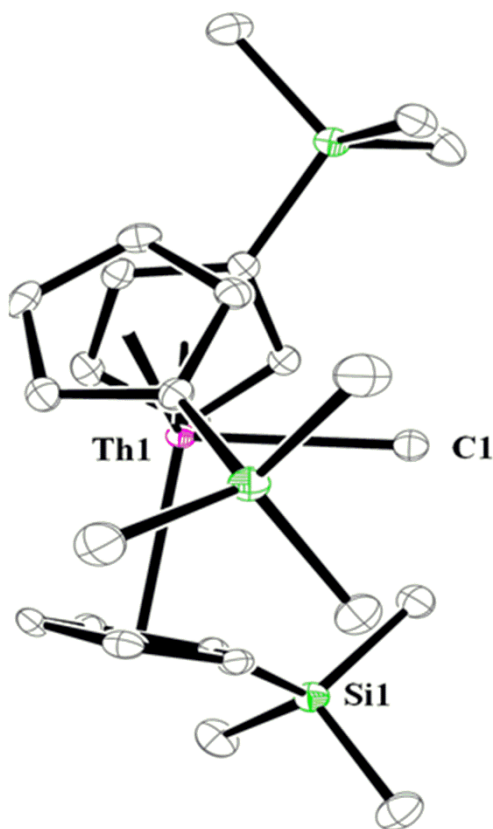


Fig. 6. Thermal ellipsoid plot of $\text{Cp}'_3\text{ThMe}$. Ellipsoids are drawn at 50% probability level and hydrogen atoms have been omitted for clarity.

An interesting structural feature of $\text{Cp}'_3\text{ThMe}$ and $\text{Cp}'_3\text{ThBr}$ in both space groups is that the three trimethylsilyl groups in each complex point in the same direction and form a pocket around the fourth ligand, Br or Me, Fig. 6 and Fig. S1. The 2.559 Å Th–centroid distance in $\text{Cp}'_3\text{ThMe}$ is surprisingly similar to the 2.569 Å Th–centroid distance in $\text{Cp}''_3\text{ThMe}$. Even more unusual is that the 2.518(3) Å Th–C(Me) distance of $\text{Cp}'_3\text{ThMe}$ is longer than the 2.477(5) Å Th–C(Me) distance in $\text{Cp}''_3\text{ThMe}$, a complex with larger ligands.

An oxide decomposition product was isolated from the reaction of **A** with C_8H_8 . This reaction gave an immediate color change from blue to orange to yellow, but only colorless crystals of $(Cp'_3Th)_2(\mu-O)$ could be isolated from this reaction, Fig. 7. The origin of the oxygen is unknown. Attempts to synthesize $(Cp'_3Th)_2(\mu-O)$ directly from Cp'_3ThMe and H_2O , or from **A** and H_2O ,^{7,37} TEMPO [TEMPO = 2,2,6,6-tetramethylpiperidin-1-yl]oxyl], pyridine-*N*-oxide,^{38,39} and epoxybutane^{38,39} were unsuccessful. In the reactions with H_2O or TEMPO, the 1H NMR spectrum showed peaks consistent with a single Cp' environment, but these products were not consistent across each reaction. The reactions with pyridine *N*-oxide and epoxybutane produced a complex mixture of products and were not pursued further.

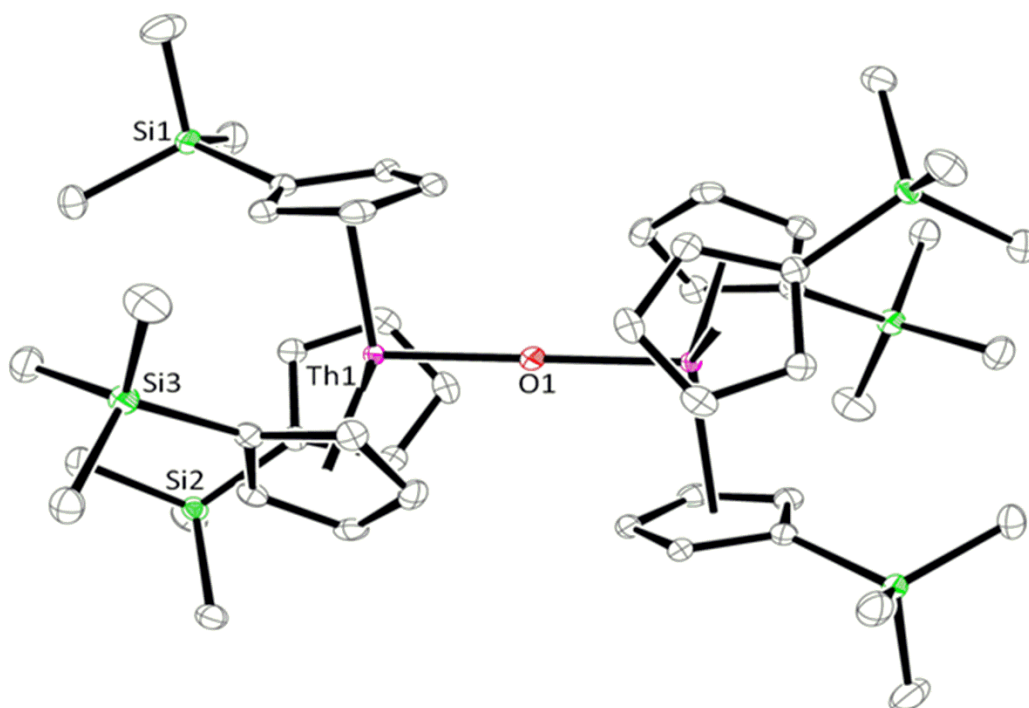


Fig. 7. Thermal ellipsoid plot of $(Cp'_3Th)_2(\mu-O)$. Ellipsoids are drawn at 50% probability level and hydrogen atoms have been omitted for clarity.

$(Cp'_3Th)_2(\mu-O)$ is isomorphous with the uranium analog, $(Cp'_3U)_2(\mu-O)$.⁴⁰ The Th–O–Th angle is rigorously 180° , as the oxygen atom sits at an inversion center of the crystal. The

trimethylsilyl substituents are staggered when observed down the Th–O–Th axis. The Th–O distance in $(\text{Cp}'_3\text{Th})_2(\mu\text{-O})$ is approximately 0.04 Å larger than the U analog, while the Th–centroid distances are all approximately 0.06 Å larger than in $(\text{Cp}'_3\text{U})_2(\mu\text{-O})$. For comparison, the difference in the six-coordinate radii between Th(IV) and U(IV) is 0.08 Å.⁴¹ The centroid–Th–centroid and centroid–Th–O angles are all similar to $(\text{Cp}'_3\text{U})_2(\mu\text{-O})$. Selected bond metrics are given in Table 2, while full details are given in the ESI.

Table 2. Selected bond distances and angles of $(\text{Cp}'_3\text{Th})_2(\mu\text{-O})$ and $(\text{Cp}'_3\text{U})_2(\mu\text{-O})$.³⁶

	$(\text{Cp}'_3\text{Th})_2(\mu\text{-O})$	$(\text{Cp}'_3\text{U})_2(\mu\text{-O})$
M–O (Å)	2.1460(1)	2.1053(2)
M–cnt (Å)	2.595 2.587 2.594	2.527 2.534 2.536
Cnt–M–cnt (°)	117.6 117.4 117.5	117.2 116.9 117.7
Cnt–M–O (°)	98.6 98.8 100.1	99.4 99.0 100.4

Discussion

Reduction of $\text{Cp}'_3\text{ThX}$ (X = Cl, Br, or I) with KC_8 yields a dark blue solution, **A**, that has the properties expected for $\text{Cp}'_3\text{Th}$. However, the instability of the complex in **A** precludes isolation and full crystallographic characterization. In contrast to other Th(III) complexes which are stable enough to be characterized by single crystal X-ray crystallography or solid-state methods such as elemental analysis, **A** decomposes within two hours at -35 °C with an approximate half-life of 5.5 min at room temperature and was not isolated.

EPR and UV-visible spectroscopy and DFT analysis support the proposed tris-cyclopentadienyl formulation. The EPR spectrum of **A** at 77 K in THF is consistent with a $6d^1$ ground state with $g_{\parallel} = 1.98$ and $g_{\perp} = 1.89$. The absorption spectrum of **A** in THF displays three strong features between 490 and 650 nm. TDDFT analysis on $\text{Cp}'_3\text{Th}$ indicates that these transitions are mainly d-f transitions, consistent with theoretical analyses of other Th(III) complexes.^{8,11-14,17,34}

Investigation of the reaction chemistry showed that **A** was not a viable precursor to $(\text{Cp}'_3\text{Th})^{1-}$. However, solutions of **A** are extremely reactive. The dark blue solution quickly loses color upon addition of substrate and the reactions produce multiple thorium-containing products. These products were difficult to separate due to the high solubility imparted by the Cp' ligand. However, NMR evidence was observed for the products expected from reactions of $\text{Cp}'_3\text{Th}$ with Me_3SiCl , I_2 , $\text{HC}\equiv\text{CPh}$, and MeI .

The instability of $\text{Cp}'_3\text{Th}$ can most likely be explained by the fact that the Cp' ligands cannot stabilize the highly reactive Th(III) center due to their small size. The analogous actinide complexes $\text{Cp}'_3\text{U}^{32}$ and $\text{Cp}'_3\text{Np}^{31}$ can be isolated and fully characterized. This is presumably because the complexes are more sterically saturated, as U and Np are 0.08 and 0.10 Å smaller than Th, respectively,⁴¹ and also because these An(III) ions are less reducing.

Conclusion

Reduction of $\text{Cp}'_3\text{ThCl}$, $\text{Cp}'_3\text{ThBr}$, and $\text{Cp}'_3\text{ThI}$ with KC_8 affords a dark blue solution with properties consistent with the presence of $\text{Cp}'_3\text{Th}$ as indicated by EPR and UV-visible spectroscopy, DFT calculations, and reactivity studies. Isolation of this complex has not been achieved, in contrast to $\text{Cp}''_3\text{Th}$.^{5,6} Evidently, the smaller Cp' ligand does not stabilize the Th(III) center well enough to allow isolation.

Experimental section

Caution! Th-232 is an alpha emitter with a specific activity of 1.1×10^{-7} Ci/g and half-life of 1.405×10^9 years. Samples should be prepared and handled only in laboratories appropriately equipped to handle radioactive materials.

Unless specifically stated, all syntheses and manipulations described below were conducted under Ar with rigorous exclusion of air and water using standard glovebox 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 before use. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a CRYO500 MHz spectrometer ($^{13}\text{C}\{^1\text{H}\}$ operating at 125 MHz) at 298 K and referenced to residual protio-solvent resonances. UV-visible spectra were collected at 298 K using a Varian Cary 50 Scan UV-visible spectrophotometer in a 1 mm quartz cuvette. X-band EPR spectra were recorded on a Bruker EMX spectrometer equipped with an ER041Xg microwave bridge and calibrated with DPPH ($g = 2.0036$). Infrared spectra were recorded as compressed solids on an Agilent Cary 630 ATR-FTIR. Elemental analyses were conducted on a PerkinElmer 2400 Series II CHNS elemental analyzer. Electrochemical measurements were recorded with a Princeton Applied Research PARSTAT 2273 Advanced Electrochemical System. MeLi (Sigma) was purchased as a 1.6 M solution in diethyl ether, and solvent was removed to yield MeLi as a bright white solid. Me₃SiCl (Alfa Aesar) was used as received. I₂ was sublimed prior to use. MeI was dried over molecular sieves and vacuum transferred before use. Me₃SiI (Sigma) was dried over molecular sieves, distilled twice under vacuum, and kept under dinitrogen until use. KC₈⁴² and Cp'₃ThCl²¹ were synthesized following literature

procedures. Electrochemical-grade [ⁿBu₄][BPh₄] was purchased from Sigma and used as received.

Synthesis of Cp'₃ThBr. This complex was prepared according to literature procedures.²¹ ¹H NMR (toluene-*d*₈): δ 6.47 (m, 6H, C₅H₄SiMe₃), 6.36 (m, 6H, C₅H₄SiMe₃), 0.37 ppm (s, 27H, SiMe₃). ¹³C NMR (C₆D₆): δ 128.67 (C₅H₄SiMe₃), 128.35 (C₅H₄SiMe₃), 121.72 (C₅H₄SiMe₃), 0.80 ppm (SiMe₃). Colorless X-ray quality crystals grown from a concentrated toluene solution at -35 °C crystallized in the space group P2₁/c, different from the P $\bar{3}$ space group in the literature.²¹

Synthesis of Cp'₃ThMe.^{19,20} A full experimental section is included here since it was not previously reported in the literature. MeLi (15 mg, 0.68 mmol) was tapped into a solution of Cp'₃ThBr (203 mg, 0.280 mmol) in Et₂O (5 mL). The colorless solution was stirred overnight at which point it had turned brown. Brown solids were removed via filtration and the solution was dried under vacuum. The mixture was extracted into hexane and dried under vacuum to yield white solids of Cp'₃ThMe (130 mg, 70%). This reaction can also be run in toluene with similar yields, but requires 72 h to reach completion. Colorless X-ray-quality crystals were grown from a concentrated hexane solution at -35 °C. ¹H NMR (C₆D₆): δ 6.25 (m, 12H, C₅H₄SiMe₃), 0.77 (s, 3H, Th-Me), 0.34 ppm (s, 27H, SiMe₃). ¹³C NMR (C₆D₆): δ 124.9 (C₅H₄SiMe₃), 124.2 (C₅H₄SiMe₃), 118.9 (C₅H₄SiMe₃), 37.0 (Th-Me), 0.40 ppm (SiMe₃). IR: 2949m, 1443m, 1402m, 1310w, 1246s, 1174s, 1086w, 1041s, 901s, 826s, 776s, 744s, 685m cm⁻¹. Anal. Calcd for C₂₅H₄₂Si₃Th: C, 45.57; H, 6.43. Found: C, 42.24; H, 5.94. Low combustion analysis was persistent across multiple samples and suggests incomplete combustion, which has been well-documented with some organoactinide complexes.^{7,10,17,35,43-45} The C to H ratio in the analytical data gives a formula of C₂₅H_{41.89} which is close to the calculated value of C₂₅H₄₂.

Synthesis of Cp₃ThCl from Cp₃ThMe and Me₃SiCl. Cp₃ThMe (38 mg, 0.058 mmol) was dissolved in hexane (3 mL) to yield a colorless solution. Neat Me₃SiCl (3 drops, excess) was added and the colorless solution was stirred for 72 h. Volatiles were removed under vacuum to yield Cp₃ThCl (35 mg, 89%), which was identified by ¹H NMR spectroscopy.²¹

Synthesis of Cp₃ThI from Cp₃ThMe and Me₃SiI. Inside the glovebox, Cp₃ThMe (59 mg, 0.090 mmol) was dissolved in hexane (10 mL) and filtered into a side-arm Schlenk flask to give a pale yellow solution. The flask was brought out of the glovebox and attached to a Schlenk line. Under a flow of nitrogen, doubly-distilled Me₃SiI (15 μL, 0.11 mmol) was added to the stirring solution via microsyringe and the solution immediately became colorless. The solution was stirred for 40 h, at which point a tan precipitate had formed. Volatiles were removed under vacuum and the flask was brought into the glovebox. The solids were extracted with hexane and brown solids were removed via filtration. Removal of solvent yielded Cp₃ThI as a colorless solid (31 mg, 45%). ¹H NMR (C₆D₆): 6.63 (m, 6H, C₅H₄SiMe₃), 6.37 (m, 6H, C₅H₄SiMe₃), 0.38 ppm (s, 27H, SiMe₃). ¹H NMR (THF-*d*₈): 6.79 (m, 6H, C₅H₄SiMe₃), 6.58 (m, 6H, C₅H₄SiMe₃), 0.37 ppm (s, 27H, SiMe₃). ¹³C NMR (THF-*d*₈): 130.50 (C₅H₄SiMe₃), 128.41 (C₅H₄SiMe₃), 122.34 (C₅H₄SiMe₃), 1.23 ppm (SiMe₃). IR: 3063w, 2949m, 2922m, 2893m, 2850m, 1442w, 1404w, 1366, 1310w, 1244s, 1172s, 1117w, 1039s, 900s, 828s, 783s, 748s, 689m cm⁻¹. Anal. Calcd for C₂₄H₃₉Si₃ThI: C, 37.40; H, 5.10. Found: C, 37.82; H, 5.36.

Synthesis of Cp₃Th(C≡CPh). LiC≡CPh (22 mg, 0.20 mmol) was tapped into a solution of Cp₃ThBr (126 mg, 0.174 mmol) in Et₂O (5 ml). The colorless solution was stirred overnight. The solution was dried under vacuum, the mixture was extracted into hexane, and insoluble material was removed via filtration before drying under vacuum to yield Cp₃Th(C≡CPh) as a colorless oil, which solidifies at -35 °C (101 mg, 78%). ¹H NMR (C₆D₆): δ 7.69 (d, 2H, *o*-Ph),

7.17 (t, 2H, *m-Ph*), 7.03 (t, 1H, *p-Ph*), 6.46 (m, 6H, C₅H₄SiMe₃), 6.34 (m, 6H, C₅H₄SiMe₃), 0.44 ppm (s, 27H, SiMe₃). ¹³C NMR (C₆D₆): δ 157.01 (Th–C≡CPh), 131.77 (C₅H₄SiMe₃), 128.60, 127.64, 127.06, 126.25, 125.17 (C₅H₄SiMe₃), 122.24, 120.00 (C₅H₄SiMe₃), 0.83 ppm (SiMe₃). IR: 3076w, 2949m, 2891m, 2062m (C≡C), 1591m, 1482s, 1441m, 1404m, 1364s, 1310w, 1241s, 1195m, 1173s, 1042s, 902s, 826s, 778s, 749s, 689s cm⁻¹. Anal. Calcd for C₃₂H₄₄Si₃Th: C, 51.59; H, 5.95. Found: C, 51.99; H, 6.35.

***In situ* Synthesis of Cp'₃Th.** Cp'₃ThBr (50 mg, 0.069 mmol) was dissolved in THF (1 mL) and chilled to –35 °C. KC₈ (12 mg, 0.089 mmol) was chilled in a separate vial to –35 °C. KC₈ was tapped into the stirring solution of Cp'₃ThBr. This immediately generated a dark blue solution, **A**. KC₈ was removed either by filtration or centrifugation after stirring for no longer than 15 min, at which time the solution begins to visibly fade in intensity. Spectroscopic data were collected immediately from these solutions, but rapid decomposition occurs and hence the extinction coefficients are probably not accurate. UV-visible (THF) λ_{max} nm (approx ε, M⁻¹cm⁻¹): 639 (150), 562 (110), 496 (180). EPR (THF, room temperature): g_{iso} = 1.90, (THF, 77 K): g_{||} = 1.98, g_⊥ = 1.89.

(Cp'₃Th)₂(μ–O). Cp'₃ThBr (28 mg, 0.039 mmol) was dissolved in THF (1 mL) and chilled to –35 °C. In a separate vial, cyclooctatetrene (8.7 mg, 0.064 mmol) was dissolved in THF (1 mL) and chilled to –35 °C. A pipette was packed with KC₈ (9 mg, 0.064 mmol) and chilled to –35 °C. The colorless solution of Cp'₃ThBr was passed through the KC₈ pipette to form **A**, and was directly eluted into the yellow stirring solution of C₈H₈. The mixture turned orange briefly before fading to yellow while it stirred. After stirring for 5 min, the solution was dried under vacuum to yield yellow and orange solids. The mixture was washed with hexane then extracted into THF. Several colorless X-ray-quality crystals were grown from a

concentrated THF solution of the mixture at $-35\text{ }^{\circ}\text{C}$, which allowed $(\text{Cp}'_3\text{Th})_2(\mu\text{-O})$ to be identified by X-ray crystallography.

X-ray crystallographic data. Crystallographic information for $\text{Cp}'_3\text{ThBr}$, $\text{Cp}'_3\text{ThMe}$, and $(\text{Cp}'_3\text{Th})_2(\mu\text{-O})$ is summarized in the ESI.

Conflicts of interest: There are no conflicts to declare.

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In Search of Tris(Trimethylsilylcyclopentadienyl) Thorium

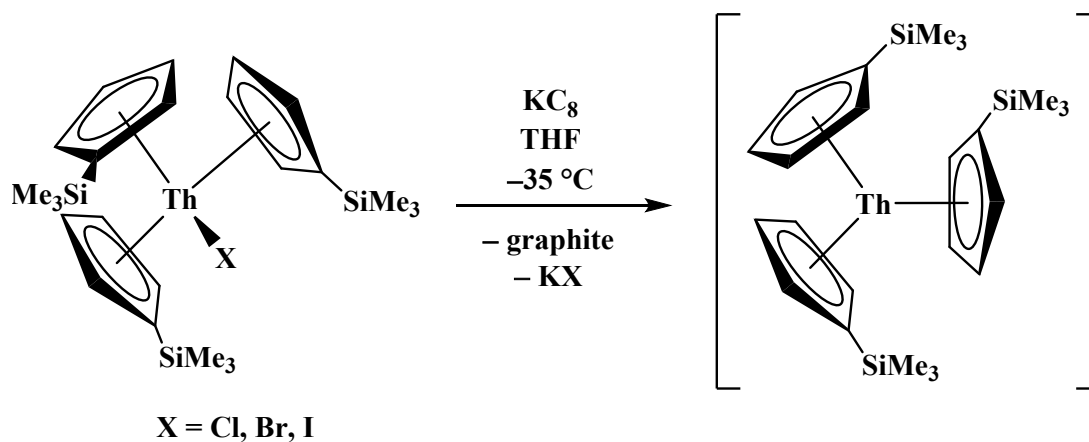
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TOC abstract:



Solution synthesis, characterization, and reactivity of a new Th(III) complex $\text{Cp}'_3\text{Th}$ ($\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$).