

Reactivity of Multimetallic Thorium Nitrides Generated by Reduction of Thorium Azides

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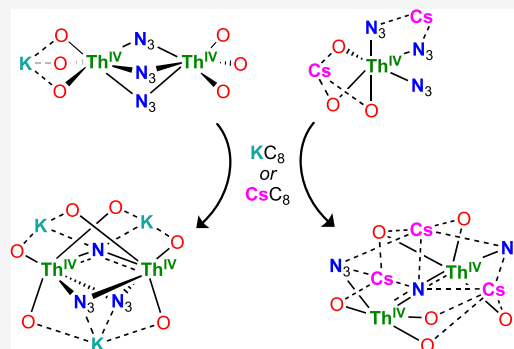


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ABSTRACT: Thorium nitrides are likely intermediates in the reported cleavage and functionalization of dinitrogen by molecular thorium complexes and are attractive compounds for the study of multiple bond formation in f-element chemistry, but only one example of thorium nitride isolable from solution was reported. Here, we show that stable multimetallic azide/nitride thorium complexes can be generated by reduction of thorium azide precursors—a route that has failed so far to produce Th nitrides. Once isolated, the thorium azide/nitride clusters, $M_3\text{Th}=\text{N}=\text{Th}$ ($M = \text{K}$ or Cs), are stable in solutions probably due to the presence of alkali ions capping the nitride, but their synthesis requires a careful control of the reaction conditions (solvent, temperature, nature of precursor, and alkali ion). The nature of the cation plays an important role in generating a nitride product and results in large structural differences with a bent $\text{Th}=\text{N}=\text{Th}$ moiety found in the K-bound nitride as a result of a strong K–nitride interaction and a linear arrangement in the Cs-bound nitride. Reactivity studies demonstrated the ability of Th nitrides to cleave CO in ambient conditions yielding CN^- .



INTRODUCTION

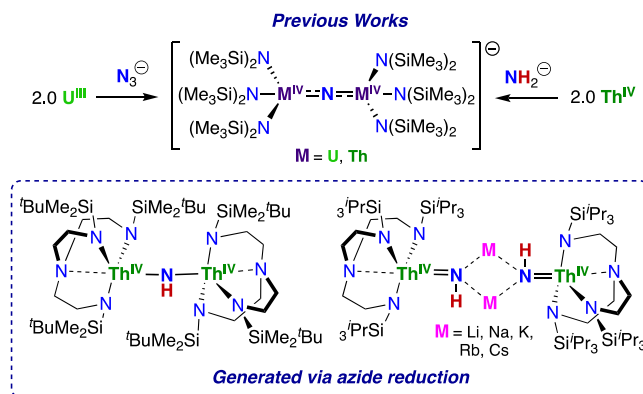
Metal nitride complexes have been extensively studied because of their key roles in the biological (nitrogenase) and industrial (Haber–Bosch) conversion of dinitrogen to ammonia and in N-transfer processes.¹ However, nitride chemistry of actinides is significantly less developed compared to the d-block metals^{1j,2} and essentially limited to uranium.

The chemistry of uranium nitride has developed significantly from their first isolation under matrix conditions³ and has now extended to the synthesis of molecular terminal and bridging nitrides that have shown high reactivity toward small molecule activation^{1h,4} and brought important information about the nature of uranium–ligand bonding.⁵ A few mononuclear^{6,5a,7} terminal nitrides and a larger number of polynuclear nitride-bridged uranium complexes^{1h,8,4a,c,j,9} have been prepared by using various synthetic methods that involve thermal, photolytic, or chemical reduction of uranium azides precursors or uranium promoted reduction of dinitrogen.^{8d,9b}

Thorium is a largely available actinide with properties close to those of group four metals that lead to unusual geometries and reactivity,¹⁰ where thorium nitrides are likely intermediates in the reported cleavage and functionalization of dinitrogen by molecular thorium complexes.¹¹ Notably, the formation of a thorium amide complex from cleavage of dinitrogen by a transient zerovalent thorium synthon reported almost 20 years ago may involve a nitride intermediate.^{11a}

However, while several thorium imido complexes have been reported (Scheme 1),¹² until 2019, the isolation of thorium nitrides was limited to matrix conditions,¹³ and attempts to

Scheme 1. Previously Reported Actinide–Nitride Complexes



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produce molecular bridging or terminal nitrides by reduction of azide precursors has so far only led to the isolation of amide and imide species.

The Liddle group had successfully used the triamidoamine ligands $\{N(CH_2CH_2NSiMe_2^tBu)_3\}^{3-}$ ($Tren^{DMBS}$) and the bulkier $\{N(CH_2CH_2NSi^tPr_3)_3\}^{3-}$ ($Tren^{TIPS}$) to isolate bridging and terminal uranium nitrides, respectively.^{7b,c,12b} However, the reduction of the thorium azide complexes supported by the $Tren^{DMBS}$ and the $Tren^{TIPS}$ ligands generated transient, highly nucleophilic nitrides that can abstract a proton from the solvent of the ligand to yield the parent bridging or terminal imido complexes.^{9a,12b} Attempts to trap the transient nitrides with electrophilic reagents were not successful.

These results suggested that Th(IV) nitrides are more reactive than the more covalent uranium analogues, an hypothesis corroborated by computational studies. Shortly after, the Hayton group¹⁴ was able to isolate the first example of a bridging thorium nitride using a different synthetic approach that involves the reaction of the $[Th\{N(R)(SiMe_2)CH_2\}(NR_2)_2]$ ($R = SiMe_3$) with $NaNH_2$. The isolated thorium nitride $[Na(18\text{-crown-6})(Et_2O)][\{(LN)_3Th\}_2(\mu-N)]$ ($LN = N(SiMe_3)_2$) did not display a higher reactivity than the analogous uranium complex $[NBu_4][\{(LN)_3U\}_2(\mu-N)]$, at least with respect to C–H bond activation.¹⁵ The latter result suggests that the high difficulty in isolating thorium nitrides may arise from the synthetic method used, which is more sensitive for the thorium system compared to uranium.

Because our group successfully isolated several terminal and bridging uranium nitrides with siloxides ($-OSi(O^tBu)_3$) as supporting ligands using the azide route, we set out to explore the possibility of preparing analogous thorium nitrides using an azide reduction route. Herein, we demonstrate that relatively stable bridging thorium nitrides can be synthesized by reduction of an azide precursor by tuning the conditions that prevent unwanted reactivity.

RESULTS AND DISCUSSION

Synthesis and Characterization of Heteroleptic Siloxide Complexes. To prepare nitride-bridged dithorium complexes, supported by $-OSi(O^tBu)_3$ ligands, we pursued the approach involving the reduction of a dithorium azide precursor. Because thorium siloxide complexes were not reported to date, we first prepared the heteroleptic complex, $[Th(OSi(O^tBu)_3)_3Cl(THF)_2]$, **1**, by reacting a THF solution of $KOSi(O^tBu)_3$ (3 equiv) with $ThCl_4(DME)_2$ ¹⁶ at $-40^\circ C$ for 16 h. Complex **1** was isolated in 69% yield from a concentrated reaction mixture in toluene at $-40^\circ C$ (Scheme S1 and Figure 1). The synthesis of **1** requires the use of low temperature to prevent ligand scrambling which is common in actinide alkoxide, aryloxide, and amide chemistry and has resulted in a scarce number of synthetic and reactivity studies of heteroleptic complexes of thorium.¹⁷

With complex **1** in hand, we pursued the synthesis of thorium azide complexes supported by $-OSi(O^tBu)_3$ ligands. Addition of excess (3.0 equiv) KN_3 to a THF solution of **1** at room temperature for 16 h led to the isolation, after removal of the KCl byproduct, of colorless crystals of the dinuclear complex $[K(OSi(O^tBu)_3)_3Th(\mu-N_3)_3Th(OSi(O^tBu)_3)_3(THF)]$ (**2-K**) in 71% yield from a concentrated toluene solution of the reaction mixture at $-40^\circ C$ (Scheme 1 and Figure 2).

Similarly, the addition of excess (3.0 equiv) CsN_3 to a THF solution of **1** at room temperature for 16 h resulted in the

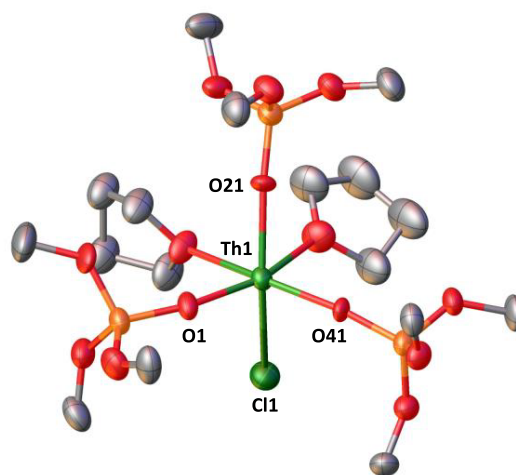


Figure 1. Molecular structure of complex $[Th(OSi(O^tBu)_3)_3Cl(THF)_2]$, **1**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and methyl groups on the $-OSi(O^tBu)_3$ ligands have been omitted for clarity.

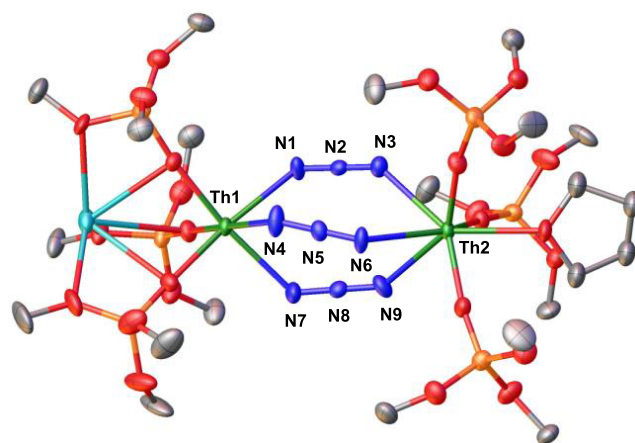
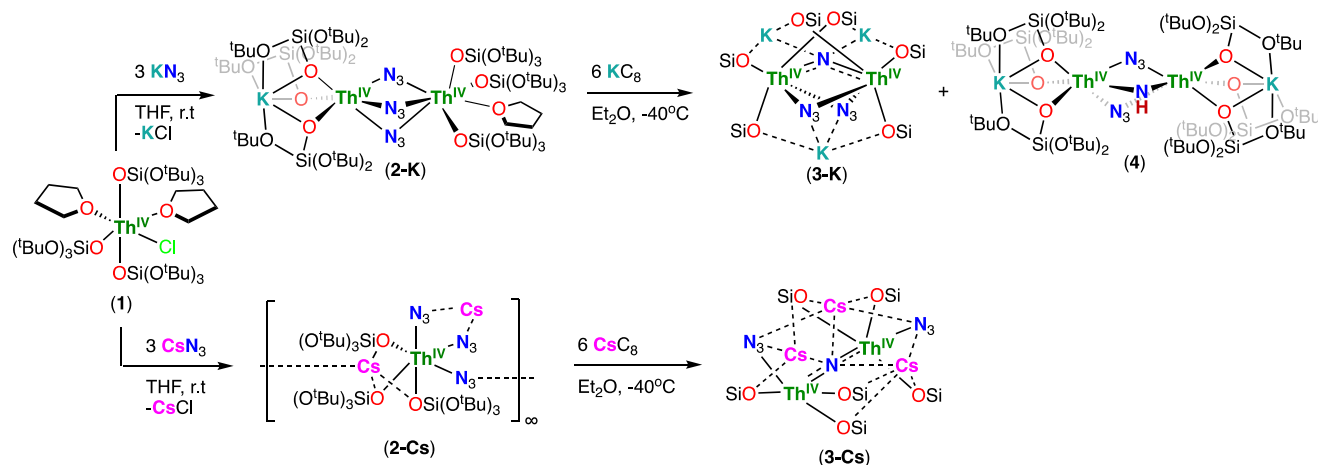


Figure 2. Molecular structure of complex $[K(OSi(O^tBu)_3)_3Th(\mu-N_3)_3Th(OSi(O^tBu)_3)_3(THF)]$, **2-K**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and methyl groups on the $-OSi(O^tBu)_3$ ligands have been omitted for clarity.

formation of a new species and full consumption of the starting material as indicated by 1H NMR studies (Figure S19). Colorless crystals of the complex $[Cs_2\{(Th(OSi(O^tBu)_3)_3(N_3)_3)\}_\infty]$ (**2-Cs**) were isolated in 69% yield from a concentrated THF solution of the reaction mixture at $-40^\circ C$ (Scheme 2 and Figure 3). Thus, the reaction with CsN_3 results in the coordination of three azide ligands to each Th center, while three azide ligands bridge two Th centers in **2-K**. In both cases, the azide replaces the chloride ligand and additional alkali azide is bound to the complex, but the Th:azide ratio is different in the two complexes (1:1.5 in **2-K** and 1:3 in **2-Cs**). Previously, two examples of azide-bridged thorium complexes were reported, one polymeric¹⁸ and one trinuclear,^{9a} which were also obtained from salt metathesis reactions, but the coordination of additional alkali azide was not observed. In contrast, the neutral thorocene was reported to react with NaN_3 to yield the azide derivative $[(18\text{-c-6}NaN_3)Th(COT)]$.¹⁹

Structural Characterization of Heteroleptic Siloxide Complexes. The solid-state molecular structures of com-

Scheme 2. Synthesis of Complexes 2-K, 2-Cs, 3-K, 3-Cs, and 4^a

^aThe siloxide ligand is written as OSi in 3-K and 3-Cs.

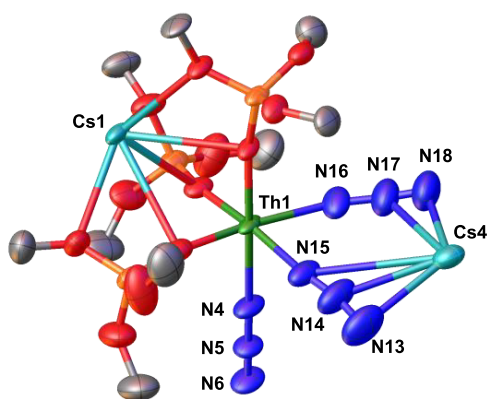


Figure 3. Molecular structure of complex $[\text{Cs}_2\{\text{Th}(\text{OSi}(\text{O}^t\text{Bu})_3)_3(\text{N}_3)_3\}]_\infty$, 2-Cs, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and methyl groups on the $-\text{OSi}(\text{O}^t\text{Bu})_3$ ligands have been omitted for clarity.

plexes 1, 2-K, and 2-Cs were determined by X-ray diffraction studies (Table S1).

The molecular structure of complex 1 (Figure 1) shows a mononuclear Th(IV) complex. The metal center is hexacoordinated and bound by three $-\text{OSi}(\text{O}^t\text{Bu})_3$, a chloride, and two THF ligands in a pseudo-octahedral geometry. The average value of the Th–O_{sil} distances (2.19(1) Å) is similar to those found in Th(IV) aryloxide and alkoxide complexes (2.189(6)–2.180(3) Å).^{17a,20} The three siloxide ligands occupy one face of the distorted octahedron.

The solid-state molecular structure of complex 2-K (Figure 2) shows a dinuclear heterometallic complex consisting of two asymmetric Th(IV) ions, bridged by three end-to-end azido ligands and a $\text{OSi}(\text{O}^t\text{Bu})_3$ -bound K⁺ cation. Th1 is hexacoordinated by the three bridging azides and three $-\text{OSi}(\text{O}^t\text{Bu})_3$ ligands, capped by the K⁺ cation. Conversely, Th2 is heptacoordinated by three bridging azides, three $-\text{OSi}(\text{O}^t\text{Bu})_3$, and one THF ligand. The average Th1–N_{azide} distance (2.506(8) Å) is slightly shorter than the average Th2–N_{azide} distance (2.64(1) Å). Such an asymmetric binding of the bridging azide has already been observed in previously reported Th(IV) polynuclear complexes^{9a,18} and was attributed to the presence of an ionic and a dative metal–azide

interaction. The values of the N–N bond distances in 2-K are similar to each other for all the three azide ligands, suggesting weak activation.

The presence of a Cs cation results in a very different structure of the azide complex 2-Cs.

The solid-state molecular structure of complex 2-Cs (Figure 3) consists of a 3D infinite coordination polymer in which the Th and Cs⁺ centers are bridged by one end-to-end and two μ_3 - $\eta^1:\eta^2$ -bridging azido ligands. The repeating unit of the coordination polymer is a mononuclear Th(IV) complex bound by three $-\text{OSi}(\text{O}^t\text{Bu})_3$ and three azide ligands. The azide ligands in 2-Cs are terminally bound to the Th center and capped by a Cs⁺ cation, while the azide ligands bridge two Th ions in 2-K. The coordination mode found in 2-Cs results in a shorter average Th^{IV}–N_{azide} bond distance (2.43(1) Å) compared to 2-K, which is only slightly longer than the value reported for the Th–N_{azide} in the complex $[\text{Th}(\text{Tren}^{\text{TIPS}})\text{N}_3]$ (2.365(3) Å).^{12b} The polymeric structure of 2-Cs is held together by the Cs cations bridging thorium bound azides. This structure differs from the Th azido coordination polymer reported by Kiplinger where azide ligands bridge thorium cations to yield an open infinite chain.¹⁸

Synthesis of Multimetallic Nitride–Azide Complexes.

To promote nitride formation, we investigated the reduction of complexes 2-K and 2-Cs with KC₈ and CsC₈, respectively (Scheme 2). Addition of excess (6.0 equiv) KC₈ to a solution of 2-K in Et₂O at -40 °C for 16 h resulted in full consumption of the starting material and the formation of the bis-azide, mononitride $[\text{K}_3\{\text{Th}(\text{OSi}(\text{O}^t\text{Bu})_3)_3(\mu\text{-N})(\mu\text{-N}_3)_2\}]$ (3-K) and bis-azide, monoimide $[\text{K}_2\{\text{Th}(\text{OSi}(\text{O}^t\text{Bu})_3)_3(\mu\text{-NH})(\mu\text{-N}_3)_2\}]$ (4) complexes in a 7:3 ratio as indicated by the ¹H NMR spectrum of the reaction mixture (Figure S8). Complex 3-K was obtained analytically pure in 48% by washing out 4 from the reaction mixture with benzene. Single crystals suitable for XRD analysis of 3-K were isolated from a concentrated toluene solution. Attempts to isolate analytically pure 4 from the reaction mixture proved unsuccessful due to contaminant precipitation of 3-K. Alternatively, when the reaction was performed at room temperature, the amount of monoimide, 4, increased to a ratio of 1:1 (3-K:4; Figure S8), whereas the reduction of 2-K with KC₈, performed in THF at -40 °C, resulted in complex 4 as the major product of the reaction (Figure S16), and only minor traces of decomposition

products could be detected. The ^1H NMR spectra of isolated complexes **3-K** and **4** display single resonances at δ 1.60 and 1.58 ppm in C_6D_6 , respectively (Figures S10 and S18). The ^1H NMR resonance of the imido ($-\text{NH}$) group in complex **4** could not be identified in various solvents, most likely due to ligand fluxionality (exchange of the imido ($-\text{NH}$) and azide groups), which could not be slowed even at lower temperatures.²¹

Complex **4** can also be independently synthesized upon protonation of **3-K** with a weak acid, $\text{HNEt}_3\text{BPh}_4$, thus confirming its Th(IV)/Th(IV) nature (see Supporting Information and Figure S17). Complex **4** is likely to be generated by proton abstraction from the solvent by a nitride intermediate generated during the reduction of the azide complex **2-K**. Such reactivity is consistent with the anticipated high nucleophilic character of the thorium bridging nitride and previous studies.^{9a,12b} Particularly, only the imido-bridged complex $[\{\text{Th}(\text{Tren}^{\text{DMBS}})(\mu\text{-NH})\}]$ could be isolated from the reduction of the $[\{\text{Th}(\text{Tren}^{\text{DMBS}})(\mu\text{-N}_3)\}]_3$ in toluene, while the use of ethereal solvents resulted in proton abstraction from the ligand.^{9a} The conditions used in the reduction (i.e., solvent and temperature) are crucial for isolating the nitride, **3-K**, in good yield.

It should be noted that, once isolated, complex **3-K** is stable in benzene and toluene solutions at room temperature for up to 2 weeks but only stable in THF for 1 week (Figures S13–S15). These results indicate that the presence of bound potassium azides is likely to play an important role both during the nitride formation and on the stability of the final complex.

To probe the role of the cation in the synthesis of the thorium nitride from the azide precursor and on the stability of the nitride, we performed the reduction of **2-Cs** with 6.0 equiv of CsC_8 at -40°C in Et_2O . The reduction proceeds with the clean formation of the bis-azide, mononitride complex $[\text{Cs}_3\{\text{Th}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-N})(\text{N}_3)_2\}]$ (**3-Cs**), which was isolated in 71% yield from a concentrated toluene solution at -40°C (Figure S22). Complex **3-Cs** is stable in benzene and toluene solutions at room temperature for up to 2 weeks but begins to decompose in THF at room temperature immediately (Figures S24–S26). The clean formation of **3-Cs** from **2-Cs** suggests the important role the cation plays, not only in stabilizing the isolated product but also in preventing the reaction with ligands or solvents during the reduction of **2-Cs**.

Complexes **3-K** and **3-Cs** are the second examples of dinuclear thorium nitrides isolated and the first thorium nitrides obtained by the reduction of azide precursors. They also provide the first example of a nitride–azide multimetallic cluster, associating thorium and alkali ions, allowing a comparative analysis of the $\text{Th}=\text{N}=\text{Th}$ moiety in the presence of different capping alkali ions.

It should be noted that reduction of the products obtained after reaction of **1** with 1.0 equiv of KN_3 or CsN_3 azide so far has not allowed the isolation and characterization of a thorium nitride complex.

Structural Characterization of Nitride and Imido Complexes. The solid-state molecular structures of complexes **3-K**, **3-Cs**, and **4** were determined by X-ray diffraction studies (Table S2).

The molecular structures of complexes **3-K** and **3-Cs** are presented in Figures 4a and 4b, respectively. They both display a dinuclear Th(IV) complex, featuring a bridging nitride and two azide ligands, but the presence of two different

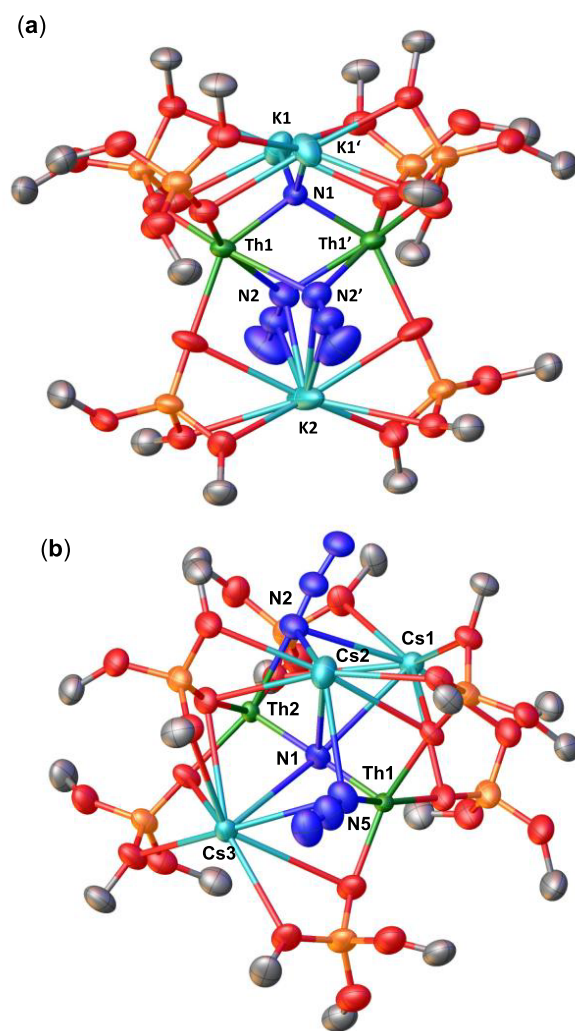
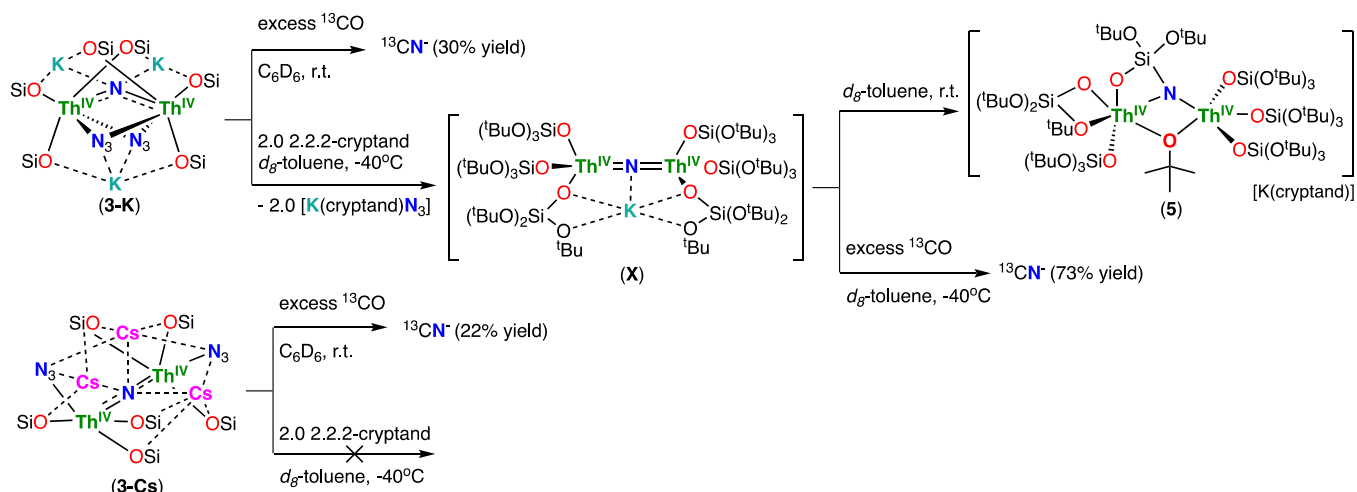


Figure 4. Molecular structures of complexes (a) $[\text{K}_3\{\text{Th}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-N})(\mu\text{-N}_3)_2\}]$, **3-K**, and (b) $[\text{Cs}_3\{\text{Th}(\text{OSi}(\text{O}^t\text{Bu})_3)_2(\mu\text{-N})(\text{N}_3)_2\}]$, **3-Cs**, with thermal ellipsoids drawn at the 50% probability level. The methyl groups on the $-\text{OSi}(\text{O}^t\text{Bu})_3$ ligands have been omitted for clarity.

counterions gives rise to paramount structural differences in the two complexes.

In complex **3-K**, each Th(IV) ion is bound by three $-\text{OSi}(\text{O}^t\text{Bu})_3$ ligands, a bridging nitride, and the two bridging azide ligands. Two K^+ cations bind the bridging nitride at a short distance (average $\text{K}-\text{N}_{\text{nitride}} = 2.760(3)$ Å), while the third K^+ is bound by the two bridging azide ligands. Conversely, the Th(IV) ions in complex **3-Cs** are bound by three $-\text{OSi}(\text{O}^t\text{Bu})_3$ ligands, one terminal azide ligand, and a bridging nitride ligand. The three Cs^+ cations bind the bridging nitride (average $\text{Cs}-\text{N}_{\text{nitride}} = 3.49(6)$ Å) at significantly longer distance compared to the K^+ ion. One of the Cs^+ cations ($\text{Cs}2$) also binds both terminal azides, whereas $\text{Cs}1$ and $\text{Cs}3$ bind only one azide ligand.

In complex **3-K**, the $\text{Th}=\text{N}=\text{Th}$ ($2.185(4)$ Å) and the two $\text{Th}-\text{N}_3-\text{Th}$ moieties are bent at $114.4(3)^\circ$ and $86.1(2)^\circ$, respectively. A similar geometry has been observed in an analogous dinuclear U(IV) bridging nitride bridging azide complex $[\text{K}_2\{\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_3(\mu\text{-N})(\mu\text{-N}_3)\}]$ ($\text{U}-\text{N}_{\text{nitride}}-\text{U} = 124.6(6)^\circ$ and $\text{U}-\text{N}_{\text{azide}}-\text{U} = 91.4(5)^\circ$),^{4c} suggesting that the bridging mode of the azide ligand promotes the bending of

Scheme 3. Reactivity of Complexes 3-K and 3-Cs^a

^aThe siloxide ligand is written as OSi in 3-K and 3-Cs.

the Th=N=Th moiety. The value of the Th=N=Th bond distances are shorter than those found in the previously reported bridging imido complexes (Th–N_{imido} = 2.264(15)–2.331(4) Å),^{9a,22} in agreement with the presence of Th=N multiple bonding. The bent geometry found in 3-K differs significantly from the linear geometry found in the only reported nitride bridged thorium complex [K(18-crown-6)(THF)₂][(R₂N)₃Th(μ-N)Th(NR₂)₃]¹⁴ ((Th=N=Th:178.1(15)°).

In contrast, in complex 3-Cs, the Th=N=Th moiety adopts a linear geometry with Th=N bond distances (2.11(3) and 2.15(3) Å) and bond angle (178.1(15)°) consistent with those found in the linear thorium bridging nitride [K(18-crown-6)(THF)₂][(R₂N)₃Th(μ-N)Th(NR₂)₃]¹⁴ (Th1–N1 = 2.14(2) Å, Th2–N1 = 2.11(2) Å). In both 3-K and 3-Cs, the bond distances in the azide ligands are comparable, suggesting weak activation in both cases. The structural differences between the two complexes are likely due to combined steric and electronic effect, resulting from the larger size and lower Lewis acidity of the Cs⁺ counterion compared to K⁺. The absence of bridging azides in the nitride complex 3-Cs mirrors the terminal nature of the azides ligands in the mononuclear precursor 2-Cs, suggesting that the structure of the azide precursors may play a key role in determining the final structure of the nitride.

The solid-state molecular structure of 4 shows a dinuclear Th(IV) complex bridged by two azido ligands and an imido (–NH) ligand. Each Th(IV) center is bound by three –OSi(O^tBu)₃ which also bind a K⁺ ion. The metrical parameters are in agreement with the presence of a bridging imide (Figure S54). Notably, the Th–N_{imido} bond distances (Th2–N1 = 2.274(18) Å, Th1–N1 = 2.351(17) Å) are comparable to those reported for the bridging Th–NH linkage in the complex [{Th(Tren^{DMBS})₂(μ-NH)] (2.331(4) and 2.312(4) Å)^{9a} and are significantly longer than the Th–nitride distances found in 3-K (*vide infra*) and in previously reported terminal imido complexes (2.038(3)–2.165(3) Å).^{12c,d,23}

Reactivity of Thorium Nitrides. Inspired by the high nucleophilic reactivity toward unreactive small molecules reported for multimetallic U(IV) bridging nitrides supported by siloxide ligands,^{4b,e,f,24} we next investigated the reactivity of

the nitride complexes, 3-K and 3-Cs, toward protonation (H⁺), CO, and CO₂.

Addition of a 2 M ethereal HCl solution to 3-K and 3-Cs led to the quantitative (100%) formation of NH₄Cl as indicated by the quantitative ¹H NMR spectroscopy (Figures S28 and S29), confirming the presence of nucleophilic nitride ligands.

Addition of excess ¹³CO (5 equiv) to a C₆D₆ solution of 3-K or 3-Cs led to slight changes in the ¹H NMR spectrum monitored over 24 h (Figures S31 and S34). Attempts to isolate single crystals from the reaction mixtures proved unsuccessful, but after removal of the volatiles and hydrolysis with D₂O (pD = 13) of the reaction residue, ¹³CN⁻ was observed by quantitative ¹³C NMR spectroscopy (Figures S33 and S36) in 30% (3-K) and 22% yield (3-Cs).

This reactivity parallels that of the reported nitride-bridged diuranium(IV) complex, [NBu₄][((^tBuO)₃SiO)₃U₂(μ-N)],¹⁵ and its Cs-capped analogue, [Cs((^tBuO)₃SiO)₃U₂(μ-N)],^{4e} that were reported to cleave CO to yield CN⁻ and an oxide diuranium complex, although higher yields in cyanide were observed (60–100%). The computed reaction mechanism involved CO binding to the uranium, followed by CO migratory insertion onto the U–nitride bond.^{4e} A similar mechanism can be anticipated for the thorium nitride complexes.

Complex 3-Cs also reacts with excess ¹³CO₂ (5 equiv), yielding a mixture of compounds that could not be isolated. After removal of the volatiles and hydrolysis with D₂O (pD = 13) of the reaction residue, D¹³CO₃⁻ and ¹³CO₃²⁻ were observed by quantitative ¹³C NMR spectroscopy (Figures S47 and S48) in 48% combined yield as previously observed for the hydrolysis of uranium dicarbamates derived from the reaction of uranium nitrides with CO₂.¹⁵

On the basis of these results, we postulated that the reactivity of the bridging nitride could be altered by removal of the bound alkali azides. We hypothesized that removal of the K⁺ or Cs⁺ might favor the loss of the azide ligands, affecting both the overall nucleophilicity of the nitride ligand and the coordination of the CO to the thorium center.

Addition of 2.0 equiv of 2,2,2-cryptand to a solution of 3-Cs in *d*₈-toluene did not lead to any changes in the ¹H NMR spectrum, indicating that the Cs⁺ cations are most likely still bound in the core (Scheme 3 and Figure S37).

In contrast, addition of 2.0 equiv of 2.2.2-cryptand to a solution of 3-K in toluene at $-40\text{ }^{\circ}\text{C}$ resulted in full consumption of the starting material and clean formation of a new species, resonating at δ 1.81 ppm in the ^1H NMR spectrum and assigned to the putative nitride complex, “[{KTh₂(OSi(O^tBu)₃)₆(μ -N)}]”, X (Scheme 3 and Figure S39). Attempts to grow single crystals from the reaction mixture proved unsuccessful. However, [K(2.2.2-cryptand)N₃] could be isolated and was confirmed by XRD analysis, providing further evidence of the removal of the K⁺ and azide ligands by addition of 2.2.2-cryptand. The intermediate species, “[{KTh₂(OSi(O^tBu)₃)₆(μ -N)}]” (X), is stable at $-40\text{ }^{\circ}\text{C}$ for up to 2 weeks in toluene but is unstable at room temperature after 12 h, affording a mixture of unidentifiable species (Scheme 3 and Figure S38). Decomposition at room temperature was also reported for the analogous [NBu₄]-[(^tBuO)₃SiO₃U]₂(μ -N)¹⁵ and Cs-capped [Cs-(^tBuO)₃SiO₃U]₂(μ -N)^{4e} nitrides.

Recrystallization of the reaction mixture from hexane at room temperature afforded few colorless crystals identifiable as the decomposition product, [K(2.2.2-cryptand)][{Th₂(OSi(O^tBu)₃)₅(μ -O^tBu)(μ -NOSi(O^tBu)₂)}] (5) (Figure 5). At-

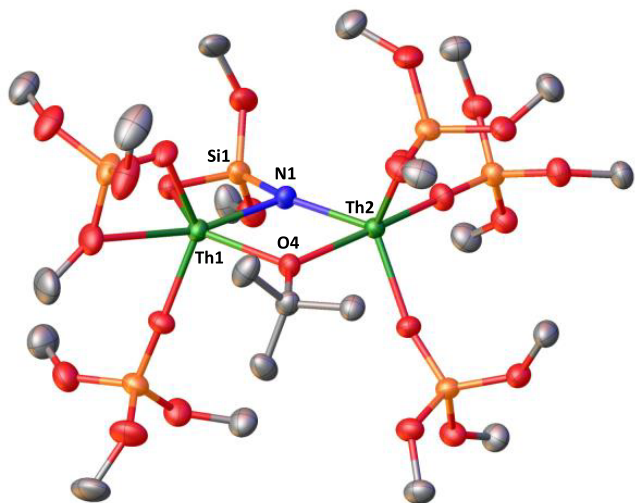


Figure 5. Molecular structures of the anion in complex [K(2.2.2-cryptand)][{Th₂(OSi(O^tBu)₃)₅(μ -O^tBu)(μ -NOSi(O^tBu)₂)}], 5, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, [K(2.2.2-cryptand)], and methyl groups on the $-\text{OSi}(\text{O}^t\text{Bu})_3$ and silanolimido ligands have been omitted for clarity.

tempts to isolate analytically pure complex 5 proved unsuccessful due to the concomitant formation of multiple unidentified products. The solid-state molecular structure of 5 shows an ion pair in which the anion is a dinuclear Th(IV) complex bridged by a *tert*-butoxy group and a silylimido group of the polydentate silanolimido ligand generated by the cleavage of the Si–O bond by the nitride. Th1 is hexacoordinated in a distorted octahedral geometry and is bound by the bridging *tert*-butoxide, one monodentate siloxide, a bidentate siloxide, and the bidentate silanolimido ligand. Th2 is, instead, pentacoordinated in a distorted trigonal-bipyramidal geometry and is bound by the bridging ligands and three siloxide ligands. The Th–O_{tBuO} bond distances are Th1–O4 = 2.368(4) Å and Th2 O_{tBuO} = 2.441(3) Å. The Th–N_{imido} distances are Th1–N1 = 2.387(4) Å and Th2–N1 = 2.252(4)

Å. The structure is completed by an outer-sphere [K(2.2.2-cryptand)]⁺ cation.

To probe the increased nucleophilic character of the bridging nitride in the intermediate X, its reactivity toward CO was investigated (Scheme 3). Addition of excess ¹³CO to *in situ* generated complex X, in *d*₈-toluene at $-40\text{ }^{\circ}\text{C}$, led to the formation of new resonances in the ^1H NMR spectrum (Figure S41). After addition of ¹³CO, the reaction mixture was monitored over 12 h. There were no observable changes or formation of decomposition products in the ^1H NMR spectra (Figure S41). Attempts to grow single crystals from the reaction mixture proved unsuccessful.

However, after removal of the volatiles, and hydrolysis with D₂O (pD = 13) of the reaction residue, ¹³CN[−] was observed by ¹³C NMR spectroscopy (Figure S43) in 70% yield. The higher yield of CN[−] in the reaction of X with ¹³CO, when compared to the ¹³CO reactivity with 3-K (30% yield after 12 h), suggests that the removal of the K⁺ counterions and azide ligands via 2.2.2-cryptand addition to 3-K results in a more reactive complex. The increased reactivity is likely to be the result of a less crowded Th center allowing for easier CO binding.

Next, we investigated the addition of excess 2.2.2-cryptand to 3-K to promote the complete abstraction of K⁺ cations in the core of the complex and compare the subsequent reactivity with CO. Addition of 3.0 equiv of 2.2.2-cryptand to a solution of 3-K in *d*₈-toluene at $-40\text{ }^{\circ}\text{C}$ led to the clean formation of complex X and unreacted 2.2.2-cryptand (~1 equiv), as displayed in the ^1H NMR spectrum (Figure S40), suggesting that only two out of the 3 K⁺ ions are removed by 2.2.2-cryptand addition. Next, 5.0 equiv of ¹³CO was added to the reaction mixture, resulting in the formation of new resonances in the ^1H NMR spectrum (Figure S44). After removal of the volatiles and hydrolysis with D₂O (pD = 13) of the reaction residues after 1 day, ¹³CN[−] was observed by quantitative ¹³C NMR spectroscopy (Figure S46) in 73% yield. This result suggests that addition of excess 2.2.2-cryptand does not increase the reactivity of the nitride toward CO.

Computational Studies. The electronic structures of the two nitrides 3-K and 3-Cs were further investigated by computational studies (DFT, B3PW91 functional). In both cases, the optimized geometry is in very good agreement with the experimental values. In 3-K, the two Th–N_{nitride} distances are found to be 2.16 Å (versus 2.18 Å experimentally), where the bent structure (Th–N–Th angle of 115°) and the two bridging azide ligands were also found. The K–N distance was found to be relatively short at 2.77 Å. Thus, the bonding was investigated by using both the molecular orbital (MO analysis) and natural bonding orbital (NBO) methods. Scrutinizing the MOs of the complex, it was found that the HOMO, HOMO–1, and HOMO–2 (Figure 6) orbitals display the Th–N–Th bonding, which involves three 3 center–2 electron interactions of σ - and π -type (with an overall 3c–6e interaction). This is in line with the anticipated description of the interaction between a strongly nucleophilic nitride ligand and two strongly electrophilic thorium centers. The NBO vision of the bonding is somewhat more localized than the MO. The two σ Th–N bonds appear to be strongly polarized toward N (90%). These bonds involve a sp orbital on N and a spdf orbital on Th (see the Supporting Information for details). At the second order donor–acceptor level, a donation from the N π lone pair toward an empty pdf orbital on the two Th is also observed, in line with 3c–2e π -type interaction. These strongly polarized

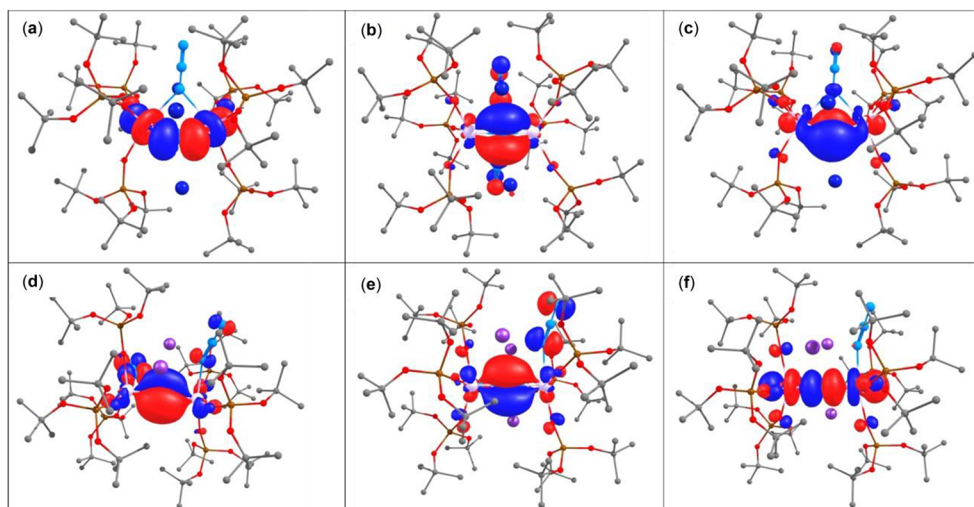


Figure 6. Molecular orbitals of complexes 3-K (a–c) and 3-Cs (d–f).

bonds are in line with a Th–N Wiberg index (WBI) of 1.1. Interestingly, a donation from the Th–N σ bonds to the potassium is observed and is in line with the short distance. This interaction explains the bent structure observed in this complex. Some K–O orbital interactions are also found at the second-order donor–acceptor level in 3-K as well as some Cs–N_{azide} orbital interactions in 3-Cs.

In the case of 3-Cs, the main geometrical parameters are also reproduced computationally. The two Th–N distances are found to be equal to 2.14 Å (versus 2.11/2.15 Å experimentally), and the structure is linear (Th–N–Th angle of 178° as in the experimental structure). The Cs–N distance is 3.40 Å, which is much longer than the K–N bond in 3-K. The bonding was thus investigated similarly as for 3-K. The MO picture is quite similar to the one found for 3-K with the presence of 3c–2e bonding interactions of σ - and π -type (Figure 6). There is, however, an interesting difference between these two systems in the ordering of the MOs. In the bent nitride structure, the π orbitals are found to be lower in energy than the σ orbital, whereas in the linear nitride structure the σ is the lowest one. The $\sigma > \pi$ phenomenon is known for uranyl²⁵ and uranium nitrides^{7b,c} but only recently identified in thorium complexes and was assigned to the “pushing from below effect”.^{12b} Similar to 3-K, the NBO description of the bonding is more localized with two Th–N σ bonds strongly polarized toward N (90%). It is interesting to note that at the second-order level only a weak donation from the N π lone pair toward an empty pdf orbital on the two Th is found. This lack of donation is replaced by a delocalization of the two Th–N σ bonds, which are strongly polarized toward N and toward the other Th center. This is in line with the presence of 3c–2e bonds found in the MO analysis. Again, these strongly polarized bonds explain the WBI of 1.12.

To further investigate the influence of the alkali centers, the bonding of the putative bare Th–N–Th nitride intermediate as well as the capped-version of it (X) was investigated. Computationally, the formation of X from 3-K in the presence of 2.2.2-cryptand is found to be 1.0 kcal mol^{−1}, where X is a plausible intermediate (the formation of 5 is exothermic by 12.0 kcal mol^{−1} from X in line with the experiment). Furthermore, the bonding situations in the bare nitride and in X are very similar (see the Supporting Information for details), and therefore we decided to describe the bare nitride

for comparison. As expected, this complex exhibits a linear Th–N–Th moiety (Th–N–Th angle of 177°). The two Th–N distances are 2.09 and 2.13 Å, which are quite similar to the experimental structure of 3-Cs. The MOs of this bare system are similar to the one found for 3-K and 3-Cs (Figures S55–S57). However, despite the linear arrangement, the ordering of the orbitals in the bare complex are similar to the one found for 3-K rather than for 3-Cs, where the σ interaction is the highest in energy. Therefore, suggesting the presence of the Cs atom has an influence on the energy of the molecular orbitals by stabilizing the σ interaction and therefore stabilizing the system. At the NBO level, the bonding situation is very similar to that found for 3-Cs with two polarized Th–N σ bonds (90% on N) and delocalization of these bonds toward the other Th center (3c–2e bonds). Finally, the bonding was compared with the bare uranium analogue [NBu₄][((^tBuO)₃SiO)₃U]₂(μ -N)].¹⁵ This complex also exhibits a linear U–N–U moiety (angle of 177°) and the U–N bond distances are short (2.03 and 2.07 Å). Once again for this system, the MOs describing the U–N–U bonding are similar to that found for the three Th systems describe above (Figure S59). It is also interesting to note that, like the bare thorium nitride system, the σ interaction is higher than the two π ones. The NBO description is quite similar to the one found for 3-K and X, with two strongly polarized U–N σ bonds and strong donation from the N π lone pair toward empty df orbital on the two U is also observed, in line with 3c–2e π -type interaction. This bonding description is in line with the reactivity described for X (Scheme 2), which is reminiscent of the reactivity reported for the uranium nitride analogues.

CONCLUSION

In conclusion, we have synthesized the first multimetallic Th₂K₃ and Th₂Cs₃ azido/nitrido complexes, 3-K and 3-Cs, which are the second examples of isolable molecular thorium nitrides. These complexes were generated by using a synthetic route involving the reduction of the thorium azide precursors, 2-K and 2-Cs, respectively. This route had previously failed to produce isolable Th nitrides and only led to the isolation of imido products resulting from the reaction of a putative nitride intermediate with solvents or supporting ligand. We found that, once isolated, the generated azide/nitride clusters are stable in solutions, but their synthesis requires a careful control

of the reaction conditions (solvent, temperature, nature of precursor, and alkali ion). Notably, the reduction of the cesium azide precursor proceeds without significant formation of byproducts while the reduction of the potassium azide precursor always results in the concomitant formation of the imido decomposition product. Overall, the unprecedented generation of stable thorium nitrides via the azide reduction route is explained in terms of the stabilization provided by the siloxide supporting ligand and more importantly by the presence of alkali azides bound to the metal center both in the precursors and in the final products. Notably, the presence of the three alkali ions binding the nitride in the final complexes results in a higher stabilization of the nucleophilic nitride. This translates into a lower reactivity both toward solvents, supporting ligand, or added reagents and is clearly illustrated by the higher reactivity of the putative bare (no azides bound) intermediate $[K\{(\text{tBuO})_3\text{SiO}\}_3\text{Th}\}_2(\mu\text{-N})$, **X**, obtained by addition of cryptand to **3-K**, toward CO and supporting ligand.

All the thorium nitride complexes reported here, although in different extent, effect the cleavage of CO to yield cyanide as previously reported for the analogous uranium nitrides. The lower reactivity of **3-K** and **3-Cs** compared to that of **X** is the result of a lower access to the Th center due to the presence of two additional azide ligands and to the presence of two additional nitride-capping alkali ion. The nature of the cation plays an important role in generating a nitride product and results in large structural differences with a bent $\text{Th}=\text{N}=\text{Th}$ moiety found in **3-K** as a result of a strong K–nitride interaction and a linear arrangement in **3-Cs**. Computational studies of the thorium nitrides and of their uranium analogue showed the presence of M–N–M bonding which involves three 3-center–2-electron interactions (3C–2e) of σ - and π -type for all complexes but identified significant differences in the electronic structures of the **3-K** and **3-Cs** nitrides with an inversion in the ordering of the σ - and π -type orbitals. Interestingly, in the bare nitride **X** and in its uranium analogue, despite the linear $\text{An}=\text{N}=\text{An}$ arrangement the ordering of the orbitals is similar to that of **3-K**, with the σ interaction highest in energy. This difference in bonding is in line with the observed differences in reactivity. We anticipate that the synthetic route presented here, which takes advantage of alkali azides to stabilize both the reactions intermediates and the final nitride, will lead to the development of thorium nitride chemistry.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.1c13150>.

Additional crystallographic details, experimental procedures, ^1H NMR spectra, FTIR spectra, and computational details (PDF)

Accession Codes

CCDC 2104497, 2128273–2128276, and 2128474–2128475 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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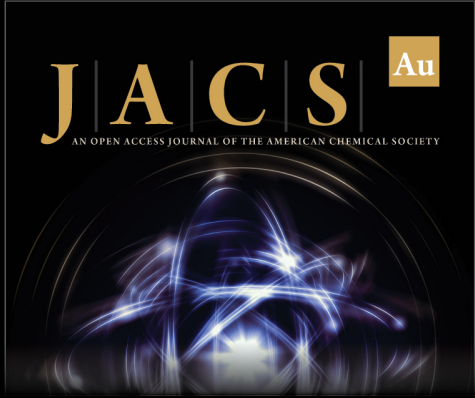
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