

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

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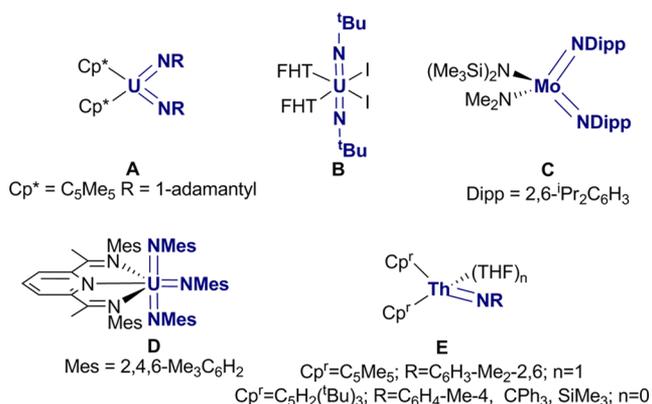
**S** Supporting Information

**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,  $K[\text{Th}(=\text{NAr})\text{N}''_3]$  and  $K_2[\text{Th}(=\text{NAr})_2\text{N}''_2]$ , are readily made from insertion reactions ( $\text{Ar} = \text{aryl}$ ,  $\text{N}'' = \text{N}(\text{SiMe}_3)_2$ ) into the Th–C bond of the cyclometalated thorium amides  $[\text{ThN}''_2(\text{N}(\text{SiMe}_3)(\text{SiMe}_2\text{CH}_2))]$  and  $K[\text{ThN}''(\text{N}(\text{SiMe}_3)(\text{SiMe}_2\text{CH}_2))_2]$ . 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.

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  $\text{O}=\text{U}=\text{O}$  unit in the uranyl dication  $[\text{UO}_2]^{2+}$ , in which the ligating atoms strongly donate electron density to the metal through one  $\sigma$  bond and two  $\pi$  bonds in an unreactive and formally triple bond.<sup>1</sup> Studies of multiple bonds between actinide ions and other heteroatoms are still rare<sup>2</sup> 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.<sup>3</sup>

Imido ligands are strong  $\sigma$ - and  $\pi$ -donors, and uranium imido bonds have a formal order of 3, like uranyl oxos. All known  $\text{U}^{\text{VI}}$  uranyl complexes contain *trans*-dioxo ions, and nearly 90% of  $\text{U}^{\text{VI}}$  bis(imido) complexes have a close to linear ( $>150^\circ$ ) geometry; examples of *cis*- and *trans*- $\text{U}^{\text{VI}}$  bis(imido) complexes respectively are  $(\text{Cp}^*)_2\text{U}(=\text{NR})_2$  (**A** in Figure 1) and the landmark, linear uranyl analogue  $[\text{U}(=\text{NR})_2]_2(\text{THF})_2$  (**B**).<sup>4</sup> 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  $\text{U}^{\text{VI}}$  tris(imido) structures (**D** in Figure 1).<sup>5</sup> Their bonding has been studied in terms of proving molecular analogues of actinide nitride nuclear fuels,<sup>6</sup> and their reactivities have been studied in the search for catalytic properties



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

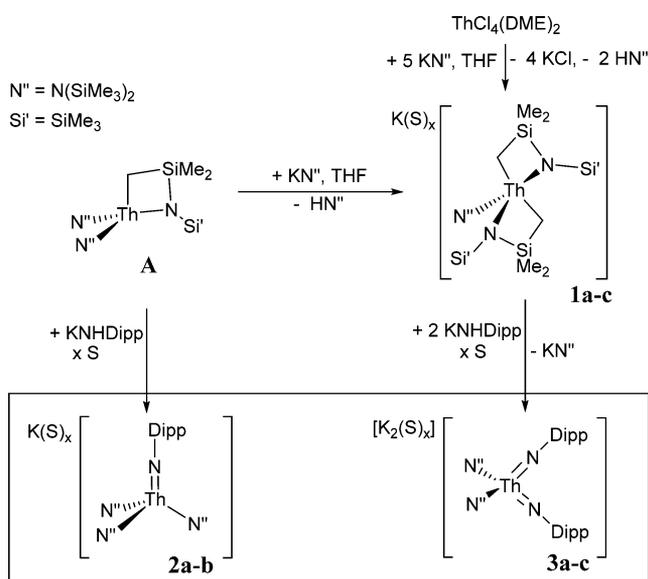
which might differ from those of the d-block complexes.<sup>7</sup> An intramolecular ligand C–H bond addition reaction was initiated by diazoalkane binding to a  $\text{U}^{\text{VI}}=\text{NR}$  bond in the complex  $(\text{C}_5\text{Me}_5)_2\text{U}(=\text{NC}_6\text{H}_2\text{tBu}_3)(\text{N}_2\text{CPh}_2)$ ,<sup>8</sup> the strong donation of the N(2p) orbitals and involvement of the uranium 5f orbitals is not conducive to the most desirable intermolecular hydrocarbon C–H bond addition chemistry, for which the more polar transition metal  $\text{M}=\text{N}$  bonds have been celebrated.<sup>9</sup>

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).<sup>10</sup> Early reports on the small-molecule activation reactivity of **E** include silane Si–H bond cleavage chemistry.<sup>11</sup> This supports the suggestion of more d-block-like behavior of thorium (cf. uranium), which is indicated by its ground-state  $[\text{Rn}]s^2d^2$  configuration, and a therefore greater potential for the reactivity of the  $\text{Th}=\text{NR}$  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  $[(\text{C}_5\text{H}_5)_2\text{Th}(=\text{NPh})_2]^{2-}$  ion find much weaker metal–nitrogen bonding than in the uranium complex),<sup>12</sup> and also to the difficulty in stabilizing low coordination numbers at the large  $\text{Th}^{\text{IV}}$  center.<sup>13</sup>

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

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Scheme 1. Synthetic Routes to the Bis(metallacyclic) Amido, and Mono- and Bis(imido) Thorium(IV) Complexes<sup>a</sup>

<sup>a</sup>Two syntheses of  $[\text{K}(\text{S})_x][\text{Th}\{\text{N}(\text{Si}')(\text{SiMe}_2\text{CH}_2)\}_2\text{N}'']$  (**1**), and the conversions of the mono- and bis(metallacyclic) into the mono- and bis(imido) complexes  $[\text{K}(\text{S})_x][\text{Th}(\text{=NDipp})\text{N}''_3]$  (**2**) and  $[\text{K}_2(\text{S})_x][\text{Th}(\text{=NDipp})_2\text{N}''_2]$  (**3**), respectively. For **1a**,  $x = 0$ ; for **1b**,  $\text{S} = 18\text{-c-6}$ ,  $x = 1$ ; for **1c**,  $\text{S} = \text{DME}$ ,  $x = 1$ ; for **2a**,  $x = 0$ ; for **2b**,  $\text{S} = 18\text{-c-6}$ ,  $x = 1$ ; for **3a**,  $\text{S} = \text{THF}$ ,  $x = 2$ ; for **3b**,  $\text{S} = 18\text{-c-6}$ ,  $x = 1$ ; for **3c**,  $\text{S} = 18\text{-c-6}$ ,  $x = 2$ .  $18\text{-c-6} = \text{C}_{12}\text{H}_{24}\text{O}_6$  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  $\text{Th}^{\text{IV}}$  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  $\text{Th}\{\text{N}(\text{Si}')(\text{SiMe}_2)\text{CH}_2\}_2\text{N}''_2$  (**A**, where  $\text{N}'' = \text{N}(\text{SiMe}_3)_2$ ,  $\text{Si}' = \text{SiMe}_3$ ) with 1 equiv of  $\text{KN}''$  affords the bis(metallacycle)  $[\text{K}(\text{S})_x][\text{Th}\{\text{N}(\text{Si}')(\text{SiMe}_2\text{CH}_2)\}_2\text{N}'']$  (**1**) as a colorless solid (Scheme 1). **1** can be also made from  $\text{ThCl}_4(\text{DME})_2$  and 5 equiv of  $\text{KN}''$  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,  $[\text{K}(18\text{-c-6})][\text{Th}\{\text{N}(\text{Si}')(\text{SiMe}_2\text{CH}_2)\}_2]$  (**1b**), and DME,  $[\text{K}(\text{DME})][\text{Th}\{\text{N}(\text{Si}')(\text{SiMe}_2\text{CH}_2)\}_2\text{N}'']$  (**1c**) ( $18\text{-c-6} = 18\text{-crown-6}$ ,  $\text{C}_{12}\text{H}_{24}\text{O}_6$ ). This “ate” complex is the direct analogue of the  $\text{U}^{\text{IV}}$  complex  $[\text{K}(\text{THF})][\text{U}\{\text{N}(\text{Si}')(\text{SiMe}_2)\text{CH}_2\}_2\text{N}'']$  reported by Ephritikhine.<sup>14</sup> At room temperature, NMR spectroscopy in  $\text{C}_6\text{D}_6/\text{THF}$  solution shows the diastereotopic relationship of the metallacyclic groups in **1**. In spectra of **1a**, the  $\text{CH}_2$  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  $\text{Si}(\text{CH}_3)_2$  hydrogens are observed as a single broad resonance at 0.49 ppm ( $W_{1/2} \approx 59$  Hz, 12 H). The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum shows a broad resonance for the  $\text{Th}-\text{CH}_2$  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  $\text{Si}(\text{CH}_3)_2$  carbons. The  $^{29}\text{Si}$ -INEPT spectrum shows the three anticipated resonances at  $\delta = -28.9$ ,  $-16.9$ , and  $-11.8$ , which compare closely with  $\delta = -32.9$ ,  $-12.1$ , and  $-9.4$  for **A**. Complex **1** does not react with further  $\text{KN}''$  in our hands.

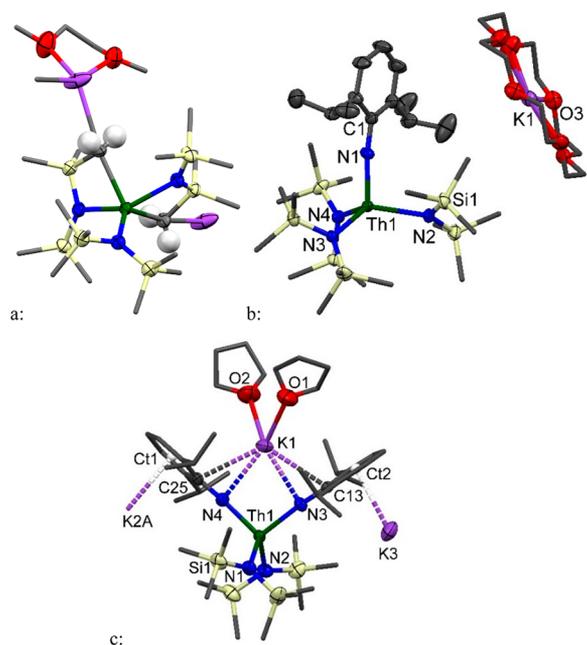
Treatment of **A** with  $\text{KNHNDipp}$  ( $\text{Dipp} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ ) in  $\text{C}_6\text{H}_6/\text{THF}$  or  $\text{THF}$  provides straightforward access to the colorless crystalline thorium imide  $[\text{K}(\text{S})_x][\text{Th}(\text{=NDipp})\text{N}''_3]$  (**2**, Scheme 1), isolable as a variety of solvates, depending on the workup procedure.<sup>15</sup> For example, from  $\text{THF}$  solution unsolvated **2a** ( $\text{S} = 0$ ) is isolated in quantitative yield, but addition of crown ether (18-c-6) and a small quantity of  $\text{THF}$  (10% by volume) to the benzene reaction mixture affords the separated ion-pair  $[\text{K}(18\text{-c-6})][\text{Th}(\text{=NDipp})\text{N}''_3]$  (**2b**). Complex **2** is highly oxygen and moisture sensitive but thermally stable for at least 14 days in a refluxing toluene/ $\text{THF}$  solution (ca. 10%  $\text{THF}$ ). NMR spectroscopy and X-ray diffraction (XRD) studies (see below) of **2** confirm the addition of the  $[\text{HNDipp}]$  group across the  $\text{Th}-\text{C}$  bond to form the  $\text{Th}=\text{NDipp}$  aryl imido complex. No NH resonance is observable in the spectra, and in the aliphatic region a lone singlet at  $\delta$  0.28 (54H) confirms the equivalence of the two original silylamide ligands and regenerated  $\text{N}''$  amido ligand. Finally,  $^{29}\text{Si}$ -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  $\text{KNHNDipp}$  in a  $\text{C}_6\text{H}_6/\text{THF}$  mixture (ca. 5:1 ratio) yields the first bis(imido) complex of thorium,  $[\text{K}_2(\text{S})_x][\text{Th}(\text{=NDipp})_2\text{N}''_2]$  (**3**), as a colorless crystalline solid in essentially quantitative yield (Scheme 1). Again, different solvated forms can be isolated, but the simple  $\text{THF}$  adduct (**3a**, with  $\text{S} = \text{THF}$ ,  $x = 2$ , 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:  $^1\text{H}$  NMR spectra of **3a** in  $\text{C}_6\text{D}_6$ , solubilized with a few drops of  $\text{THF}$ , contain a singlet at  $\delta$  0.26 (36H), demonstrating a single silylamide environment.  $^1\text{H}$  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  $[\text{K}(18\text{-c-6})]_2[\text{Th}(\text{=NDipp})_2\text{N}''_2]$ . The MALDI spectrum clearly shows a molecular ion peak at 901.5  $m/z$ , corresponding to  $[\text{Th}(\text{=NDipp})_2\text{N}''_2 - \text{H}]^+$ . 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  $\text{KN}''$  byproduct, over 8 h at room temperature solutions begin to degrade to multiple products, as determined by  $^1\text{H}$  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  $\text{ThCl}_4(\text{DME})_2$ . X-ray-quality crystals of **2b** were grown by slow cooling of a  $\text{C}_6\text{D}_6/\text{THF}$  solution, while single crystals of **3a** were grown by slow diffusion of hexane into a  $\text{C}_6\text{H}_6/\text{THF}$  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  $\text{Th}-\text{C}$  bonds of 2.562(5) and 2.576(5) Å fall within the expected range for single  $\text{Th}-\text{C}$  bonds (2.4–2.8 Å).

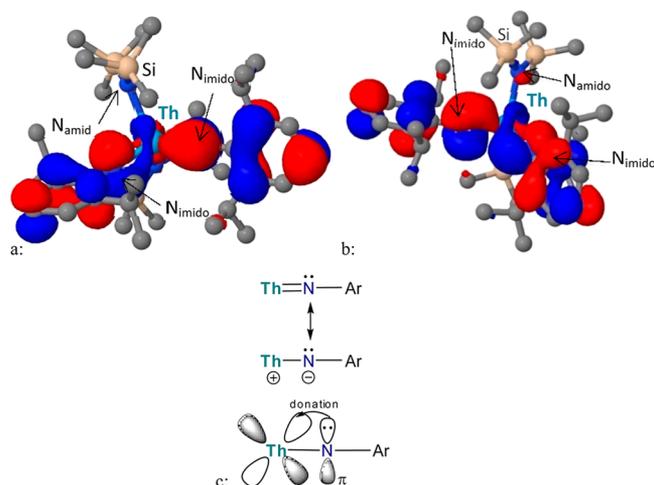
The molecular structure of **2b** (Figure 2b) shows a tetrahedral thorium environment with a  $\text{Th1}-\text{N1}$  imido bond length of 2.072(3) Å that is significantly shorter than a single  $\text{Th}-\text{N}$  amido bond (range 2.2–2.4 Å for thorium dialkylamides) but is one of the longest  $\text{Th}-\text{N}$  imido bonds observed to date. The four reported terminal thorium imido complexes **E** all contain two cyclopentadienyl co-ligands, either  $[(\text{C}_5\text{Me}_5)_2]^{10\text{b}}$  or



**Figure 2.** Solid-state molecular structure of (a)  $[\text{K}(\text{DME})][\text{Th}\{\text{N}(\text{Si}^i\text{-}(\text{SiMe}_2\text{CH}_2)_2\text{N}''\}_2]$  (**1c**), (b)  $[\text{K}(18\text{-c-}6)][\text{Th}(=\text{NDipp})\text{N}''_3]$  (**2b**), and (c)  $[\text{K}_2(\text{THF})_2][\text{Th}(=\text{NDipp})_2\text{N}''_2]$  (**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), N2–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).

$[(\text{C}_5\text{H}_2(\text{tBu})_3\text{-}1,2,4)_2]$ .<sup>11a</sup> 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<sup>IV</sup> 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.<sup>16</sup>

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<sub>imido</sub>–C<sub>Dipp</sub> 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



**Figure 3.** Calculated  $\pi$  Th–N<sub>imido</sub> 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.

both the nitrogen and *ipso*-aryl carbon atoms of each imido group, a feature observed previously in related uranium systems.<sup>7f</sup> 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<sub>imido</sub> bond in **2** at the second-order donor–acceptor level, with a polarized covalent  $\sigma$  bond and an ionic  $\pi$  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,<sup>17</sup> and a greater d orbital involvement than f, in line with previous studies by us.<sup>18</sup>

In **3'**, these double bonds can be described as a polarized covalent  $\sigma$  bond (90% 2p N; 10% 6d(65)–5f(35) Th) and an ionic  $\pi$  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<sub>imido</sub> bonds. Thus, the Th–N<sub>imido</sub> bonds in both mono- and bis(imido) compounds are correspondingly more polarized than in a typical uranium analogue.<sup>18</sup> The Wiberg bond indices are 0.88 in **3**, twice the indices of the Th–N<sub>amido</sub> 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 counter-cation 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,  $[\text{K}(\text{S})_x][\text{Th}(=\text{NDipp})\text{N}''_2]$  (**2**), and the first bis(imido)

thorium complex,  $[K_2(S)_x][Th(=NDipp)_2N''_2]$  (**3**), are both readily accessible from the simple, well-known thorium amidometallacycle,  $Th\{N(Si')(SiMe_2CH_2)\}_2N''_2$  (**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.

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## ■ REFERENCES

(1) (a) Denning, R. G. *J. Phys. Chem. A* **2007**, *111*, 4125. (b) Vallet, V.; Wahlgren, U.; Grenthe, I. *J. Phys. Chem. A* **2012**, *116*, 12373. (2) (a) Burns, C. J. *Science* **2005**, *309*, 1823. (b) Hayton, T. W. *Chem. Commun.* **2013**, *49*, 2956. (c) Smiles, D. E.; Wu, G.; Kaltsoyannis, N.; Hayton, T. W. *Chem. Sci.* **2015**, *6*, 3891. (3) (a) Wu, Q.-Y.; Wang, C.-Z.; Lan, J.-H.; Xiao, C.-L.; Wang, X.-K.; Zhao, Y.-L.; Chai, Z.-F.; Shi, W.-Q. *Inorg. Chem.* **2014**, *53*, 9607. (b) Minasian, S. G.; Keith, J. M.; Batista, E. R.; Boland, K. S.; Clark, D. L.; Kozimor, S. A.; Martin, R. L.; Shuh, D. K.; Tylliszczak, T. *Chem. Sci.* **2014**, *5*, 351. (c) La Pierre, H. S.; Meyer, K. *Inorg. Chem.* **2013**, *52*, 529.

(d) Kaltsoyannis, N. *Inorg. Chem.* **2013**, *52*, 3407. (e) Hayton, T. W. *Dalton Trans.* **2010**, *39*, 1145.

(4) (a) Hayton, T. W.; Boncella, J. M.; Scott, B. L.; Palmer, P. D.; Batista, E. R.; Hay, P. J. *Science* **2005**, *310*, 1941. (b) Brown, D. R.; Denning, R. G. *Inorg. Chem.* **1996**, *35*, 6158.

(5) Anderson, N. H.; Odoh, S. O.; Yao, Y.; Williams, U. J.; Schaefer, B. A.; Kiernicki, J. J.; Lewis, A. J.; Goshert, M. D.; Fanwick, P. E.; Schelther, E. J.; Walensky, J. R.; Gagliardi, L.; Bart, S. C. *Nat. Chem.* **2014**, *6*, 919.

(6) (a) Thomson, R. K.; Cantat, T.; Scott, B. L.; Morris, D. E.; Batista, E. R.; Kiplinger, J. L. *Nat. Chem.* **2010**, *2*, 723. (b) King, D. M.; McMaster, J.; Tuna, F.; McInnes, E. J. L.; Lewis, W.; Blake, A. J.; Liddle, S. T. *J. Am. Chem. Soc.* **2014**, *136*, 5619.

(7) (a) Jilek, R. E.; Tomson, N. C.; Shook, R. L.; Scott, B. L.; Boncella, J. M. *Inorg. Chem.* **2014**, *53*, 9818. (b) Schmidt, A.-C.; Heinemann, F. W.; Maron, L.; Meyer, K. *Inorg. Chem.* **2014**, *53*, 13142. (c) Camp, C.; Pécaut, J.; Mazzanti, M. *J. Am. Chem. Soc.* **2013**, *135*, 12101. (d) Matson, E. M.; Crestani, M. G.; Fanwick, P. E.; Bart, S. C. *Dalton Trans.* **2012**, *41*, 7952. (e) Turner, Z. R.; Bellabarba, R.; Tooze, R. P.; Arnold, P. L. *J. Am. Chem. Soc.* **2010**, *132*, 4050. (f) Fox, A. R.; Cummins, C. C. *J. Am. Chem. Soc.* **2009**, *131*, 5716. (g) Graves, C. R.; Yang, P.; Kozimor, S. A.; Vaughn, A. E.; Clark, D. L.; Conradson, S. D.; Schelther, E. J.; Scott, B. L.; Thompson, J. D.; Hay, P. J.; Morris, D. E.; Kiplinger, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 5272. (h) Bart, S. C.; Anthon, C.; Heinemann, F. W.; Bill, E.; Edelstein, N. M.; Meyer, K. *J. Am. Chem. Soc.* **2008**, *130*, 12536. (i) Spencer, L. P.; Yang, P.; Scott, B. L.; Batista, E. R.; Boncella, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 2930. (j) Arney, D. S. J.; Burns, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 9448.

(8) Kiplinger, J. L.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Chem. Commun.* **2002**, *30*.

(9) (a) Scott, J.; Basuli, F.; Fout, A. R.; Huffman, J. C.; Mendiola, D. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 8502. (b) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.

(10) (a) Haskel, A.; Straub, T.; Eisen, M. S. *Organometallics* **1996**, *15*, 3773. (b) Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5017. (c) Ren, W.; Zi, G.; Fang, D.-C.; Walter, M. D. *J. Am. Chem. Soc.* **2011**, *133*, 13183. (d) Ren, W.; Zi, G.; Walter, M. D. *Organometallics* **2012**, *31*, 672.

(11) (a) Ren, W.; Zi, G.; Fang, D.-C.; Walter, M. D. *Chem. - Eur. J.* **2011**, *17*, 12669. (b) Ren, W.; Zhou, E.; Fang, B.; Zi, G.; Fang, D.-C.; Walter, M. D. *Chem. Sci.* **2014**, *5*, 3165. (c) Zhou, E.; Ren, W.; Hou, G.; Zi, G.; Fang, D. C.; Walter, M. D. *Organometallics* **2015**, *34*, 3637.

(12) Belkhir, L.; Lissillour, R.; Boucekkine, A. *J. Mol. Struct.: THEOCHEM* **2005**, *757*, 155.

(13) Schelther, E. J.; Morris, D. E.; Scott, B. L.; Kiplinger, J. L. *Chem. Commun.* **2007**, 1029.

(14) Bénaud, O.; Berthet, J.-C.; Thuéry, P.; Ephritikhine, M. *Inorg. Chem.* **2010**, *49*, 8117.

(15) The drawing of a double bond is used as a shorthand representation of the dianionic group, and not an indication of the degree of multiple bonding.

(16) (a) Chan, H.-S.; Li, H.-W.; Xie, Z. *Chem. Commun.* **2002**, 652. (b) Zuckerman, R. L.; Bergman, R. G. *Organometallics* **2000**, *19*, 4795. (c) Gehrman, T.; Lloret Fillol, J.; Wadepohl, H.; Gade, L. H. *Organometallics* **2012**, *31*, 4504.

(17) Smiles, D.; Wu, G.; Kaltsoyannis, N.; Hayton, T. W. *Chem. Sci.* **2015**, *6*, 3891.

(18) Barros, N.; Maynau, D.; Maron, L.; Eisenstein, O.; Zi, G. F.; Andersen, R. A. *Organometallics* **2007**, *26*, 5059.

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