Thorium Mono- and Bis(imido) Complexes Made by Reprotonation of *cyclo*-Metalated Amides

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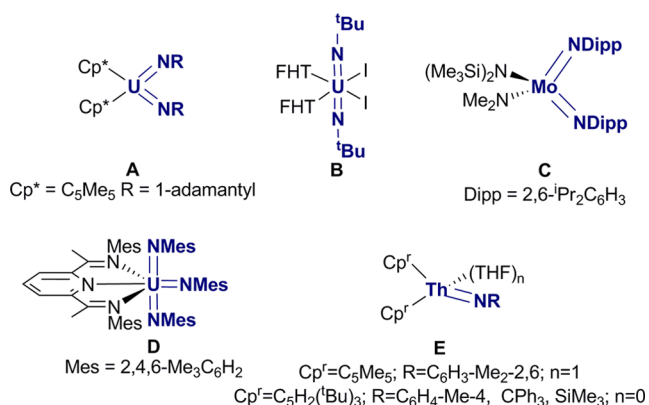
S *Supporting Information*

ABSTRACT: Molecules containing actinide−nitrogen multiple bonds are of current interest as simple models for new actinide nitride nuclear fuels, and for their potential for the catalytic activation of inert hydrocarbon C−H bonds. Complexes with up to three uranium−nitrogen double bonds are now being widely studied, yet those with one thorium−nitrogen double bond are rare, and those with two are unknown. A new, simple mono(imido) thorium complex and the first bis(imido) thorium complex, $K[Th(=NAr)N''_3]$ and $K_2[Th(=NAr)_2N''_2]$, are readily made from insertion reactions (Ar = aryl, $N'' = N(SiMe_3)_2$) into the Th−C bond of the cyclometalated thorium amides $[ThN''_2(N(SiMe_3)(SiMe_2CH_2))]$ and $K[ThN''(N(SiMe_3)(SiMe_2CH_2))_2]$. X-ray and computational structural analyses show a "transition-metal-like" *cis*-bis(imido) geometry and polarized Th=N bonds with twice the Wiberg bond order of the formally single Th−N bond in the same molecule.

Figure 1. Terminal imido complexes of the f- and d-block. Examples of the *cis*- and the more common *trans*-bis(imido) U(VI) motifs (**A**, **B**), the common bis(imido) Mo(VI) motif (**C**), the first tris(imido) U(VI) complex (**D**), and the known thorium imido complexes (**E**).

Strong and covalent multiple bond formation between actinide cations and oxo groups is a ubiquitous feature of actinide chemistry, most famously represented by the linear $O=U=O$ unit in the uranyl dication $[UO_2]^{2+}$, in which the ligating atoms strongly donate electron density to the metal through one σ bond and two π bonds in an unreactive and formally triple bond.[1] Studies of multiple bonds between actinide ions and other heteroatoms are still rare[2] but are gaining momentum due to their unique contributions to our understanding of the role of the 5f and other orbitals in covalent actinide bonding.[3]

Imido ligands are strong σ- and π-donors, and uranium imido bonds have a formal order of 3, like uranyl oxos. All known U^{VI} uranyl complexes contain *trans*-dioxo ions, and nearly 90% of U^{VI} bis(imido) complexes have a close to linear (>150°) geometry; examples of *cis*- and *trans*-U^{VI} bis(imido) complexes respectively are $(Cp^*)_2U(=NR)_2$ (**A** in Figure 1) and the landmark, linear uranyl analogue $[U(=NR)_2I_2(THF)_2]$ (**B**).[4] Meanwhile, the majority (ca. 95%) of the numerous transition metal bis(imido) complexes exhibit *cis* geometries (e.g., **C** in Figure 1).

Recent years have seen a great increase in the number and variety of terminal imido uranium complexes, including bis-(imido) and most recently U^{VI} tris(imido) structures (**D** in Figure 1).[5] Their bonding has been studied in terms of proving molecular analogues of actinide nitride nuclear fuels,[6] and their reactivities have been studied in the search for catalytic properties

which might differ from those of the d-block complexes.[7] An *intra*molecular ligand C−H bond addition reaction was initiated by diazoalkane binding to a $U^{VI}=NR$ bond in the complex $(C_5Me_5)_2U(=NC_6H_2{}^tBu_3)(N_2CPh_2)$,[8] the strong donation of the N(2p) orbitals and involvement of the uranium 5f orbitals is not conducive to the most desirable *inter*molecular hydrocarbon C−H bond addition chemistry, for which the more polar transition metal M=N bonds have been celebrated.[9]

Only four terminal thorium imido complexes have been reported, all of which are supported by the bulky, clam-shaped bis(cyclopentadienyl) co-ligand set (**E** in Figure 1).[10] Early reports on the small-molecule activation reactivity of **E** include silane Si−H bond cleavage chemistry.[11] This supports the suggestion of more d-block-like behavior of thorium (cf. uranium), which is indicated by its ground-state $[Rn]s^2d^2$ configuration, and a therefore greater potential for the reactivity of the Th=NR group. No bis(imido) complexes have been reported to date, which could be due to their anticipated higher reactivity compared to the uranium analogues (calculations on the model $[(C_5H_5)_2Th(=NPh)_2]^{2-}$ ion find much weaker metal−nitrogen bonding than in the uranium complex),[12] and also to the difficulty in stabilizing low coordination numbers at the large Th^{IV} center.[13]

Given that **A** has no equivalent in transition-metal chemistry, we were interested in thorium imido complexes of monodentate,

Scheme 1. Synthetic Routes to the Bis(metallacyclic) Amido, and Mono- and Bis(imido) Thorium(IV) Complexes[a]
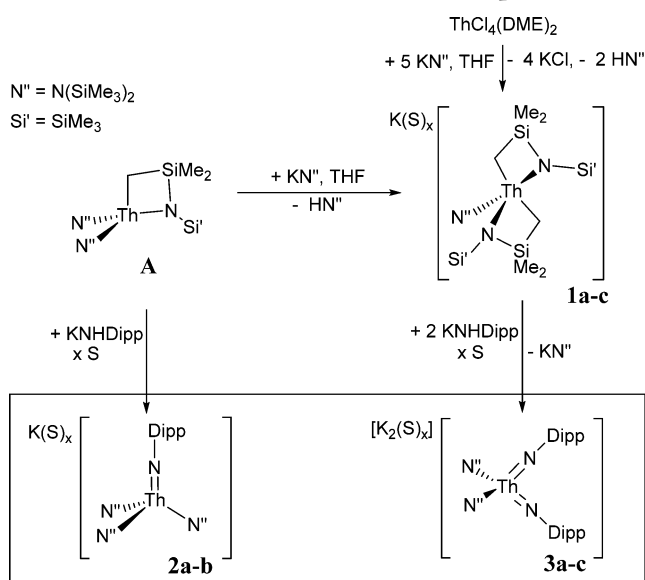
[a]Two syntheses of $[K(S)_x][Th\{N(Si')(SiMe_2CH_2)\}_2N'']$ (**1**), and the conversions of the mono- and bis(metallacycles) into the mono- and bis(imido) complexes $[K(S)_x][Th(=NDipp)N''_3]$ (**2**) and $[K_2(S)_x]$-$[Th(=NDipp)_2N''_2]$ (**3**), respectively. For **1a**, x = 0; for **1b**, S = 18-c-6, x = 1; for **1c**, S = DME, x = 1; for **2a**, x = 0; for **2b**, S = 18-c-6, x = 1; for **3a**, S = THF, x = 2; for **3b**, S = 18-c-6, x = 1; for **3c**, S = 18-c-6, x = 2. 18-c-6 = $C_{12}H_{24}O_6$ crown ether.

monoanionic ligands which would not be sterically protected or geometrically directed by the "clam-shell" configuration of the bis(cyclopentadienyl) framework. Herein we report a new, straightforward route to amido-imido Th^{IV} complexes and the first thorium bis(imido) complex. We also discuss their bonding and geometries with the support of density functional theory (DFT) calculations.

Treatment of a THF solution of the thorium metallacycle Th$\{N(Si')(SiMe_2)CH_2\}N''_2$ (**A**, where N'' = N(SiMe_3)_2, Si' = SiMe_3) with 1 equiv of KN'' affords the bis(metallacycle) $[K(S)_x][Th\{N(Si')(SiMe_2CH_2)\}_2N'']$ (**1**) as a colorless solid (Scheme 1). **1** can be also made from ThCl_4(DME)_2 and 5 equiv of KN'' in toluene and is isolable solvent-free in 70% yield (**1a**) or as a variety of solvates, depending on the precursor and workup procedure, including crown ether, [K(18-c-6)][ThN''{N(Si')-(SiMe_2CH_2)}_2] (**1b**), and DME, [K(DME)][Th{N(Si')-(SiMe_2CH_2)}_2N''] (**1c**) (18-c-6 = 18-crown-6, $C_{12}H_{24}O_6$). This "ate" complex is the direct analogue of the U^{IV} complex [K(THF)][U{N(Si')(SiMe_2)CH_2}_2N''] reported by Ephritikhine.[14] At room temperature, NMR spectroscopy in C_6D_6/THF solution shows the diastereotopic relationship of the metallacyclic groups in **1**. In spectra of **1a**, the CH_2 protons are observed as two broad resonances at 0.04 ($W_{1/2} \approx 47$ Hz) and −0.37 ($W_{1/2} \approx 42$ Hz) ppm, which coalesce at 343 K; the Si(CH_3)_2 hydrogens are observed as a single broad resonance at 0.49 ppm ($W_{1/2} \approx 59$ Hz, 12 H). The ^{13}C{^{1}H} NMR spectrum shows a broad resonance for the Th−CH_2 group at 53.4 ppm (the corresponding resonance in **A** is 68.8 ppm). Two broad resonances at 6.8 and 8.7 ppm are assigned as the diastereotopic Si(CH_3)_2 carbons. The ^{29}Si-INEPT spectrum shows the three anticipated resonances at δ = −28.9, −16.9, and −11.8, which compare closely with δ = −32.9, −12.1, and −9.4 for **A**. Complex **1** does not react with further KN'' in our hands.

Treatment of **A** with KNHDipp (Dipp = 2,6-^{i}Pr_2C_6H_3) in C_6H_6/THF or THF provides straightforward access to the colorless crystalline thorium imide $[K(S)_x][Th(=NDipp)N''_3]$ (**2**, Scheme 1), isolable as a variety of solvates, depending on the workup procedure.[15] For example, from THF solution unsolvated **2a** (S = 0) is isolated in quantitative yield, but addition of crown ether (18-c-6) and a small quantity of THF (10% by volume) to the benzene reaction mixture affords the separated ion-pair [K(18-c-6)][Th(=NDipp)N''_3] (**2b**). Complex **2** is highly oxygen and moisture sensitive but thermally stable for at least 14 days in a refluxing toluene/THF solution (ca. 10% THF). NMR spectroscopy and X-ray diffraction (XRD) studies (see below) of **2** confirm the addition of the [HNDipp] group across the Th−C bond to form the Th=NDipp aryl imido complex. No NH resonance is observable in the spectra, and in the aliphatic region a lone singlet at δ 0.28 (54H) confirms the equivalence of the two original silylamide ligands and regenerated N'' amido ligand. Finally, ^{29}Si-INEPT NMR spectra show a single silicon environment with a chemical shift of −11.2 ppm. A number of other arylimido analogues of **2** were also made and are discussed in the Supporting Information (SI).

Analogously, treatment of **1a** with 2 equiv of KNHDipp in a C_6H_6/THF mixture (ca. 5:1 ratio) yields the first bis(imido) complex of thorium, $[K_2(S)_x][Th(=NDipp)_2N''_2]$ (**3**), as a colorless crystalline solid in essentially quantitative yield (Scheme 1). Again, different solvated forms can be isolated, but the simple THF adduct (**3a**, with S = THF, x = 2, 85% yield) most readily forms single crystals suitable for XRD studies (see Figure 2). The mono- and bis-18-c-6 analogues **3b** and **3c** are described in the SI, section IVc. The complex is mononuclear in solution as well as in the solid state: ^{1}H NMR spectra of **3a** in C_6D_6, solubilized with a few drops of THF, contain a singlet at δ 0.26 (36H), demonstrating a single silylamide environment. ^{1}H DOSY NMR spectroscopic experiments (SI, section V) show the hydrodynamic radius of **3a** (7.1 Å) to be similar to that of **2a** (6.9 Å), suggesting that **3** remains monomeric in solution. The highest mass peak in the electron ionization mass spectrum of **3c** is at 1509.2 m/z, corresponding to the ion-pair [K(18-c-6)]_2[Th(=NDipp)_2N''_2]. The MALDI spectrum clearly shows a molecular ion peak at 901.5 m/z, corresponding to [Th(=NDipp)_2N''_2 − H]$^-$. No ion with higher mass was observed by either method.

Once isolated, **3** is stable for several days in solution, but if stored in contact with the soluble KN'' byproduct, over 8 h at room temperature solutions begin to degrade to multiple products, as determined by ^{1}H NMR spectroscopy. Other bis(imido) analogues were also targeted, but none was as stable as **3**; see SI, section IV for details.

X-ray-quality crystals of **1c** were grown by slow cooling of the hexane filtrate of a sample made from ThCl_4(DME)_2. X-ray-quality crystals of **2b** were grown by slow cooling of a C_6D_6/THF solution, while single crystals of **3a** were grown by slow diffusion of hexane into a C_6H_6/THF solution. The molecular structure of **1c** (Figure 2a) confirms the metalation of both amido ligands. Although the solid-state structure of **A** is not known, the two Th−C bonds of 2.562(5) and 2.576(5) Å fall within the expected range for single Th−C bonds (2.4−2.8 Å).

The molecular structure of **2b** (Figure 2b) shows a tetrahedral thorium environment with a Th1−N1 imido bond length of 2.072(3) Å that is significantly shorter than a single Th−N amido bond (range 2.2−2.4 Å for thorium dialkylamides) but is one of the longest Th−N imido bonds observed to date. The four reported terminal thorium imido complexes **E** all contain two cyclopentadienyl co-ligands, either $[(C_5Me_5)_2]$[10b] or
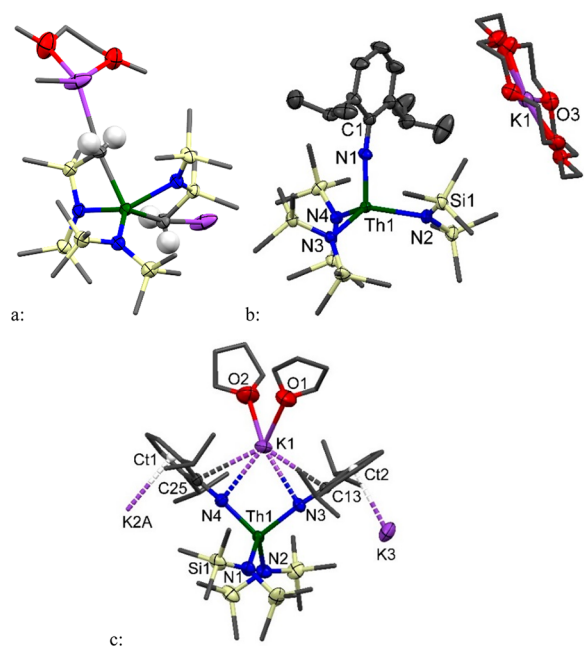
Figure 2. Solid-state molecular structure of (a) [K(DME)][Th{N(Si′)-(SiMe$_2$CH$_2$)}$_2$N″] (**1c**), (b) [K(18-c-6)][Th(=NDipp)N″$_3$] (**2b**), and (c) [K$_2$(THF)$_2$][Th(=NDipp)$_2$N″$_2$] (**3a**). Displacement ellipsoid in all structures are drawn with 50% ellipsoid probability for all atoms except for peripheral C atoms and, in (b), the Dipp carbons. All hydrogen atoms other than those on the two metalated carbons in (a) are omitted for clarity. Selected distances (Å) and angles (deg): (a) Th1–N2 2.352(3), Th1–N1 2.363(4), Th1–N3 2.381(4), Th1–C6 2.562(5), Th1–C10 2.576(5), N2–Th1–N1 138.15(14), N2–Th1–N3 109.52(13), N1–Th1–N3 112.14(13), N2–Th1–C6 86.24(14), N3–Th1–C6 123.40(16), N2–Th1–C10 67.93(14), N1–Th1–C10 89.37(14), N2–Th1–C6 86.24(14), N3–Th1–C10 127.55(15), N1–Th1–C6 67.85(15), C6–Th1–C10 108.91(18); (b) Th1–N1 2.072(3), Th1–N2 2.424(3), Th1–N3 2.449(3), Th1–N4 2.406(3), N1–Th1–N4 103.56(11), N1–Th1–N2 98.57(12), N4–Th1–N2 122.64(11), N1–Th1–N3 115.59(12), N4–Th1–N3 103.73(10), N2–Th1–N3 112.93(11), C1–N1–Th1 172.0(3); (c) Th1–N3 2.165(3), Th1–N4 2.165(3), Th1–N1 2.448(3), Th1–N2 2.474(3), K1–N4 2.840(3), K1–C25 3.086(3), K2A–C25 3.130(4), K2A–Ct1 2.851, N1–Th1–N4 107.08(11), N1–Th1–N2 111.73(11), N4–Th1–N2 116.10(11), N1–Th1–N3 115.33(11), N4–Th1–N3 97.34(12), N2–Th1–N3 108.70(11), C13–N3–Th1 169.1(3), C25–N4–Th1 171.4(3).

[[(C$_5$H$_2$(^{t}Bu)$_3$-1,2,4)$_2$].[11a] It is likely that the Th–N lengthening in **2** reflects the electron richness of the metal center due to both the formal negative charge on the Th^{IV} center and the presence of electron-donating silylamide ligands, each of which has been shown to result in a measurable M=N lengthening in d-block analogues.[16]

The structure of **3a** (Figure 2c) shows a pseudo-tetrahedral thorium environment and a *cis* arrangement of the two imido ligands with a N4–Th1–N3 bond angle of 97.34(12)°, close to that which has been theoretically predicted (see below). The two thorium imido Th–N bonds (both 2.165(3) Å) are longer than that in **2b** (2.072(3) Å) but significantly shorter than the thorium amido Th–N bonds (Th1–N1, 2.448(3) Å and Th1–N2, 2.474(3) Å). Both Th–N$_{imido}$–C$_{Dipp}$ angles are also very close to linear, as would be anticipated for a Th–N bond order of 2 or 3 (C13–N3–Th1, 169.1(3)° and C25–N4–Th, 1171.4(3)°). One of the two potassium counter-cations (K1) occupies the gap between the two imido groups, with relatively close contacts to
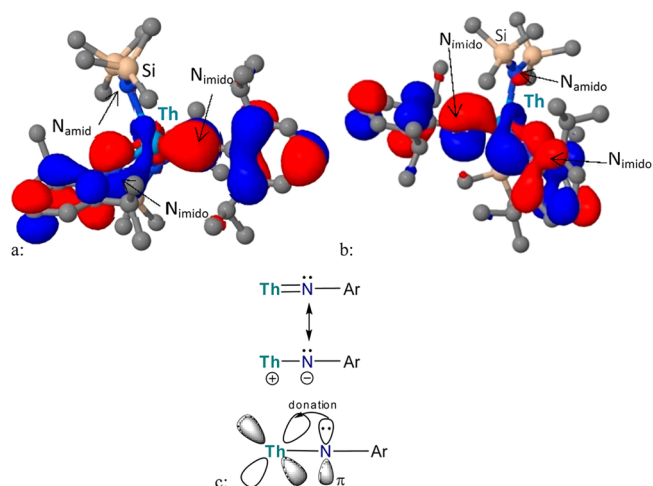
both the nitrogen and *ipso*-aryl carbon atoms of each imido group, a feature observed previously in related uranium systems.[7j] The other, K2A/K3 (disordered over two sites), is weakly bound in an approximately bis(arene) sandwich-type geometry through coordination to the imido aryl rings of adjacent molecules, resulting in the formation of one-dimensional chains in the solid state.

The mono- (**2**) and bis(imido) **3** structures were studied using theoretical methods (DFT) on model compounds **2′** and **3′**, with potassium counterions omitted (see SI, section VIII for details and further analysis of the data). The computational method reproduced the geometry of **2** and **3** very well, indicating the suitability of the chosen method. Analysis of the bonding in **2**, using NBO, indicates double-bond character in the Th–N$_{imido}$ bond in **2** at the second-order donor–acceptor level, with a polarized covalent σ bond and an ionic π interaction involving donation from the nitrogen 2p orbital toward an empty 6d/5f hybrid orbital on Th. There is a greater polarization than the bonding in the recently reported Th=O analogue, as expected,[17] and a greater d orbital involvement than f, in line with previous studies by us.[18]

In **3′**, these double bonds can be described as a polarized covalent σ bond (90% 2p N; 10% 6d(65)-5f(35) Th) and an ionic π interaction involving donation from the nitrogen 2p orbital toward an empty 6d orbital on Th (second-order NBO, 44.2 kcal/mol). Figure 3 shows the calculated HOMO and HOMO–1, which are the Th–N$_{imido}$ bonds. Thus, the Th–N$_{imido}$ bonds in both mono- and bis(imido) compounds are correspondingly more polarized than in a typical uranium analogue.[18] The Wiberg bond indices are 0.88 in **3**, twice the indices of the Th–N$_{amido}$ bonds, which are 0.47, but significantly lower than 2.0, which would represent a pure covalent double bond.

It is gratifying to find that both the predicted and found bis(imido) geometries are cisoid, 117° and 97.34(12)° (for **3c**). The difference of *ca.* 20° is presumably due to the weak interaction between one potassium countercation and the two imido N atoms that is likely to exaggerate the *cis* geometry. Optimizations from both *cis*- and *trans*-imido starting points converged to the 117° *cis* geometry, underlining the relative instability of the *trans*.

To summarize, a rare thorium terminal imido complex, [K(S)$_x$][Th(=NDipp)N″$_2$] (**2**), and the first bis(imido)

Figure 3. Calculated π Th–N$_{imido}$ interaction in **3′**. (a) HOMO and (b) HOMO–1 orbitals shown at the default isosurface value of 0.025. (c) Schematic of the thorium imido bonding.

thorium complex, $[K_2(S)_x][Th(=NDipp)_2N''_2]$ (**3**), are both readily accessible from the simple, well-known thorium amidometallacycle, $Th\{N(Si')(SiMe_2CH_2)\}N''_2$ (**A**) and a doubly metalated analogue, $K[Th\{N(Si')(SiMe_2CH_2)\}_2N'']$ (**1**). These are the first thorium-imido-containing complexes to be isolated without the support of the sterically constraining, clam-shell-shaped bis(cyclopentadienyl) ligand set. The Th=N bonds are relatively long in both **2** and **3**, presumably reflecting the electron-richness of the metal center compared to those in the bis(cyclopentadienyl)-supported examples and the formal anionic charge associated with the "ate" nature. Our inability to synthesize more bulky analogues, or to isolate less bulky analogues, suggests that steric protection is a key enabler in the isolation of the bis(imido) unit, in agreement with calculations that suggest the thorium imido bonds are more polarized than their uranium congeners. The Th=N bond orders calculated by DFT (Wiberg) methods are twice the value of the single Th–N amido bonds in the same molecule, suggesting a much more polar Th=N bond than compared with uranium analogues, more like some of the most reactive early d-block M=N complexes. Thus, both experiments and calculations suggest the potential for reactivity closer to the transition-metal imido complexes that can activate hydrocarbon C–H bonds. Work is in progress to explore their capacity for new small-molecule activation chemistry.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06630. Crystallographic files are also deposited in the CCDC, numbers 1062064−1062066. Experimental raw data are openly available through the University of Edinburgh's DataShare archive, DOI:10.7488/ds/289.

> X-ray crystallographic data for **1c**, **2b**, and **3a** (CIF)
> Experimental procedures and characterization data for the real and computed complexes (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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■ NOTE ADDED AFTER ASAP PUBLICATION

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