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Anion-Induced Disproportionation of Th(III) Complexes to Form Th(II) and Th(IV) Products

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A new synthesis of Th(II) complexes has been identified involving addition of simple MX salts (M = Li, Na, K; X = H, Cl, Me, N₃) to Cp"₃Th^{III} [Cp" = [C₅H₃(SiMe₃)₂] in the presence of 18-crown-6 or 2.2.2-cryptand, forming [M(chelate)][Cp"₃Th^{II}] and Cp"₃Th^{IV}X. Cp^{tet}₃Th^{III} (Cp^{tet} = C₅Me₄H) reacts with KH to form Cp^{tet}₃Th^{IV}H and the C–H bond activation product, [K(crypt)]{[Cp^{tet}₂Th^{IV}H[η^1:η^5-C₅Me₃H(CH₂)]}.

There are less than a dozen crystallographically characterized Th(III) complexes[1–10] and only five Th(II) crystal structures, all of which involve the [Cp"₃Th^{II}]$^{1-}$ anion with different countercations [Cp" = C₅H₃(SiMe₃)₂].[11,12] As a result, the reaction chemistry of organometallic Th(III) and Th(II) complexes is not extensively developed. Recently, electrochemical data have been obtained on organothorium complexes Cp"₃Th^{IV}Cl, Cp"₃Th^{III}, and [Cp"₃Th^{II}]$^{1-}$ that show that the Th(IV)/Th(III) and Th(III)/Th(II) redox couples are surprisingly similar: −2.96 V vs Fc$^+$/Fc[12,13] and −2.85 V vs Fc$^+$/Fc,[12] respectively. This similarity suggested that Th(II) complexes could be synthesized directly from Th(IV) precursors with strong reductants like potassium, and this was confirmed experimentally.[12]

While studying the reaction of Cp"₃Th^{III}, **1**, with KH in hopes of synthesizing a new Th(III) complex, such as [Cp"₃Th^{III}H]$^{1-}$, the characteristic green color of the Th(II) anion [Cp"₃Th^{II}]$^{1-}$, **2**, was observed instead of the blue-purple of Th(III). Since KH is not a strong enough reductant to affect the Th(III)/Th(II) couple measured electrochemically, this was puzzling. We now report that not only KH, but also many other alkali metal salts, MX, will react with **1**, to form the Th(II) anion **2** and the Th(IV) complex, Cp"₃Th^{IV}X, **3-X**, as a co-product. Hence, there are many routes to Th(II) complexes by disproportionation which evidently can occur due to the similarity of the Th(IV)/Th(III) and Th(III)/Th(II) redox couples. We report here the details of these reactions and extension of this chemistry to Cp^{tet}₃Th^{III} (Cp^{tet} = C₅Me₄H).[3]

A dark blue solution of **1**[2,11,14] in THF reacts with KH and 2.2.2-cryptand (crypt) or 18-crown-6 (crown) at room temperature to generate a deep blue/green solution, indicative of the presence of a Th(II) species, over a few hours. From this reaction, crystals of [K(chelate)][**2**][11] can be isolated after workup in addition to Cp"₃Th^{IV}H, **3-H**,[15] and **1**[2,11,14] as determined by X-ray crystallography and UV-visible and^{1}H NMR spectroscopy (Scheme 1).

This type of reaction with **1** was found to also occur with other MX salts such as LiMe, NaN₃, and even KCl, generating [M(chelate)][**2**],[11,12] **3-X**, and some amount of **3-H** (Scheme 1). Minimal Cp"₃Th^{IV}Cl, **3-Cl**, was observed in the reaction of **1** with KCl. This is likely because once the reaction occurs to form **2** and **3-Cl** (Scheme 2), these then react to reform **1** and KCl in a reaction analogous to the previously observed reaction between [Na(crown)₂][**2**] and Cp"₃Th^{IV}Br, **3-Br**.[12] The reaction between [K(crypt)][**2**] and **3-Cl** was independently confirmed to form **1** in near quantitative yield. The formation of Th(II) is also observed in reactions with LiMe without the use of a chelate.

The reactions with alkyl lithium reagents other than LiMe were also studied. The reaction of 1, LiCH₂SiMe₃, and crypt in THF again formed [Li(crypt)][**2**]. In this reaction, **3-H** and **1** were the only other Cp"-containing compounds observable in the ^{1}H NMR spectrum. Interestingly, the reaction of **1** with ^{n}BuLi formed [Li(crypt)][**2**] in 66% yield, but neither the expected Th(IV) product, Cp"₃Th^{IV}(^{n}Bu), nor its β–H elimination product, **3-H**,[15] were observed in the ^{1}H NMR spectrum. In this case, ^{n}BuLi appeared to act only as a reductant. It is not clear where the hydride product originates in these reactions, but we note that analogous C₅H₄SiMe₃ (Cp') and C₅Me₅ hydrides, Cp'₃Th^{IV}H and (C₅Me₅)₃Th^{IV}H, have also been found to be ubiquitous byproducts in reactions with Cp'₃Th^{III} and (C₅Me₅)₃Th^{III}.[6,18]

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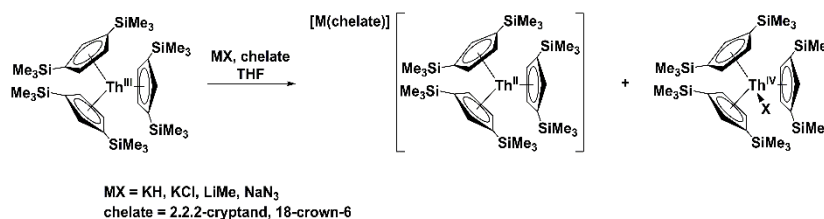
Scheme 1 Reaction of Cp"$_3$Th^{III}, **1**, with MX salts

A mechanism can be proposed for the reaction of **1** and MX based on the analogous reactions of Cp'$_3$U^{III} and Cp"$_3$U^{III} with KH and chelate, eqn (1). The uranium reactions form the U(III) anions [K(crypt)][Cp'$_3$U^{III}] and [K(crown)(THF)$_2$][Cp"$_3$U^{III}], respectively, which can be isolated as single crystals.[16,17] The fact that these do not disproportionate is consistent with their electrochemistry.[13]

R = H, SiMe$_3$
chelate = 2.2.2-cryptand, 18-crown-6
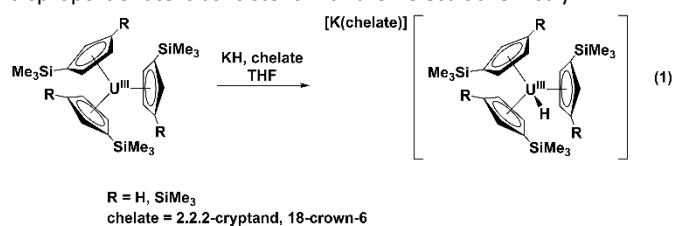
If a reaction analogous to eqn (1) occurs between **1** and MX, then [Cp"$_3$Th^{III}X]$^{1-}$ would form as shown in Scheme 2. This species will likely have a reduction potential more negative than the −2.96 V value for **1**.[12] This claim is supported by electrochemical measurements on Cp"$_3$Th^{IV}Me, **3-Me**. Only a cathodic event with E_{PC} = −3.48 V vs Fc$^+$/Fc was observed in the voltammogram for **3-Me** (Fig. 1). For comparison, Cp"$_3$Th^{III}, Cp"$_3$Th^{IV}Br, and Cp"$_3$Th^{IV}Cl have cathodic events at E_{PC} = −2.92, −3.00 and −3.04 V, respectively.[12]
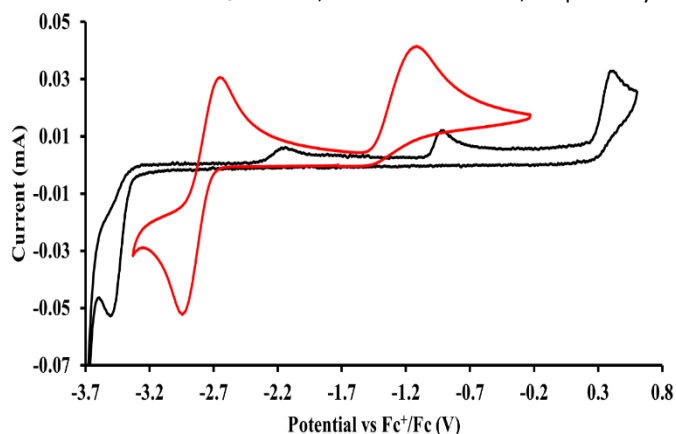
Fig. 1 Voltammogram of Cp"$_3$Th^{IV}Me, **3-Me**, (black) and Cp"$_3$Th^{III}, **1**, (red) at v = 200 mV/s in 200 mM [^{n}Bu$_4$N][PF$_6$] / THF. The events for **3-Me** occur at −3.48 V [E_{PC}, Th(IV)/Th(III)], −2.045 V (E_{PA1}, related to E_{PC}), −0.90 V (E_{PA2}, likely Cp" oxidation[12]), and 0.415 V (E_{PA3}). The event at −2.045 V is related to E_{PC} as is it only present after E_{PC} occurs. The events for **1** occur at −2.94 V (E_{PC}), −2.73 V (E_{PA1}), and −1.09 V (E_{PA2}, Cp" oxidation).[12]

Thus, electron transfer from [Cp"$_3$Th^{III}X]$^{1-}$ to **1** would be thermodynamically favorable and could occur to form **3-X** and **2**, which is isolated as the [M(chelate)]$^{1+}$ salt. The formation of **1** in some cases can be explained by the reaction of **3-X** with **2**. The amount of **1** formed likely depends on the relative rate of the

reaction between [Cp"$_3$Th^{III}X]$^{1-}$ and **3-X** versus the disproportionation rate.

Attempts to observe the proposed intermediate [Cp"$_3$Th^{III}H]$^{1-}$ generated by reaction of **1** and KH via UV-visible spectroscopy were unsuccessful. Due to the large (~5000 M^{-1}cm^{-1}) attenuation coefficients of **1**[2,14] UV-visible measurements were performed at roughly 0.15 mM concentrations, in contrast to the bulk reactions which were performed at approximately 15 mM concentrations. Even while stirring the reaction inside the UV-visible cell, no evidence of disproportionation could be observed. Instead, the solution slowly became colorless, indicative of decomposition to Th(IV) products. Control reactions performed inside the glovebox at the same 0.15 mM concentration confirmed that the reaction in Scheme 2 does not proceed at low concentrations, possibly because [Cp"$_3$Th^{III}H]$^{1-}$ reacts with solvent molecules instead of **1**. The reaction with LiMe and **1** was probed at −80 °C and 0.15 mM concentrations to evaluate if an intermediate could be observed at low temperature. However, only new absorption bands attributable to **2** were observed with concomitant disappearance of the spectrum of **1** (Fig. 2).
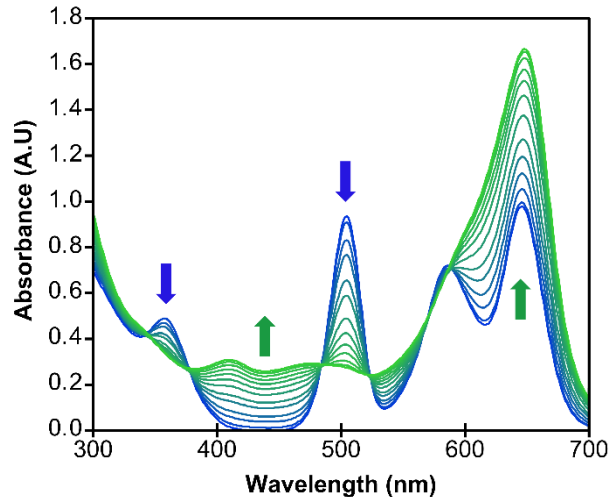

Fig. 2 UV-visible spectra during the reaction of Cp"$_3$Th^{III}, **1**, (blue) and LiMe at −80 °C, showing the appearance of a strong absorption at 650 nm indicative of [Cp"$_3$Th^{II}]$^{1-}$, **2**, (green) with concomitant disappearance of the four bands at 655, 590, 510, and 362 nm. The final spectrum matches that of **2**.[11,12]

The possibility that the low-valent Th(II) compound **2** is actually a Th(III)–H species is dispelled by the fact that **2** has a diamagnetic NMR spectrum and no EPR spectrum.[12] A Th(III)–H species would exhibit a characteristic EPR spectrum and distinct crystallographic properties as shown for the U(III)–H compounds in eqn (1) compared to their related U^{II} complexes.[16,17]

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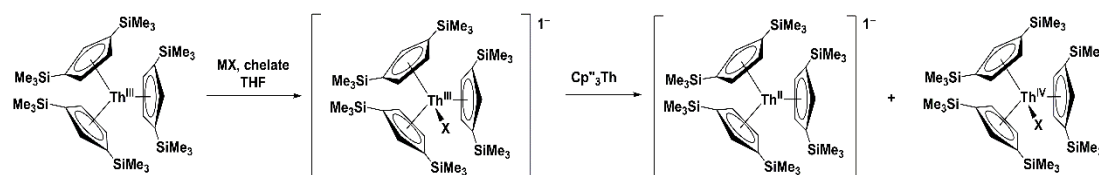
Scheme 2 Possible disproportionation mechanism for the reaction of Cp"$_3$Th^{III}, **1**, with simple MX salts (M = Li, Na, K; X = H, Cl, Me, N$_3$).

Since the Th(IV)/Th(III) and Th(III)/Th(II) reduction potentials in complexes of the (Cp^{tet})$_3$ ligand set are also similar,[12] the reaction of KH, Cp$^{tet}_3$Th^{III}, and crypt in THF was examined. The initially purple solution turns orange after 45 minutes and Cp$^{tet}_3$Th^{IV}H, [K(crypt)][Cp^{tet}], and [K(crypt)]{Cp$^{tet}_2$Th^{IV}H[η^5:η^1-C$_5$Me$_3$H(CH$_2$)]} were identified from the reaction mixture by ^{1}H NMR spectroscopy and X-ray crystallography.[5] These same products are isolated from the reaction of Cp$^{tet}_3$Th^{III}, KC$_8$, and crypt in THF, which forms a dark green solution which may be "[K(crypt)][Cp$^{tet}_3$Th^{II}]" that quickly decomposes.[5] The formation of the C–H bond activation product, [K(crypt)]{Cp$^{tet}_2$Th^{IV}H[η^5:η^1-C$_5$Me$_3$H(CH$_2$)]}, may explain why [K(crypt)][Cp$^{tet}_3$Th^{II}] has proven difficult to isolate. C–H bond activation has been observed before with U(II) complexes[19,20] and may result from Th(II) in this case. These results suggest that Cp$^{tet}_3$Th^{III} undergoes a similar disproportionation reaction as **1** and a mechanism like Scheme 2 may be operative.

In summary, a new synthetic route to [Cp"$_3$Th^{II}]$^{1-}$ via the disproportionation of Cp"$_3$Th^{III} has been discovered. The reaction of Cp"$_3$Th^{III} with simple MX salts leads to the formation of Cp"$_3$Th^{IV}X and [Cp"$_3$Th^{II}]$^{1-}$. A highly reactive "[Cp"$_3$Th^{III}X]$^{1-}$" complex is a possible intermediate. This reaction also appears to occur with Cp$^{tet}_3$Th^{III}, which suggests that it can be generalized to other Th(III) complexes.

There are no conflicts to declare.

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