

Convenient access to the anhydrous thorium tetrachloride complexes $\text{ThCl}_4(\text{DME})_2$, $\text{ThCl}_4(1,4\text{-dioxane})_2$ and $\text{ThCl}_4(\text{THF})_{3.5}$ using commercially available and inexpensive starting materials†

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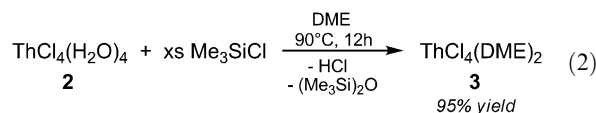
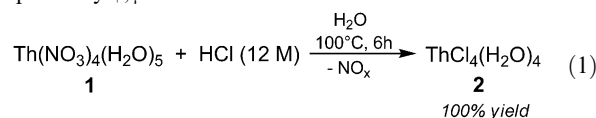
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Anhydrous thorium tetrachloride complexes $\text{ThCl}_4(\text{DME})_2$, $\text{ThCl}_4(1,4\text{-dioxane})_2$, and $\text{ThCl}_4(\text{THF})_{3.5}$ have been easily accessed from inexpensive, commercially available reagents under mild conditions and serve as excellent precursors to a variety of thorium(IV) halide, alkoxide, amide and organometallic compounds.

Anhydrous halide complexes are key starting materials in the synthesis of transition metal, lanthanide and actinide complexes. For non-aqueous thorium chemistry, $\text{ThBr}_4(\text{THF})_4$ and ThCl_4 have been the most commonly used precursors, but their syntheses suffer from several inconvenient drawbacks, which have, in turn, greatly hampered progress in thorium research. For example, the synthesis of $\text{ThBr}_4(\text{THF})_4$ requires thorium(0) metal, a material available at only a small number of institutions. Furthermore, its synthesis is highly dependent on the type of thorium metal used (turnings, powder or chips) and the complex is thermally sensitive with ring-opening and subsequent polymerization of THF being a problem.¹ The syntheses for ThCl_4 require special equipment and more dangerous protocols that involve elevated temperatures (300–500 °C). One method involves reacting thoria (ThO_2) with CCl_4 vapor at 450–500 °C for several days,^{2,3} while another requires heating thorium metal with NH_4Cl at 300 °C for 30 h to initially generate $(\text{NH}_4)_2\text{ThCl}_6$, which is then heated at 350 °C under high vacuum to ultimately give ThCl_4 .⁴

The increasing use of thorium in catalysis^{5–8} and materials science, coupled with the growing interest in developing a proliferation-resistant thorium nuclear fuel cycle,⁹ calls for straightforward access to anhydrous thorium(IV) starting materials. To address this need and circumvent the above issues with current thorium(IV) halide syntheses, we have explored the use of commercially available thorium nitrate $\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_5$ (**1**) as a safe and economically viable entry point for non-aqueous thorium chemistry and research. Herein, we show that anhydrous thorium(IV) chloride complexes can be prepared from thorium nitrate, and that the use of anhydrous HCl and Me_3SiCl serves as a new powerful drying reagent.

As shown in eqn (1), quantitative conversion of $\text{Th}(\text{NO}_3)_4(\text{H}_2\text{O})_5$ (**1**) into the thorium(IV) chloride tetrahydrate complex $\text{ThCl}_4(\text{H}_2\text{O})_4$ (**2**) was conveniently achieved by refluxing **1** in concentrated aqueous HCl (12 M) solution. Complex **2** is a white solid, which is insoluble in hydrocarbons but soluble in tetrahydrofuran (THF), dimethoxyethane (DME) and 1,4-dioxane. Its formulation as a tetrahydrate was determined from elemental analysis as well as recrystallization from THF or 1,4-dioxane, which afforded $\text{ThCl}_4(\text{H}_2\text{O})_4 \cdot (\text{THF})_5$ (**2**·(THF)₅) and $\text{ThCl}_4(\text{H}_2\text{O})_4 \cdot (1,4\text{-dioxane})_3$ (**2**·(1,4-dioxane)₃), respectively.†,‡



Attempts to dehydrate thorium(IV) chlorides using thionyl chloride (SOCl_2) have been reported.^{10–12} However, these reactions require long reaction times, elevated temperatures and are not reproducible.² Furthermore, SOCl_2 requires distillation prior to use and is a severe lachrymator that releases dangerous gases upon contact with water. Since chlorotrimethylsilane (Me_3SiCl) has been successfully used to dehydrate a variety of transition metal¹³ and uranyl chlorides,¹⁴ our initial efforts focused on exploiting the more benign Me_3SiCl as a drying reagent for $\text{ThCl}_4(\text{H}_2\text{O})_4$ (**2**).

Unfortunately, reaction between $\text{ThCl}_4(\text{H}_2\text{O})_4$ (**2**) and Me_3SiCl in THF resulted in THF polymerization, which precluded the isolation of a thorium compound. This behavior is a well established and problematic side reaction in both uranium and thorium chemistry, whereby coordination of THF to the electrophilic actinide metal center leads to ring-opening following nucleophilic attack from another molecule of THF.^{15,16} Reasoning that anhydrous HCl would not only serve as an effective drying reagent but also convert any generated thorium alkoxide back to the tetrachloride complex, the same reaction was performed in the presence of an excess of anhydrous HCl (2.0 M/diethyl ether). Under these conditions, the known monohydrate complex $\text{ThCl}_4(\text{H}_2\text{O})(\text{THF})_3$ ¹⁷ formed rapidly; however, removal of the residual H_2O results in THF polymerization.

Replacing THF by DME as a solvent proved to be the solution for the successful dehydration of $\text{ThCl}_4(\text{H}_2\text{O})_4$ (**2**) using Me_3SiCl (eqn (2)). The reaction is complete after 12 h at 90 °C and $\text{ThCl}_4(\text{DME})_2$ (**3**) is easily isolated in nearly quantitative

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† Electronic supplementary information (ESI) available: General experimental details, synthetic procedures for complexes **2–11** and crystallographic details for **2**·(THF)₅, **2**·(1,4-dioxane)₃ and **3**. CCDC 753730–753732. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b923558b

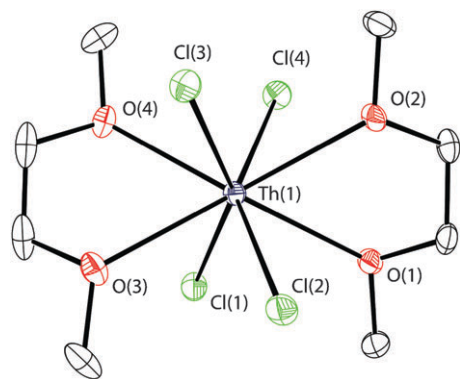


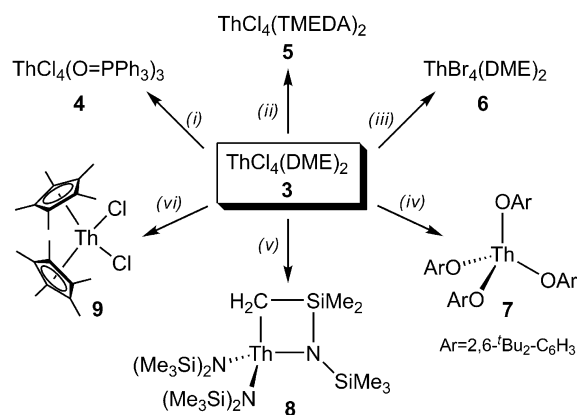
Fig. 1 Molecular structure of $\text{ThCl}_4(\text{DME})_2$ (**3**) with thermal ellipsoids projected at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Th(1)–Cl(1) 2.697(1), Th(1)–Cl(2) 2.675(1), Th(1)–Cl(3) 2.697(1), Th(1)–Cl(4) 2.692(1), Th(1)–O(1) 2.616(3), Th(1)–O(2) 2.598(3), Th(1)–O(3) 2.603(3), Th(1)–O(4) 2.567(3), O(1)–Th(1)–O(2) 63.37(10), O(3)–Th(1)–O(4) 64.67(11).

yield (95%) after precipitation with hexane.¹⁸ Complex **3** was characterized by combination of ^1H and ^{13}C NMR spectroscopy, elemental analysis and X-ray crystallography.

The molecular structure of **3** is presented in Fig. 1.† The thorium(IV) metal center features a distorted dodecahedron geometry with the oxygen and chloride atoms located in the A and B sites, respectively. The average Th–Cl bond distance of 2.690 Å compares well to those presented by other reported Th(IV) tetrachloride complexes (e.g. $\text{ThCl}_4(\text{O}=\text{PPh}_3)_3$ (**4**), $\text{Th}-\text{Cl}_{(\text{ave})} = 2.736$ Å¹⁹; $\text{ThCl}_4(\text{TMEDA})_2$ (**5**), $\text{Th}-\text{Cl}_{(\text{ave})} = 2.689$ Å²⁰) and the average Th–O bond length of 2.596 Å is consistent with those measured in $\text{ThBr}_4(\text{DME})_2$ (**6**) ($\text{Th}-\text{O}_{(\text{ave})} = 2.588$ Å).²¹

$\text{ThCl}_4(\text{DME})_2$ (**3**) proved to be an excellent synthetic precursor to a wide range of thorium(IV) halide, alkoxide, amide and organometallic complexes as outlined in Scheme 1. Displacement of the DME ligands by monodentate ligands such as triphenylphosphine oxide or bidentate ligands such as *N,N*-tetramethylethylenediamine (TMEDA) readily afforded the known complexes $\text{ThCl}_4(\text{O}=\text{PPh}_3)_3$ (**4**)¹⁹ and $\text{ThCl}_4(\text{TMEDA})_2$ (**5**),²² respectively. Transmetalation chemistry^{23–27} using excess Me_3SiBr smoothly converted **3** to $\text{ThBr}_4(\text{DME})_2$ (**6**).¹ Salt metathesis between 4 equiv. potassium 2,6-di-*tert*-butylphenoxide and $\text{ThCl}_4(\text{DME})_2$ (**3**) quantitatively afforded the homoleptic alkoxide complex $\text{Th}(\text{O}-2,6\text{-}^t\text{Bu}_2\text{-C}_6\text{H}_3)_4$ (**7**).²⁸ Similarly, reaction of 4 equiv. sodium hexamethyldisilazide with $\text{ThCl}_4(\text{DME})_2$ (**3**) yielded the known cyclometallated $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Th}[\kappa^2\text{-}(\text{C},\text{N})\text{-CH}_2\text{Si}(\text{CH}_3)_2\text{N}(\text{SiMe}_3)]$ (**8**)²⁸ complex in 93% yield. Finally, the bis(pentamethylcyclopentadienyl) complex $(\text{C}_5\text{Me}_5)_2\text{ThCl}_2$ (**9**)²⁹ was prepared in 88% yield from $\text{ThCl}_4(\text{DME})_2$ (**3**) and 2 equiv. $(\text{C}_5\text{Me}_5)\text{MgCl}\cdot\text{THF}$. Overall, the reaction chemistry with $\text{ThCl}_4(\text{DME})_2$ (**3**) has been performed on multigram scales and is high yielding (> 88%).

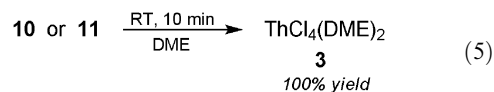
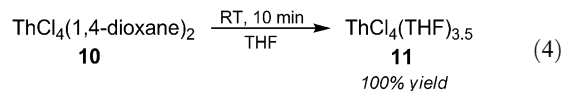
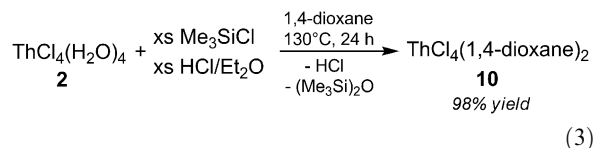
Despite this great synthetic profile, the DME ligand in **3** is not displaced by weak donor ligands such as THF. To prevent this from being an issue for chemistry, we examined other donors as alternatives to DME. The insolubility of $\text{ThCl}_4(\text{H}_2\text{O})_4$ (**2**) in most organic solvents precluded its reaction with Me_3SiCl . Although $\text{ThCl}_4(\text{H}_2\text{O})_4$ (**2**) is fairly soluble in 1,4-dioxane, no reaction was observed with Me_3SiCl , even



Scheme 1 Reagents and conditions: (i) 3 equiv. $\text{Ph}_3\text{P}=\text{O}$, THF, 100% yield; (ii) excess TMEDA, THF, 100% yield; (iii) excess Me_3SiBr , toluene, 24 h, 100% yield; (iv) 4 equiv. KOAr ($\text{Ar} = 2,6\text{-}^t\text{Bu}_2\text{-C}_6\text{H}_3$), THF, 99% yield; (v) 4 equiv. $\text{Na}[\text{N}(\text{SiMe}_3)_2]$, toluene, reflux, 12 h, 93% yield; (vi) 2 equiv. $(\text{C}_5\text{Me}_5)\text{MgCl}\cdot\text{THF}$, toluene, reflux, 24 h, 88% yield.

after several days at 150 °C. Interestingly, addition of anhydrous HCl (2.0 M/diethyl ether) to the reaction medium leads to the quantitative formation of the new thorium(IV) tetrachloride complex $\text{ThCl}_4(1,4\text{-dioxane})_2$ (**10**) after 12 h at 130 °C (eqn (3)). The insolubility of **10** in non-coordinating solvents did not permit its characterization using NMR spectroscopy; however, its identity as $\text{ThCl}_4(1,4\text{-dioxane})_2$ (**10**) was confirmed by elemental analysis. Although only poor quality crystallographic data could be obtained for **10**, connectivity was established and showed bridging 1,4-dioxane ligands, leading to the formation of an extended polymeric structure. This observation accounts for the apparent low coordination number of 6 suggested by the stoichiometry in $\text{ThCl}_4(1,4\text{-dioxane})_2$ (**10**).

In contrast to the DME ligands in **3**, the 1,4-dioxane ligands in **10** are easily displaced by THF, leading to the new complex $\text{ThCl}_4(\text{THF})_{3.5}$ (**11**) (eqn (4)), which was fully characterized using ^1H NMR spectroscopy and elemental analysis. Whereas the dioxane adduct **10** is stable in solution and in the solid state at 130 °C, the THF adduct **11** is thermally sensitive and undergoes rapid THF ring-opening at room temperature. It is remarkable that this new route permits access to the THF adduct **11**, whereas direct synthesis from $\text{ThCl}_4(\text{H}_2\text{O})_4$ (**2**) systematically failed. This clearly establishes the synthetic utility of the dioxane adduct **10**. Both complexes **10** and **11** are easily converted to **3** by reaction with DME (eqn (5)).



In conclusion, we have developed three convenient and safe solution routes to anhydrous thorium(IV) tetrachloride complexes using inexpensive, commercially available starting materials, and have demonstrated that the combination of anhydrous HCl and Me₃SiCl provides a powerful reagent for the dehydration of thorium halide hydrates. Importantly, the thorium complexes ThCl₄(DME)₂ (**3**), ThCl₄(1,4-dioxane)₂ (**10**) and ThCl₄(THF)_{3,5} (**11**) are easy to prepare on a large scale and display a wide range of reactivity. We anticipate that this advance will enable future progress in thorium chemistry, materials science, and nuclear fuel cycle research.

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Notes and references

‡ *Crystal data for ThCl₄(H₂O)₄(THF)₅ (2·(THF)₅):* C₂₀H₄₈Cl₄O₉Th, *M* = 806.42, triclinic, space group *P* $\bar{1}$, *a* = 10.744(5) Å, *b* = 10.896(5) Å, *c* = 13.900(6) Å, α = 99.515(5)°, β = 107.115(5)°, γ = 92.690(5)°, *V* = 1525.9(11) Å³, *Z* = 2, *D*_c = 1.755 Mg m⁻³, μ = 5.278 mm⁻¹, *F*(000) = 796, *T* = 140(1) K, 14 789 measured reflections, 5562 independent (*R*_{int} = 0.0831), *R*₁ = 0.0471, *wR*₂ = 0.1213 for *I* > 2σ(*I*). CCDC 753730. *Crystal data for ThCl₄(H₂O)₄(1,4-dioxane)₃ (2·(1,4-dioxane)₃):* C₁₂H₃₂Cl₄O₁₀Th, *M* = 710.22, orthorhombic, space group *Pbna*, *a* = 10.2963(13) Å, *b* = 12.3952(15) Å, *c* = 18.491(2) Å, α = 90.00°, β = 90.00°, γ = 90.00°, *V* = 2359.9(5) Å³, *Z* = 4, *D*_c = 1.999 Mg m⁻³, μ = 6.813 mm⁻¹, *F*(000) = 1368, *T* = 140(1) K, 24 922 measured reflections, 2861 independent (*R*_{int} = 0.0529), *R*₁ = 0.0318, *wR*₂ = 0.0698 for *I* > 2σ(*I*). CCDC 753731. *Crystal data for ThCl₄(DME)₂ (3):* C₈H₂₀Cl₄O₄Th, *M* = 554.08, monoclinic, space group *P*2₁/*c*, *a* = 16.644(3) Å, *b* = 7.3263(15) Å, *c* = 14.877(3) Å, α = 90.00°, β = 115.356(2)°, γ = 90.00°, *V* = 1639.3(6) Å³, *Z* = 4, *D*_c = 2.245 Mg m⁻³, μ = 9.747 mm⁻¹, *F*(000) = 1032, *T* = 120(1) K, 17 216 measured reflections, 3819 independent (*R*_{int} = 0.0489), *R*₁ = 0.0313, *wR*₂ = 0.0746 for *I* > 2σ(*I*). CCDC 753732.

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