

Actinide Metallocene Hydride Chemistry: C–H Activation in Tetramethylcyclopentadienyl Ligands to Form $[\mu-\eta^5\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2)\text{-}\kappa\text{C}]^{2-}$ Tuck-over Ligands in a Tetrathorium Octahydride Complex

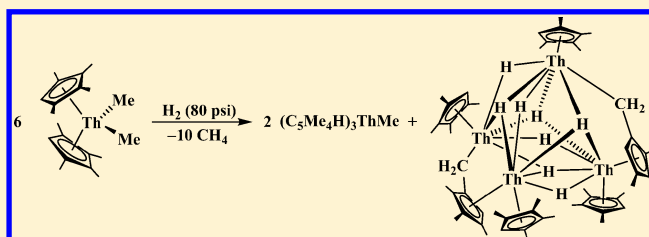
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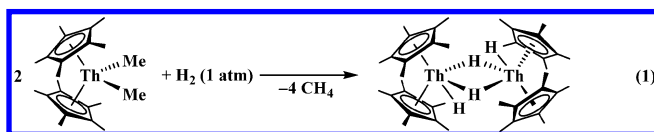
Supporting Information

ABSTRACT: Hydrogenolysis of the dimethyl actinide metallocenes $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ume}_2$ and $(\text{C}_5\text{Me}_4\text{H})_2\text{AnMe}_2$ (An = Th, U) was examined for comparison with the hydrogenolysis of $(\text{C}_5\text{Me}_5)_2\text{AnMe}_2$ that forms the hydrides $[(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$, $[(\text{C}_5\text{Me}_5)_2\text{UH}_2]_2$, and $[(\text{C}_5\text{Me}_5)_2\text{UH}]_2$. Parallel reactivity is not found with the $(\text{C}_5\text{Me}_4\text{SiMe}_3)^-$ and $(\text{C}_5\text{Me}_4\text{H})^-$ complexes. Instead, this study led to the first example of a “tuck-over” $[\mu-\eta^5\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2)\text{-}\kappa\text{C}]^{2-}$ dianion derived from $(\text{C}_5\text{Me}_4\text{H})^-$ ligands by C–H bond activation and rare examples of a polymetallic thorium polyhydride compound and an organometallic Th^{3+} complex. $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ume}_2$ reacts with H_2 to form the bis(tethered alkyl) complex $(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2\text{-}\kappa\text{C})_2\text{U}$, a product of C–H bond activation of the silylmethyl groups. The only identifiable product of hydrogenolysis of $(\text{C}_5\text{Me}_4\text{H})_2\text{Ume}_2$ is $(\text{C}_5\text{Me}_4\text{H})_3\text{U}$. The first thorium complex of $(\text{C}_5\text{Me}_4\text{H})^-$ was synthesized by reaction of 2 equiv of $(\text{C}_5\text{Me}_4\text{H})\text{MgCl}(\text{THF})$ with $\text{ThBr}_4(\text{THF})_4$ to produce $(\text{C}_5\text{Me}_4\text{H})_2\text{ThBr}_2$. This complex reacts with MeLi to make $(\text{C}_5\text{Me}_4\text{H})_2\text{ThMe}_2$. The latter complex reacts with H_2 to form the ligand redistribution product $(\text{C}_5\text{Me}_4\text{H})_3\text{ThMe}$ and the tetrametallic octahydride tuck-over complex $(\text{C}_5\text{Me}_4\text{H})_4[\mu-\eta^5\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2)\text{-}\kappa\text{C}]_2\text{Th}_4(\mu\text{-H})_4(\mu_3\text{-H})_4$. For comparison with the $(\text{C}_5\text{Me}_4\text{H})_3\text{U}$ product, the thorium analogue, $(\text{C}_5\text{Me}_4\text{H})_3\text{Th}$, was synthesized by potassium reduction of a $[(\text{C}_5\text{Me}_4\text{H})_3\text{Th}][\text{BPh}_4]$ intermediate obtained in situ from $(\text{C}_5\text{Me}_4\text{H})_3\text{ThMe}$ and $[\text{HNEt}_3][\text{BPh}_4]$. $(\text{C}_5\text{Me}_4\text{H})_3\text{Th}$ can also be prepared from KC_8 and $(\text{C}_5\text{Me}_4\text{H})_3\text{ThBr}$, obtained from $\text{KC}_5\text{Me}_4\text{H}$ and $\text{ThBr}_4(\text{THF})_4$.

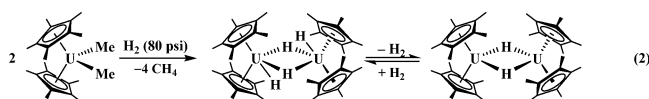


INTRODUCTION

The formation of isolable and crystalline organoactinide hydride complexes was first demonstrated by Marks et al. utilizing the bis(pentamethylcyclopentadienyl) ligand set that has dominated the organometallic chemistry of the f elements.^{1,2} The uranium and thorium hydrides $[(\text{C}_5\text{Me}_5)_2\text{UH}_2]_2$ and $[(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$ were synthesized from straightforward hydrogenation of dimethyl precursors $(\text{C}_5\text{Me}_5)_2\text{AnMe}_2$ (An = Th, U). In the thorium case, eq 1, the only product is the Th^{4+} hydride.^{1–3}



With uranium, as shown in eq 2, the initially formed U^{4+} hydride loses H_2 to form a mixture containing a U^{3+} hydride.^{1,2,4} The difference in the two systems reflects the fact that Th^{3+} is not



nearly as accessible as U^{3+} . In fact, Th^{3+} complexes are relatively rare.^{5–8}

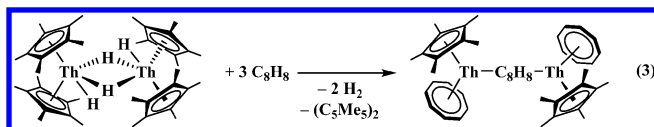
Since their discovery, the bis(pentamethylcyclopentadienyl) actinide metallocene hydride complexes have been extensively studied both experimentally^{2,4,9–26} and theoretically.²⁷ Reactivity studies on $[(\text{C}_5\text{Me}_5)_2\text{UH}_2]_2$ and $[(\text{C}_5\text{Me}_5)_2\text{ThH}_2]_2$ have revealed that these hydride complexes engage in traditional electropositive metal hydride chemistry^{2,14,15,17–26} and can also act as four-, six-, and eight-electron reductants⁹ in reactions involving a $\text{H}^- \rightarrow \frac{1}{2} \text{H}_2 + \text{e}^-$ half-reaction. The redox behavior of the hydride ligands enables reduction reactivity to occur with complexes of the redox-inactive Th^{4+} , as shown in the reduction of 1,3,5,7-cyclooctatetraene, eq 3.⁹

Although hydrides of the $[(\text{C}_5\text{Me}_5)_2\text{An}]^{2+}$ metallocene unit have been heavily investigated, relatively few examples of bis(cyclopentadienyl) actinide hydrides with ligands other than $(\text{C}_5\text{Me}_5)^-$ have been crystallographically characterized.^{13,28} Tris(cyclopentadienyl) actinide hydrides $[(\text{C}_5\text{R}_5)_3\text{AnH}]^{n-}$ (R = H, silyl, alkyl; $n = 0, 1$) are known,^{13,29–35} but bis(cyclopentadienyl)

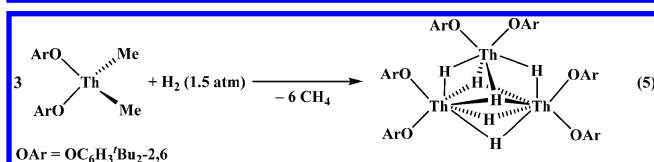
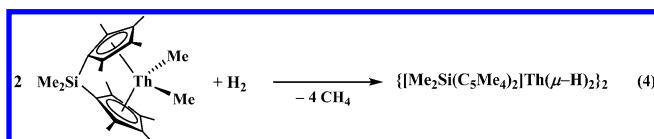
Received: August 22, 2013

Published: October 23, 2013





variants are rare. One involves the chelating silylalkylbis-(tetramethylcyclopentadienyl) ligand, $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]^{2-}$, which has been employed to generate $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Th}(\mu\text{-H})_2\}_2$, eq 4.¹⁸ The popular aryloxy ancillary ligand $(2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3\text{O})^-$, $(\text{ArO})^-$, has also been utilized with thorium to make the inorganic polyhydride $(2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_6\text{Th}_3(\mu\text{-H})_4(\mu_3\text{-H})_2$, eq 5.³⁶



Recently, it has become clear in actinide chemistry, as well as in transition metal and lanthanide chemistry, that small changes in polyalkylated cyclopentadienyl complexes can have large effects on the chemistry.^{37–41} For example, changing from $(\text{C}_5\text{Me}_5)^-$ to $(\text{C}_5\text{Me}_4\text{H})^-$ had a major effect in the dinitrogen reduction chemistry of zirconium metallocenes,³⁸ and $(\text{C}_5\text{Me}_4\text{H})^-$ proved to be the key ligand in the isolation of the first $(\text{NO})^-$ complex of an f element.⁴¹

Efforts to explore the uranium chemistry of the $(\text{C}_5\text{Me}_4\text{H})^-$ ligand^{42–45} and the $(\text{C}_5\text{Me}_4\text{SiMe}_3)^-$ group^{46–48} have now led to an exploration of the synthesis of metallocene hydrides with these cyclopentadienyl ligands. We report here on the hydrogenolysis reactions analogous to eqs 1 and 2 with the dimethyl actinide metallocene complexes of $(\text{C}_5\text{Me}_4\text{SiMe}_3)^-$ and $(\text{C}_5\text{Me}_4\text{H})^-$, as well as theoretical studies on the latter system. These experiments have led to a new type of organothorium polyhydride that contains the first example of “tuck-over”^{10,11,49–52} $[\mu\text{-}\eta^5\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2\text{-}\kappa\text{C})]^{2-}$ ligands derived from $(\text{C}_5\text{Me}_4\text{H})^-$ ligands by C–H bond activation. Metalation of methyl groups in $(\text{C}_5\text{Me}_5)^-$ ligands is well known^{11,49–55} and includes examples with uranium^{11,54} and thorium,⁵⁶ but to our knowledge, this is the first example of a metalated tetramethylcyclopentadienyl ligand. The byproduct of the thorium reaction proved to be a useful precursor for the preparation of a rare organometallic Th^{3+} complex^{5–8} that is also reported here.

EXPERIMENTAL DETAILS

The syntheses and manipulations described below were conducted with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques under an Ar atmosphere unless otherwise specified. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves. C_6D_6 (Cambridge Isotope Laboratories) was dried over NaK alloy, degassed by three freeze–pump–thaw cycles, and vacuum transferred before use. $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ume}_2$,⁴⁶ $(\text{C}_5\text{Me}_4\text{H})_2\text{Ume}_2$,⁴² $(\text{C}_5\text{Me}_4\text{H})\text{MgCl}(\text{THF})$,⁴⁵ $\text{ThBr}_4(\text{THF})_4$,⁵⁷ and potassium graphite (KC_8) ⁵⁸ were prepared as previously reported. LiMe was obtained as a 2 M diethyl ether solution, and the solvent was removed under reduced pressure to yield bright white solid LiMe before use. Ultra-high-purity H_2 was purchased from Airgas and used as received. NMR experiments were

conducted with a Bruker DRX 500 MHz spectrometer at 298 K unless otherwise stated. Infrared spectra were recorded as KBr pellets on a Varian 1000 FT-IR Scimitar Series spectrometer. Elemental analyses were performed with a Perkin-Elmer 2400 CHNS elemental analyzer. X-band EPR spectra were recorded on a Bruker 300 spectrometer equipped with an Oxford ESR-910 liquid helium cryostat and a dual-mode microwave cavity.

Reaction of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ume}_2$, 1, with H_2 . A red solution of $(\text{C}_5\text{Me}_4\text{SiMe}_3)_2\text{Ume}_2$ (224 mg, 0.342 mmol) in toluene (10 mL) was added to a Fisher-Porter vessel and charged with 80 psi of H_2 . After 24 h, the solution was red-brown. The system was evacuated, and the solvent was removed to yield a tacky brown-red solid. ^1H NMR analysis of this crude mixture showed the major product to be the previously reported complex $(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3\text{CH}_2\text{-}\kappa\text{C})_2\text{U}$, 2.⁴⁶ Washing the crude material with cold hexane gave pure 2 (197 mg, 93%) by ^1H NMR spectroscopy.

Reaction of $(\text{C}_5\text{Me}_4\text{H})_2\text{Ume}_2$, 3, with H_2 . A red solution of $(\text{C}_5\text{Me}_4\text{H})_2\text{Ume}_2$ (86 mg, 0.17 mmol) in toluene (10 mL) was added to a Fisher-Porter vessel and charged with 80 psi of H_2 . After 24 h, the solution was black. The apparatus was evacuated, and the solvent was removed to yield a tacky black solid (70 mg). ^1H NMR analysis of this crude mixture showed resonances for the previously reported complex $(\text{C}_5\text{Me}_4\text{H})_3\text{U}$,²⁴ 4, as well as several other resonances between +50 and –50 ppm. Washing the crude material with cold hexane gave pure 4 (35 mg, 0.058 mmol) by ^1H NMR spectroscopy. Crystalline samples of the other product(s) could not be obtained.

$(\text{C}_5\text{Me}_4\text{H})_2\text{ThBr}_2$, 5. In a glovebox containing coordinating solvents, $(\text{C}_5\text{Me}_4\text{H})\text{MgCl}(\text{THF})$ (3.12 g, 12.3 mmol) was added to $\text{ThBr}_4(\text{THF})_4$ (5.00 g, 5.95 mmol) in toluene (250 mL) in a 500 mL Schlenk flask equipped with a condenser and a gas inlet. This apparatus was removed from the glovebox and heated to reflux for two days under nitrogen on a Schlenk line. The solvent was then removed under reduced pressure to yield a tacky solid, and the apparatus was brought into a glovebox without coordinating solvents. The tacky solid was dissolved in toluene and filtered to remove insoluble material. The solvent was removed under reduced pressure to yield 5 as a white powder (2.9 g, 77%). Crystals suitable for X-ray diffraction were grown from a saturated solution in toluene at -35°C . ^1H NMR (C_6D_6): δ 5.70 (s, 2H, $\text{C}_5\text{Me}_4\text{H}$), 2.16 (s, 12H, $\text{C}_5\text{Me}_4\text{H}$), 2.05 (s, 12H, $\text{C}_5\text{Me}_4\text{H}$). ^{13}C NMR (C_6D_6): δ 132.28 ($\text{C}_5\text{Me}_4\text{H}$), 129.68 ($\text{C}_5\text{Me}_4\text{H}$), 117.79 ($\text{C}_5\text{Me}_4\text{H}$), 13.88 ($\text{C}_5\text{Me}_4\text{H}$), 12.78 ($\text{C}_5\text{Me}_4\text{H}$). IR (cm^{-1}): 2974m, 2911s, 2860s, 2730w, 1498m, 1475m, 1434m, 1388s, 1314m, 1147w, 1026m, 830m, 801vs, 605w. Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{Br}_2\text{Th}$: C, 34.09; H, 4.13. Found: C, 34.21; H, 3.79.

$(\text{C}_5\text{Me}_4\text{H})_2\text{ThMe}_2$, 6. LiMe (50 mg, 2.3 mmol) was added to a stirred solution of 5 (520 mg, 0.820 mmol) in toluene (20 mL). An excess of LiMe was used since this has been observed to give higher yields. After 16 h, a white precipitate was removed by centrifugation, and the solvent was removed under vacuum to yield 6 as a pale yellow, microcrystalline solid (340 mg, 82%). Crystals suitable for X-ray diffraction were grown from a saturated toluene solution at -35°C . ^1H NMR (C_6D_6): δ 5.38 (s, 2H, $\text{C}_5\text{Me}_4\text{H}$), 2.00 (s, 12H, $\text{C}_5\text{Me}_4\text{H}$), 1.98 (s, 12H, $\text{C}_5\text{Me}_4\text{H}$), –0.18 (s, 6H, Me). ^{13}C NMR (C_6D_6): δ 125.32 ($\text{C}_5\text{Me}_4\text{H}$), 125.09 ($\text{C}_5\text{Me}_4\text{H}$), 113.62 ($\text{C}_5\text{Me}_4\text{H}$), 70.55 (Me), 13.08 ($\text{C}_5\text{Me}_4\text{H}$), 11.49 ($\text{C}_5\text{Me}_4\text{H}$). Anal. Calcd for $\text{C}_{20}\text{H}_{32}\text{Th}$: C, 47.61; H, 6.39. Found: C, 47.89; H, 6.52.

Reaction of $(\text{C}_5\text{Me}_4\text{H})_2\text{ThMe}_2$, 6, with H_2 . In a glovebox, a solution of $(\text{C}_5\text{Me}_4\text{H})_2\text{ThMe}_2$ (400 mg, 0.50 mmol) in toluene (8 mL) was placed into a Fisher-Porter vessel. The vessel was attached to a pressure manifold in a hood and charged with 80 psi of H_2 . After three days, the apparatus was evacuated, and the solvent was removed under reduced pressure to yield a yellow oil. The oil was washed with 2 mL of hexane, leaving $(\text{C}_5\text{Me}_4\text{H})_3\text{ThMe}$, 7, as a white solid (227 mg, 55%). ^1H NMR (C_6D_6): δ 5.25 (s, $\Delta\nu_{1/2} = 2$ Hz, 3H, $\text{C}_5\text{Me}_4\text{H}$), 2.10 (s, $\Delta\nu_{1/2} = 2$ Hz, 18H, $\text{C}_5\text{Me}_4\text{H}$), 1.93 (s, $\Delta\nu_{1/2} = 2$ Hz, 18H, $\text{C}_5\text{Me}_4\text{H}$), 0.26 (s, $\Delta\nu_{1/2} = 2$ Hz, 3H, Me). ^{13}C NMR (C_6D_6): δ 118 (s, $\text{C}_5\text{Me}_4\text{H}$), 13.5 (s, $\text{C}_5\text{Me}_4\text{H}$), 12.8 (s, $\text{C}_5\text{Me}_4\text{H}$). IR (cm^{-1}): 2918s, 2864s, 2772w, 1437w, 1381m, 1327w, 1280w, 1144w, 1097m, 1021w, 783s, 728w, 694w, 569w, 497m cm^{-1} . Anal. Calcd for $\text{C}_{28}\text{H}_{42}\text{Th}$: C, 55.07; H, 6.93. Found: C, 54.24; H, 6.77.

The other product isolated in this reaction is $(C_5Me_4H)_4[\mu-\eta^5-C_5Me_3H(CH_2)-\kappa C]_2Th_4(\mu-H)_4(\mu_3-H)_4$, **8**, obtained from the hexane wash of **7** by cooling these solutions to $-35^\circ C$. X-ray quality crystals of **8** were obtained from concentrated hexane solutions at $-35^\circ C$. Detailed characterization of **8** has been challenging since solutions of crystals are contaminated with **7** and other alkane-soluble products containing $(C_5Me_4H)^-$ ligands. The IR spectrum of samples of **8** contains a resonance at 1108 cm^{-1} in the region expected for actinide hydride stretches; for example, $[(C_5Me_5)_2ThH_2]_2$ has Th–H absorptions at 1406, 1361, 1215, and 1114 cm^{-1} .²

$(C_5Me_4H)_3ThBr$, **9.** $ThBr_4(THF)_4$ (960 mg, 1.14 mmol) was dissolved in toluene (80 mL) in a 250 mL round-bottom flask capped with a greaseless high-vacuum stopcock. It was charged with KC_5Me_4H (732 mg, 4.57 mmol) and a stirbar, evacuated to the vapor pressure of the solvent, sealed, and placed in an oil bath at $100^\circ C$. An excess of KC_5Me_4H was used since this has been observed to give higher yields. After stirring for 48 h, the temperature was lowered and the system evacuated to dryness before being brought inside a glovebox. The solids were extracted with toluene, and the solution was centrifuged to remove white solids and yield a clear solution. The supernatant was dried under reduced pressure to yield $(C_5Me_4H)_3ThBr$, **9** (512 mg, 66%). 1H NMR (C_6D_6): δ 5.71 (s, 3H, C_5Me_4H), 2.12 (s, 18H, C_5Me_4H), 2.08 (s, 18H, C_5Me_4H). ^{13}C NMR (C_6D_6): δ 130.3 (s, C_5Me_4H), 120.6 (s, C_5Me_4H), 13.9 (s, C_5Me_4H), 13.8 (s, C_5Me_4H). IR (cm^{-1}): 2910s, 2860s, 2724w, 1571w, 1438w, 1375m, 1321w, 1260w, 1017m, 790s, 728w cm^{-1} . Anal. Calcd for $C_{27}H_{39}ThBr$: C, 48.00; H, 5.82. Found: C, 48.39; H, 5.46. Single crystals suitable for X-ray analysis were grown in concentrated toluene solutions at $-35^\circ C$.

$(C_5Me_4H)_3Th$, **10.** Addition of $[HNEt_3][BPh_4]$ (42 mg, 0.099 mmol) to a solution of $(C_5Me_4H)_3ThMe$ (40 mg, 0.066 mmol) in toluene (15 mL) generates a bright orange precipitate (99 mg) that presumably contains $[(C_5Me_4H)_3Th][BPh_4]$. A sample of the orange solid (40 mg) was dissolved in 5 mL of THF to give a colorless solution. Addition of freshly prepared KC_8 (8 mg) to the stirred solution caused an immediate color change to dark purple. After stirring for 1 h, the purple solution was filtered to remove black and white insoluble materials, and the solution was placed in a freezer at $-35^\circ C$. After 2 days, dark purple crystals of $(C_5Me_4H)_3Th$ were isolated (12 mg), which were used to identify this complex by X-ray diffraction.

Synthesis of $(C_5Me_4H)_3Th$, **10, from $(C_5Me_4H)_3ThBr$.** KC_8 (105 mg, 0.777 mmol) was slowly added over 1 min to a stirred solution of $(C_5Me_4H)_3ThBr$, **9** (500 mg, 0.74 mmol), in THF (40 mL) that had been chilled in a $-35^\circ C$ freezer for 30 min. An immediate color change from colorless to dark blue/violet was observed along with the appearance of black solids assumed to be graphite. The mixture was stirred for 1 h, centrifuged, and filtered. The insoluble solids were washed with additional THF, and the washings were centrifuged, filtered, and added to the original supernatant. The solvent was removed from the supernatant via reduced pressure to give $(C_5Me_4H)_3Th$, **10**, as a microcrystalline blue/black solid. Single crystals suitable for X-ray diffraction were grown from THF solutions at $-35^\circ C$ (255 mg, 58%). EPR (toluene, room temperature): singlet; $g_{iso} = 1.92$. IR (cm^{-1}): 2965w, 2915s, 2854s, 2719w, 1531w, 1432m, 1378m, 1367m, 1322w, 1138w, 1018m, 973w, 774s cm^{-1} . Anal. Calcd for $C_{27}H_{39}Th$: C, 54.44; H, 6.60. Found: C, 54.38; H, 6.55. UV–vis (toluene) λ_{max} , nm (ϵ , $M^{-1}\text{ cm}^{-1}$): 380 (1400 shoulder), 400 (1600), 522 (7100), 565 (3900), 622 (3400).

X-ray Crystallographic Data. Crystallographic information for complexes **6**, **8**, **9**, and **10** is summarized in Table S10 of the Supporting Information.

Density Functional Calculations. Quantum chemical calculations on $[(C_5Me_4H)_2UH_2]_2$ and $[(C_5Me_4H)_2UH]_2$ were performed using density functional theory (DFT).^{59,60} Starting structures for geometry optimizations were obtained from the available experimental crystal structures of $[(C_5Me_5)_2UH_2]_2$ and $[(C_5Me_5)_2UH]_2$.²⁷ For $[(C_5Me_4H)_2UH_2]_2$ and $[(C_5Me_4H)_2UH]_2$, two initial structures were chosen where the C–H bond of the cyclopentadienyl ring was either pointing toward or away from the U–(μ -H)–U metallic wedge.

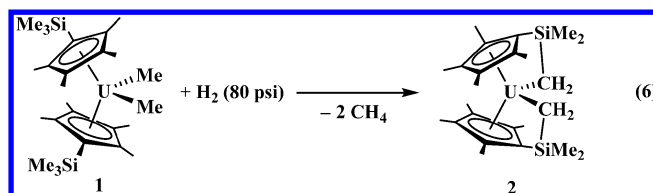
Furthermore, geometry optimizations for $[(C_5Me_4H)_2UH_2]_2$ and $[(C_5Me_4H)UH]_2$ were performed imposing C_2 symmetry constraints.

Geometry optimizations were performed at the DFT level with the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional⁶¹ and a triple- ζ valence plus polarization (def-TZVP)^{62,63} basis set on all atoms. Quasi-relativistic pseudopotentials were used for U atoms with a core of 60 electrons.^{62,64} Additional single-point calculations were performed utilizing a larger def-TZVPP basis set on all atoms in order to accurately determine the dependence of the interconversion energy on the size and quality of the basis set. The tetravalent and trivalent uranium hydride complexes, with $5f^2$ and $5f^3$ uranium configurations, respectively, were assumed to have an open-shell quintet and septet ground states, respectively. Therefore, geometry optimizations were performed solely for these highest spin states. Vibrational harmonic frequencies were calculated analytically to ensure the optimized uranium hydride structures are indeed minima that are not characterized by any imaginary frequencies. The zero-point energies were also included in calculating the interconversion energy. All DFT calculations were performed with the TURBOMOLE 5.10 program package.^{62,65}

Relative energies at the PBE optimized geometries were computed also with the Complete Active Space followed by second-order perturbation theory, CASPT2, method.⁶⁶ All-electron double- ζ valence plus polarization basis sets of ANO type, with relativistic correction (ANO-RCC-VDZP),⁶⁷ were employed. The active space was formed by molecular orbitals that are linear combinations of the U 7s, 6d, and 5f orbitals with the bonding and antibonding π -orbitals on the cyclopentadienyl ligands. The single-point CASPT2 calculations were performed with the MOLCAS 7.3 package.⁶⁸

RESULTS

$(C_5Me_4SiMe_3)_2UME_2$ Reactions. The hydrogenolysis reaction successfully demonstrated with $(C_5Me_5)_2AnMe_2$ ($An = Th, U$) to form $[(C_5Me_5)_2ThH_2]_2$ and $[(C_5Me_5)_2UH_2]_2$, eqs 1 and 2, was examined with $(C_5Me_4SiMe_3)_2UME_2$, **1**. Exposure of toluene solutions of **1** to H_2 at 80 psi did not lead to isolation of a hydride product, but instead the bis(tethered alkyl) metallocene complex $(\eta^5-C_5Me_4SiMe_3)_2U(CH_2CH_2-\kappa C)_2$, **2**, was generated, eq 6. If hydrogenolysis occurred to form a uranium



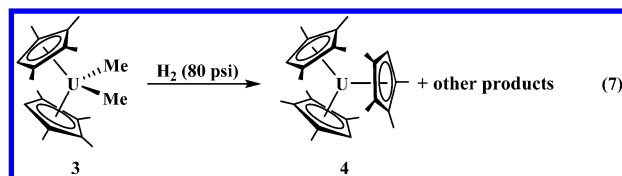
hydride such as $[(C_5Me_4SiMe_3)_2UH_2]_n$, it was not isolable. Complex **2** was previously isolated by heating **1** to $100^\circ C$, which causes C–H bond activation of the trimethylsilyl groups by the methyl ligands to form **2** and methane.⁴⁶ Since hydride ligands can engage in C–H bond activation as well as the methyl groups in **1**, any $[(C_5Me_4SiMe_3)_2UH_2]_n$ formed by hydrogenolysis of **1** could also form **2** by C–H bond activation. The byproduct of this C–H bond activation, H_2 , would not be detectable in this reaction since it is performed under a hydrogen atmosphere. The fact that **2** is formed from **1** at $100^\circ C$, while eq 6 occurs at room temperature, suggests that any uranium hydride compound formed in the reaction of **1** with H_2 contains hydride ligands that are more reactive than the methyl groups in **1**.

This observed reactivity is consistent with the research of Hou et al. on the hydrogenation of $[(\eta^5-C_5Me_4SiMe_3)_2U(\kappa C)-Ln(C_5Me_4SiMe_3)(THF)]$ complexes, where $Ln = Y, Nd, Sm, Dy$, and Lu .⁶⁹ The smaller metals Y, Dy, and Lu yielded isolable $(C_5Me_4SiMe_3)_2LnH$ complexes from exposure to hydrogen, but for the larger metals, Nd and Sm, the unsolvated forms

of the starting materials, the metalated complexes (η^5 -C₅Me₄-SiMe₂CH₂- κ C)Ln(C₅Me₄SiMe₃), were isolated. It was postulated that hydrogenolysis of the tethered alkyl occurred to form a transient hydride species, but it was unstable with the larger metals and subsequently metalated the (C₅Me₄SiMe₃)[−] ligand.⁶⁹ Since eight-coordinate U⁴⁺ has an ionic radius close to that of seven-coordinate Sm³⁺, 1.00 vs 1.02 Å,⁷⁰ respectively, a similar situation may occur in eq 6. Any “[(C₅Me₄SiMe₃)₂UH₂]_n” that formed would be expected to be capable of C–H bond activation.

(C₅Me₄H)₂UMe₂ Reactions. The hydrogenolysis reaction of the tetramethylcyclopentadienyl complex (C₅Me₄H)₂UMe₂,⁴² **3**, also failed to produce a hydride product analogous to the [(C₅Me₅)₂AnH₂]₂ complexes of eqs 1 and 2. A reaction occurred, and several highly soluble paramagnetic products were observed by ¹H NMR spectroscopy, but the U³⁺ complex (C₅Me₄H)₃U,⁴⁵ **4**, is the only product that could be definitively identified, eq 7.

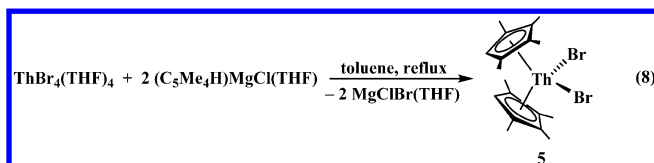
Formation of a U³⁺ product in a U⁴⁺ hydrogenolysis has precedent in eq 2 above.^{1,2,4} If any intermediate “(C₅Me₄H)₂UH₂” is formed in eq 7, it could lose H₂ like the (C₅Me₅)[−] analogue. That



“(C₅Me₄H)₂UH” product would be sterically unsaturated and could ligand redistribute to the observed **4**. Ligand redistribution reactions to form (C₅Me₄H)₃U^{42,43,45} as well as (C₅Me₄H)₃Ln⁷¹ are common. Analogous reactions would not be expected with (C₅Me₅)[−] and (C₅Me₄SiMe₃)[−] ligands since (C₅Me₅)₃U⁷² and (C₅Me₄SiMe₃)₃U⁴⁷ are sterically crowded complexes that can only be made by carefully designed syntheses that leave no other option than to form the tris(cyclopentadienyl) complex. In contrast, with the (C₅Me₄H)[−] ligand, (C₅Me₄H)₃M complexes readily form.

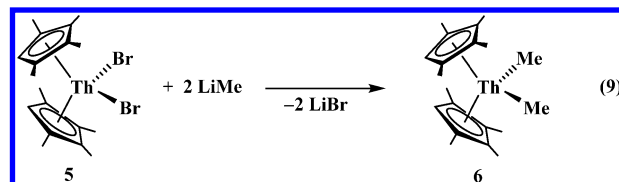
(C₅Me₄H)₂ThMe₂ Reactions. To reduce the possibility of forming An³⁺ byproducts like **4** in eq 7, it was desirable to examine the analogous tetramethylcyclopentadienyl thorium chemistry since Th³⁺ organometallic complexes are rare and not readily formed.^{5–8} However, to our surprise, there were no reports of thorium complexes of the (C₅Me₄H)[−] ligand. This necessitated the synthesis of several (C₅Me₄H)[−] complexes starting from ThBr₄(THF)₄.⁵⁷

(C₅Me₄H)₂ThBr₂, **5**, was prepared from ThBr₄(THF)₄ and 2 equiv of (C₅Me₄H)MgCl(THF) in refluxing toluene, eq 8, in a



manner similar to the synthesis of (C₅Me₅)₂ThBr₂.⁷³ Complex **5** was characterized by standard methods, and X-ray crystallography established the connectivity, but did not provide data good enough for detailed structural analysis.

The reaction of **5** with excess LiMe produces (C₅Me₄H)₂ThMe₂, **6**, according to eq 9, a reaction similar to the formation of (C₅Me₄H)₂UMe₂ and (C₅Me₅)₂AnMe₂.^{2,43} The ¹H NMR spectrum of **6** has a ThMe₂ resonance at −0.18 ppm that is very similar to the −0.19 ppm analogue of (C₅Me₅)₂ThMe₂.² Complex **6** was characterized by standard techniques, and the X-ray crystal



structure showed no unusual structural features, Table 1. The (C₅Me₄H)[−] rings are eclipsed with the hydrogen substituent at the

Table 1. Selected Bond Distances (Å) and Angles (deg) for (C₅Me₄H)₂ThMe₂, **6**, (C₅Me₄H)₄[μ - η^5 -C₅Me₃H(CH₂)- κ C]₂Th₄(μ -H)₄(μ_3 -H)₄, **8**, (C₅Me₄H)₃ThBr, **9**, and (C₅Me₄H)₃Th, **10**, as well as (C₅Me₅)₂ThMe₂,² (C₅Me₅)₃ThH,³⁵ (C₅Me₄H)₃UCl,⁷⁵ and (C₅Me₄H)₃U⁴⁵

| | (Cp centroid)–M | (Cp centroid)–M–(Cp centroid) | M–R/M–X/M–H |
|--|-----------------|-------------------------------|-------------|
| (C ₅ Me ₄ H) ₂ ThMe ₂ , 6 | 2.518 | 135.7 | 2.497(2) |
| (C ₅ Me ₅) ₂ ThMe ₂ | 2.518 | 133.9 | 2.471 |
| (C ₅ Me ₄ H) ₂ UMe ₂ | 2.444 | 134.3 | 2.426(2) |
| 8 , Th1 | 2.560/2.562 | 121.6 | |
| 8 , Th2 | 2.526 | | 2.503(4) |
| 8 , Th3 | 2.534 | | 2.508(4) |
| 8 , Th4 | 2.566/2.568 | 120.1 | |
| (C ₅ Me ₄ H) ₃ ThBr, 9 | 2.576 | 117.7 | 2.8372(8) |
| (C ₅ Me ₅) ₃ ThH | 2.614 | 120.0 | 2.33(13) |
| (C ₅ Me ₄ H) ₃ UCl | 2.520 | 117.9 | 2.637 |
| (C ₅ Me ₄ H) ₃ Th, 10 | 2.551 | 120.0 | |
| (C ₅ Me ₄ H) ₃ U | 2.523 | 120.0 | |

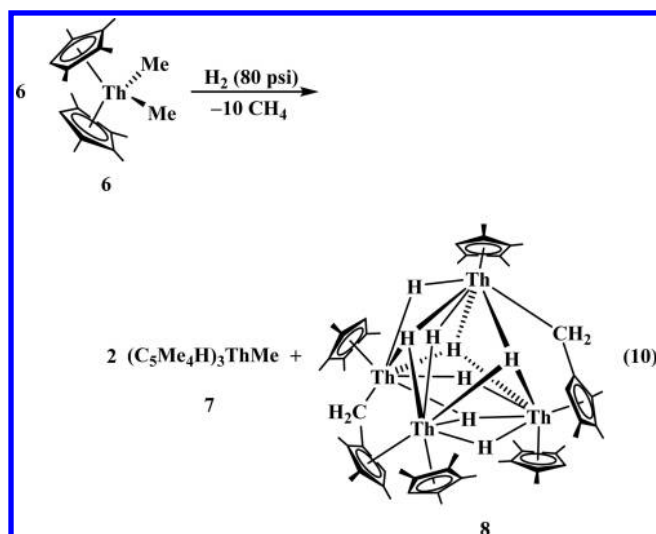
back of the wedge, as found for (C₅Me₄H)₂UCl₂,⁴⁵ (C₅Me₄H)₂UMe₂,⁴² and (C₅Me₄H)₂UMeCl.⁴² This is the optimum orientation to relieve steric crowding.

Hydrogenolysis of **6** gave very different results from eqs 1 and 2. Exposure of toluene solutions of **6** to H₂ (80 psi) generated the tris(cyclopentadienyl)methyl complex (C₅Me₄H)₃ThMe, **7**, in about 55% yield, as well as crystals of a polymetallic polyhydride, (C₅Me₄H)₄[μ - η^5 -C₅Me₃H(CH₂)- κ C]₂Th₄(μ -H)₄(μ_3 -H)₄, **8**, eq 10. Compound **8** was identified by X-ray crystallography, Figure 1.

Compound **7** could be cleanly separated from the reaction mixture since it is less soluble than **8** in hexane. However, isolation of pure samples of **8** has been challenging since **7** is partially soluble in hexane and other unidentified hexane-soluble products are also produced in the reaction in eq 10. Multiple crystallization attempts on samples of **8** from hexane extractions gave crystals that when dissolved for ¹H NMR characterization still contained both **7** and unidentified byproducts in addition to **8**.

The isolation of the tris(ring) complex **7** has parallels to the ligand redistribution reactivity observed in the uranium reaction that forms (C₅Me₄H)₃U in eq 7. The difference in the thorium reaction is that Th³⁺ is not easily generated and (C₅Me₄H)₃Th would not be expected to readily form. A tris(ring) thorium ligand redistribution product does form in eq 10, but it has another ligand. The formation of the three-ring **7** suggests there should be a coproduct with less than two rings per metal. This is the case with **8** since it has six rings for the four metals.

The formation of **8** has parallels with eq 6 in that it is the result of C–H bond activation. However, in **8** it is methyl groups of the (C₅Me₄H)[−] ligand that are metalated to form



$[\text{C}_5\text{Me}_3\text{H}(\text{CH}_2)]^{2-}$ ligands. Metalation of the methyl groups in $(\text{C}_5\text{Me}_5)^-$ ligands is well established^{11,49–55} with both uranium^{11,54} and thorium⁵⁶ examples, but metalation of a tetramethylcyclopentadienyl ligand has not been reported to our knowledge. Metalated $(\text{C}_5\text{Me}_5)^-$ ligands, i.e., $[\text{C}_5\text{Me}_4(\text{CH}_2)]^{2-}$, have been shown to chelate in a “tuck-in”^{55,56,74} mode and bridge in

a “tuck-over” orientation.^{49–53} In **8**, the $[\text{C}_5\text{Me}_3\text{H}(\text{CH}_2)]^{2-}$ ligands “tuck-over” to connect two metals.

Although the ligand redistribution and C–H bond activation have parallels, the tetrathorium octahydride complex **8** represents a new type of organometallic thorium hydride. The most closely related complex in the literature is $(2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_6\text{Th}_3(\mu\text{-H})_4(\mu_3\text{-H})_2$, eq 5, which can be viewed as a trimer of “ $(2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_2\text{ThH}_2$ ”. This makes it similar to $[(\text{C}_5\text{Me}_5)_2\text{ThH}(\mu\text{-H})]_2$, the dimer of “ $(\text{C}_5\text{Me}_5)_2\text{ThH}_2$ ”. Complex **8** differs in that two of the thorium ions, Th2 and Th3, are bound to just one $(\text{C}_5\text{Me}_4\text{H})^-$ ancillary ligand; that is, they are not bis(cyclopentadienyl) metallocene moieties. The other two thorium ions are attached to one $(\text{C}_5\text{Me}_4\text{H})^-$ ligand and the pentahapto part of the bridging $[\mu\text{-}\eta^5\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2)\text{-}\kappa\text{C}]^{2-}$ tuck-over ligand. The bridging methylene groups of the tuck-over ligands, C15 and C42, attach to the thorium ions ligated with only a single $(\text{C}_5\text{Me}_4\text{H})^-$ ligand.

Complex **8** contains a distorted tetrahedron of thorium atoms. The magnitude of the distortion can be seen from the values of the six Th···Th nonbonding distances, which are (in order of decreasing distance in Å) as follows: Th3···Th4, 4.1822(3); Th1···Th2, 4.1707(3); Th1···Th4, 3.8407(3); Th2···Th4, 3.7412(3); Th1···Th3, 3.7192(3); Th2···Th3, 3.6960(3). This broad range of Th···Th distances matches the wide range found in other thorium hydrides: 3.588(1) to 3.818(1) Å in $(2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3\text{O})_6\text{Th}_3(\mu\text{-H})_4(\mu_3\text{-H})_2$,³⁶ 4.007(8) Å in

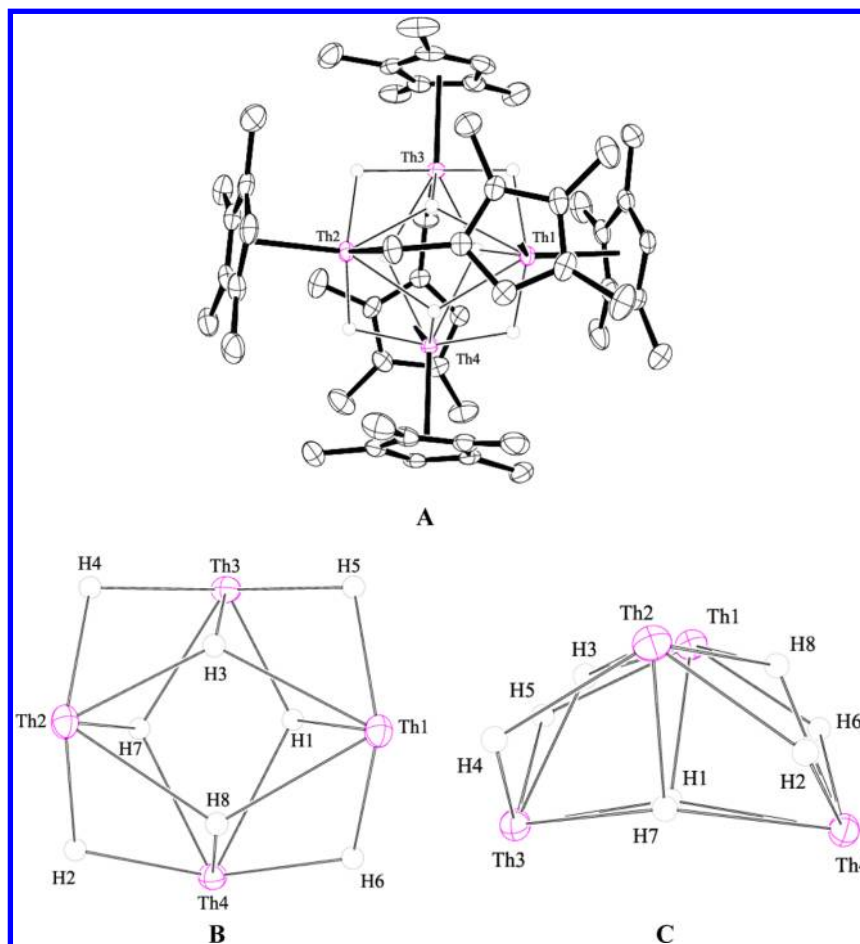


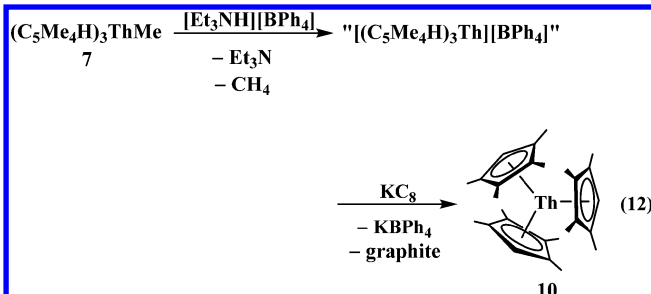
Figure 1. (A) Thermal ellipsoid plot of $(\text{C}_5\text{Me}_4\text{H})_4[\mu\text{-}\eta^5\text{-C}_5\text{Me}_3\text{H}(\text{CH}_2)\text{-}\kappa\text{C}]_2\text{Th}_4(\mu\text{-H})_4(\mu_3\text{-H})_4$, **8**, drawn at the 50% probability level with hydrogen atoms omitted for clarity except for the hydride ligands in the core. (B) Identical orientation of the thorium hydride core with atom labels. (C) Alternative view of the thorium hydride core.

$[(C_5Me_5)_2ThH(\mu-H)]_2$, $2.3632(2)$ Å in $\{[Me_2Si(C_5Me_4)_2]Th(\mu-H)_2\}_2$.¹⁸ The distances are such that the Th2–Th3–Th4 triangle is more compact than the other three faces of the tetrahedron, but this is the only aspect in which this face is special. Each face of the tetrahedron has a μ_3 -H ligand. The other four hydrides bridge four of the six edges of the tetrahedron: Th1–Th3, Th1–Th4, Th2–Th3, and Th2–Th4. The remaining two edges of the tetrahedron, Th1–Th2 and Th3–Th4, are spanned by the tuck-over methylene moieties from the $[\mu-\eta^5-C_5Me_3H(CH_2)-\kappa C]^{2-}$ ligands that lead to the Th2–C15 and Th3–C42 bonds involving the thorium sites with only one $(C_5Me_4H)^-$ ligand.

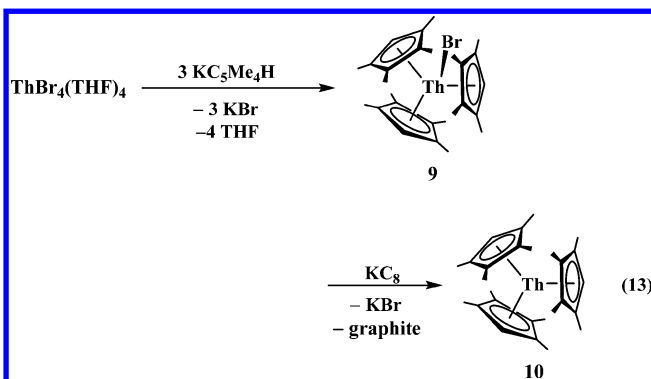
Although the composition of **8** is unusual, most of the structural parameters, Table 1, are similar to those in other thorium hydride complexes.^{3,18,36} For Th1 and Th4, which are ligated by an intact $(C_5Me_4H)^-$ ligand and a $[C_5Me_3H-(CH_2)]^{2-}$ group, the Th–(ring centroid) distances fall in the narrow range 2.560–2.568 Å. These distances are not very different from the 2.518 Å analogue in **6** and the 2.526 and 2.534 Å Th–(ring centroid) distances of mono(cyclopentadienyl) Th2 and Th3 in complex **8**. The 2.503(4) Å Th2–C15 and 2.508(4) Å Th3–C42 metal carbon single-bond distances involving the bridging methylene groups of the $[\mu-\eta^5-C_5Me_3H-(CH_2)-\kappa C]^{2-}$ tuck-over ligands are typical of Th–C bonds^{76,77} such as the 2.497(2) Å Th–Me distance in **6** and the 2.471(8) Å Th–Me length in $(C_5Me_5)_2ThMe_2$.⁷⁶ Although the hydride ligands were located and refined, the relatively large error associated with the Th–H distances does not allow meaningful discussion. The 2.11(5) to 2.56(6) Å values generated by the model of the structural data are consistent with the 2.0(1) to 2.3(1) Å³⁶ range reported for $(2,6\text{-}^iBu_2C_6H_3O)_6Th_3(\mu-H)_4(\mu_3-H)_2$ and the 2.29(3) Å Th–(μ -H) distance for $[(C_5Me_5)_2ThH-(\mu-H)]_2$.³ The most unusual structural parameters in **8** are the 121.6° and 120.1° $[(C_5Me_4H)^- \text{ ring centroid}]$ –Th– $\{[C_5Me_3H-(CH_2)]^{2-} \text{ ring centroid}\}$ angles for Th1 and Th4. These are very small angles for actinide metallocenes and are typically found only in extremely crowded molecules, e.g., the 120° angles in $(C_5Me_5)_3U$ ⁷² and $(C_5Me_5)_3Th$.³⁵ In comparison, the (C_5Me_4H) –Th– (C_5Me_4H) angle in $(C_5Me_4H)_2ThMe_2$, **6**, is 135.7°. The angles in **8** suggest steric crowding around those metallocene units.

Synthesis of $(C_5Me_4H)_3Th$, **10.** Since a major difference between the hydrogenolyses of $(C_5Me_4H)_2UMe_2$ and $(C_5Me_4H)_2ThMe_2$ is the facile formation of $(C_5Me_4H)_3U$, it was of interest to have information about the thorium analogue $(C_5Me_4H)_3Th$, **10**. Accordingly, its synthesis was attempted. The formation of $(C_5Me_4H)_3ThMe$ as a byproduct in the hydrogenolysis of $(C_5Me_4H)_2ThMe_2$, eq 10, provided a convenient starting point for generating **10** in analogy with the synthesis of the bis(cyclopentadienyl) Th^{3+} amidinate, $(C_5Me_5)_2Th[{}^iPrNC(Me)N^iPr]$, shown in eq 11. In that case, a

Th^{4+} methyltriphenylborate salt, formed in situ, was reducible to the Th^{3+} product. In this case, **7** was treated with $[HNEt_3][BPh_4]$ to generate an orange toluene-insoluble material presumably containing $[(C_5Me_4H)_3Th][BPh_4]$ that can be reduced in THF to form $(C_5Me_4H)_3Th$, **10**, eq 12. This was used to make **10** for the first time and obtain its X-ray crystal structure.



Subsequently, an additional synthesis of **10** was developed that involved reduction of a fully characterizable precursor, $(C_5Me_4H)_3ThBr$, **9**, a complex that can be prepared from $ThBr_4(THF)_4$ and excess KC_5Me_4H according to eq 13. In



each case, the KC_8 reductions generate dark purple solutions. Complexes **9** and **10** were identified by X-ray crystallography, Figure 2, Table 1.

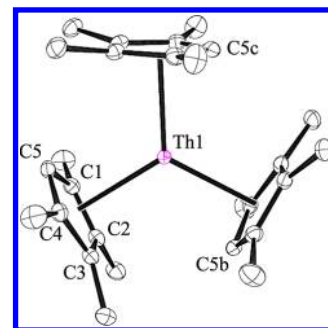
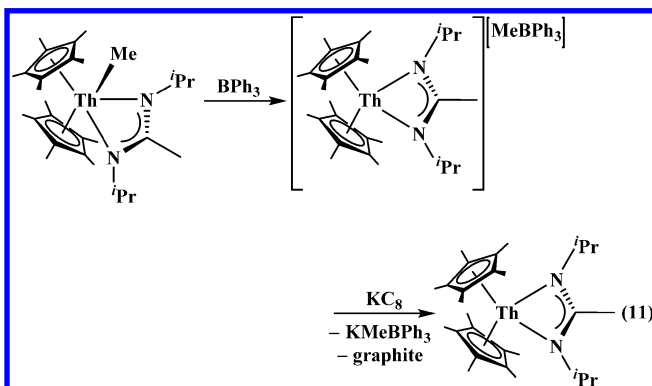


Figure 2. Thermal ellipsoid plot of $(C_5Me_4H)_3Th$, **10**, shown at the 50% probability level with the hydrogen atoms omitted for clarity.

All three rings in the X-ray crystal structure of **10** are equivalent such that the molecule has rigorous trigonal planar symmetry with 120° $(C_5Me_4H \text{ ring centroid})$ –Th– $(C_5Me_4H \text{ ring centroid})$ angles. The rings are staggered with respect to each other so that the H-bearing ring carbon, C5, is in between methyl-substituted carbons, C2 and C3. The 2.551 Å Th– $(C_5Me_4H \text{ ring centroid})$ distance is slightly larger than the 2.518 Å distance in $(C_5Me_4H)_2ThMe_2$, **6**, and less than the



2.614 Å value in sterically crowded $(C_5Me_5)_3ThH$.³⁵ In comparison, $(C_5Me_5)_2Th[PrNC(Me)N^iPr]$ has 2.541 and 2.545 Å Th–(C_5Me_4H ring centroid) distances compared to 2.584 and 2.598 Å analogues in the Th^{4+} complex $(C_5Me_5)_2[PrNC(Me)N^iPr]ThMe$.⁷⁸

The EPR spectrum of **10**, Figure 3, contains a singlet at $g_{iso} = 1.92$ that is consistent with a Th^{3+} oxidation state. The g

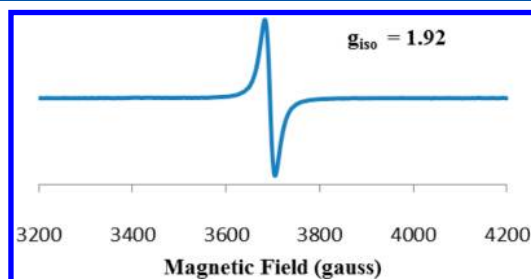


Figure 3. Room-temperature X-band EPR spectrum of a microcrystalline sample of $(C_5Me_4H)_3Th$, **10**, in toluene.

values for the other known Th^{3+} complexes are similar: 1.916 for $[\eta^8-C_8H_6(SiMe_2^tBu)_2-1,4]_2ThK(DME)_2$,^{5,7} 1.910 for both $[C_5H_3(SiMe_2^tBu)_2-1,3]_3Th^6$ and $[C_5H_3(SiMe_3)_2-1,3]_3Th$,^{5,6} and 1.871 for $(C_5Me_5)_2Th[PrNC(Me)N^iPr]$.⁸

The UV–vis spectrum of **10**, Figure 4, is also consistent with those of other Th^{3+} complexes that contain strong absorptions

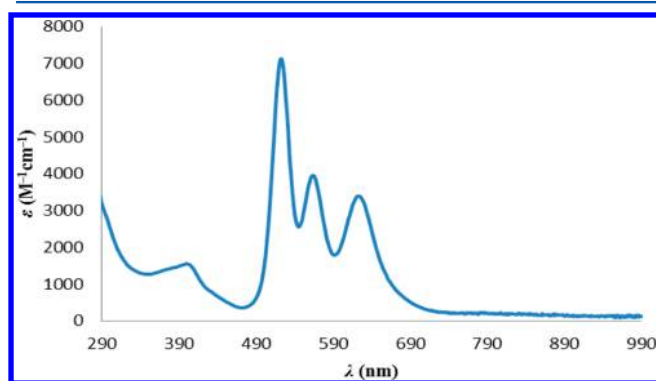
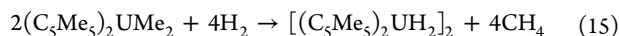
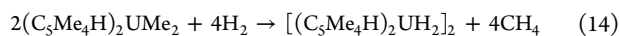


Figure 4. UV–vis spectrum of $(C_5Me_4H)_3Th$, **10**.

in the visible region. These have been attributed in the past to transitions from a $6d^1$ ground state to higher lying orbitals of odd parity.

Theoretical Studies. Density functional theory calculations were performed on the tetramethylcyclopentadienyl uranium system, eq 7, for comparison with the pentamethylcyclopentadienyl analogue, eq 2, to search for a theoretical basis for the differing results. Calculations were carried out on the hydrogenolysis of each dimethyl U^{4+} complex to the corresponding U^{4+} dihydride, i.e., eqs 14 and 15.



The enthalpy of eq 14 is predicted to be exothermic at -64.4 kcal/mol at the electronic energy level and -46.1 kcal/mol when including $\Delta H_{rxn}(ZPE) = 18.3$ kcal/mol. The energies for eq 15 are very similar: at the electronic energy level, the enthalpy is predicted to be -63.2 kcal/mol, which increases to

-44.0 kcal/mol when including the $\Delta H_{rxn}(ZPE) = 19.2$ kcal/mol. Therefore, the enthalpy of the reaction that forms the U^{4+} hydride complexes is exothermic in both cases and predicted to be within 2.0 kcal/mol for $(C_5Me_4H)^-$ vs $(C_5Me_5)^-$.

DFT calculations were also performed on $[(C_5Me_4H)_2UH_2]_2$ and $[(C_5Me_4H)_2UH]_2$ to investigate the structure, vibrational spectra, and interconversion energy for these tetramethylcyclopentadienyl complexes (details in the Supporting Information). The initial geometry optimizations were performed for two structures of $[(C_5Me_4H)_2UH_2]_2$ and $[(C_5Me_4H)_2UH]_2$ where the ring C–H bond was pointing either toward or away from the $U-(\mu-H)_2-U$ metallic wedge, respectively. For both $[(C_5Me_4H)_2UH_2]_2$ and $[(C_5Me_4H)_2UH]_2$, the final optimized structure with the C–H bond pointing away from the $U-(\mu-H)_2-U$ part of the molecule was lower in energy by 2.9 and 4.4 kcal/mol, respectively, based on electronic energies. This puts the H-substituted ring carbon atoms in the most congested spot, which relieves steric crowding overall.

The interconversion of $[(C_5Me_4H)_2UH_2]_2$ to $[(C_5Me_4H)_2UH]_2 + H_2$, similar to eq 2, was predicted to be thermoneutral at 2.1 kcal/mol, based on just the electronic energies. Including the zero-point energy of the reaction ($\Delta H_{rxn}(ZPE) = -1.7$ kcal/mol) results in a marginally endothermic reaction at 0.4 kcal/mol. Furthermore, increasing the quality of the basis set does not alter the reaction energy, which was predicted to be 0.4 kcal/mol, indicating that $[(C_5Me_4H)_2UH_2]_2$ will readily release molecular hydrogen to form $[(C_5Me_4H)_2UH]_2$.

Additionally, these tetramethylcyclopentadienyl energies do not differ considerably from the energies predicted to interconvert the pentamethylcyclopentadienyl complexes, $[(C_5Me_5)_2UH_2]_2$ and $[(C_5Me_5)_2UH]_2$, eq 2, of -2.2 and 2.2 kcal/mol at the CASPT2/ANO-RCC-VDZP and PBE/def-TZVP levels, respectively. The CASPT2 result is marginally exothermic and consistent with the spontaneous release of hydrogen from isolated samples of $[(C_5Me_5)_2UH_2]_2$ and formation of an equilibrium mixture of $[(C_5Me_5)_2UH_2]_2$ and $[(C_5Me_5)_2UH]_2$. On the basis of the reaction thermodynamics of the pentamethylcyclopentadienyl reaction, the $[(C_5Me_4H)_2UH_2]_2/[(C_5Me_4H)_2UH]_2$ interconversion at the CASPT2 level is estimated to be -4 kcal/mol. Moreover, the interconversion energy is not significantly altered by the removal of a single methyl group from the pentamethylcyclopentadienyl ligand, and from a thermodynamic standpoint, there should be no hindrance to the spontaneous release of hydrogen from $[(C_5Me_4H)_2UH_2]_2$ and accompanying formation of $[(C_5Me_4H)_2UH]_2$.

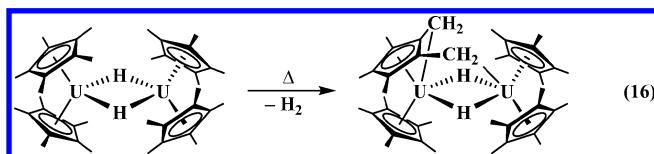
The relative stabilities of the tetravalent $[(C_5Me_4H)_2UH_2]_2$ vs $[(C_5Me_5)_2UH_2]_2$ and trivalent $[(C_5Me_4H)_2UH]_2$ vs $[(C_5Me_5)_2UH]_2$ complexes were determined from an isodesmic reaction approach (Table S3). Considering just the electronic energies, $[(C_5Me_5)_2UH_2]_2$ is more stable than $[(C_5Me_4H)_2UH_2]_2$ by a mere 1.3 kcal/mol. However, including $\Delta H_{rxn}(ZPE) = -4.8$ kcal/mol further increases the stability to 6.0 kcal/mol. Similarly, the trivalent pentamethyl complex $[(C_5Me_5)_2UH]_2$ is more stable than its trivalent tetramethyl analogue $[(C_5Me_4H)_2UH]_2$ by 2.3 kcal/mol at the electronic energy level, which increases to 8.4 kcal/mol when including $\Delta H_{rxn}(ZPE) = -6.0$ kcal/mol. Therefore, in both cases the trivalent and tetravalent pentamethyl hydride complexes are more stable than the tetramethyl analogues by at least 6.0 kcal/mol.

These DFT and CASPT2 studies suggest that the $(C_5Me_4H)^-$ and $(C_5Me_5)^-$ systems are very similar. The calculations indicate

that the U^{3+} hydride could readily form. Since ligand redistribution to form $(C_5Me_4H)_3U$ is facile whereas formation of $(C_5Me_5)_3U$ is difficult, this is likely the reason for the difference in the reactivity of these systems. Further details of the calculations on $[(C_5Me_4H)_2UH_2]_2$ and $[(C_5Me_4H)_2UH]_2$ are in the Supporting Information.

DISCUSSION

Neither $(C_5Me_4SiMe_3)_2UMe_2$, **1**, nor $(C_5Me_4H)_2UMe_2$, **3**, nor $(C_5Me_4H)_2ThMe_2$, **6**, undergoes hydrogenolysis to form bimetallic hydrides as found for $(C_5Me_5)_2ThMe_2$, eq 1, and $(C_5Me_5)_2UMe_2$, eq 2. In the case of $(C_5Me_4SiMe_3)_2UMe_2$, eq 6, the formation of the metalated product, $(\eta^5-C_5Me_4SiMe_2CH_2-\kappa C)_2U$, **2**, instead of a hydride can be rationalized by a conventional hydrogenolysis of the U–Me linkage to form U–H bonds followed by C–H bond activation of the silylmethyl substituents by the hydride ligands. This scenario has precedent in the 100 °C C–H bond activation reactivity of $(C_5Me_4SiMe_3)_2UMe_2$ that forms **2** and in the results of Hou et al. with $(C_5Me_4SiMe_3)^-$ lanthanide complexes.⁶⁹ Precedent for C–H bond activation by uranium hydrides is known from the 110 °C reactions of the $[(C_5Me_5)_2UH_2]_2/[(C_5Me_5)_2UH]_2$ mixture that generates the tuck-in, tuck-over complex $[(C_5Me_5)U[\mu-\eta^5-C_5Me_3(CH_2)_2-\kappa C:\kappa C](\mu-H)_2U(C_5Me_5)_2]$, eq 16.⁴⁶ The fact that **2** is formed at



room temperature in the hydrogenolysis of $(C_5Me_4SiMe_3)_2UMe_2$ suggests that any $[(C_5Me_4SiMe_3)_2UH_2]_n$ formed is more reactive than $(C_5Me_4SiMe_3)_2UMe_2$ and has highly reactive U–H bonds.

The hydrogenolysis of $(C_5Me_4H)_2UMe_2$ to form $(C_5Me_4H)_3U$, **4**, eq 7, can also be rationalized by an initial conventional step followed in this case by ligand redistribution. The theoretical calculations indicate that hydrogenolysis of $(C_5Me_4H)_2UMe_2$ to form a $[(C_5Me_4H)_2UH_2]_2/[(C_5Me_4H)_2UH]_2$ mixture analogous to that found in eq 2 is completely reasonable. The energy differences between the $(C_5Me_5)^-$ and $(C_5Me_4H)^-$ systems are so small that similar chemistry should be expected. Since $(C_5Me_4H)_3U$, **4**, is observed instead of these analogous hydrides, it appears that this system channels into this stable tris(cyclopentadienyl) end product. The tendency to form $(C_5Me_4H)_3M$ complexes is a significant difference between $(C_5Me_4H)^-$ and $(C_5Me_5)^-$ in the lanthanide and actinide area: the sterically crowded $(C_5Me_5)_3M$ complexes form only when there is no other reasonable option,⁷⁹ while $(C_5Me_4H)_3M$ often are observed as byproducts in reactions involving $(C_5Me_4H)^{1-}$ complexes.^{40,71} If the U^{3+} component of the $[(C_5Me_4H)_2UH_2]_2/[(C_5Me_4H)_2UH]_2$ equilibrium, $[(C_5Me_4H)_2UH]_2$, ligand redistributes to $(C_5Me_4H)_3U$, this will shift the equilibrium to the U^{3+} side and eventually take both bimetallic hydrides to $(C_5Me_4H)_3U$. The other product of the ligand redistribution should be hydride rich and cyclopentadienyl poor and could have a composition such as $[(C_5Me_4H)UH_2]_x$. This sterically unsaturated species would be expected to be highly reactive. It could ligand redistribute further to make more $(C_5Me_4H)_3U$ and insoluble UH_3 ,^{80,81} or it could engage in the type of C–H bond activation seen in the thorium case discussed below. $[(C_5Me_4H)UH_2]_x$ species could be so reactive that they would metalate indiscriminately, leading to a complicated intractable mixture of byproducts, as was observed in this case.

The hydrogenolysis of $(C_5Me_4H)_2ThMe_2$, **6**, to form $(C_5Me_4H)_3ThMe$, **7**, and $(C_5Me_4H)_4[\mu-\eta^5-C_5Me_3H(CH_2)-\kappa C]_2Th_4-(\mu-H)_4(\mu_3-H)_4$, **8**, eq 10, is the most difficult to rationalize. The generation of the tris(tetramethylcyclopentadienyl) product **7** has parallels in the ligand redistribution chemistry that forms $(C_5Me_4H)_3U$ except that ligand redistribution to make $(C_5Me_4H)_3AnX$ complexes has not been observed to our knowledge. The fact that **8** has less than two $(C_5Me_4H)^-$ ligands per thorium is consistent with the ligand redistribution. The formation of the $[C_5Me_3H(CH_2)]^{2-}$ ligands in **8** has parallels in the hydrogenolysis of $(C_5Me_4SiMe_3)_2UMe_2$, where C–H bond activation chemistry is postulated, eq 6. However, neither the composition nor the structure of **8** has precedent. Overall, these results re-emphasize the importance of the specific pattern of substitution on the cyclopentadienyl rings in this prototypical type of organoactinide reaction.

The formation of the fifth example of a Th^{3+} organometallic complex, $(C_5Me_4H)_3Th$, **10**, eqs 12 and 13, does follow precedented synthetic routes. The isolation of $(C_5Me_4H)_3ThMe$, **7**, as a byproduct in the hydrogenolysis of $(C_5Me_4H)_2ThMe_2$ provided a facile route to **10**. On the basis of the previous syntheses of Th^{3+} complexes, it is likely that other Th^{3+} complexes of formula $(C_5Me_4R')_2ThX$ ($R' = H$, alkyl, silyl; $X = \text{anion}$) will be synthetically accessible whenever $(C_5Me_4R')_2ThX(X')$ complexes are available that have an easily removed X' anionic ligand.

CONCLUSIONS

The reactions described here highlight the significant effects achievable in organoactinide chemistry by varying the substitution pattern in the polyalkylcyclopentadienyl ancillary ligands. Changing from $(C_5Me_5)^-$ to $(C_5Me_4SiMe_3)^-$ leads to C–H bond activation and formation of the tethered metallocene $(\eta^5-C_5Me_4SiMe_2CH_2-\kappa C)_2U$, **2**. Changing from $(C_5Me_5)^-$ to $(C_5Me_4H)^-$ enhances ligand redistribution reactivity to form $(C_5Me_4H)_3An$ species, which can be trivalent, as in the case of $(C_5Me_4H)_3U$, or tetravalent, as in the case of $(C_5Me_4H)_3ThMe$. These studies also demonstrate that the $(C_5Me_4H)^-$ ligand can be metalated as well as $(C_5Me_5)^-$ and that tuck-over dianions, $[\mu-\eta^5-C_5Me_3H(CH_2)-\kappa C]^{2-}$, can be formed with tetramethylcyclopentadienyl precursors. The isolation of $(C_5Me_4H)_4[\mu-\eta^5-C_5Me_3H(CH_2)-\kappa C]_2Th_4-(\mu-H)_4(\mu_3-H)_4$, **8**, suggests that other polymetallic actinide hydrides are likely to be accessible. Since **8** is not a simple tetramer, it seems likely that other arrangements of thorium metallocenes with combinations of bridging hydride or alkyl ligands and mono(cyclopentadienyl) thorium moieties could assemble to make polymetallic species of this type. Likewise, the isolation of $(C_5Me_4H)_3Th$, **10**, suggests that other Th^{3+} complexes should be accessible if the appropriate synthetic pathways can be defined.

ASSOCIATED CONTENT

Supporting Information

X-ray data collection, structure solution and refinement (PDF), and X-ray diffraction details of compounds **6**, **8**, **9**, and **10** (CIF, CCDC nos. 948005–948007; 956330) are available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the Department of Energy under grant DE-SC0004739 (W.J.E.) and by the Director, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract No. USDOE/DE-SC002183 (L.G.).

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