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C-H Bond Activation by an Isolated Dinuclear U(III)/U(IV) Nitride

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ABSTRACT: Synthetic studies of bimetallic uranium nitride complexes with the N(SiMe₃)₂ ligand have generated a new nitride complex of U(III), which is highly reactive toward C–H bonds and H₂. Treatment of the previously reported U(IV)/U(IV) nitride complex [Na(DME)₃][[(Me₃Si)₂N]₂U(μ-N)(μ-κ²-C,N-CH₂SiMe₂NSiMe₃)U(N(SiMe₃)₂)₂], **1**, with 2 equivalents of HNEt₃BPh₃ yielded the cationic U(IV)/U(IV) nitride complex, [([(Me₃Si)₂N]₂U(THF))₂(μ-N)][BPh₄], **3**, by successive protonolysis of one N(SiMe₃)₂ ligand and the uranium–methylene bond. Reduction of **3** with KC₈ afforded a rare example of a U(III) nitride, namely, the U(III)/U(IV) complex, [([(Me₃Si)₂N]₂U(THF))₂(μ-N)], **4**. Complex **4** is highly reactive and undergoes 1,2-addition of the C–H bond of the N(SiMe₃)₂ ligand across the uranium–nitride moiety to give the U(III)/U(IV) imide cyclometalate complex, [([(Me₃Si)₂N]₂(THF)U(μ-NH)(μ-κ²-C,N-CH₂SiMe₂NSiMe₃)U(N(SiMe₃)₂))(THF)], **5**. Complex **4** also reacts with toluene at –80 °C to yield an inverse sandwich imide complex arising from C–H bond activation of toluene, [([(Me₃Si)₂N]₂U(THF))₂(μ-N)][([(Me₃Si)₂N]₃U(μ-NH)U(N(SiMe₃)₂)(C₇H₈))], **6**. Complex **4** effects the heterolytic cleavage of the C–H of phenylacetylene to yield the imide acetylidyde [([(Me₃Si)₂N]₂U(THF))₂(μ-N)][([(Me₃Si)₂N]₂U(κ⁴-CCPh)(μ₂-NH)(μ₂-η²:η¹-CCPh)U(N(SiMe₃)₂)₂], **7**. Complex **4** also reacts with H₂ to produce an imide hydride U(III)/U(IV) complex, [([(Me₃Si)₂N]₂U(THF))₂(μ-NH)(μ-H)], **9**. These data demonstrate that nitride complexes of U(III) are accessible with amide ligands and show the high reactivity of molecular U(III) nitrides in C–H bond activation.

Introduction

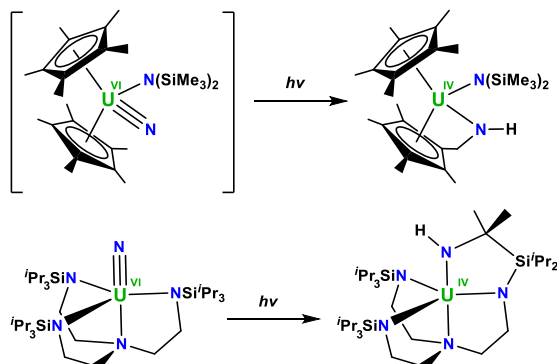
C–H bond functionalization remains of great interest in modern chemistry. Compared to analogous metal–oxo or metal–imido species, only a few examples of C–H bond activation by metal–nitrides have been reported, and in most cases the nitride species have not been isolated.¹ Actinide nitrides have recently been the subject of an increasing number of reports that have provided fundamental insight into the nature of actinide–ligand multiple bonding² and shown novel reactivity toward small unreactive molecules

such as CO₂, N₂, H₂, and CO,³ and the ability to promote C–H bond activation.^{1e, 4}

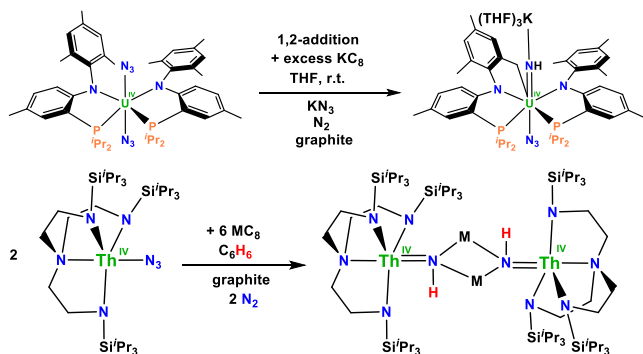
In particular, molecular uranium nitride compounds can be viewed as models of inorganic uranium(III) nitride materials (UN) which have proven effective as catalysts in the Haber-Bosch conversion of dinitrogen and hydrogen into ammonia.⁵ However, the majority of terminal and bridging uranium nitrides isolated in recent years contain uranium in high oxidation states ranging from U(VI) to U(IV).^{2a, 3b, 4c, 6} Only one example of a nitride bridged

diuranium(III) complex was reported so far,⁷ and it was shown to effect the complete cleavage and functionalization of dinitrogen^{3d} confirming the interest of uranium(III) complexes as uranium nitride analogues. Nitride-bridged U(III)-U(IV) and U(III)-U(III) complexes have only been reported in the presence of the siloxide ligand OSi(O^{*i*}Bu)₃, despite that several U(IV)-U(IV) bridging nitrides are known with different supporting ligands.^{2f, 4c, 6d, 6k} Hence, most studies of uranium nitride reactivity are so far limited to U(IV) and U(VI).

Reactivity studies on uranium nitrides include rare examples of dihydrogen cleavage^{3c, 6a} and C–H activation reactivity.^{1e, 4a, 4b, 6f, 8} Isolated^{6f} or transient^{1e} terminal U(VI) nitrides showed high reactivity resulting in C–H activation and reductive 1,1-insertion of the nitride into the C–H bond to afford U(IV) amide complexes, Scheme 1. More recently, the reductive denitrogenation of An(IV) azides was reported to lead to formation of parent imido An(IV) complexes, Scheme 2. On the basis of computational studies, it was proposed that the reaction proceeds via 1,2-addition reactivity of the ligand C–H bond across the An≡N moiety of transient Th(IV)^{4c} and U(IV)^{4b} nitrides, but they were neither isolated nor observed.



Scheme 1. Previously reported intramolecular insertion reactions of transient^{1e} and isolated^{6f} uranium(VI) nitride complexes.



Scheme 2. Previously reported addition reactivity by transient actinide(IV) nitride complexes.^{4c, 4b}

We recently became interested in the study of uranium nitrides supported by the N(SiMe₃)₂ ligand and showed that the reactivity of the nitride ligand is

significantly modified in the diuranium(IV) complexes [NBu₄][{[(Me₃Si)₂N]₃U}₂(μ-N)]⁹ and [Na(dme)₃][{[(Me₃Si)₂N]₂U(μ-N)(μ-κ²:C,N-CH₂SiMe₂NSiMe₃)U(N(SiMe₃)₂)₂}]^{1,6c} compared to the siloxide analogue [{U(OSi(O^{*i*}Bu)₃)₃]₂Cs(μ-N)]^{6e, 10}

Here we show that a U(III)/U(IV) nitride can be prepared using N(SiMe₃)₂ as the supporting ligand and report examples of intramolecular and intermolecular C–H activation by the isolated U(III)/U(IV) diuranium nitride. The U(III)/U(IV) diuranium complex [{[(Me₃Si)₂N]₂U(thf)₂(μ-N)]}, **4**, can be prepared by reduction of the U(IV)/U(IV) analogue at –80 °C. Upon raising the temperature to –40 °C, complex **4** undergoes intramolecular C–H bond activation by 1,2-addition of a C–H bond from the N(SiMe₃)₂ ligand across the U^{III}=N=U^{IV} bond affording the first example of a NH bridged U(III)/U(IV) diuranium complex. Complex **4** also cleaves H₂ and the C–H bonds of phenylacetylene and toluene.

Results and discussion

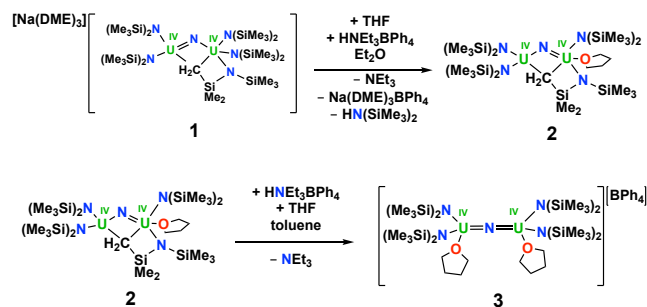
Preparation of a Cationic U(IV)/U(IV) Nitride.

With the aim of synthesizing new U(III) nitrides, we first attempted the reduction of the previously reported anionic complexes [NBu₄][{[(Me₃Si)₂N]₃U}₃(μ-N)]⁹ and [Na(dme)₃][{[(Me₃Si)₂N]₂U(μ-N)(μ-κ²:C,N-CH₂SiMe₂NSiMe₃)U(N(SiMe₃)₂)₂}]^{1,6c}. In contrast to the reduction of the siloxide U(IV)/U(IV) complex [Cs{U(OSi(O^{*i*}Bu)₃)₃]₂(μ-N)] that led to isolable U(III)/U(IV) and U(III)/U(III) complexes, [Cs₂{U(OSi(O^{*i*}Bu)₃)₃]₂(μ-N)] and [Cs₃{U(OSi(O^{*i*}Bu)₃)₃]₂(μ-N)], such attempts failed to lead to the reduction of the uranium center.

The inability to access the +III oxidation state was attributed to the more electron-rich character of the anionic N(SiMe₃)₂ complexes compared to the siloxide analogues. Therefore, we targeted a cationic N(SiMe₃)₂ complex of uranium(IV) which was expected to be more easily reduced.

Treatment of the previously reported U(IV)/U(IV) nitride complex **1** with HNEt₃BPh₄ resulted in protonolysis of a metal–amide bond to yield the neutral THF adduct, [{[(Me₃Si)₂N]₂U(μ-N)(μ-κ²:C,N-CH₂SiMe₂NSiMe₃)U(N(SiMe₃)₂)(THF)]}, **2**, according to Scheme 3. Large single crystals of **2** are obtained in 78% yield upon addition of several drops of THF to a concentrated hexane solution of **2** obtained after extraction of the reaction residue. The thermal ellipsoid plot and detailed structural analysis of **2** are given in the Supporting Information, Figure S35.

Addition of HNEt₃BPh₄ to a solution of **2** in toluene-*d*₈ caused an immediate change in the ¹H NMR spectrum; new resonances at 2.4 ppm, 1.3 ppm, and –0.74 ppm due to BPh₄[–] were observed along with the N(SiMe₃)₂ resonance at –3.0 ppm and those of the coordinated THF at –18.0 ppm and –29.9 ppm, Figure S3. Brown needle crystals of the cationic U(IV)/U(IV) nitride complex, [{[(Me₃Si)₂N]₂U(thf)₂(μ-N)][BPh₄]}], **3**, Scheme 3, Figure 1, were obtained from toluene. The crystals are insoluble in Et₂O, toluene, and hexane but are soluble in THF.



Scheme 3. Synthesis of complexes $[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\mu\text{-N})(\mu\text{-}\kappa^2\text{:C,N-CH}_2\text{SiMe}_2\text{NSiMe}_3)\text{U}(\text{N}(\text{SiMe}_3)_2)(\text{THF}))_2(\text{BPh}_4)]$, **2**, and $[(((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF}))_2(\mu\text{-N})][\text{BPh}_4]$, **3**.

Complex **3** crystallizes in the space group $P\bar{1}$ with one molecule per asymmetric unit. Its solid state structure can be described as an ion pair consisting of an outer sphere BPh_4^- anion and a U(IV)/U(IV) nitride cation. The cation is comprised of two $[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})]^{2+}$ units bridged by a nitride ligand. The SiMe_3 groups are staggered with respect to those on the adjacent uranium, and the THF ligands are nearly eclipsed. The coordination around the U(IV) ions resembles that of the previously reported⁹ $[\text{NBu}_4][(((\text{Me}_3\text{Si})_2\text{N})_3\text{U})_2(\mu\text{-N})]$, except that two $\text{N}(\text{SiMe}_3)_2$ ligand have been replaced by neutral THF molecules. The positive charge of $[(((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF}))_2(\mu\text{-N})]^+$ evidently leads to slightly shorter $\text{U-N}_{\text{nitride}}$ bond distances (2.055(3) Å and 2.064(3) Å) compared to $[\text{NBu}_4][(((\text{Me}_3\text{Si})_2\text{N})_3\text{U})_2(\mu\text{-N})]$ (2.075(2)-2.083(5) Å). The $\text{U-(N}_{\text{amide}})_{\text{avg}} = 2.282(4)$ Å in **3** is also shorter than that of $[\text{NBu}_4][(((\text{Me}_3\text{Si})_2\text{N})_3\text{U})_2(\mu\text{-N})]$, 2.35(1) Å. The U-N-U angle is ca. 169° in **3** whereas it is linear in $[\text{NBu}_4][(((\text{Me}_3\text{Si})_2\text{N})_3\text{U})_2(\mu\text{-N})]$.

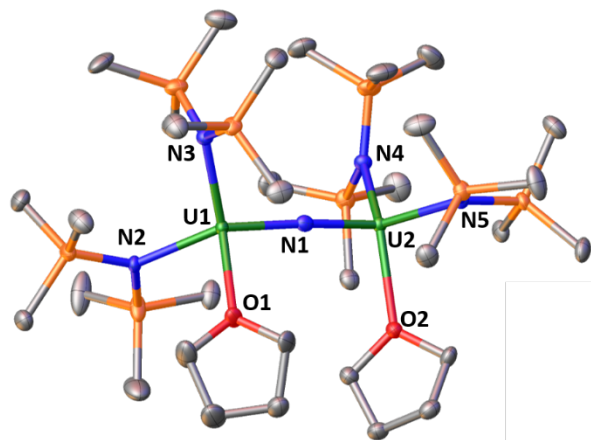
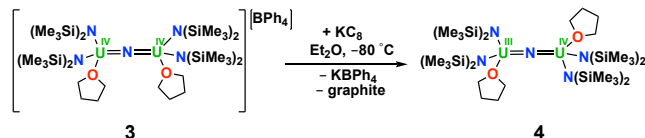


Figure 1. Molecular structure of the cation of $[(((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF}))_2(\mu\text{-N})][\text{BPh}_4]$, **3**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and the BPh_4^- anion have been omitted for clarity.

Synthesis of a U(III)-U(IV) nitride.

We found that in contrast to the previously reported anionic nitride complexes supported by $\text{N}(\text{SiMe}_3)_2$ ligands,^{6c,9} complex **3** can be reduced to afford a new example of U(III)-U(IV) nitride. The addition of 1 equiv of KC_8 to **3** at room

temperature resulted in immediate reaction and yielded a ^1H NMR spectrum with several resonances. However, when the reduction was performed at -80°C , the low temperature ^1H NMR spectrum (-60°C) showed only a single broad resonance at -5.1 ppm, Figure S6. Crystallization from Et_2O of the low temperature species at -80°C yielded dark brown crystals of the mixed valent U(III)/U(IV) nitride complex, $[(((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF}))_2(\mu\text{-N})]$, **4**, Scheme 4, which were characterized by X-ray crystallography, Figure 2.



Scheme 4. Reduction of $[(((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{thf}))_2(\mu\text{-N})][\text{BPh}_4]$, **3**, to yield $[(((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF}))_2(\mu\text{-N})]$, **4**.

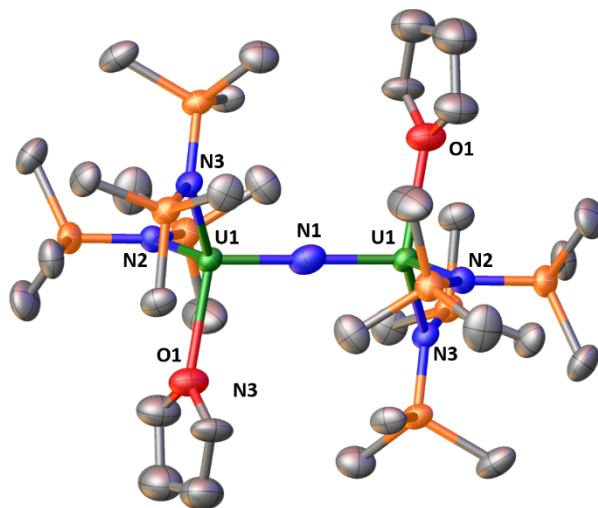


Figure 2. Molecular structure of $[(((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF}))_2(\mu\text{-N})]$, **4**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms and one component of the THF disorder have been omitted for clarity.

Complex **4** crystallizes in the $P\bar{1}$ space group as a neutral $[(((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF}))_2(\mu\text{-N})]$ complex composed of two $[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})]^{n+}$ ($n = 1, 2$) moieties that are bridged by a μ -nitride ligand. The overall structure is similar to the cation in **3** but the THF ligands are staggered. The metrical parameters of **4** are fully consistent with reduction to U(III) . The 2.340(5)-2.351(5) Å range of $\text{U-N}_{\text{amide}}$ bond distances is significantly longer than the 2.277(3)-2.287(3) Å range displayed by its parent compound **3**. Further, the U-O_{THF} distances are elongated by 0.091 Å in **4**. However, the uranium-nitride distances do not change significantly ($\text{U-N}_{\text{nitride}} = 2.0634(3)$ Å in **4** and 2.055(3) Å and 2.064(3) Å in **3**), but this is not unexpected. The complexes of $\text{OSi}(\text{O}^t\text{Bu})_3$ do not show significant changes in their $\text{U-N}_{\text{nitride}}$ distances from U(IV)/U(IV) to U(III)/U(IV) ($\Delta_{\text{U-Nitride}} = 0.02$ Å), nor do the U(V)/U(IV) and U(IV)/U(IV) complexes, $[(((\text{Me}_3\text{Si})_2\text{N})_3\text{U})_2(\mu\text{-N})]$ and $[\text{NBu}_4][(((\text{Me}_3\text{Si})_2\text{N})_3\text{U})_2(\mu\text{-N})]$ ($\Delta_{\text{U-Nitride}} = \text{ca. } 0.04$ Å),⁹ or the U(V)/U(IV) and U(IV)/U(IV) complexes reported by Cummins, $\text{Na}[(\mu\text{-N})(\text{U}(\text{N}[\text{t-Bu}]\text{Ar})_3)_2]$ and $[(\mu\text{-N})(\text{U}(\text{N}[\text{t-Bu}]\text{Ar})_3)_2]$, ($\Delta_{\text{U-Nitride}} = \text{ca. } 0.02$ Å).^{6d} The U-N-U angle is completely linear in **4**. The metrical parameters of **3** and **4** are shown in Table 1 below.

Table 1. Selected bond lengths (Å) and angles (°) of $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF}))_2(\mu\text{-N})][\text{BPh}_4]$, **3**, and $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF}))_2(\mu\text{-N})]$, **4**.

	3	4
U–N _{nitride}	2.055(3), 2.064(3)	2.0634(3)
U–N _{amide}	2.277(3)–2.287(3)	2.340(5)–2.351(5)
U–(N _{amide}) _{avg}	2.282(4)	2.346(6)
U–O _{THF}	2.453(3)	2.544(5)
U–N–U	168.97(14)	180.000(15)

The plots of the magnetic susceptibility (χ) and of the χT data (Figures S23–S34) versus T for **3**, **4** and **5** are in agreement with the presence of U(IV)/U(IV) and U(III)/U(IV) complexes respectively¹¹ and show no evidence of exchange coupling.

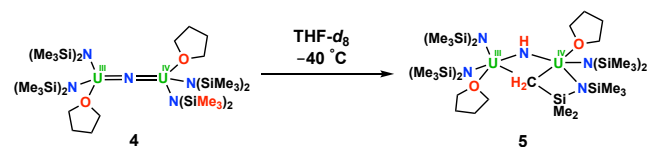
The UV/Visible spectra recorded for complexes **3** and **5** are compatible with the presence of U(IV)/U(IV) and U(III)/U(IV) complexes respectively.

Complex **4** is only the third example of a crystallographically characterized nitride complex of U(III). The only reported U(III)/U(IV) and U(III)/U(III) bridging nitride complexes are anionic and were isolated using $\text{OSi}(\text{O}^t\text{Bu})_3$ as a supporting ligand.⁷

Reactivity of the U(III)/U(IV) nitride.

The nitride in the U(III)/U(IV) complex **4** is highly reactive and reacts immediately with the C–H bonds of $\text{N}(\text{SiMe}_3)_2$, toluene, and phenylacetylene, and it readily cleaves the H–H bond of dihydrogen. In contrast, the parent complex **3** does not react with any of these substrates.

Complex **4** above -40°C reacts rapidly to afford quantitatively a new species. Single crystals of this product were grown from a concentrated hexane solution at -40°C , and X-ray crystallography allowed the identification of a metalate product arising from the 1,2-addition of a C–H bond of $\text{N}(\text{SiMe}_3)_2$ across the uranium–nitride bond, $[[((\text{Me}_3\text{Si})_2\text{N})\text{U}(\text{THF})(\mu\text{-NH})(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)\text{-U}(\text{N}(\text{SiMe}_3)_2)_2]$, **5**, Scheme 5, Figure 3. Complex **5** displays SiMe_3 resonances at 56.4 ppm, -2.93 ppm, and -45.1 ppm in $\text{THF-}d_8$ at room temperature, Figure S7. The methylene resonances of **4** were identified at -240 ppm and -300 ppm and the NH resonates at 471 ppm.



Scheme 5. Intramolecular C–H activation by the U(III)/U(IV) nitride **4**, to yield $[[((\text{Me}_3\text{Si})_2\text{N})\text{U}(\text{THF})(\mu\text{-NH})(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)\text{U}(\text{N}(\text{SiMe}_3)_2)_2]$, **5**.

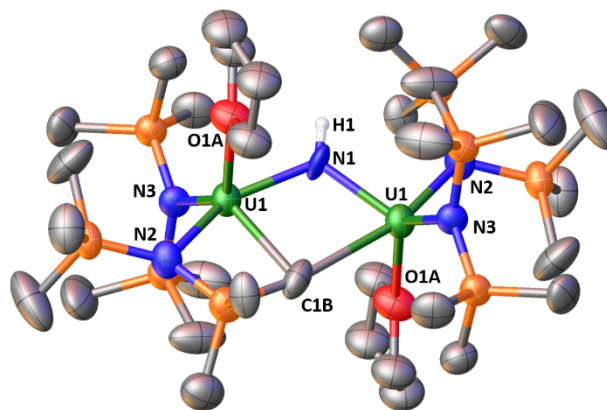


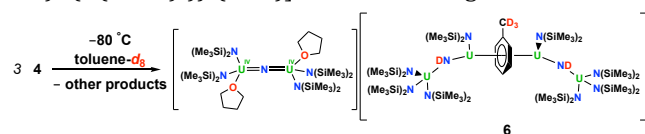
Figure 3. Molecular structure of $[[((\text{Me}_3\text{Si})_2\text{N})\text{U}(\text{THF})(\mu\text{-NH})(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)\text{U}(\text{N}(\text{SiMe}_3)_2)_2]$, **5**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms except H1, disorder in the coordinated THF, and one orientation of **5** have been omitted for clarity. Selected bond lengths (Å) and angles (°): U1–N1 = 2.151(15) Å, U1–N1 = 2.139(12) Å, U1–N2 = 2.309(7) Å, U1–N3 = 2.329(7) Å, U1–C1B = 2.45(2) Å, U1–O1A = 2.473(11) Å, U1–N1–U1 = 117.5(7)°, U1–C1B–U1 = 89.5(9)°.

There are numerous examples^{6c,12} of silylmethyl metalation in uranium/ $\text{N}(\text{SiMe}_3)_2$ chemistry including the metalation reaction of the nitride complex $[\text{NBu}_4][[((\text{Me}_3\text{Si})_2\text{N})_3\text{U}]_2(\mu\text{-N})]$ leading to $[\text{NBu}_4]\text{-1}$,⁹ but most occur with concomitant loss of one $\text{N}(\text{SiMe}_3)_2$ ligand to yield $\text{HN}(\text{SiMe}_3)_2$ and the dianionic bidentate ligand $[\text{N}(\text{SiMe}_3)(\text{SiMe}_2\text{CH}_2)]^{2-}$. Reactivity by 1,2-addition across the uranium–nitride bond was previously proposed by Schelter and coworkers for a putative terminal uranium(IV) nitride (Scheme 2).^{4b} The difference in the observed reactivity (insertion vs addition) between the proposed nitrides of U(IV) and U(VI) was inferred from the high energy profile of a reductive insertion process for U(IV) that would give a U(II) product. The reaction of **4** to generate **5** represents an unambiguous example of this chemistry from a *bona fide* isolated uranium–nitride and corroborates the argument presented by Schelter and coworkers that 1,2-addition reactivity is favored when lower oxidation states are inaccessible.

The overall structure of **5** features a bimetallic U(III)/U(IV) imide cyclometalate complex with two 5-coordinate uranium ions that are bridged by two dianionic ligands, namely an imide $\mu\text{-NH}$ and a $\mu\text{-}\kappa^2\text{-N,C-CH}_2\text{SiMe}_2\text{NSiMe}_3$ ligand. The $\mu\text{-}\kappa^2\text{-N,C-CH}_2\text{SiMe}_2\text{NSiMe}_3$ ligand binds one uranium through both the amide nitrogen and the μ -methylene while the other uranium is bound only through the μ -methylene. Charge localization is not evident from the structural data; the U1–N1 = 2.151(15) Å and 2.139(12) Å bond distances are within error. The hydrogen atom H1 could not be located in the Fourier map but the elongation of the U1–N1 bond distances with respect to those of the nitride **4** (U–N1 = 2.0634(3) Å) along with the ^1H NMR data (chemical shift = 471 ppm) are fully consistent with the assignment of **5** as an imide complex of uranium.

Complex **4** was also found to activate the toluene C–H bond. Notably, addition of toluene (2 mL) to solid **4** at -80°C resulted in an immediate reaction and precipitated dark red crystalline material that gave a complicated ^1H

NMR spectrum after dissolution in THF-*d*₈, Figure S8. Recrystallization of the dark crystalline material by slow diffusion of hexane into a dilute toluene solution at –40 °C gave crystals characterizable by X-ray crystallography as the tetranuclear arene imide complex, $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})_2(\mu\text{-N}))]-[(((\text{Me}_3\text{Si})_2\text{N})_3\text{U}(\mu\text{-NH})\text{U}(\text{N}(\text{SiMe}_3)_2)_2(\text{C}_7\text{H}_8))]$, **6**, Scheme 6, Figure 4, Table 2.



Scheme 6. Reaction of **4**, with toluene to yield $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})_2(\mu\text{-N}))][(((\text{Me}_3\text{Si})_2\text{N})_3\text{U}(\mu\text{-NH})\text{U}(\text{N}(\text{SiMe}_3)_2)_2(\text{C}_7\text{H}_8))]$, **6**.

Complex **6** crystallizes in the $P\bar{1}$ space group, and the structure is consistent with an ion pair composed of a $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})_2(\mu\text{-N}))]^+$ cation similar to that found in **3** and a tetranuclear arene inverse-sandwich imide-bridged anion, $[[((\text{Me}_3\text{Si})_2\text{N})_3\text{U}(\mu\text{-NH})\text{U}(\text{N}(\text{SiMe}_3)_2)_2(\text{C}_7\text{H}_8))^-]$. In contrast to the cation in **3**, the $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})_2(\mu\text{-N}))]^+$ cation in **6** shows staggered THF ligands suggesting their orientation is influenced from packing forces in the crystal. The 2.260(5)-2.272(6) Å range of U–N_{amide} bond distances in the cation is consistent with the U(IV)/U(IV) designation and similar to the 2.277(3)-2.287(3) Å range observed in **3**. The formal charge on the uranium ions of the anion $[[((\text{Me}_3\text{Si})_2\text{N})_3\text{U}(\text{NH})\text{U}(\text{N}(\text{SiMe}_3)_2)_2(\text{C}_7\text{H}_8))^-]$ is ambiguous as is often the case for arene inverse-sandwich complexes of uranium.¹³ Two formulations are plausible for the $[[((\text{Me}_3\text{Si})_2\text{N})_3\text{U}(\text{NH})\text{U}(\text{N}(\text{SiMe}_3)_2)_2(\text{C}_7\text{H}_8))^-]$ anion: (1) a combination of three U(III) ions, one U(IV), and a toluenide dianion (C₇H₈)²⁻, or (2) that with four U(III) ions and a toluenide monoanion (C₇H₈)¹⁻. The 154.2(3)° and 155.7(4)° U–NH–U angles are fully consistent with an imide ligand and the hydrogens could be located on the difference Fourier map. The NH resonances were also identified in the ¹H NMR spectrum of **6** in THF-*d*₈ as two signals at 231 ppm and 216 ppm at –80 °C and as one signal at 177 ppm at –40 °C, Figure S8. Consistent with this assignment, when **4** is reacted with toluene-*d*₈, an identical complicated ¹H NMR spectrum is obtained, but the foresaid resonances are absent, Figure S9. This confirms that the NH group is formed from the cleavage of the toluene C–H bond; the fate of the benzyl anion and the source of two electron equivalents remain undetermined.

While the reaction of **4** with toluene to produce **6** was not optimized on a larger scale, the attainment of analytically pure crystals is reproducible. Its crystal structure and ¹H NMR spectra clearly show the ability of the highly reactive nitride in **4** to promote C–H activation of toluene. It should be noted that activation of the toluene C–H was previously reported for a transient U(V) terminal nitride^{6f} and more recently for a putative bridging thorium nitride that could not be isolated.^{2c} However, the previously reported U(III)/U(IV) nitride complex supported by the OSi(O^tBu)₃,⁷ was reported to be stable in toluene, suggesting a higher nucleophilic character for the nitride in **4**.

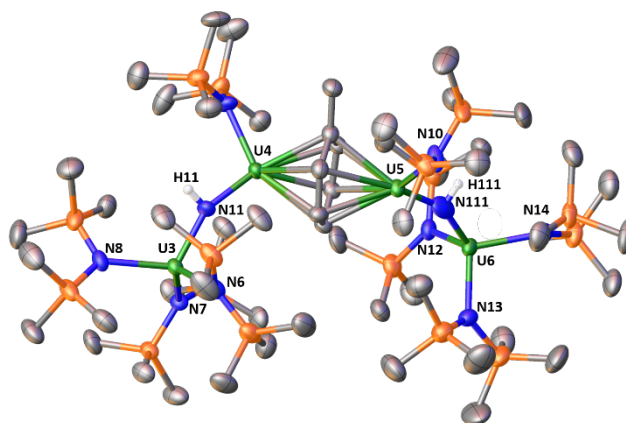


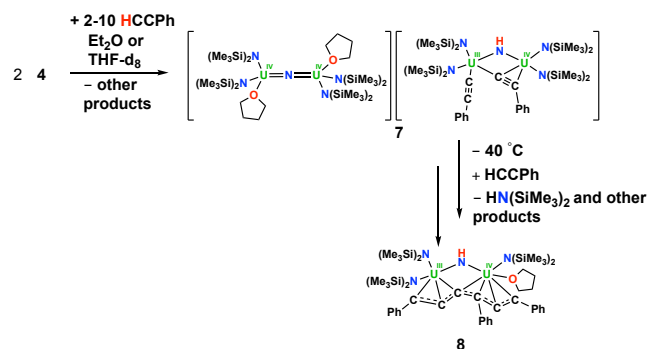
Figure 4. Molecular structure of the anion $[[((\text{Me}_3\text{Si})_2\text{N})_3\text{U}(\mu\text{-NH})\text{U}(\text{N}(\text{SiMe}_3)_2)_2(\text{C}_7\text{H}_8))^-]$ in **6**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms except H11 and H111 have been omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) of the cation and anion of $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})_2(\mu\text{-N}))][(((\text{Me}_3\text{Si})_2\text{N})_3\text{U}(\text{NH})\text{U}(\text{N}(\text{SiMe}_3)_2)_2(\text{C}_7\text{H}_8))]$, **7**.

	Cation	Anion
U–N	2.040(6), 2.044(6)	-
U–NH	-	2.045(5), 2.130(10), 1.940(10), 2.049(5)
U–N _{amide} range	2.260(5)- 2.272(6)	2.301(5)-2.341(6)
U–N _{amide} mean		
U–N(H)–U angle	176.7(4)	154.2(3), 155.7(4)
U–C range	-	2.564(7)-2.669(6)
U–C mean	-	2.62(3)
C–C range	-	1.425(9)-1.492(9)
C–C _{avg}	-	1.44(1)

In view of its high reactivity with toluene, the reaction of complex **4** with phenylacetylene was also investigated and allowed the discovery that **4** heterolytically cleaves the C–H bond of phenylacetylene at –80 °C. The reaction of a THF-*d*₈ solution of **4** with of phenylacetylene (2–5 equivalents) at –80 °C caused an immediate color change from dark brown to dark red and led to ¹H NMR spectra showing a common product, Figure S10. In one attempt, single dark red crystals of $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})_2(\mu\text{-N}))][((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\eta^1\text{-CCPh})(\mu_2\text{-NH})(\mu\text{-}\eta^2\text{:}\eta^1\text{-CCPh})\text{U}(\text{N}(\text{SiMe}_3)_2)_2]$, **7**, Scheme 7, Figure 5, formed from the reaction mixture in Et₂O at –80 °C, and the ¹H NMR spectra of the crystals showed that **7** is the common product, Figure S11. NMR studies of the reaction mixture containing **7** show that even at –80 °C, the mixture evolves to give a

complicated spectrum; after 2 d at $-80\text{ }^{\circ}\text{C}$, **7** is fully consumed and $\text{HN}(\text{SiMe}_3)_2$ is produced, Figure S12. Crystals of a complex arising from the coupling of three equivalents of phenylacetylene and loss of one $\text{HN}(\text{SiMe}_3)_2$ ligand, $[[((\text{Me}_3\text{Si})_2\text{N})\text{U}(\text{THF})(\mu_2\text{-NH})(\text{PhCCC}(\text{Ph})\text{CCC}(\text{Ph}))\text{U}(\text{N}(\text{SiMe}_3)_2)_2]$, **8**, were isolated after crystallization of the reaction residue from hexane at $-40\text{ }^{\circ}\text{C}$. Structural details of complex **8** can be found in the Supporting Information, Figure S35.



Scheme 7. Reaction of $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})_2(\mu\text{-N})]]$, **4**, with phenylacetylene to yield $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})_2(\mu\text{-N})][[(\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\eta^1\text{-CCPh})(\mu_2\text{-NH})(\mu_2\text{-}\eta^2\text{:}\eta^1\text{-CCPh})\text{U}(\text{N}(\text{SiMe}_3)_2)_2]]$, **7** and $[[((\text{Me}_3\text{Si})_2\text{N})\text{U}(\text{THF})(\mu_2\text{-NH})(\text{PhCCC}(\text{Ph})\text{CCC}(\text{Ph}))\text{U}(\text{N}(\text{SiMe}_3)_2)_2]$, **8**.

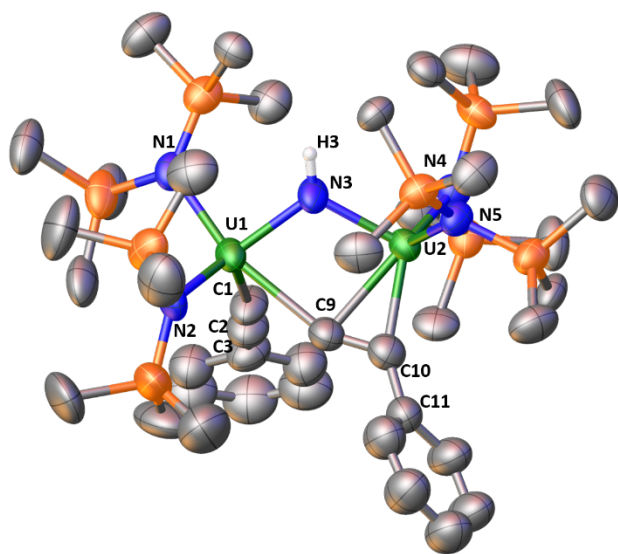


Figure 5. Molecular structure of the anion of $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\eta^1\text{-CCPh})(\mu_2\text{-NH})(\mu_2\text{-}\eta^2\text{:}\eta^1\text{-CCPh})\text{U}(\text{N}(\text{SiMe}_3)_2)_2]]^-$ in **7**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms except H3 have been omitted for clarity. $\text{U1-N3} = 2.146(11)\text{ \AA}$, $\text{U2-N3} = 2.163(13)\text{ \AA}$, $\text{U1-N1} = 2.307(14)\text{ \AA}$, $\text{U1-N2} = 2.306(15)\text{ \AA}$, $\text{U2-N4} = 2.310(13)\text{ \AA}$, $\text{U2-N5} = 2.279(11)\text{ \AA}$, $\text{U1-C1} = 2.466(16)\text{ \AA}$, $\text{U1-C9} = 2.641(18)\text{ \AA}$, $\text{U2-C9} = 2.470(16)\text{ \AA}$, $\text{U2-C10} = 2.317(17)\text{ \AA}$, $\text{C1-C2} = 1.22(2)\text{ \AA}$, $\text{C2-C3} = 1.39(3)\text{ \AA}$, $\text{C9-C10} = 1.33(2)\text{ \AA}$, $\text{C10-C11} = 1.48(3)\text{ \AA}$, $\text{U1-N3-U2} = 114.3(5)^{\circ}$, $\text{U1-C9-U2} = 90.1(5)^{\circ}$, $\text{C1-C2-C3} = 178(3)^{\circ}$, $\text{C9-C10-C11} = 124.2(16)^{\circ}$.

In the solid state, **7** crystallizes in the $P\bar{1}$ space group with one molecule per asymmetric unit. The overall

structure shows an ion pair consisting of the U(IV)/U(IV) cation $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})_2(\mu\text{-N})]]^+$ as observed in **3** and **6** and the bis(acetylide) U(III)/U(IV) imide anion, $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\kappa^1\text{-CCPh})(\mu\text{-NH})(\mu_2\text{-}\eta^2\text{:}\eta^1\text{-CCPh})\text{U}(\text{N}(\text{SiMe}_3)_2)_2]]^-$. Each uranium ion in the anion of **7** is bound by two $\text{N}(\text{SiMe}_3)_2$ and one $\mu\text{-NH}$ ligands and the $\text{U1-N3} = 2.146(11)\text{ \AA}$ and $\text{U2-N3} = 2.163(13)\text{ \AA}$ bond distances are consistent with the uranium-imide assignment. The two phenylacetylide ligands show different binding modes. One is bound η^1 to one uranium and the other is bound to both in a $\mu_2\text{-}\eta^1\text{:}\eta^2$ fashion with one carbon bridging both metals. The η^1 binding has been observed in numerous crystallographically characterized uranium-acetylide complexes, but there are no other examples structurally characterized displaying the $\mu_2\text{-}\eta^1\text{:}\eta^2$ -acetylide binding mode in uranium chemistry. The $2.466(16)\text{ \AA}$ U1-C1 bond distance is at the longer end of the $2.34\text{--}2.47\text{ \AA}$ range typical of uranium(IV)-acetylide bond distances.¹⁴ There is only one other structurally characterized acetylide complex of U(III) ,¹⁵ and its $2.589(9)\text{ \AA}$ $\text{U-C}_{\text{acetylide}}$ distance is significantly longer than the $2.466(16)\text{ \AA}$ distance of the terminal acetylide in **7**.

The formation of complex **7** results from the heterolytic cleavage of the phenylacetylene C–H bond by the electrophilic uranium centers and the highly nucleophilic nitride ligand.

Intrigued by the propensity of complex **4** to heterolyze C–H bonds, we examined its reactivity with H_2 . Complex **4** reacts immediately with H_2 upon thawing a THF-d_8 solution of **4** and the ^1H NMR spectrum of the reaction mixture showed the presence of two sets of signals that were assigned to complex **5** and a new species identified by X-ray crystallography as the imide hydride complex, $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})_2(\mu\text{-NH})(\mu\text{-H}))]$, **9**, Scheme 8, Figure 6. Complex **9** crystallizes in the $P\bar{1}$ space group with one molecule per asymmetric unit and can be described as a mixed valent U(III)/U(IV) imide hydride complex. The overall structure consists of a diamond core formed by two $[[((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})]^{n+}]$ ($n = 1, 2$) units along with $\mu\text{-NH}$ and $\mu\text{-H}$ ligands. Each uranium ion is 5-coordinate. The $\text{U1-N1} = 2.158(9)\text{ \AA}$ and the $\text{U2-N1} = 2.140(9)\text{ \AA}$ bond distances are fully consistent with an imide ligand and delocalized charge on the uranium ions is indicated by the nearly symmetrical $\text{U-N}_{\text{imide}}$ metrical parameters. Variable temperature ^1H NMR studies showed that the reaction of **4** with H_2 occurs only above *ca.* $-40\text{ }^{\circ}\text{C}$, a temperature at which the 1,2-addition reaction that gives **5** competes with H_2 heterolysis. Thus, at $-40\text{ }^{\circ}\text{C}$, a mixture of **5** / **9** is observed, and the ratio of **5** / **9** was *ca.* 1:1 in all cases. The ^1H NMR spectrum of **9** in THF-d_8 shows one resonance for the SiMe_3 groups at -4.4 ppm , Figure S13. The hydride resonance was observed at 597 ppm and the NH resonance at 197 ppm . Consistent with this, when **4** is reacted with D_2 , both of these resonances disappear, and the ratio of **5** / **9** changes to about 8:1, Figure S14. The NH and CH_2 resonances of **5** do not change in intensity when 1 atm of D_2 is used suggesting that H/D exchange does not occur under these conditions. Previously, Andersen and coworkers showed that the uranium(IV) metallate $[\text{U}(\text{N}(\text{SiMe}_3)_2)_2(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)]$ can be fully deuterated via H/D exchange, but only under high pressure of D_2 .^{12a, 12c} When the headspace of H_2 is removed, **9** slowly

decomposes and a complicated ^1H NMR spectrum is obtained. Attempts to independently prepare **9** or to separate **9** from **5** on a preparatory scale were unsuccessful. Complex **9** is a remarkable addition to the rare examples of uranium hydride complexes reported in the literature which are mostly supported by carbocyclic ligands.¹⁶



Scheme 8. Reaction of $[\{((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})\}_2(\mu\text{-N})]$, **4**, with H_2 to yield $[\{((\text{Me}_3\text{Si})_2\text{N})\text{U}(\text{THF})(\mu\text{-NH})(\text{CH}_2\text{SiMe}_2\text{NSiMe}_3)\text{U}(\text{N}(\text{SiMe}_3)_2)_2\}]$, **5**, and $[\{((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})\}_2(\mu\text{-NH})(\mu\text{-H})]$, **9**.

Heterolytic cleavage of H_2 by U(IV)/U(IV) nitride bridged complexes was previously reported by our group,^{3c, 9} but this is the first example reported for a U(III) nitride and adds to the handful of reports of heterolytic splitting of H_2 by nitride complexes.¹⁷ Hydrogenolysis by metal nitride intermediates has been identified as a key step in the Haber-Bosch process.¹⁸ As such, the cleavage of H_2 by a molecular U(III) nitride provides a molecular model for the activity of inorganic UN materials as catalysts^{5, 19} in the formation of ammonia from N_2 and H_2 .

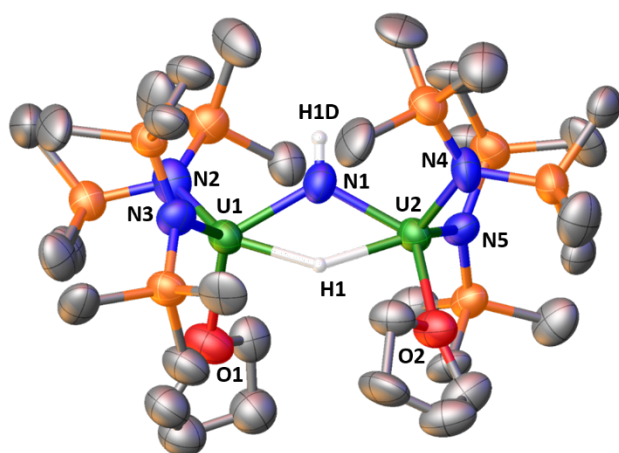


Figure 6. Molecular structure of $[\{((\text{Me}_3\text{Si})_2\text{N})_2\text{U}(\text{THF})\}_2(\mu\text{-NH})(\mu\text{-H})]$, **9**, with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms except H1 have been omitted for clarity. $\text{U1-N1} = 2.158(9)$ Å, $\text{U2-N1} = 2.140(9)$ Å, $\text{U1-N2} = 2.30(3)$ Å, $\text{U1-N3} = 2.37(2)$ Å, $\text{U2-N4} = 2.30(2)$ Å, $\text{U2-N5} = 2.26(2)$ Å, $\text{U1-O1} = 2.59(2)$ Å, $\text{U2-O2} = 2.58(2)$ Å.

Conclusion

The $\text{N}(\text{SiMe}_3)_2$ ligand system allowed us to isolate a cationic U(IV)/U(IV) nitride that can be further reduced to afford the neutral U(III)/U(IV) nitride (**4**) that has been fully characterized. Complex **4** is only the third example of a molecular nitride complex of U(III) and the first isolated with a ligand other than $\text{OSi}(\text{O}^t\text{Bu})_3$. The high reactivity of **4** was demonstrated by its rapid decomposition at -40 °C to afford a U(III)/U(IV) imido metalated product. This result demonstrated C–H bond addition across the uranium–nitride bond

and the first unambiguous example of 1,2-addition chemistry from an isolated uranium nitride complex which behaves as a strong nucleophile. This result also provides evidence of the key role of the uranium oxidation state in favoring 1,2-addition reactivity over reductive C–H insertion. The high reactivity of the uranium–nitride bond toward C–H bonds was also demonstrated by the reaction of **4** with toluene which resulted in the isolation a tetranuclear arene inverse-sandwich complex which contains imide ligand bridges. The U(III)/U(IV) nitride (**4**) was also shown to heterolytically cleave the C–H bond of phenylacetylene at low temperature to give a U(III)/U(IV) imide acetylide complex. Additionally, **4** effects the heterolytic cleavage of H_2 to yield a U(III)/U(IV) imide hydride complex. These results show that U(III) nitrides can be isolated with strong sigma donor amide supporting ligands upon careful choice of reaction condition. The resulting U(III) nitride displays unusually high reactivity toward C–H bond activation resulting in the first examples of 1,2 addition of C–H bonds across an isolated nitride. Thus, the nature of the supporting ligands can be used to tune the reactivity of U(III) nitrides for the discovery of novel and unusual transformations.

ASSOCIATED CONTENT

Supporting Information.

X-ray data for **2**, **3**, **4**, **5**, **6**, **7**, **8**, and **9** (CIF) and additional crystallographic details (PDF), experimental procedures, spectroscopic details, and magnetic data of **2**, **3**, **4** and **5**.

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

THF: tetrahydrofuran, DME:1,2-dimethoxyethane.

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