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In search of tris(trimethylsilylcyclopentadienyl) thorium†

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Reduction of Cp'_3ThCl, Cp'_3ThBr, and Cp'_3ThI ($Cp' = C_5H_4SiMe_3$) with potassium graphite generates dark blue solutions with reactivity and spectroscopic properties consistent with the formation of Cp'_3Th. The EPR and UV-visible spectra of the solutions are similar to those of crystallographically-characterized tris (cyclopentadienyl) Th(III) complexes: $[C_5H_3(SiMe_3)_2]_3Th$, $(C_5Me_4H)_3Th$, $(C_5{}^tBu_2H_3)_3Th$, and $(C_5Me_5)_3Th$. Density functional theory (DFT) analysis indicates that the UV-visible spectrum is consistent with Cp'_3Th and not $[Cp'_3ThBr]^{1-}$. Although single crystals of Cp'_3Th have not been isolated, the blue solution reacts with Me_3SiCl, I_2, and HC≡CPh to afford products expected from Cp'_3Th, namely, Cp'_3ThCl, Cp'_3ThI, and $Cp'_3Th(C{\equiv}CPh)$, respectively. Reactions with MeI give mixtures of Cp'_3ThI and Cp'_3ThMe. Evidence for further reduction of the blue solutions to a Cp′-ligated Th(II) complex has not been observed. The crystal structures of Cp'_3ThMe and $(Cp'_3Th)_2(\mu\text{-}O)$ were also determined as part of these studies.

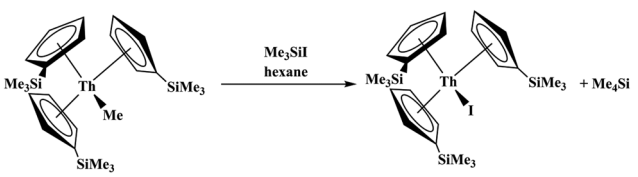
Introduction

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 = $(C_5H_5)_2Fe$].[4] Although careful choice of ligand environment and synthetic procedures can allow isolation of Th(III) complexes, to our knowledge, there are currently only eleven crystallographically-characterized Th(III) complexes.[5–14] There are also synthetic reports of $(C_5H_5)_3Th$, $(C_5H_4Me)_3Th$, and $(indenyl)_3Th$ from β-hydride elimination[15] and $[(Cp^*{}_2ThH_2)_2]^{1-}$ from reduction of $(Cp^*{}_2ThH_2)_2$ [Cp^* = C_5Me_5],[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'' = $C_5H_3(SiMe_3)_2$, chelate = 2.2.2-cryptand or $(18\text{-crown-6})(THF)_2$][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′ = $C_5H_4(SiMe_3)$] 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 $Cp'_3Th(C{\equiv}CPh)$ were developed and X-ray crystal structures of Cp'_3ThMe[19,20] and $(Cp'_3Th)_2(\mu\text{-}O)$ 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 $ThCl_4(DME)_2$ or $ThBr_4(THF)_4$ and KCp′, respectively.[21] Cp'_3ThI was synthesized for the first time by reaction of Me_3SiI with Cp'_3ThMe[19,20] in a metathesis reaction which generated Me_4Si as a product, eqn (1). The Cp'_3ThMe precursor in eqn (1) was prepared from Cp'_3ThBr and MeLi and was crystallographically characterized (*vide infra*, Fig. 5).



(1)

Reaction of Cp'_3ThBr with KC_8 in THF at −35 °C generates a dark blue solution, **A**, and a black precipitate, presumably

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graphite, eqn (2). The solution displays an axial EPR signal at 77 K with $g_{\|}$ = 1.98 and $g_{\perp}$ = 1.89, and an isotropic signal at room temperature with g_{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 Cp''_3Th[7] and has three main features between 490 and 650 nm, Fig. 2. The measured 100–200 M^{-1} 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 Cp'_3ThBr to Cp'_3Th with no decomposition and hence are minimum values. Since further studies (*vide infra*, ESI, Fig. S10†) show that Cp'_3Th decomposes rapidly, the measured extinction coefficients are not likely to be accurate.

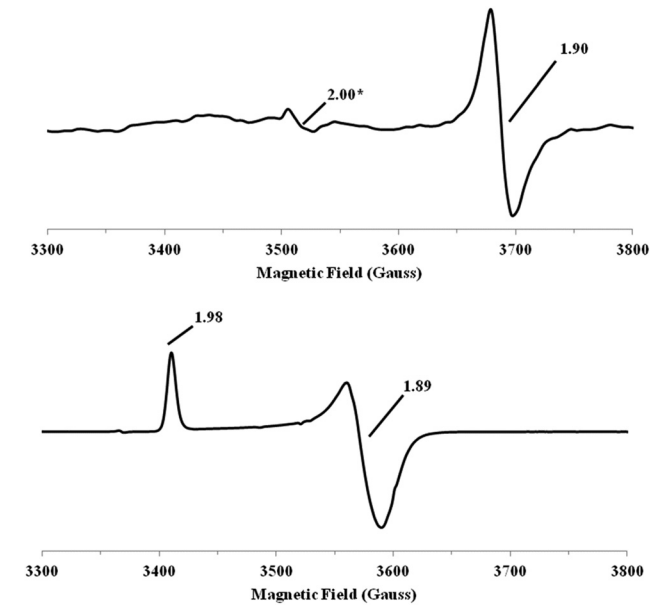


Fig. 1 X-band EPR of **A** in THF at room temperature (top; mode: perpendicular, ν = 9.816566 GHz, P = 2.021, modulation amplitude = 2 mT) and at 77 K (bottom; mode: perpendicular, ν = 9.45551 GHz, P = 2.138; modulation amplitude = 2 mT). *the feature at g = 2.00 is attributed to electride.[22]

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

	Room temperature g_{iso}	77 K $g_{\|}$, $g_{\perp}$
$[C_5H_3(SiMe_2{}^tBu)_2]_3Th$[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 Fig. S7.†

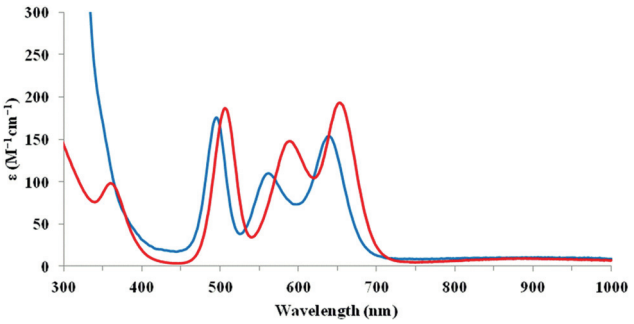
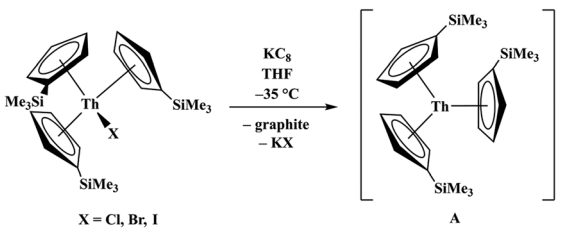


Fig. 2 UV-visible spectrum of **A** (blue) in THF and Cp''_3Th,[7] (red) scaled down by a factor of 30, in THF.

Reduction of Cp'_3ThCl[17] and Cp'_3ThI 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 Cp'_3ThBr, which indicates that this reaction scheme is independent of the halide ligand, eqn (2). The reduction of Cp'_3ThBr can also be done in Et_2O and toluene with KC_8. However, crystallization attempts at −35 °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 °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.



(2)

The first electrochemical redox couples of thorium complexes have been published recently by Inman and Cloke.[4] Common electrolytes, such as $[^nBu_4][PF_6]$, are decomposed by Th(III) complexes, but Inman and Cloke were able to use $[^nBu_4][BPh_4]$ 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^{-1}, 500 mV s^{-1}, and 1 V s^{-1}, 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.

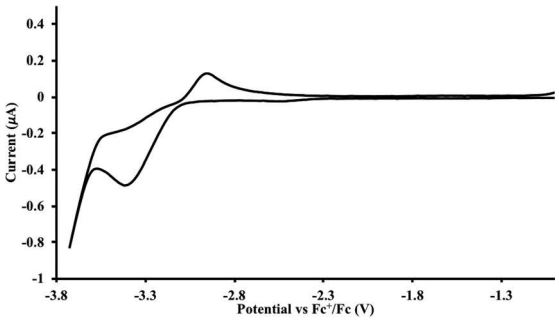


Fig. 3 Cyclic voltammogram of Cp'_3ThCl in 0.50 mM $[^nBu_4][BPh_4]$/THF with a scan rate of 1 V s^{-1}. Details can be found in the ESI.†

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 C_6D_6 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. Cp'_3ThH also appears as a byproduct in reactions with **A** as described below.

Geometry optimization calculations on Cp'_3Th, Cp'_3ThBr, and its possible reduction product, $(Cp'_3ThBr)^{1-}$, were carried out at the density functional level of theory using the TPSSh functional.[23] Scalar relativistic effective core potentials (ECPs)[24] with the def-TZVP[25] basis set were used for thorium and polarized split-valence basis sets with diffuse functions def2-SVPD[26] were used for the other atoms. DFT calculations on Cp'_3ThBr matched the known structure within 0.009 Å in bond distances and within degrees in angles. The calculations yielded a Cp'_3Th minimum structure that has a trigonal planar arrangement of the cyclopentadienyl rings as found in crystallographically characterized Cp''_3Th.[5,6] Two $SiMe_3$ substituents point the direction opposite the third, which is consistent with structure of other Cp'_3M complexes (M = Y,[27] La–Nd,[28,29] Sm–Lu,[28–30] U,[18] Np[31]). In order to directly compare the geometry of Cp'_3Th with previously analyzed Cp''_3Th,[10] Cp'_3Th 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 Cp''_3Th, 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 Cp'_3U[32] and Cp''_3U,[33] respectively.

The HOMO calculated for Cp'_3Th 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 Cp'_3Th in good agreement with the experimental spectrum, Fig. 5. In contrast, the predicted spectrum of the possible reduction product, $[Cp'_3ThBr]^{1-}$, has only a single excitation between 300–800 nm, and an excitation between 900–1000 nm (ESI Fig. S8†), neither

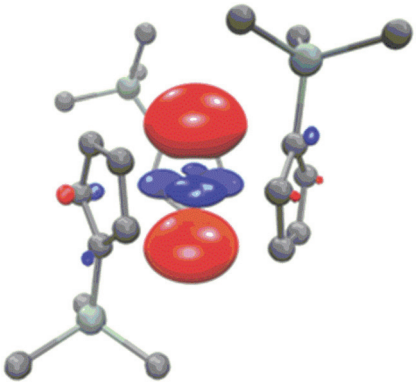


Fig. 4 Calculated d_{z^2}-like HOMO of Cp'_3Th obtained using DFT with the TPPSSh functional, plotted with a contour value of 0.06.

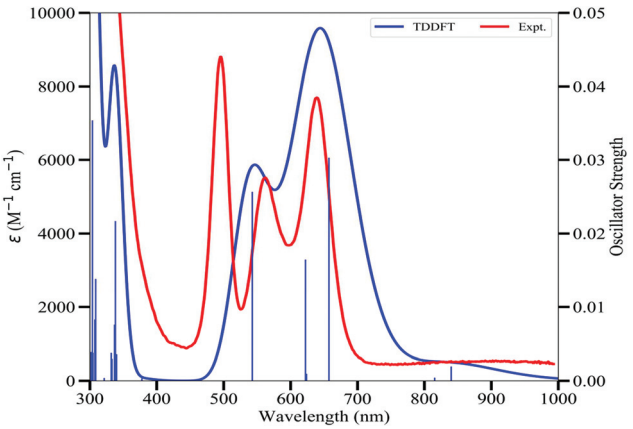


Fig. 5 Experimental UV-visible spectrum of **A** in THF (red) scaled by a factor of 50 compared to the simulated TDDFT spectrum of Cp'_3Th (blue). The computed electronic excitation spectrum was empirically blue-shifted by 0.4 eV and broadened using Gaussians with root mean squared width of 0.12 eV, see the ESI† for details.

of which are observed in the experimental spectrum. The electronic transitions of Cp'_3Th 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 $(Cp'_3ThBr)^{1-}$ is less stable than Cp'_3Th by 2.2 kcal mol^{-1}. Further thermochemical calculations indicate that $[Cp'_3ThBr]^{1-}$ is unstable with respect to Cp'_3Th and a bromide ion. Hence, these calculations are consistent with Cp'_3Th being the product of the reduction of Cp'_3ThBr.

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 Cp''_3Th is reduced to the green Th(II) complex, $[Cp''_3Th]^{1-}$.[7,17] However, no green color was observed in reactions of Cp'_3ThBr 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 Cp'_3ThBr gave Cp'_3ThCl as the major

product, along with Cp'_3ThH 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 Cp'_3ThI and Cp'_3ThBr were identified by ^1H NMR spectroscopy in a 10 : 1 ratio, along with at least two other Cp′ environments. No Cp'_3ThH was observed in this reaction.

Addition of HC≡CPh to the dark blue solution **A** gave an immediate color change to orange. $Cp'_3Th(C{\equiv}CPh)$, Cp'_3ThBr, and Cp'_3ThH were identified in approximately 9 : 8 : 1 ratio by ^1H NMR spectroscopy. Small signals consistent with other Cp′ environments were also observed. $Cp'_3Th(C{\equiv}CPh)$ was synthesized independently from Cp'_3ThBr and LiC≡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. Cp'_3ThMe, Cp'_3ThI, Cp'_3ThH, and Cp'_3ThBr could be identified in approximately a 4 : 1.5 : 1 : 9 ratio. This differs from the reactivity of $(C_5Me_5)_3Th$ with MeI, which cleanly affords a 2 : 3 mixture of $(C_5Me_5)_3ThMe$ and $(C_5Me_5)_3ThI$ 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 Cp'_3ThMe 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. Cp'_3ThMe crystallizes in the $P\bar{3}$ space group and is only the third example of a tris(cyclopentadienyl)thorium methyl structure after Cp''_3ThMe[35] and $(C_5Me_5)_3ThMe$.[12] Cp'_3ThMe is isomorphous with Cp'_3ThBr[21] just as Cp''_3ThMe is isomorphous with Cp''_3ThCl.[36] Interestingly, Cp'_3ThCl does not readily crystallize in our hands. In the course of these studies, Cp'_3ThBr was crystallized in the space group $P2_1/c$, a different unit cell from the $P\bar{3}$ space group of the literature.[21]

An interesting structural feature of Cp'_3ThMe and Cp'_3ThBr 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 Cp'_3ThMe is surprisingly similar to the 2.569 Å Th–centroid distance in Cp''_3ThMe. Even more unusual is that the 2.518(3) Å Th–C(Me) distance of Cp'_3ThMe is longer than the 2.477(5) Å Th–C(Me) distance in Cp''_3ThMe, 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 $(Cp'_3Th)_2(\mu\text{-}O)$ could be isolated from this reaction, Fig. 7. The origin of the oxygen is unknown. Attempts to synthesize $(Cp'_3Th)_2(\mu\text{-}O)$ 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.

$(Cp'_3Th)_2(\mu\text{-}O)$ is isomorphous with the uranium analog, $(Cp'_3U)_2(\mu\text{-}O)$.[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 $(Cp'_3Th)_2(\mu\text{-}O)$ is approximately 0.04 Å larger than the U analog, while the Th–centroid distances are all approximately 0.06 Å larger than in

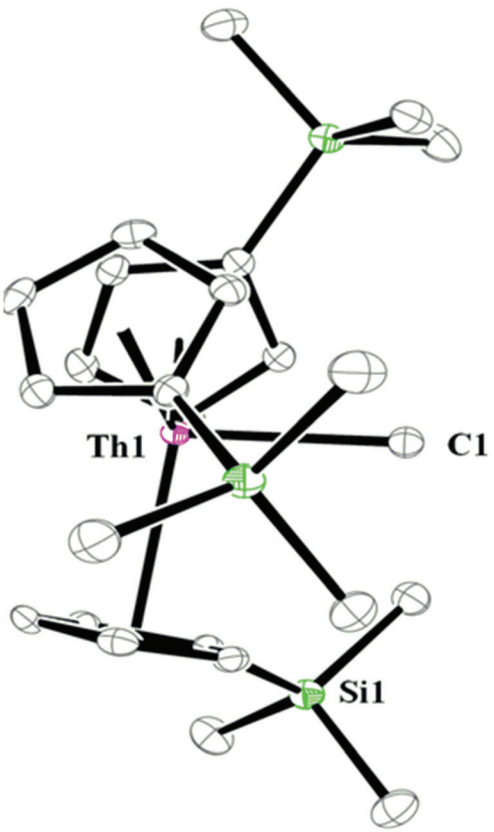


Fig. 6 Thermal ellipsoid plot of Cp'_3ThMe. Ellipsoids are drawn at 50% probability level and hydrogen atoms have been omitted for clarity.

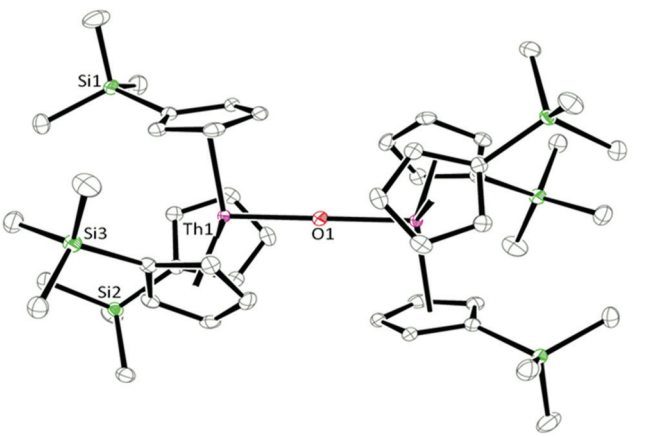


Fig. 7 Thermal ellipsoid plot of $(Cp'_3Th)_2(\mu\text{-}O)$. Ellipsoids are drawn at 50% probability level and hydrogen atoms have been omitted for clarity.

Table 2 Selected bond distances and angles of $(Cp'_3Th)_2(\mu\text{-}O)$ and $(Cp'_3U)_2(\mu\text{-}O)$[36]

	$(Cp'_3Th)_2(\mu\text{-}O)$	$(Cp'_3U)_2(\mu\text{-}O)$
M–O (Å)	2.1460(1)	2.1053(2)
M–cnt (Å)	2.595	2.527
	2.587	2.534
	2.594	2.536
Cnt–M–cnt (°)	117.6	117.2
	117.4	116.9
	117.5	117.7
Cnt–M–O (°)	98.6	99.4
	98.8	99.0
	100.1	100.4

$(Cp'_3U)_2(\mu\text{-}O)$. 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 $(Cp'_3U)_2(\mu\text{-}O)$. Selected bond metrics are given in Table 2, while full details are given in the ESI.†

Discussion

Reduction of Cp'_3ThX (X = Cl, Br, or I) with KC_8 yields a dark blue solution, **A**, that has the properties expected for Cp'_3Th. 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 values $g_\parallel = 1.98$ and $g_\perp = 1.89$. The absorption spectrum of **A** in THF displays three strong features between 490 and 650 nm. TDDFT analysis on Cp'_3Th 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 $(Cp'_3Th)^{1-}$. 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 Cp'_3Th with Me_3SiCl, I_2, HC≡CPh, and MeI.

The instability of Cp'_3Th 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 Cp'_3U[32] and Cp'_3Np[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 Cp'_3ThCl, Cp'_3ThBr, and Cp'_3ThI with KC_8 affords a dark blue solution with properties consistent with the presence of Cp'_3Th as indicated by EPR and UV-visible spectroscopy, DFT calculations, and reactivity studies. Isolation of this complex has not been achieved, in contrast to Cp''_3Th.[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^{-1} 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 $^{13}C\{^1H\}$ NMR spectra were recorded on a CRYO500 MHz spectrometer ($^{13}C\{^1H\}$ 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. Me_3SiCl (Alfa Aesar) was used as received. I_2 was sublimed prior to use. MeI was dried over molecular sieves and vacuum transferred before use. Me_3SiI (Sigma) was dried over molecular sieves, distilled twice under vacuum, and kept under dinitrogen until use. KC_8[42] and Cp'_3ThCl[21] were synthesized following literature procedures. Electrochemical-grade [^{n}Bu$_4$][BPh$_4$] 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, $C_5H_4SiMe_3$),

6.36 (m, 6H, $C_5H_4SiMe_3$), 0.37 ppm (s, 27H, SiMe_3). ^{13}C NMR (C_6D_6): δ 128.67 ($C_5H_4SiMe_3$), 128.35 ($C_5H_4SiMe_3$), 121.72 ($C_5H_4SiMe_3$), 0.80 ppm (SiMe_3). Colorless X-ray quality crystals grown from a concentrated toluene solution at −35 °C crystallized in the space group $P2_1/c$, different from the $P\bar{3}$ space group in the literature.[21]

Synthesis of Cp′$_3$ThMe[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′$_3$ThBr (203 mg, 0.280 mmol) in Et_2O (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′$_3$ThMe (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. ^{1}H NMR (C_6D_6): δ 6.25 (m, 12H, $C_5H_4SiMe_3$), 0.77 (s, 3H, Th–*Me*), 0.34 ppm (s, 27H, SiMe_3). ^{13}C NMR (C_6D_6): δ 124.9 ($C_5H_4SiMe_3$), 124.2 ($C_5H_4SiMe_3$), 118.9 ($C_5H_4SiMe_3$), 37.0 (Th–*Me*), 0.40 ppm (SiMe_3). IR: 2949m, 1443m, 1402m, 1310w, 1246s, 1174s, 1086w, 1041s, 901s, 826s, 776s, 744s, 685m cm^{-1}. Anal. Calcd for $C_{25}H_{42}Si_3Th$: 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 $C_{25}H_{41.89}$ which is close to the calculated value of $C_{25}H_{42}$.

Synthesis of Cp′$_3$ThCl from Cp′$_3$ThMe and Me$_3$SiCl

Cp′$_3$ThMe (38 mg, 0.058 mmol) was dissolved in hexane (3 mL) to yield a colorless solution. Neat Me_3SiCl (3 drops, excess) was added and the colorless solution was stirred for 72 h. Volatiles were removed under vacuum to yield Cp′$_3$ThCl (35 mg, 89%), which was identified by ^{1}H NMR spectroscopy.[21]

Synthesis of Cp′$_3$ThI from Cp′$_3$ThMe and Me$_3$SiI

Inside the glovebox, Cp′$_3$ThMe (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 Me_3SiI (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 Cp′$_3$ThI as a colorless solid (31 mg, 45%). ^{1}H NMR (C_6D_6): 6.63 (m, 6H, $C_5H_4SiMe_3$), 6.37 (m, 6H, $C_5H_4SiMe_3$), 0.38 ppm (s, 27H, SiMe_3). ^{1}H NMR (THF-d_8): 6.79 (m, 6H, $C_5H_4SiMe_3$), 6.58 (m, 6H, $C_5H_4SiMe_3$), 0.37 ppm (s, 27H, SiMe_3). ^{13}C NMR (THF-d_8): 130.50 ($C_5H_4SiMe_3$), 128.41 ($C_5H_4SiMe_3$), 122.34 ($C_5H_4SiMe_3$), 1.23 ppm (SiMe_3). IR: 3063w, 2949m, 2922m, 2893m, 2850m, 1442w, 1404w, 1366m, 1310w, 1244s, 1172s, 1117w, 1039s, 900s, 828s, 783s, 748s, 689m cm^{-1}. Anal. Calcd for $C_{24}H_{39}Si_3ThI$: C, 37.40; H, 5.10. Found: C, 37.82; H, 5.36.

Synthesis of Cp′$_3$Th(C≡CPh)

LiC≡CPh (22 mg, 0.20 mmol) was tapped into a solution of Cp′$_3$ThBr (126 mg, 0.174 mmol) in Et_2O (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 Cp′$_3$Th(C≡CPh) as a colorless oil, which solidifies at −35 °C (101 mg, 78%). ^{1}H NMR (C_6D_6): δ 7.69 (d, 2H, *o-Ph*), 7.17 (t, 2H, *m-Ph*), 7.03 (t, 1H, *p-Ph*), 6.46 (m, 6H, $C_5H_4SiMe_3$), 6.34 (m, 6H, $C_5H_4SiMe_3$), 0.44 ppm (s, 27H, SiMe_3). ^{13}C NMR (C_6D_6): δ 157.01 (Th–*C*≡CPh), 131.77 ($C_5H_4SiMe_3$), 128.60, 127.64, 127.06, 126.25, 125.17 ($C_5H_4SiMe_3$), 122.24, 120.00 ($C_5H_4SiMe_3$), 0.83 ppm (SiMe_3). 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 $C_{32}H_{44}Si_3Th$: C, 51.59; H, 5.95. Found: C, 51.99; H, 6.35.

In situ synthesis of Cp′$_3$Th

Cp′$_3$ThBr (50 mg, 0.069 mmol) was dissolved in THF (1 mL) and chilled to −35 °C. KC_8 (12 mg, 0.089 mmol) was chilled in a separate vial to −35 °C. KC_8 was tapped into the stirring solution of Cp′$_3$ThBr. This immediately generated a dark blue solution, **A**. KC_8 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^{-1} cm^{-1}): 639 (150), 562 (110), 496 (180). EPR (THF, room temperature): g_{iso} = 1.90, (THF, 77 K): $g_{\|}$ = 1.98, $g_{\perp}$ = 1.89.

(Cp′$_3$Th)$_2$(μ-O)

Cp′$_3$ThBr (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 KC_8 (9 mg, 0.064 mmol) and chilled to −35 °C. The colorless solution of Cp′$_3$ThBr was passed through the KC_8 pipette to form **A**, and was directly eluted into the yellow stirring solution of C_8H_8. 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 °C, which allowed (Cp′$_3$Th)$_2$(μ-O) to be identified by X-ray crystallography.

X-ray crystallographic data

Crystallographic information for Cp′$_3$ThBr, Cp′$_3$ThMe, and (Cp′$_3$Th)$_2$(μ-O) is summarized in the ESI.†

Conflicts of interest

There are no conflicts to declare.

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