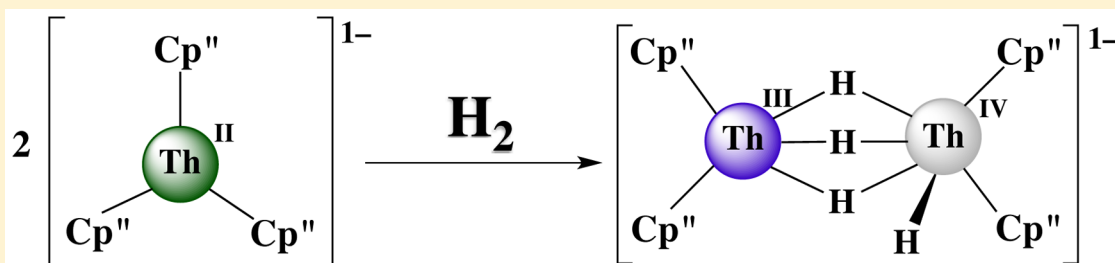


# Expanding Thorium Hydride Chemistry Through $\text{Th}^{2+}$ , Including the Synthesis of a Mixed-Valent $\text{Th}^{4+}/\text{Th}^{3+}$ Hydride Complex

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**S** Supporting Information



**ABSTRACT:** The reactivity of the recently discovered  $\text{Th}^{2+}$  complex  $[\text{K}(18\text{-crown-6})(\text{THF})_2][\text{Cp}''_3\text{Th}]$ , **1** [ $\text{Cp}'' = \text{C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}$ ], with hydrogen reagents has been investigated and found to provide syntheses of new classes of thorium hydride compounds. Complex **1** reacts with  $[\text{Et}_3\text{NH}][\text{BPh}_4]$  to form the terminal  $\text{Th}^{4+}$  hydride complex  $\text{Cp}''_3\text{ThH}$ , **2**, a reaction that formally involves a net two-electron reduction. Complex **1** also reacts in the solid state and in solution with  $\text{H}_2$  to form a mixed-valent bimetallic product,  $[\text{K}(18\text{-crown-6})(\text{Et}_2\text{O})][\text{Cp}''_2\text{ThH}_2]_2$ , **3**, which was analyzed by X-ray crystallography, electron paramagnetic resonance and optical spectroscopy, and density functional theory. The existence of **3**, which formally contains  $\text{Th}^{3+}$  and  $\text{Th}^{4+}$ , suggested that  $\text{KC}_8$  could reduce  $[(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$ . In the presence of 18-crown-6, this reaction forms an analogous mixed-valent product formulated as  $[\text{K}(18\text{-crown-6})(\text{THF})][(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$ , **4**. A similar complex with  $(\text{C}_5\text{Me}_4\text{H})^{1-}$  ligands was not obtained, but reaction of  $(\text{C}_5\text{Me}_4\text{H})_3\text{Th}$  with  $\text{H}_2$  in the presence of  $\text{KC}_8$  and 2.2.2-cryptand at  $-45^\circ\text{C}$  produced two monometallic hydride products, namely,  $(\text{C}_5\text{Me}_4\text{H})_3\text{ThH}$ , **5**, and  $[\text{K}(2.2.2\text{-cryptand})]\{(\text{C}_5\text{Me}_4\text{H})_2[\eta^1:\eta^5\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2)]\text{ThH}\}$ , **6**. Complex **6** contains a metalated tetramethylcyclopentadienyl dianion,  $[\text{C}_5\text{Me}_3\text{H}(\text{CH}_2)]^{2-}$ , that binds in a tuck-in mode.

## INTRODUCTION

One of the fundamental aspects of the chemistry of any element is its reactivity with the simplest element, hydrogen. Although the first molecular example of a thorium hydride complex was made in 1978<sup>1</sup> (eq 1) and was characterized by neutron diffraction,<sup>2</sup> few other crystallographically characterizable thorium hydrides have been reported subsequently. Only three monometallic examples,  $(\text{C}_5\text{Me}_5)_3\text{ThH}$ ,<sup>3</sup>  $(\text{C}_5\text{H}_3^t\text{Bu}_2\text{-1,3})_3\text{ThH}$ ,<sup>4</sup> and  $(\text{C}_5\text{H}_2^t\text{Bu}_3\text{-1,2,4})_2\text{ThH}[\text{N}(p\text{-tolyl})(\text{SiH}_2\text{Ph})]$ ,<sup>5</sup> and three poly-metallic examples,  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Th}(\mu\text{-H})_2\}_2$ ,<sup>6</sup>  $(2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_6\text{Th}_3(\mu_2\text{-H})_4(\mu_3\text{-H})_2$ ,<sup>7,8</sup> and  $(\text{C}_5\text{Me}_4\text{H})_4[\mu\text{-}\eta^1:\eta^5\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2)]_2\text{Th}_4(\mu\text{-H})_4(\mu_3\text{-H})_4$ ,<sup>9</sup> are in the literature. All involve  $5f^06d^0 \text{Th}^{4+}$ , the predominant oxidation state of this metal. The lack of  $\text{Th}^{3+}$  hydrides is not unexpected because there are only five crystallographically characterized examples of any type of  $\text{Th}^{3+}$  complex,<sup>9–13</sup> all of which contain  $6d^1$  ions.

Recently, the first molecular complex of a  $\text{Th}^{2+}$  ion,  $[\text{K}(18\text{-crown-6})(\text{THF})_2][\text{Cp}''_3\text{Th}]$ ,<sup>14</sup> **1** [ $\text{Cp}'' = \text{C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}$ ], was synthesized by reduction of the first  $\text{Th}^{3+}$  complex,  $\text{Cp}''_3\text{Th}$ ,<sup>11</sup> with  $\text{KC}_8$  (eq 2). Structural, spectroscopic, magnetic, and density functional theory (DFT) analysis suggested that this ion was the first example of a  $6d^2$  ion, the electron configuration expected for ions of the fourth row transition metal superheavy elements such as  $\text{Rf}^{2+}$  and  $\text{Db}^{3+}$ .<sup>14</sup> This new oxidation state for

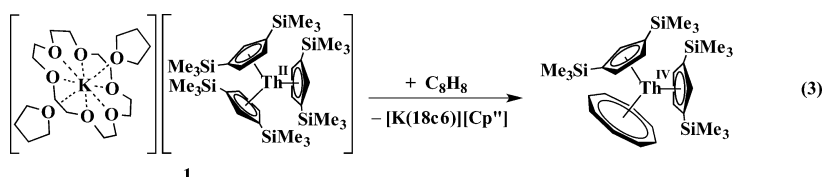
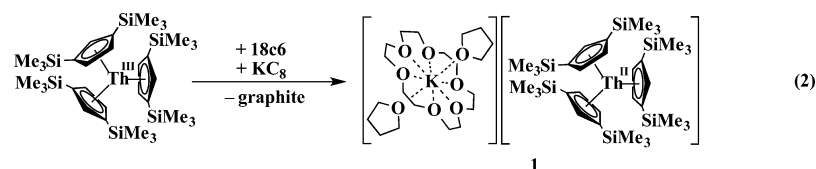
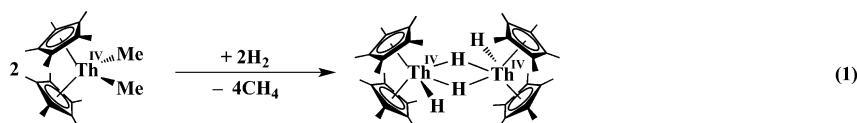
thorium and this unique electron configuration provide opportunities to explore new aspects of f element and transition metal chemistry in the same species. This paper addresses the reactivity of this  $6d^2 \text{Th}^{2+}$  ion with hydrogen.

An additional aspect of the chemistry of **1** is that it is the first thorium complex capable of a two-electron metal-based reduction from a single metal center.<sup>14</sup> Redox-active ligands have been used with  $\text{Th}^{4+}$  complexes to enable reduction chemistry,<sup>15–18</sup> but prior examples of metal-based reductions were limited to one-electron processes because thorium chemistry was previously limited to only the +3 and +4 oxidation states. The formal two-electron metal-based reduction chemistry of **1** was first identified in its reaction with cyclooctatetraene to form  $(\text{C}_8\text{H}_8)^{2-}$  (eq 3).<sup>14</sup>

We report here that the  $\text{Th}^{2+}$  complex **1** opens up a new avenue to develop thorium hydride chemistry. We describe how **1** can expand the number of  $\text{Th}^{4+}$  hydrides and provide the first  $\text{Th}^{3+}$  hydride in a mixed-valent  $\text{Th}^{3+}/\text{Th}^{4+}$  complex. We also present comparisons between  $\text{Th}^{3+}$  and  $\text{Th}^{4+}$  with  $(\text{C}_5\text{Me}_5)^{1-}$ ,  $(\text{C}_5\text{Me}_4\text{H})^{1-}$ , and  $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]^{1-}$  ligands.

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## EXPERIMENTAL DETAILS

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk and high-vacuum line and glovebox techniques under an argon atmosphere. 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 sodium benzophenone ketyl, degassed by three freeze–pump–thaw cycles, and vacuum transferred before use.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{29}\text{Si}$  NMR spectra were recorded on Bruker GN500 or CRYO500 spectrometers operating at 500, 125, and 99.2 MHz, respectively, at 298 K unless otherwise noted.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were referenced internally to residual protio-solvent resonances, and  $^{29}\text{Si}$  NMR spectra were referenced externally to  $\text{SiMe}_4$ . Electron paramagnetic resonance (EPR) spectra were collected using X-band frequency (9.3–9.8 GHz) on a Bruker EMX spectrometer equipped with an ER041XG microwave bridge. The magnetic field was calibrated with 2,2-diphenyl-1-picrylhydrazyl (DPPH) ( $g = 2.0036$ ). IR samples were prepared as KBr pellets and analyzed using a Jasco 4700 FT-IR spectrometer. Elemental analyses were conducted on a PerkinElmer 2400 series II CHNS elemental analyzer.  $[\text{K}(18\text{-crown-6})(\text{THF})_2][\text{Cp}^*_3\text{Th}]$ ,  $[(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$ ,  $^{19}\text{C}_5\text{Me}_5\text{H}_3\text{Th}$ ,  $^9[\text{Et}_3\text{NH}][\text{BPh}_4]$ ,  $^{20}\text{ThCl}_4(\text{DME})_2$ ,  $^{21}\text{AgBPh}_4$ ,  $^{22}$  and  $\text{KC}_8$ ,  $^{23}$  were prepared according to the literature. 18-Crown-6 (abbreviated 18c6 in equations) (Aldrich) was sublimed before use, and 2.2.2-cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, Aldrich), CuI (Aldrich), and CuBr (Aldrich) were placed under vacuum ( $10^{-3}$  Torr) for 12 h before use.  $\text{H}_2$  (Praxair) and  $\text{D}_2$  (Aldrich) were used as received.

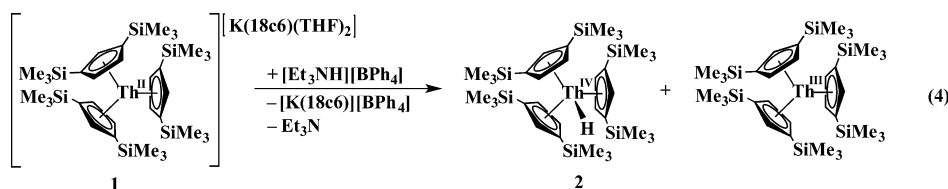
**$\text{Cp}^*_3\text{ThH}_2$ , 2.** In an argon-containing glovebox, a dark green THF solution (18 mL) of  $[\text{K}(18\text{-crown-6})(\text{THF})_2][\text{Cp}^*_3\text{Th}]$ , **1** (202 mg, 0.154 mmol), was added dropwise over 15 min to a stirred THF (2 mL) slurry of  $[\text{Et}_3\text{NH}][\text{BPh}_4]$  (263 mg, 0.618 mmol). The resulting blue solution was dried under reduced pressure to yield blue and white solids. The mixture was extracted into hexane, filtered, and dried to yield blue and white solids. The solids were dissolved in a minimal amount of hexane and stored at  $-30^\circ\text{C}$  for 4 days, producing blue crystals of  $\text{Cp}^*_3\text{Th}$  (73 mg, 55%) identified by X-ray crystallography. The colorless mother liquor was transferred to a new vessel and dried under vacuum to yield **2** as a white solid (41 mg, 30%). X-ray quality crystals were grown from a pentane solution at  $-30^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  12.60 [s, 1H, Th-H], 6.32 [m, 6H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 5.88 [s, 3H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 0.46 [s, 54H,  $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  130.38 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 128.35 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 123.52 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ], 1.73 [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ].  $^{29}\text{Si}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$   $-8.16$  [ $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ ]. IR: 3082 w, 3053 w, 2951 s, 2893 m, 1995 w, 1636 w, 1464 m, 1402 m, 1358 w, 1319 w, 1243 s, 1206 m, 1079 s, 1056 w, 919 s, 828 s, 789 s, 750 s, 687 m, 638 m, 620 m. Anal. Calcd for  $\text{C}_{33}\text{H}_{64}\text{Si}_6\text{Th}$ : C, 46.01; H, 7.49. Found: C, 44.66; H, 7.86. Low carbon values were obtained even after multiple analysis attempts using different batches of material that had

been recrystallized several times. This may be due to the high silicon content in **2**, as observed in other systems.<sup>24</sup>

**Solid–Gas Preparation of  $[\text{K}(18\text{-Crown-6})(\text{Et}_2\text{O})][\text{Cp}^*_2\text{ThH}_2]$ , **3.**** In an argon-containing glovebox, crystals of **1** (648 mg, 0.496 mmol) were crushed to a powder and placed into a Fischer–Porter high-pressure apparatus. The vessel was sealed and attached to a high-pressure gas line. The pressure in the vessel was reduced to half an atmosphere and then charged with  $\text{H}_2$  (60 psi). After 16 h, the vessel was evacuated and returned to an argon-containing glovebox. Washing the dark solids with hexane (20 mL) removed blue  $\text{Cp}^*_3\text{Th}$  (155 mg, 0.18 mmol, 35%), which was identified by X-ray crystallography. The remaining purple solids were then extracted with a minimal amount of cold  $\text{Et}_2\text{O}$ , filtered to remove  $\text{K}(18\text{-crown-6})\text{Cp}^*$ , and dried to a purple oil. The oil was extracted twice more in the same manner and dried under reduced pressure to produce pure **3** as a purple oil by elemental analysis (316 mg, 0.18 mmol, 35%). X-ray quality crystals were grown by pentane vapor diffusion into a concentrated  $\text{Et}_2\text{O}$  solution of **3** at  $-15^\circ\text{C}$ . EPR (THF, room temperature):  $g_{\text{iso}} = 1.89$ ; (THF, 77 K):  $g = 1.98$ , 1.94, 1.76. IR: 3036 w, 3035 w, 2953 m, 2900 m, 1475 w, 1456 w, 1442 w, 1406 w, 1353 m, 1288 m, 1249 m, 1229 w, 1114 s, 1082 m, 963 m, 925 m, 836 s, 779 w, 753 m, 685 w, 639 w, 632 w, 480  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{60}\text{H}_{122}\text{KO}_7\text{Si}_8\text{Th}_2$ : C, 42.81; H, 7.30. Found: C, 42.58; H, 7.09. UV–vis (THF)  $\lambda_{\text{max}}$  nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 330 (2500 shoulder), 530 (2300), 670 (3100).

**Solution Preparation of  $[\text{K}(18\text{-Crown-6})(\text{Et}_2\text{O})][\text{Cp}^*_2\text{ThH}_2]$ , **3.**** In an argon-containing glovebox, crystals of **1** (145 mg, 0.111 mmol) were placed in a Schlenk flask containing a stir bar, dissolved in THF (9 mL), fitted with a greaseless Teflon high-vacuum adapter, and removed from the glovebox. The flask was attached to a high-vacuum line, chilled to  $0^\circ\text{C}$ , and evacuated to the solvent pressure three times before the addition of 1 atm of  $\text{H}_2$ . The initially dark green solution was allowed to stir at  $0^\circ\text{C}$  for 10 min during which time it turned dark blue. The solution was allowed to stir for an additional 10 min at room temperature, dried under reduced pressure, and brought into an argon-containing glovebox. The resulting oily solids were washed extensively with hexane to remove  $\text{Cp}^*_3\text{Th}$ , which left behind purple oily material. The purple oil was extracted into a minimal amount of  $\text{Et}_2\text{O}$  several times to remove a  $\text{K}(18\text{-crown-6})\text{Cp}^*$  impurity. The resulting solution was dried under reduced pressure to yield **3** as a purple oil (63 mg, 34%) as identified by X-ray crystallography and elemental analysis.

**$[\text{K}(18\text{-Crown-6})(\text{THF})][(\text{C}_5\text{Me}_5)_2\text{ThH}_2]$ , **4.**** In an argon-containing glovebox,  $\text{KC}_8$  (19 mg, 0.14 mmol) was added to a stirred colorless THF solution (5 mL) containing  $[(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$  (92 mg, 0.091 mmol) and 18-crown-6 (25 mg, 0.094 mmol). The solution immediately turned dark blue and was allowed to mix for 5 min before being centrifuged to remove black insolubles (presumably graphite) and filtered. The graphite was washed twice with 4 mL of THF, and the supernatants were combined and dried under reduced pressure to yield blue solids. The solids were washed with hexane (5 mL) and dried to yield **4** (102



mg, 80%) as a blue solid. Single crystals were grown by pentane vapor diffusion into a concentrated THF solution of **4** at  $-15\text{ }^{\circ}\text{C}$  but were not of sufficient quality to obtain useful structural information by X-ray crystallography. EPR (THF, room temperature):  $g_{\text{iso}} = 1.88$ , (THF, 77 K):  $g = 1.97, 1.91, 1.77$ . UV-vis (THF)  $\lambda_{\text{max}}$  nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 370 (1200 shoulder), 580 (2100 shoulder), 640 (2500). IR: 2970 m, 2903 s, 2890 s, 1453 w, 1353 w, 1252 w, 1108 s, 962 w, 843 w, 717 w. Anal. Calcd for  $\text{C}_{56}\text{H}_{98}\text{KO}_7\text{Th}_2$ : C, 48.51; H, 7.12. Found: C, 48.82; H, 7.05.

**(C<sub>5</sub>Me<sub>4</sub>H)<sub>3</sub>ThH, 5, and [K(2.2.2-Cryptand)][(C<sub>5</sub>Me<sub>4</sub>H)<sub>2</sub>[ $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>H(CH<sub>2</sub>)ThH]], 6.** In an argon-containing glovebox, solid (C<sub>5</sub>Me<sub>4</sub>H)<sub>3</sub>Th (103 mg, 0.173 mmol), K<sub>2</sub>C<sub>8</sub> (35 mg, 0.26 mmol), and 2.2.2-cryptand (65 mg, 0.173 mmol) were placed in a high-vacuum greaseless Teflon sealable Schlenk flask with a stir bar and attached to a high-vacuum line. THF (20 mL) was condensed onto the solids at 77 K. H<sub>2</sub> (1 atm) was introduced, and the mixture was allowed to warm to  $-45\text{ }^{\circ}\text{C}$ . The initially dark purple solution turned dark blue and was allowed to mix for 1 h at  $-45\text{ }^{\circ}\text{C}$  before being allowed to warm to room temperature. This caused the color to change to pale yellow. After an additional 30 min, the mixture was dried under reduced pressure, brought into an argon-containing glovebox, and extracted into THF (20 mL). The solution was filtered and dried under reduced pressure to yield oily yellow-orange solids that were extracted with toluene (40 mL), leaving an orange oil (see below). The toluene extracts were filtered and dried under reduced pressure to yield **5** as pale yellow solids (82 mg, 80%). X-ray quality crystals of **5** were grown from THF at  $-30\text{ }^{\circ}\text{C}$ . <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  15.34 [s, 1H, Th-H], 5.22 [s, 3H, C<sub>5</sub>Me<sub>4</sub>H], 2.34 [s, 18H, C<sub>5</sub>Me<sub>4</sub>H], 2.05 [s, 18H, C<sub>5</sub>Me<sub>4</sub>H]. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  125.02 [C<sub>5</sub>Me<sub>4</sub>H], 121.63 [br, C<sub>5</sub>Me<sub>4</sub>H], 118.45 [C<sub>5</sub>Me<sub>4</sub>H], 14.16 [C<sub>5</sub>Me<sub>4</sub>H], 12.56 [C<sub>5</sub>Me<sub>4</sub>H]. IR: 3089 w, 2957 m, 2945 m, 2897 s, 2853 s, 2720 w, 1550 w, 1483 w, 1480 w, 1429 m, 1402 m, 1367 m, 1360 m, 1325 w, 1170 w, 1140 w, 1102 w, 1065 w, 1020 m, 997 s, 782 s, 629 w, 611 m, 586 m. Anal. Calcd for C<sub>27</sub>H<sub>40</sub>Th: C, 54.35; H, 6.76. Found: C, 54.22; H, 6.93. The toluene extraction left behind an orange oil, from which X-ray quality crystals of **6** were grown by pentane vapor diffusion into a 1 mL THF solution of the oil at  $-30\text{ }^{\circ}\text{C}$ . This process also produces crystals of [K(2.2.2-cryptand)][C<sub>5</sub>Me<sub>4</sub>H] and other products that could not be separated.

**(C<sub>5</sub>Me<sub>4</sub>H)<sub>3</sub>ThCl.** This complex was made by a variation of the literature method that used LiC<sub>5</sub>Me<sub>4</sub>H.<sup>25</sup> In an argon-containing glovebox, ThCl<sub>4</sub>(DME)<sub>2</sub> (44 mg, 0.079 mmol) was dissolved in toluene (10 mL), and solid K<sub>2</sub>C<sub>5</sub>Me<sub>4</sub>H was added with mixing. The white slurry was stirred for 18 h before being centrifuged and filtered to remove white insoluble material. The colorless supernatant was dried to yield (C<sub>5</sub>Me<sub>4</sub>H)<sub>3</sub>ThCl<sup>25</sup> as a white crystalline solid (45 mg 90%). Purification was achieved by crystallization from toluene at  $-30\text{ }^{\circ}\text{C}$ , which yielded colorless crystals (30 mg, 60%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  5.72 [s, 3H, C<sub>5</sub>Me<sub>4</sub>H], 2.13 [s, 18H, C<sub>5</sub>Me<sub>4</sub>H], 2.06 [s, 18H, C<sub>5</sub>Me<sub>4</sub>H]. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  129.24 [C<sub>5</sub>Me<sub>4</sub>H], 119.98 [C<sub>5</sub>Me<sub>4</sub>H], 13.22 [C<sub>5</sub>Me<sub>4</sub>H], 12.91 [C<sub>5</sub>Me<sub>4</sub>H]. IR: 2976 m, 2936 m, 2903 s, 2860 s, 2723 w, 1560 w, 1485 w, 1432 w, 1381 m, 1368 m, 1322 w, 1243 w, 1140 w, 1071 w, 1015 w, 971 w, 933 w, 822 w, 792 m, 787 s, 730 w, 696 w, 601 w. Anal. Calcd for C<sub>27</sub>H<sub>39</sub>ClTh: C, 51.39; H, 6.23. Found: C, 51.54; H, 6.58.

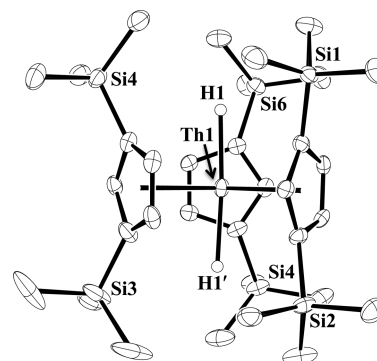
**X-ray Data Collection, Structure Determination, and Refinement.** Crystallographic details for compounds Cp<sup>''</sup><sub>3</sub>ThH, **2**, [K(18-crown-6)(Et<sub>2</sub>O)][Cp<sup>''</sup><sub>2</sub>ThH<sub>2</sub>]<sub>2</sub>, **3**, (C<sub>5</sub>Me<sub>4</sub>H)<sub>3</sub>ThH, **5**, and [K(2.2.2-cryptand)][(C<sub>5</sub>Me<sub>4</sub>H)<sub>2</sub>[ $\mu$ - $\eta^5$ -C<sub>5</sub>Me<sub>3</sub>H(CH<sub>2</sub>)ThH]], **6**, are summarized in the Supporting Information.

**Computational Details.** DFT calculations were carried out on the anion of [K(18-crown-6)(Et<sub>2</sub>O)][Cp<sup>''</sup><sub>2</sub>ThH<sub>2</sub>]<sub>2</sub> as well as the potential reduction product {[Cp<sup>''</sup><sub>2</sub>ThH<sub>2</sub>]<sub>2</sub>}<sup>2-</sup> using the hybrid meta-generalized gradient approximation functional TPSSH.<sup>26</sup> Scalar-relativistic effective

core potentials<sup>27</sup> and triple- $\zeta$  valence basis sets, def-TZVP,<sup>28</sup> with the two tight  $g$  functions removed, were used for Th. All calculations were performed using the Turbomole quantum chemistry software.<sup>29</sup> Time-dependent DFT (TDDFT) calculations<sup>30</sup> were also performed to simulate the UV-vis spectrum for {[Cp<sup>''</sup><sub>2</sub>ThH<sub>2</sub>]<sub>2</sub>}<sup>1-</sup>. A full description of the computational methods is reported in the Supporting Information.

## RESULTS

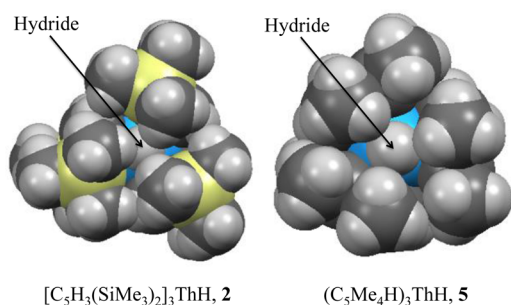
**Th<sup>4+</sup> Hydride from Th<sup>2+</sup>.** A dark green THF solution of the 6d<sup>2</sup> Th<sup>2+</sup> complex, [K(18-crown-6)(THF)<sub>2</sub>][Cp<sup>''</sup><sub>3</sub>Th], **1** [Cp<sup>''</sup> = C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>-1,3], reacted with a slurry of excess white [Et<sub>3</sub>NH][BPh<sub>4</sub>] to form a solution with a blue color characteristic of 6d<sup>1</sup> Th<sup>3+</sup>. Blue and white solids were isolated from the reaction and characterized by X-ray crystallography as Cp<sup>''</sup><sub>3</sub>Th<sup>11</sup> (55% yield) and Cp<sup>''</sup><sub>3</sub>ThH, **2** (30% yield), respectively (reaction 4 and Figure 1).



**Figure 1.** Molecular structure of Cp<sup>''</sup><sub>3</sub>ThH, **2**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except the two disordered hydride positions, H1 and H1', are omitted for clarity.

The <sup>1</sup>H NMR spectrum of **2** contains a resonance at 12.6 ppm that is similar to the 15.4 ppm value for (C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>ThH<sup>3</sup> and the 12.95 ppm shift for (C<sub>5</sub>H<sub>3</sub><sup>t</sup>Bu<sub>2</sub>-1,3)<sub>3</sub>ThH.<sup>4</sup> Attempts to prepare the deuterium analogue of **2** by reaction with [Et<sub>3</sub>ND][BPh<sub>4</sub>] gave an analogous product, but a deuteride resonance was not observed in the <sup>2</sup>H NMR spectrum. The <sup>1</sup>H spectrum contained a resonance at 12.6 ppm that suggested that hydride/deuteride exchange had occurred as is common with actinide hydride species.<sup>19,31,32</sup> The <sup>2</sup>H NMR experiments were not helpful in identifying at what site the exchange was occurring, but this is difficult because a large excess of deuterium was not used. A reaction of **2** with CCl<sub>4</sub> was examined to determine if HCCl<sub>3</sub> would form and to confirm the presence of a hydride ligand according to this classic test reaction for metal hydrides. However, no reaction was observed even with excess CCl<sub>4</sub>. This may be due to steric protection of the hydride ligand by the trimethylsilyl groups. Space-filling models of the complex are consistent with this (Figure 2).

**Structure of Cp<sup>''</sup><sub>3</sub>ThH, 2.** The three Cp<sup>''</sup> ring centroids form a trigonal plane around the Th<sup>4+</sup> ion with 120° (ring centroid)–Th–(ring centroid) angles. Similar angles are found with the



**Figure 2.** Space-filling models of compounds  $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{ThH}$ , **2**, and  $(\text{C}_5\text{Me}_4\text{H})_3\text{ThH}$ , **5**.

only other monometallic thorium hydride complexes,  $(\text{C}_5\text{Me}_5)_3\text{ThH}$ ,<sup>3</sup>  $(\text{C}_5\text{H}_3^t\text{Bu}_2-1,3)_3\text{ThH}$ ,<sup>4</sup> and  $(\text{C}_5\text{H}_2^t\text{Bu}_3)_2\text{Th}(\text{H})[\text{N}(p\text{-tolyl})\text{SiH}_2\text{Ph}]$ .<sup>5</sup> The hydride ligand in **2** is disordered on either side of the trigonal plane as is also observed in  $(\text{C}_5\text{Me}_5)_3\text{ThH}^3$  and  $(\text{C}_5\text{H}_3^t\text{Bu}_2-1,3)_3\text{ThH}$ .<sup>4</sup> The 2.54 Å Th–(ring centroid) distance in **2** is similar to the 2.56 Å distance in  $\text{Cp}''_3\text{ThCl}^{33}$  and to the 2.52 Å distances found in both the  $\text{Th}^{2+}$  complex, **1**, and its  $\text{Th}^{3+}$  precursor,  $\text{Cp}''_3\text{Th}$ .<sup>11</sup> This is consistent with previous analyses of  $\text{Th}^{2+}$ ,  $\text{Th}^{3+}$ , and  $\text{Th}^{4+}$  complexes that show that Th–(ring centroid) distances do not change greatly when electrons are added to  $d_z^2$  orbitals.<sup>14,24,34–37</sup> Comparisons with the 2.58 and 2.61 Å Th–(ring centroid) distances in  $(\text{C}_5\text{H}_3^t\text{Bu}_2-1,3)_3\text{ThH}^4$  and  $(\text{C}_5\text{Me}_5)_3\text{ThH}$ ,<sup>3</sup> respectively, show that tris(cyclopentadienyl)thorium hydride complexes can exist with a range of metal ligand distances.

**Mixed-Valent  $\text{Th}^{3+}/\text{Th}^{4+}$  Hydride from  $\text{Th}^{2+}$ .** The  $\text{Th}^{2+}$  complex  $[\text{K}(18\text{-crown-6})][\text{Cp}''_3\text{Th}]$ , **1**, was treated with  $\text{H}_2$  to determine if a  $\text{Th}^{3+}$  hydride complex such as  $[\text{K}(18\text{-crown-6})][\text{Cp}''_3\text{ThH}]$  would form in analogy to the complex formed by reaction of the  $\text{U}^{2+}$  complex,  $[\text{K}(2.2.2\text{-cryptand})][\text{Cp}_3\text{U}]$  ( $\text{Cp}' = \text{C}_5\text{H}_4\text{SiMe}_3$ ), with  $\text{H}_2$ .<sup>36</sup> (eq 5). However, the  $\text{Th}^{2+}$  complex does not react analogously. Instead, **1** reacts with 1 atm of  $\text{H}_2$  in THF at 0 °C within minutes to form  $\text{Cp}''_3\text{Th}$  (35% yield) and the bimetallic complex,  $[\text{K}(18\text{-crown-6})(\text{Et}_2\text{O})][\text{Cp}''_2\text{Th}(\mu\text{-H})_3\text{ThHCp}''_2]$ , **3** (35% yield) (eq 6), identified by X-ray crystallography (Figure 3). Complex **1** also reacts in the solid state with  $\text{H}_2$  at 60 psi over several hours to form **3**.<sup>38</sup> The reaction of  $\text{CCl}_4$  with **3** was found to produce  $\text{CHCl}_3$ , but the simple chloride product that may have formed,  $\text{Cp}''_2\text{ThCl}_2$ ,<sup>39</sup> was not observed.

**Structure of  $[\text{K}(18\text{-Crown-6})\text{Et}_2\text{O}][\text{Cp}''_2\text{Th}(\mu\text{-H})_3\text{ThHCp}''_2]$ , **3**.** The crystallographic data show that the  $[\text{Cp}''_2\text{Th}(\mu\text{-H})_3\text{ThHCp}''_2]^{1-}$  anion in **3** contains two bent metallocene units with the four cyclopentadienyl ring centroids in a roughly tetrahedral arrangement. The dihedral angle between the planes defined by the two ring centroids and the metal of each metallocene unit is 58.6°, but these two planes do not intersect along the Th···Th vector because **3** is not as symmetrical as many  $(\text{C}_5\text{R}_5)_2\text{M}[\text{bridging ligand(s)}]\text{M}(\text{C}_5\text{R}_5)_2$  compounds in the literature.<sup>40–45</sup> Four hydride ligands were located between the two metallocenes, three in bridging

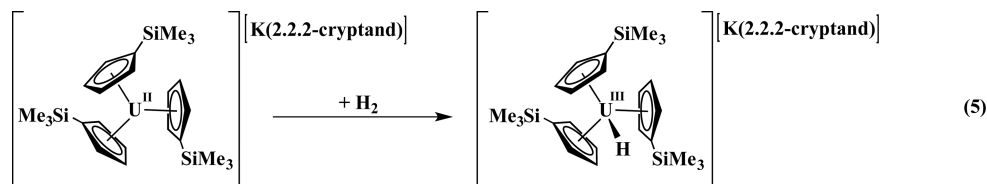
positions and one terminal hydride, H4, attached to Th1. Charge balance in the  $[\text{Cp}''_2\text{Th}(\mu\text{-H})_3\text{ThHCp}''_2]^{1-}$  anion requires this to be a mixed-valent  $\text{Th}^{3+}/\text{Th}^{4+}$  complex, an assignment that is supported by spectroscopic and theoretical data described later.

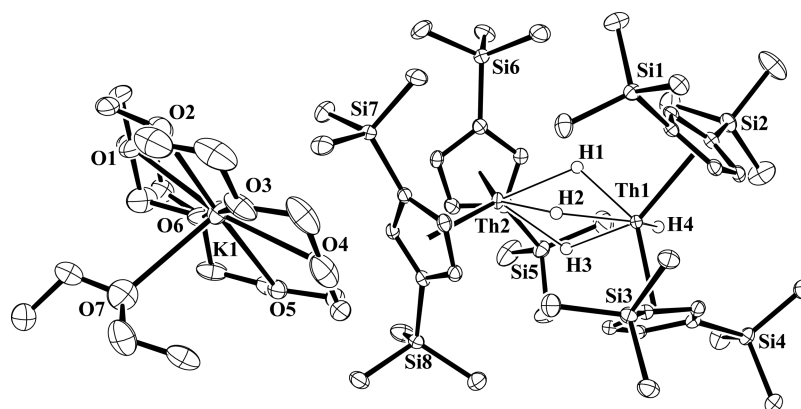
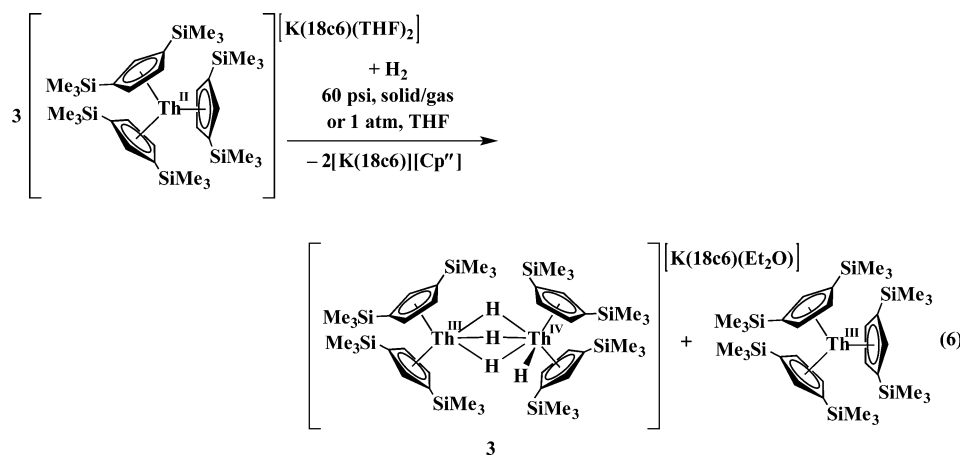
Identifying  $\text{Th}^{3+}$  versus  $\text{Th}^{4+}$  from the thorium–( $\text{Cp}''$  ring centroid) distances in **3** is complicated because these distances do not change much with oxidation state (Table 1) and because the formally nine-coordinate Th2 has two different distances, 2.583 and 2.536 Å. The former distance is similar to the 2.589 and 2.583 Å distances for formally 10-coordinate Th1, which is bound by the terminal hydride. The 2.536 Å distance, on the other hand, is what might be expected based on the 0.04 Å difference in Shannon ionic radius for 10-coordinate  $\text{Th}^{4+}$  versus nine-coordinate  $\text{Th}^{4+}$ .<sup>46</sup>

The 3.6622(1) Å Th···Th distance is much smaller than the 4.007(8) Å distance in the bis(pentamethylcyclopentadienyl)  $\text{Th}^{4+}$  hydride dimer containing two bridging hydrides, namely,  $[(\text{C}_5\text{Me}_5)_2\text{ThH}(\mu\text{-H})]_2$  (eq 1).<sup>19</sup> The distance is very close to the 3.632 Å distance in  $\{[(\text{CH}_3)_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Th}(\mu\text{-H})_2\}_2$ ,<sup>6</sup> which contains four bridging hydrides and two  $\text{Th}^{4+}$  centers. It is also close to the 3.59 Å distance between thorium atoms in thorium metal.<sup>2</sup>

**Mixed-Valent  $\text{Th}^{3+}/\text{Th}^{4+}$  Hydride from Reduction of a Bimetallic  $\text{Th}^{4+}$  Hydride:  $[\text{K}(18\text{-Crown-6})(\text{THF})][(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$ , **4**.** The existence of the mixed-valent tetrahydride, **3**, raised the possibility that a similar complex could be made by reduction of the first isolated thorium hydride,  $[(\text{C}_5\text{Me}_5)_2\text{ThH}(\mu\text{-H})]_2$ ,<sup>1,49</sup> if a change from  $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]^{1-}$  to  $(\text{C}_5\text{Me}_5)^{1-}$  was not too big a perturbation. Since  $\text{Th}^{3+}$  complexes are traditionally difficult to synthesize, it seemed possible that reduction of this compound had never been considered. Addition of  $\text{KC}_8$  to a THF solution of colorless  $[(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$  in the presence of 18-crown-6 immediately generates a dark blue color characteristic of  $\text{Th}^{3+}$ . Crystals of the product, **4**, were isolated from this reaction; however, the quality of multiple samples of the crystals was not high enough to provide structural data by X-ray crystallography (eq 7). Similar crystallographic problems were encountered with crystals formed in the presence of 2.2.2-cryptand. Elemental analysis was consistent with the formula of  $[\text{K}(18\text{-crown-6})(\text{THF})][(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$  for **4**, analogous to **3**, and other data on **4** also parallel those of **3** as described below. Compound **4** reacts with  $\text{CCl}_4$  in  $\text{C}_6\text{D}_6$ , and the filtered product showed  $^1\text{H}$  NMR signals consistent with  $\text{CHCl}_3$  as well as several resonances in the  $\text{C}_5\text{Me}_5$  region but not the resonance of  $(\text{C}_5\text{Me}_5)_2\text{ThCl}_2$ .<sup>39</sup> Only one THF molecule is assumed to be coordinated to the potassium in **4** based on elemental analysis and in analogy to the cation in **3**.

**Spectroscopy of **3** and **4**.** The IR spectra of **3** and **4** show absorptions in the area expected for terminal/bridging actinide hydrides, that is,  $\approx 1300\text{--}1500\text{ cm}^{-1}$  for terminal and  $\approx 1100\text{--}1300\text{ cm}^{-1}$  for bridging asymmetrical stretches,<sup>50</sup> but deuterium experiments did not result in conclusive assignments. In each case, the IR spectrum of the deuterated analogue matched exactly that of the hydride product, even when reactions were done in





**Figure 3.** Molecular structure of  $[\text{K}(18\text{-crown-}6)(\text{Et}_2\text{O})][\text{Cp}^*_2\text{Th}(\mu\text{-H})_3\text{ThHCp}^*_2]$ , **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except H1–H4, as well as cocrystallized  $\text{Et}_2\text{O}$  and disorder about the potassium-bound  $\text{Et}_2\text{O}$ , are omitted for clarity.

**Table 1. Comparison of Th–(Ring Centroid) Distances in Structurally Similar Thorium Compounds in Varying Oxidation States**

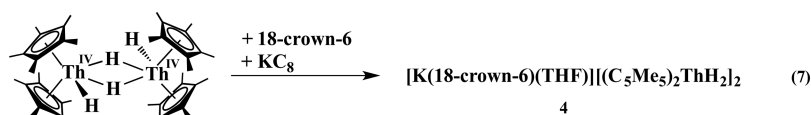
| compound   | metal oxidation state | M–CNT (Å, ave) |
|--|-----------------------|----------------|
| $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{ThCl}^{47}$  | +4                    | 2.565          |
| $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{Th}^{11}$  | +3                    | 2.520          |
| $[\text{K}(2.2.2\text{-cryptand})]\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{Th}\}^{14}$           | +2                    | 2.521          |
| $[\text{K}(18\text{-crown-}6)(\text{THF})_2]\{[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]_3\text{Th}\}^{14}$ | +2                    | 2.525          |
| $(\text{C}_5\text{Me}_4\text{H})_3\text{ThBr}^9$   | +4                    | 2.576          |
| $(\text{C}_5\text{Me}_4\text{H})_3\text{Th}^9$   | +3                    | 2.551          |
| $(\text{C}_5\text{Me}_5)_2[\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]\text{Th}(\text{Me})^{48}$          | +4                    | 2.591          |
| $(\text{C}_5\text{Me}_5)_2[\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]\text{Th}^3$                        | +3                    | 2.543          |
| $[\text{C}_5\text{H}_3(\text{SiMe}_2^t\text{Bu})_2]_3\text{ThCl}^{47}$                                   | +4                    | 2.581          |
| $[\text{C}_5\text{H}_3(\text{SiMe}_2^t\text{Bu})_2]_3\text{Th}^{10}$                                     | +3                    | 2.533          |

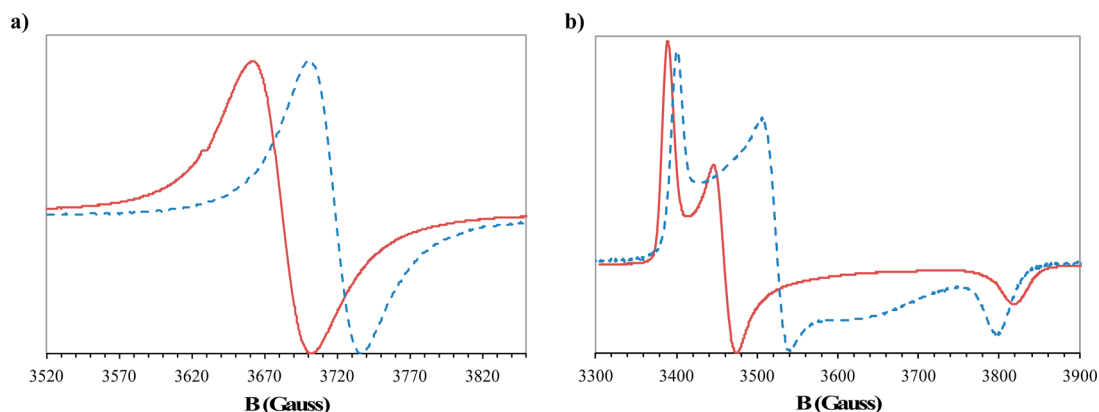
the solid state and infrared spectra were obtained directly on the resulting solid without any contact with solvent. This is consistent with H/D exchange, which has been a common problem in molecular actinide hydride chemistry.<sup>19,31,32</sup> NMR spectroscopy was not helpful in resolving this matter, as the

paramagnetism of **3** and **4** prevented the identification of the hydride/deuteride resonances in both cases.

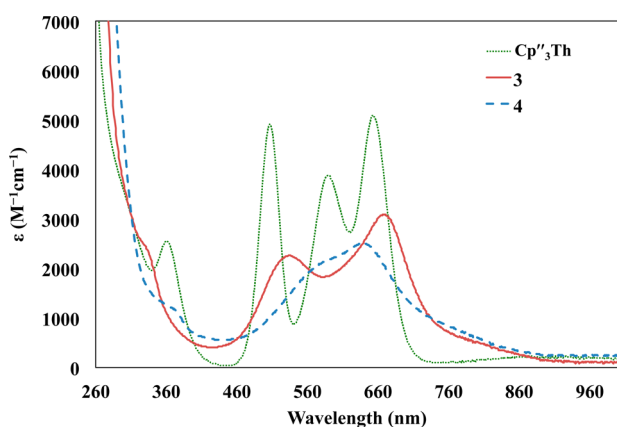
The room temperature EPR spectra of **3** and **4** in THF show isotropic signals with  $g = 1.89$  and  $1.88$ , respectively. These values are similar to those of the other five  $\text{Th}^{3+}$  compounds that have been crystallographically characterized:  $\text{Cp}^*_3\text{Th}$  (1.91),<sup>10,11,51</sup>  $[\text{C}_5\text{H}_3(\text{SiMe}_2^t\text{Bu})_2]_3\text{Th}$  (1.91),<sup>10</sup>  $(\text{C}_5\text{Me}_4\text{H})_3\text{Th}$  (1.92),<sup>9</sup>  $[\text{K}(\text{DME})_2]\{[\text{C}_8\text{H}_6(\text{SiMe}_2^t\text{Bu})_{2-1,4}]_2\text{Th}\}$  (1.92),<sup>12</sup> and  $(\text{C}_5\text{Me}_5)_2[\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]\text{Th}$  (1.87),<sup>13</sup> and are consistent with a  $6d^1$  ground state. The line widths of ca. 300 G for **1** and **3** at room temperature lie between the ca. 200 and 500 G values for  $(\text{C}_5\text{Me}_4\text{H})_3\text{Th}^9$  and  $(\text{C}_5\text{Me}_5)_2[\text{PrNC}(\text{Me})\text{N}^i\text{Pr}]\text{Th}$ ,<sup>13</sup> respectively. The spectra at 77 K in THF show rhombic signals with  $g = 1.98$ , 1.94, and 1.76 for **3** and  $g = 1.97$ , 1.91, and 1.77 for **4** (Figure 4). No hyperfine coupling is observed in either case. In contrast, axial or pseudoaxial signals are observed at low temperature and in the solid state for the monometallic species  $\text{Cp}^*_3\text{Th}$ ,  $[\text{C}_5\text{H}_3(\text{SiMe}_2^t\text{Bu})_2]_3\text{Th}$ , and  $[\text{K}(\text{DME})_2]\{[\text{C}_8\text{H}_6(\text{SiMe}_2^t\text{Bu})_{2-1,4}]_2\text{Th}\}$ .

The optical spectra of both complexes **3** and **4** display features similar to the known  $\text{Th}^{3+}$  complex  $\text{Cp}^*_3\text{Th}$ ,<sup>10,11,53</sup> with intense absorptions in the 500–650 nm range (Figure 5). Complexes **3** and **4** have extinction coefficients of 3000 and 2500  $\text{M}^{-1} \text{cm}^{-1}$ ,





**Figure 4.** EPR spectra of  $[\text{K}(\text{18-crown-6})(\text{Et}_2\text{O})][\text{Cp}''_2\text{ThH}_2]_2$ , **3** (red, solid), and  $[\text{K}(\text{18-crown-6})(\text{THF})][(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$ , **4** (blue, dashed), in THF at (a) room temperature and (b) 77 K.



**Figure 5.** Optical spectra of  $[\text{K}(\text{18-crown-6})(\text{Et}_2\text{O})][\text{Cp}''_2\text{Th}(\mu\text{-H})_3\text{ThHCp}''_2]_2$ , **3** (red, solid),  $[\text{K}(\text{18-crown-6})(\text{THF})][(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$ , **4** (blue, dashed), and  $\text{Cp}'''_3\text{Th}$  (green, dotted) solutions in THF.

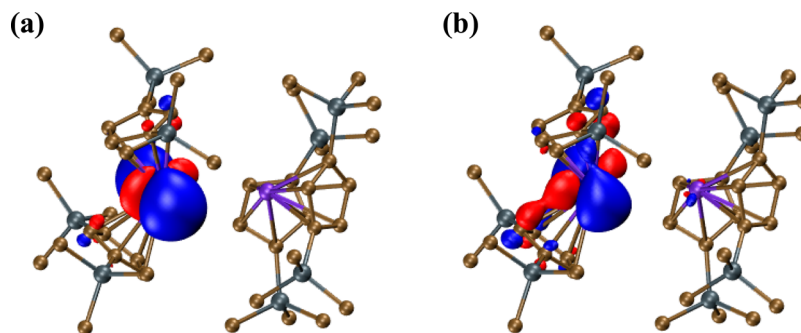
respectively, which are about half that of  $\text{Cp}'''_3\text{Th}$ . Assignments are presented below in the [theory section](#).

**Density Functional Theory Analysis of 3.** DFT calculations on the anion of **3**,  $[\text{Cp}''_2\text{Th}(\mu\text{-H})_3\text{ThHCp}''_2]^{1-}$ , reveal a structural minimum that agrees very well with the crystallographic data. The HOMO and LUMO ([Figure 6](#)) are both metal-based d orbitals, localized on the thorium metal center without a terminal hydride, which is Th2 in the crystal structure ([Figure 3](#)). Natural population analysis (NPA) calculations on the anion give a 0.69 d orbital and 0.86 overall

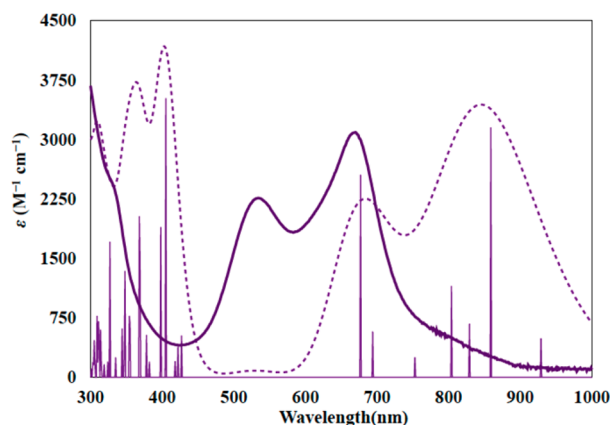
spin density at the Th2 metal center, while the NPA calculations describe no d orbital spin density at the Th1 metal center to which the terminal hydride is attached. This matches the formal assignment of nine-coordinate Th2 being  $\text{Th}^{3+}$  and 10-coordinate Th1 being  $\text{Th}^{4+}$ . The localization of the metal electron in a  $d_{z^2}$  orbital is consistent with experimental data on other known  $\text{Th}^{3+}$  complexes which have been characterized as  $6d^1$  ions<sup>9–13</sup> and previous calculations of a hypothetical  $\text{Th}^{3+}/\text{Th}^{3+}$  hydride dimer of the formula  $[(\text{C}_5\text{H}_5)_2\text{Th}(\mu\text{-H})]_2$ .<sup>15</sup>

TDDFT calculations were performed to simulate the UV–vis spectrum of the anion in **3**. The overall shape of the experimental spectrum is well matched in the simulated spectrum ([Figure 7](#)), but the energies of the excitations are predicted to be lower in energy than what is observed experimentally. This observation was also seen in the simulated spectrum of **1**<sup>14</sup> and is often seen in these calculations.<sup>52</sup> The two broad, low-energy absorptions are primarily metal-to-metal transitions containing d→f character, while the higher-energy absorptions are a combination of metal-to-metal and metal-to-ligand transitions. This is very similar to the analysis of the simulated UV–vis spectrum of **1**.

Calculations were carried out on the possible product of reducing the monoanion of **3** by one electron to form the dianion,  $[\text{Cp}''_2\text{Th}(\text{H})(\mu\text{-H})_3\text{ThCp}''_2]^{2-}$ . Although it was anticipated that reduction of **3** would reduce the  $\text{Th}^{4+}$  metal center, Th1, to make a  $\text{Th}^{3+}/\text{Th}^{3+}$  bimetallic complex, the LUMO of the anion of **3** suggested that reduction of the  $\text{Th}^{3+}$  metal center, Th2, was more likely. Indeed, in the structural minimum for the  $[\text{Cp}''_2\text{Th}(\text{H})(\mu\text{-H})_3\text{ThCp}''_2]^{2-}$  dianion, the  $\text{Th}^{2+}/\text{Th}^{4+}$  singlet state was found to be the ground state, with the triplet state being approximately  $2100\text{ cm}^{-1}$  (6 kcal/mol) higher in energy than the



**Figure 6.** Molecular orbital plots of the (a) 263a orbital (HOMO) and (b) 263b orbital (LUMO) of the anion in **3**,  $[\text{Cp}''_2\text{Th}(\mu\text{-H})_3\text{ThHCp}''_2]^{1-}$ , using a contour value of 0.05. The metal center on the left is Th2, and the metal center on the right is Th1.



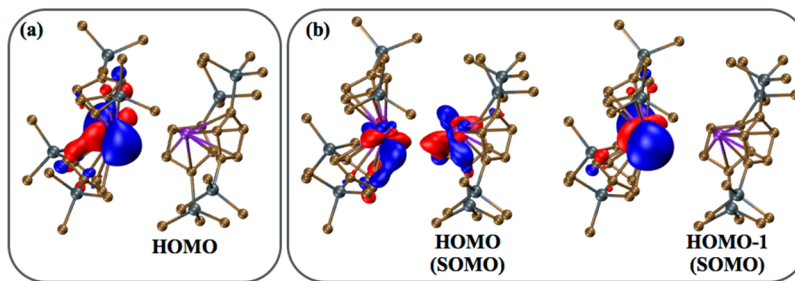
**Figure 7.** Experimental (solid line) and calculated (dotted line) UV-vis spectra of  $[\text{K}(18\text{-crown-6})\text{Et}_2\text{O}][\text{Cp}''_2\text{Th}(\mu\text{-H})_3\text{ThHCp}''_2]$ , **3**, in THF at 298 K, with pertinent theoretical excitations shown as vertical lines and theoretical extinction coefficients scaled down by a factor of 1.5.

singlet state. The HOMO of the singlet state is a doubly occupied orbital localized on the Th2 metal center (Figure 8a). NPA calculations support the description of the singlet ground state as a  $\text{Th}^{2+}/\text{Th}^{4+}$  bimetallic complex with no evidence for a Th–Th bond. Since semilocal DFT has a tendency to overdelocalize electrons,<sup>53</sup> the prediction of a  $\text{Th}^{2+}/\text{Th}^{4+}$  compound by the present calculations is significant.

Calculations of the higher-lying triplet state reveal two singly occupied molecular orbitals (SOMOs): the higher orbital (HOMO) is spread across both metals and the ligands, while the lower orbital is localized on the Th2 metal center (Figure 8b). NPA calculations show increased spin density on both Th1 and Th2, providing further support that the triplet state cannot be described as a simple  $\text{Th}^{3+}/\text{Th}^{3+}$  bimetallic species.

**Redox Chemistry of 3 and 4.** Experimental attempts to reduce **3** and **4** further to make the dianion described above have not been successful. Only transient species have been generated. No diamagnetic products have been observed, and EPR measurements suggest the formation of organic radicals.

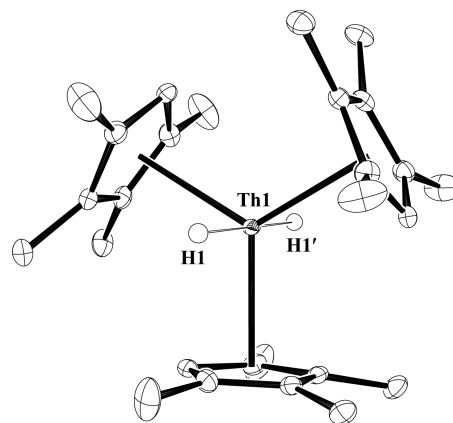
Attempts were also made to oxidize **3** and **4** to form the corresponding  $\text{Th}^{4+}/\text{Th}^{4+}$  dimers with several oxidizing agents.  $\text{AgBPh}_4$  gave the cleanest results in both cases. Oxidation of **4** forms the expected  $[(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$  complex,<sup>1,49</sup> while oxidation of **3** forms a tris(cyclopentadienyl) monometallic complex,  $\text{Cp}''_3\text{ThH}$ , **2**, as the major product. Reactions of **3** and **4** with  $\text{CuBr}$ ,  $\text{CuI}$ , and  $\text{AgI}$  also form the products described above but as mixtures with several other unidentified products.



**Figure 8.** Molecular orbital plots of the (a) doubly occupied 263a orbital (HOMO) of the singlet state and (b) singly occupied 264a (HOMO) and 263a (HOMO–1) orbitals of the triplet state of the dianion,  $[\text{Cp}''_2\text{Th}(\text{H})(\mu\text{-H})_3\text{ThCp}''_2]^{2-}$ , using a contour value of 0.05. The metal center on the left is Th2, and the metal center on the right is Th1.

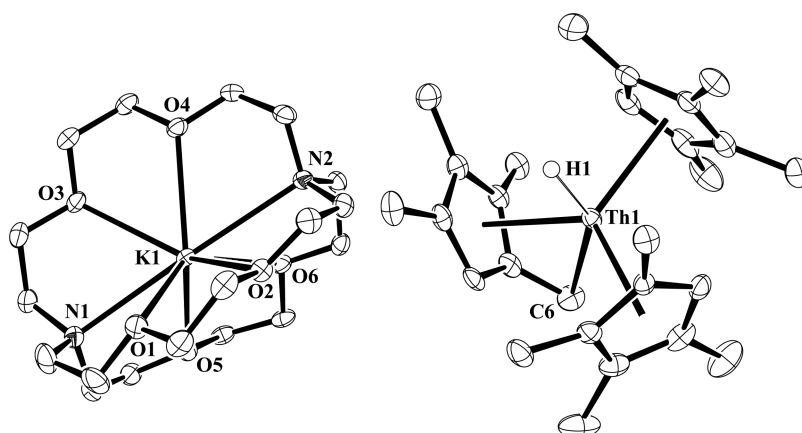
**Tetramethylcyclopentadienyl  $\text{Th}^{4+}$  Hydrides from Reduction of  $\text{Th}^{3+}$ .** Since the tetramethylcyclopentadienyl ligand can be viewed as intermediate between  $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]^{1-}$  and  $(\text{C}_5\text{Me}_5)^{1-}$  both sterically and electronically, it seemed possible that  $(\text{C}_5\text{Me}_4\text{H})^{1-}$  analogues of **3** and **4** could also be accessible. However, it is known that the reaction of  $(\text{C}_5\text{Me}_4\text{H})_2\text{ThMe}_2$  with  $\text{H}_2$  does not produce a dimer of formula  $[(\text{C}_5\text{Me}_4\text{H})_2\text{ThH}_2]_2$ , as in the  $(\text{C}_5\text{Me}_5)^{1-}$  case in eq 1. Instead, the tetramethylcyclopentadienyl reaction forms an octahydride cluster containing four thorium atoms and metalated tuck-over<sup>54–59</sup> ligands,  $[\mu\text{-}\eta^1:\eta^5\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2)]^{2-}$ , namely,  $(\text{C}_5\text{Me}_4\text{H})_4[\mu\text{-}\eta^1:\eta^5\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2)]_2\text{Th}_4(\mu\text{-H})_4(\mu_3\text{-H})_4$ , as well as the ligand redistribution product,  $(\text{C}_5\text{Me}_4\text{H})_3\text{ThMe}$ .<sup>9</sup> The synthesis of an analogue of **3** according to eq 6 would require the existence of the  $\text{Th}^{2+}$  complex  $[(\text{C}_5\text{Me}_4\text{H})_3\text{Th}]^{1-}$ . Although such a species has not yet been isolated, it is possible that this could be generated in situ according to eq 2.

To test these ideas, a dark purple THF solution of  $(\text{C}_5\text{Me}_4\text{H})_3\text{Th}^9$  was treated with  $\text{KC}_8$  under 1 atm of  $\text{H}_2$  in the presence of 18-crown-6 at  $-78^\circ\text{C}$ . Upon being warmed to  $-45^\circ\text{C}$ , the solution turned dark blue, not the green color of **1**, and when allowed to warm slightly above  $-45^\circ\text{C}$ , the color turned pale yellow. Two  $\text{Th}^{4+}$  hydride products were isolated from the reaction:  $(\text{C}_5\text{Me}_4\text{H})_3\text{ThH}$ , **5** (Figure 9), as the major product,

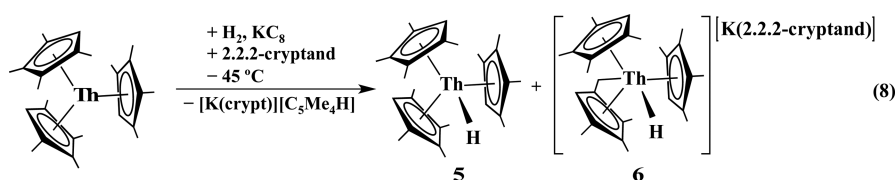


**Figure 9.** Molecular structure of  $(\text{C}_5\text{Me}_4\text{H})_3\text{ThH}$ , **5**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except H1 and H1', are omitted for clarity.

and  $[\text{K}(2.2.2.\text{cryptand})]\{(\text{C}_5\text{Me}_4\text{H})_2[\eta^1:\eta^5\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2)]\text{-ThH}\}$ , **6** (Figure 10, reaction 8). The predominant product, **5**, is an analogue of  $\text{Cp}''_3\text{ThH}$ , **2**, and of the previously reported  $(\text{C}_5\text{Me}_5)_3\text{ThH}$ .<sup>3</sup> The minor product contains a ligand in which



**Figure 10.** Molecular structure of  $[K(2.2.2\text{-cryptand})]\{(C_5Me_4H)_2[\eta^1:\eta^5\text{-}C_5Me_3H(CH_2)]ThH\}$ , **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, except H1, as well as cocrystallized THF, are omitted for clarity.



C–H bond activation has occurred with one of the methyl groups of a  $(\eta^5\text{-}C_5Me_4H)^{1-}$  ligand to make a  $(\eta^1:\eta^5\text{-}CH_2C_5Me_3H)^{2-}$  dianion, which binds to a single metal as a “tuck-in”<sup>60</sup> rather than “tuck-over”<sup>54–59</sup> ligand. The only other example of a tuck-in complex with a tetramethylcyclopentadienyl ligand with any metal is  $\{\eta^5\text{-}C_5HMe_2[CH_2CH(tBu)CH=CHCH(tBu)CH_2]\}[\eta^3:\eta^4\text{-}C_5HMe_2(CH_2)_2]Ti$ , which is described as a  $Ti^{2+}$   $\eta^3$ -allylcyclopentadienyl  $\eta^4$ -diene complex.<sup>61</sup>

Complex **5** could be isolated from the mixture in 80% yield by extraction into toluene followed by drying under reduced pressure. The toluene-insoluble material could be dried to an orange oil containing **6**,  $[K(2.2.2\text{-cryptand})][C_5Me_4H]$ , and other unidentified  $(C_5Me_4H)$ -containing products that could not be readily separated on a preparative scale. The presence of hydride ligands in **5** and **6** was confirmed by  $^1H$  NMR spectroscopy. The resonances at 15.3 ppm for **5** and 19.8 ppm for **6** are both shifted further downfield from the 12.6 ppm value of **2**. When the reaction was carried out with deuterium, resonances could be seen at 15.3 for **5** and 19.8 ppm for **6** in both the  $^1H$  and  $^2H$  NMR for the terminal hydride/deuteride, indicating H/D exchange.<sup>19,31,32</sup> Once again,  $^2H$  NMR experiments were not helpful in determining with which species the exchange was occurring. Complex **5** reacts with  $CCl_4$  in  $C_6D_6$  to form  $CHCl_3$  and  $(C_5Me_4H)_3ThCl$ ,<sup>25</sup> which was confirmed by  $^1H$  NMR spectroscopy on a sample independently prepared from  $ThCl_4(DME)_2$  and  $KC_5Me_4H$ .

Control experiments were run in order to see if complexes **5** or **6** could be formed in the presence of some, but not all, of the reactants in eq 7. The reaction of  $(C_5Me_4H)_3Th$  with 1 atm of  $H_2$  in THF does produce NMR signals consistent with the generation of a small amount of **5** after 15 h, but too many other products are formed to make this a useful route to **5**. Interestingly, in a reaction of  $(C_5Me_4H)_3Th$  with  $KC_8$  and  $H_2$  without 2.2.2-cryptand, the initially purple solution never turns blue, as with the reaction described in eq 7, and there is no evidence for the formation of any thorium hydride complexes. Complex **6** is one of many products formed when  $(C_5Me_4H)_3Th$  is treated with  $KC_8$  in the presence of 2.2.2-cryptand, as identified

by the 19.83 ppm hydride resonance in the  $^1H$  NMR spectrum. This reaction produces a transient green solution, possibly  $[K(2.2.2\text{-cryptand})][(C_5Me_4H)_3Th]$ , that quickly turns pale yellow.

**Structure of  $(C_5Me_4H)_3ThH$ , **5**.** Complex **5** has a structure (Figure 9) similar to that of  $Cp^*_3ThH$ , **2**,  $(C_5Me_5)_3ThH$ ,<sup>3</sup> and  $(C_5H_3^tBu)_3ThH$ .<sup>4</sup> The three  $C_5Me_4H$  ring centroids define a plane around thorium, and the hydride ligand is disordered on either side. The 2.562 Å Th–( $C_5Me_4H$  ring centroid) distances in **5** are similar to the 2.54, 2.58, and 2.61 Å distances in **2**,  $(C_5H_3^tBu)_3ThH$ ,<sup>4</sup> and  $(C_5Me_5)_3ThH$ ,<sup>3</sup> respectively, and all have 120° ( $C_5Me_4H$  ring centroid)–Th–( $C_5Me_4H$  ring centroid) angles.

**Structure of  $[K(2.2.2\text{-Cryptand})]\{(C_5Me_4H)_2[\eta^1:\eta^5\text{-}C_5Me_3H(CH_2)]ThH\}$ , **6**.** Complex **6** is also a  $(C_5R_5)_3ThH$  complex like **2** and **5** except that one ring is a chelate. This creates some asymmetry in the structure, and the 117.7, 118.6, and 123.6° (ring centroid)–Th–(ring centroid) angles are not exactly 120°. However, they sum to 359.9°, and the Th metal center is only 0.0684 Å out of the plane of the three ring centroids. The 2.523 Å Th–( $\eta^5$ -ring centroid) distance for the chelating  $[\eta^1:\eta^5\text{-}C_5Me_3H(CH_2)]^{2-}$  cyclopentadienyl ligand in **6** is substantially shorter than the 2.614 and 2.637 Å distances for the other two rings. This shorter bond length is consistent with this ligand carrying a formal  $-2$  charge compared to  $-1$  for the other cyclopentadienyl ligands. In comparison, the Th–(ring centroid) distances in  $(C_5Me_4H)_4[\mu\text{-}\eta^1:\eta^5\text{-}C_5Me_3H(CH_2)]_2Th_4(\mu\text{-}H)_4(\mu_3\text{-}H)$ , which has two formally nine-coordinate and two formally 11-coordinate metal centers, range from 2.526 to 2.568 Å, with the smallest distances for the monoanionic  $(C_5Me_4H)^{1-}$  ligands on the nine-coordinate thorium atoms. The C6 carbon atom of the methylene group derived from a methyl group by C–H activation in **6** shows a displacement of 0.649 Å from the plane formed by the five carbons of the Cp ring.



## DISCUSSION

The overall conversion of the  $6d^2$   $\text{Th}^{2+}$  reagent,  $[\text{K}(18\text{-crown-6})(\text{THF})_2][\text{Cp}''_3\text{Th}]$ , **1**, to the  $\text{Th}^{4+}$  hydride,  $\text{Cp}''_3\text{ThH}$ , **2**, involves a net two-electron transformation of  $\text{H}^{1+}$  to  $\text{H}^{1-}$ . Direct protonation of **1** by  $[\text{Et}_3\text{NH}][\text{BPh}_4]$  to form  $\text{KBPh}_4$  and **2** is conceivable, but the presence of the  $6d^1$   $\text{Th}^{3+}$  byproduct,  $\text{Cp}''_3\text{Th}$ ,<sup>11</sup> indicates that one-electron reaction pathways from **1** are operative in this reaction. Although the reaction pathway is not known, some possibilities can be considered less likely. A one-electron reduction of  $[\text{Et}_3\text{NH}][\text{BPh}_4]$  by **1** could form  $\text{KBPh}_4$ , the observed  $\text{Cp}''_3\text{Th}$ , and  $\text{H}_2$ , but examination of the reaction of **1** with  $\text{H}_2$  shows that it forms the bimetallic mixed-valent complex,  $[\text{K}(18\text{-crown-6})(\text{Et}_2\text{O})][\text{Cp}''_2\text{ThH}_2]_2$ , **3**, and not **2**. Complex **2** could form from **3** by oxidation with  $\text{AgBPh}_4$ , but this is unlikely in the reducing environment of eq 4. Since  $\text{Cp}''_3\text{Th}$  does not react with either  $\text{H}_2$  or  $[\text{Et}_3\text{NH}][\text{BPh}_4]$ , this can also be ruled out as a route to **2**.

The pathway of the reaction of the  $\text{Th}^{2+}$  complex, **1**, with  $\text{H}_2$  to form mixed-valent **3** (eq 6) is also unclear. The net reaction of **1** to **3** involves a four-electron reduction of two molecules of  $\text{H}_2$  to form the four hydride ligands in **3**. The  $\text{Th}^{4+}$  and  $\text{Th}^{3+}$  ions in **3** formally arise from a net three-electron oxidation of two  $\text{Th}^{2+}$  ions. Observation of the  $\text{Th}^{3+}$  byproduct,  $\text{Cp}''_3\text{Th}$ , again suggests one electron pathways are present, and this redox reaction could provide the fourth reducing equivalent needed in the net reaction. If divalent **1** initially reduced  $\text{H}_2$  to a  $\text{Th}^{4+}$  dihydride and it formed a dimer,  $[\text{Cp}''_2\text{ThH}_2]_2$ , analogous to the known  $[(\text{C}_5\text{Me}_5)_2\text{ThH}(\mu\text{-H})]_2$ ,<sup>1,20</sup> reduction by another equivalent of **1** could form the mixed-valent **3** with the  $\text{Cp}''_3\text{Th}$  byproduct. In such a scenario, the  $\text{Th}^{2+}$  complex is formally acting as both a one- and two-electron reductant.

Compounds **3** and **4** are the first known mixed-valent molecular compounds of thorium. This is a consequence of the rare nature of any oxidation state other than +4 for this metal. Since this complex appears to have localized oxidation states, the Robin–Day classification<sup>62</sup> would be type I. The  $6d^1$   $\text{Th}^{3+}$  center in **3** can be compared with those in the five other crystallographically characterized  $\text{Th}^{3+}$  complexes,  $\text{Cp}''_3\text{Th}$ ,<sup>10,11,53</sup>  $[\text{C}_5\text{H}_3(\text{SiMe}_2^t\text{Bu})_2]_3\text{Th}$ ,<sup>10</sup>  $(\text{C}_5\text{Me}_4\text{H})_3\text{Th}$ ,<sup>9</sup>  $[\text{K}(\text{DME})_2]\text{-}\{[\text{C}_8\text{H}_6(\text{SiMe}_2^t\text{Bu})_2\text{-}1,4]_2\text{Th}\}$ ,<sup>12</sup> and  $(\text{C}_5\text{Me}_5)_2[\text{PrNC}(\text{Me})\text{-N}^t\text{Pr}]\text{Th}$ .<sup>13</sup> In each of the latter five compounds, the polydentate ligands provide a coordination environment such that a  $d_z^2$  orbital can be populated. Since the DFT calculations on **3** also show a  $d_z^2$ -like orbital as the HOMO on the  $\text{Th}^{3+}$  center,  $\text{Th}_2$  (Figure 6a), it appears that the  $[\text{Cp}''_2(\mu\text{-H}_3)]^{5-}$  ligand set in **3** can also provide a suitable coordination environment for this electron configuration.

The reactions of the new thorium hydrides with  $\text{AgBPh}_4$  emphasize the differences conferred by the ancillary cyclopentadienyl ligands. Oxidation of **4** forms the bis(cyclopentadienyl) dimer  $[(\text{C}_5\text{Me}_5)_2\text{ThH}(\mu\text{-H})]_2$ ,<sup>1,20</sup> while the oxidation of **3** forms the tris(cyclopentadienyl) monomer,  $\text{Cp}''_3\text{ThH}$ . This is consistent with the plethora of known bis(pentamethylcyclopentadienyl)actinide complexes and the crowded nature of the tris complexes,  $(\text{C}_5\text{Me}_5)_3\text{M}$ .<sup>3,63–67</sup> It is interesting that, while the  $\text{Th}^{3+}/\text{Th}^{4+}$   $\text{Cp}''$ -ligated complex, **3**, is an isolable complex, the  $\text{Th}^{4+}/\text{Th}^{4+}$  analogue is not isolated by oxidation of **3**, as in the case with the oxidation of **4**.

## CONCLUSION

Investigation of the reactivity of the first example of a  $6d^2$   $\text{Th}^{2+}$  complex,  $[\text{K}(18\text{-crown-6})(\text{THF})_2][\text{Cp}''_3\text{Th}]$ , **1**, with hydrogen

has led to the first example of a mixed-valent  $\text{Th}^{3+}/\text{Th}^{4+}$ ,  $[\text{K}(18\text{-crown-6})(\text{Et}_2\text{O})][\text{Cp}''_2\text{ThH}_2]_2$ , **3**. Complex **1** has also provided the first synthetic pathway to the bis(trimethylsilyl)cyclopentadienyl hydride,  $\text{Cp}''_3\text{ThH}$ , **2**. Exploration of analogous chemistry with  $(\text{C}_5\text{Me}_5)^{1-}$  and  $(\text{C}_5\text{Me}_4\text{H})^{1-}$  complexes has led to another example of a mixed-valent complex  $[\text{K}(18\text{-crown-6})(\text{THF})][(\text{C}_5\text{Me}_5)_2\text{ThH}]_2$ , **4**, and the first thorium complex with a tuck-in tetramethylcyclopentadienyl dianion,  $[\text{K}(2.2.2\text{-cryptand})]\{(\text{C}_5\text{Me}_4\text{H})_2[\eta^1:\eta^5\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2)]\text{ThH}\}$ , **6**. Isolation of  $(\text{C}_5\text{Me}_4\text{H})_3\text{ThH}$ , **5**, along with **2** means that tris(cyclopentadienyl)thorium hydrides are now known with  $(\text{C}_5\text{Me}_5)^{1-}$ ,<sup>3</sup>  $(\text{C}_5\text{Me}_4\text{H})^{1-}$ ,  $(\text{C}_5\text{H}_3^t\text{Bu}_2)^{1-}$ ,<sup>4</sup> and  $[\text{C}_5\text{H}_3(\text{SiMe}_3)_2]^{1-}$  ligands.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b11508.

Experimental and computational details; crystallographic data collection, structure solution, and refinement (PDF)  
 Crystallographic data for **2**, CCDC 1434238 (CIF)  
 Crystallographic data for **3**, CCDC 1434239 (CIF)  
 Crystallographic data for **5**, CCDC 1434240 (CIF)  
 Crystallographic data for **6**, CCDC 1434241 (CIF)

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### Notes

The authors declare no competing financial interest.

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