Uranium azide photolysis results in C–H bond activation and provides evidence for a terminal uranium nitride

Robert K. Thomson, Thibault Cantat, Brian L. Scott, David E. Morris, Enrique R. Batista* and Jaqueline L. Kiplinger*

Uranium nitride \([\text{U} = \text{N}]_2\) is an alternative nuclear fuel that has great potential in the expanding future of nuclear power; however, very little is known about the \(\text{U} = \text{N}\) functionality. We show, for the first time, that a terminal uranium nitride complex can be generated by photolysis of an azide \((\text{U} = \text{N} = \text{N} = \text{N})\) precursor. The transient \(\text{U} = \text{N}\) fragment is reactive and undergoes insertion into a ligand \(\text{C} = \text{H}\) bond to generate new \(\text{N} = \text{H}\) and \(\text{N} – \text{C}\) bonds. The mechanism of this unprecedented reaction has been evaluated through computational and spectroscopic studies, which reveal that the photochemical azide activation pathway can be shut down through coordination of the terminal azide ligand to the Lewis acid \(\text{BC}_6\text{F}_5)_3\). These studies demonstrate that photochemistry can be a powerful tool for inducing redox transformations for organometallic actinide complexes, and that the terminal uranium nitride fragment is reactive, cleaving strong \(\text{C} – \text{H}\) bonds.

As we strive to deal with a global energy crisis and anthropogenic global warming, we need to look to alternative energy sources to reduce our dependence on fossil fuels. Nuclear energy provides one possible route to the alleviation of these issues with next-generation nuclear reactors and fuels. In this regard, uranium nitride \([\text{U} = \text{N}]_2\) has emerged as a promising alternative to traditional mixed oxide fuels, with advantages such as a higher melting point and enhanced thermal conductivity\(^{1,2}\). Unlike the widely studied uranyl ion \([\text{O} = \text{U} = \text{O}]^{2+}\), very little is known about the \(\text{U} = \text{N}\) linkage or its chemical behaviour and reactivity\(^{3-6}\). A thorough understanding of the physicochemical properties of the \(\text{U} = \text{N}\) moiety is critical for predicting the long-term behaviour of the ceramic nuclear fuel \([\text{U} = \text{N}]_2\). The properties of extended ceramic materials are difficult to study, and molecular model systems are therefore ideal for the controlled investigation of this bond fragment. Uranium nitrides are rare, and the few known systems have all been generated through oxidation of reduced uranium centres with either dinitrogen\(^7\) or azide sources\(^8-12\). The nitride fragments in these complexes either form bridging linkages between uranium centres\(^7-9,11,12\) or coordinate to Lewis acids, namely \(\text{B}(\text{C}_6\text{F}_5)_3\) (ref. 10). These interactions quench any other potential reactivity of the \(\text{U} = \text{N}\) bond, making the generation of a terminal uranium nitride complex an important goal. The ability to generate a discrete molecular terminal uranium nitride would enable investigation of the fundamental reactivity of the isolated \(\text{U} = \text{N}\) fragment, which could shed light on the behaviour and properties of bulk \([\text{U} = \text{N}]_2\) under life-cycle conditions from fuel-element formulation to recovery and reprocessing.

By far the most effective way in which to access nitride species is through photochemical extrusion of \(\text{N}_2\) from metal azide complexes \((\text{M} – \text{N}_3)_x\). For example, the photolysis of iron azide complexes has been successfully applied to generate terminal iron nitrides\(^13-16\). However, to date, this reaction has not proven successful for analogous uranium complexes. In fact, with the exception of some early reports concerning the photoinduced generation of low-valent thorium and uranium complexes through \(\beta\)-hydride elimination\(^17,18\), the photochemistry of organometallic actinide complexes has remained essentially unexplored. Herein, we demonstrate that a terminal uranium nitride can be generated by photolysis of an azide precursor, and that the \(\text{U} = \text{N}\) linkage is nucleophilic, activating a \(\text{C} – \text{H}\) bond to form new \(\text{C} – \text{N}\) and \(\text{N} – \text{H}\) bonds. This is the first uranium nitride to be accessed through photolysis. Most importantly, this result demonstrates that the \(\text{U} = \text{N}\) fragment is not inert and can undergo reactions with strong bonds, with the observed \(\text{C} – \text{H}\) bond addition to the \(\text{U} = \text{N}\) moiety being strikingly similar to the oxidation of alkanes to alcohols by the cytochrome P450 family of enzymes\(^19\). It is anticipated that these first reactivity studies will open new avenues in the study of \(\text{U} = \text{N}\) bonds and provide important insights into the generation and reprocessing of \([\text{U} = \text{N}]_2\).

Additionally, these results demonstrate the utility of photochemistry for promoting redox processes for organometallic actinides.

Results and discussion

Recently, we reported that \((\text{Ph}_3\text{P})\text{Au-N}_3\) is an ideal mild oxidant for the generation of \(\text{U}^{\text{V}}\) azide complexes from \(\text{U}^{\text{VI}}\) precursors\(^20\). The solid-state structural parameters of the azide functionality in the aryloxide complex \((\text{C}_6\text{Me}_6)_2\text{U}(\text{O}-2,6-\text{Pr}_2\text{C}_6\text{H}_3)(\text{N}_3)\) (1) were consistent with a typical \(\text{U} = \text{N} = \text{N} = \text{N}\) bonding description\(^20,21\). Photolysis studies of 1 were undertaken, and although these indicated that the azide complex was consumed, the reaction led to the formation of numerous unidentified products. The \(\text{U}^{\text{V}}\) amide–azide complexes \((\text{C}_6\text{Me}_6)_2\text{U}(\text{NPh}_3)(\text{N}_3)\) (2), \((\text{C}_6\text{Me}_6)_2\text{U}[\text{N(SiMe}_3)_2](\text{N}_3)\) (3) and \((\text{C}_6\text{Me}_6)(\text{Et})\text{U}[\text{N(SiMe}_3)_2](\text{N}_3)\) (4) were also prepared by oxidation of the corresponding \(\text{U}^{\text{VI}}\) precursors with \((\text{Ph}_3\text{P})\text{Au-N}_3\) (for their solid-state molecular structures, see Fig. 1).

In contrast to the aryloxide–azide complex 1, the arylamide–azide complex 2 presents a more localized azide fragment with a \(\text{N}(1) – \text{N}(2)\) bond length of 1.20(2) Å, and a \(\text{N}(2) – \text{N}(3)\) bond length of 1.11(2) Å, consistent with a more polarized bonding description that is shifted towards a \(\text{U} = \text{N} = \text{N} = \text{N}\) form\(^21\).
Aromatic amines are known photosensitizers, and we suspect that seven distinct singlet resonances corresponding to the four
\((\text{C}_5\text{Me}_4\text{CH}_2\text{NH})\text{U}[\text{N(SiMe}_3\text{)}_2]\) is supported by 1H nuclear magnetic doublets at those for the methylene protons, which appear as diastereotopic
to the \(\text{C}_5\) Lewis acid \(\text{BPh}_3\). Furthermore, 1H NMR spectroscopy shows that there is no
interaction between the \(\text{C}_5\text{Me}_5\) ligand and the \(\text{C}_5\text{Me}_5\) ligand across a \(\text{N} = \text{U} = \text{N}\) \(\pi\)-system has been
observed upon thermolysis of the bis(imido) system (C\(_9\)Me\(_9\))U(=NAd)\(_2\) (Ad = 1-adamantyl), resulting in the formation of (C\(_9\)Me\(_9\))(C\(_9\)Me\(_9\)CH\(_2\)NAd)(NHAd), in which the methylene group is bound to one nitrogen and the transferred hydrogen is bound to the other nitrogen.

In an attempt to trap the putative nitride intermediate, photolysis was performed in the presence of Lewis acids. Photolysis of a 1:1 mixture of (C\(_9\)Me\(_9\))\(_2\)U[N(SiMe\(_3\))\(_2\)](N\(_3\)) (3) and the weak Lewis acid BPh\(_3\) gave quantitative formation of (C\(_9\)Me\(_9\))(C\(_9\)Me\(_9\)CH\(_2\)NH)U[N(SiMe\(_3\))\(_2\)] (5), showing no reaction with BPh\(_3\). Furthermore, 1H NMR spectroscopy shows that there is no interaction between 3 and 1 equiv. of BPh\(_3\) at room temperature. In contrast, the stronger Lewis acid B(C\(_9\)F\(_3\))\(_2\) forms the stable borane adducts (C\(_9\)Me\(_9\))\(_2\)U[N(SiMe\(_3\))\(_2\)][μ-\(\eta^1\)-\(\eta^1\)-N\(_3\)][B(C\(_9\)F\(_3\))\(_2\)] (6) and (C\(_9\)Me\(_9\)Et)\(_2\)U[N(SiMe\(_3\))\(_2\)][μ-\(\eta^1\)-\(\eta^1\)-N\(_3\)][B(C\(_9\)F\(_3\))\(_2\)] (7) upon reaction with azide complexes 3 and 4, respectively. In

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**Figure 1** | Generation of U\(_n\) azide complexes. a. Uranium azide complexes 1–4 were obtained through one-electron oxidation of the corresponding U\(_n\) precursors with (Ph\(_2\))P\(_2\)Au-N\(_3\). b-d. Solid-state structures of 2, 3 and 4 as determined by single-crystal X-ray diffraction, depicted with 50% probability ellipsoids (hydrogen atoms have been omitted for clarity). Selected bond lengths (Å) and angles (deg) for 2: U(1)–N(1) = 2.289(15), U(1)–N(4) = 2.325(4), N(1)–N(2) = 1.20(2), N(2)–N(3) = 1.11(2), U(1)–C(32) = 3.356, N(1)–U(1)–N(4) = 97.9(4), U(1)–N(1)–N(2) = 146.2(14), N(1)–N(2)–N(3) = 176.6(19). Selected bond lengths (Å) and angles (deg) for 3: U(1)–N(1) = 2.21(2), U(1)–N(2) = 2.26(2), N(2)–N(3) = 1.20(3), N(3)–N(4) = 1.14(4), U(1)–C(26) = 3.209, N(1)–U(1)–N(2) = 88.0(7), U(1)–N(2)–N(3) = 163.5(17), N(2)–N(3)–N(4) = 176.3(2). Selected bond lengths (Å) and angles (deg) for 4: U(1)–N(1) = 2.26(2), U(1)–N(4) = 2.286(2), N(1)–N(2) = 1.200(3), N(2)–N(3) = 1.145(4), U(1)–C(23) = 3.309, N(4)–U(1)–N(1) = 91.85(8), U(1)–N(1)–N(2) = 160.1(2), N(1)–N(2)–N(3) = 179.3(3).
Figure 2 | Photochemical generation and reactivity of terminal uranium nitride. a. Photolysis of azide complex 3 generates a transient terminal uranium nitride, C–H bond activation of the C₅Me₅ ligand leads to the formation of 5. Addition of B(C₆F₅)₃ to azide complexes 3 and 4 leads to the formation of azidoborate complexes 6 and 7, which are deactivated towards photolysis. b. Products from photolysis of azide complex 4. c. Solid-state structure of photolysis product 5 as determined by single-crystal X-ray diffraction, with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): U(1)–N(1) = 2.233(3), U(1)–N(2) = 2.192(3), N(2)–C(8) = 1.473(5), U(1)–C(22) = 2.305, N(1)–U(1)–N(2) = 99.72(11), U(1)–N(2)–C(8) = 110.62(2). d. Solid-state structure of azidoborate complex 7 as determined by single-crystal X-ray diffraction, with 50% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (deg): U(1)–N(1) = 2.233(3), U(1)–N(2) = 2.192(3), N(2)–N(3) = 1.166(4), N(3)–N(4) = 1.486(4), N(4)–B(1) = 1.605(5), U(1)–C(28) = 3.078, N(1)–U(1)–N(2) = 88.57(10), U(1)–N(2)–N(3) = 170.83, N(2)–N(3)–N(4) = 173.94, N(3)–N(4)–B(1) = 127.8(3).

Figure 3 | UV-visible–NIR absorption spectra in a toluene solution. Spectra are shown for the azide complex (C₅Me₅)₂U[N(SiMe₃)₂]₂[N₃] (3, green), the photolysis product (C₅Me₅)(C₅Me₄(CH₂)NH)U[N(SiMe₃)₂] (5, red) and the azidoborate complex (C₅Me₅)₂U[N(SiMe₃)₂][μ-η¹-η¹-N₃]-B(C₆F₅)₃ (6, blue).
higher energy (250–350 cm⁻¹), indicating that the distal borane is perturbing the ligand field at the U⁴⁺ ion.

Density functional theory (DFT) calculations were performed to gain insight into the chemical properties of the U;N linkage, as they afford a model to explain the role of photochemistry in promoting the activation of the azide complex 3 and to propose a viable mechanism for the C–H activation process. Under photolytic conditions, both singlet and triplet configurations are available for uranium complexes, and the two potential energy surfaces were computationally explored. As depicted in Fig. 4, the formation of (C₅Me₅)₂U[N(SiMe₃)₂]N₃⁻ (3’) from the starting azide complex (C₅Me₅)₂U[N(SiH₃)₂]N₃⁻ (3) is an exergonic process for both spin states, with an overall release in free energy of 36.2 kcal mol⁻¹. This large stabilization is consistent with a process releasing N₂ together with the formation of strong N–H and C–H bonds, and accounts for the quantitative nature of the reaction. The formation of the intermediate nitride complex (C₅Me₅)₂(U=N)[N(SiMe₃)₂] (5’) is slightly endergonic on the

Figure 4 | DFT calculations on the mechanism for the formation of 5 from 3. Calculated relative energies (kcal mol⁻¹) of the azide precursor (C₅Me₅)₂U[N(SiH₃)₂]N₃⁻ (3’), nitride (C₅Me₅)₂(U=≡N)[N(SiH₃)₂] (9’) and imido-tuck-in (C₅Me₅)₂(C₅Me₅CH₂)₆U=≡N[N(SiH₃)₂] (10’) intermediates, and photolysis product (C₅Me₅)₂(C₅Me₅CH₂)₆U=≡N[N(SiH₃)₂] (11’). Imido-hydride intermediates (C₅Me₅)₂(C₅Me₅CH₂)₆U=≡N[N(SiH₃)₂] (11’) from the 1,2-addition pathway are given for comparison. Transition states are labelled ‘TS’. Red structures represent the singlet (S) spin state and black structures the triplet (T) spin state. Calculations were performed on model systems using SiH₃ substituents in place of SiMe₃; this simplification has no significant impact on the energetics of the pathways. (For full details regarding the simplification from SiMe₃ to SiH₃, see Supplementary Information.)
triplet surface ($\Delta G = 4.4$ kcal mol$^{-1}$), but is exergonic for the singlet system ($\Delta G = -11.9$ kcal mol$^{-1}$), with $9'$ having a singlet ground-state configuration. Most importantly, $N_2$ loss from $3'$ is a highly energy-intensive process, requiring at least $\approx 48$ kcal mol$^{-1}$ for both the triplet and singlet configurations. Such a high energy barrier indicates that this process is not thermally accessible. Indeed, attempts to form $5$ from $3$ by thermolysis were unsuccessful at temperatures as high as $140$ °C.

Because generation of the nitride unit requires an electron transfer from uranium to the azide ligand ($f \rightarrow \pi^*$), leading to $N_2$ loss, a metal-to-ligand charge transfer (MLCT) has to take place. As determined by UV–vis-NIR spectroscopy, such an electron transfer should occur in the visible region of the spectrum at $\approx 24,300$ cm$^{-1}$ (69 kcal mol$^{-1}$), corresponding to the activation barrier for $N_2$ loss (Fig. 3). Time-dependent DFT (TD-DFT) calculations of the electronic excited states for the azide complex $3'$ describe well the three-peak structure of the experimental UV–vis spectrum (Fig. 5). (For full details of the computational methods, see Supplementary Information.) The lowest calculated excited state ($\approx 17,500$ cm$^{-1}$) after the $f \rightarrow f$ manifold contains an MLCT from U(5f) to the azide ligand ($\pi^*$). Most importantly, the excited electron orbital has no charge density on the nitrogen proximal to the metal, and all the charge is transferred to the distal $N_2$, corroborating the experimentally observed photochemically induced $N_2$ loss (Fig. 5b). This transition falls under the envelope created by the first peak in the UV–vis spectrum (centred at $20,150$ cm$^{-1}$). A similar excited state is also present in the envelope containing the second peak in the UV–vis spectrum (centred at $24,350$ cm$^{-1}$); the excited electron orbital is illustrated in Fig. 5a. In this case, the $\pi$-electron density is contained within the terminal $N_2$ unit, but also exhibits a $\pi$-bond character between uranium and the adjacent nitrogen, again supporting $N_2$ extrusion, coupled with the formation of a U=U fragment.

Irradiation in the NIR region only leads to metal-centred $f-f$ transitions, that is, no significant charge redistribution in the excited states, and thus irradiation in this region is not sufficient to promote thermal activation of the azide. The necessity of UV–vis photolysis was experimentally established by selective irradiation experiments showing that azide decomposition is not observed under strict NIR excitation. The reactive nature of the nitride intermediate (C$_5$Me$_5$)$_2$(U=SiH$_3$)$_2$ ($9'$) is supported by the low observed selectivity in the thermal C–H activation of the C$_5$Me$_5$Et ligand by the nitride generated upon photolysis of the azide complex (C$_5$Me$_5$Et)U[N(SiMe$_3$)$_2$](N$_2$) ($4'$). This reaction produces all possible C–H activation products ($8'$) as determined by $^1$H NMR spectroscopy (Fig. 2b; see Supplementary Information for full details of the photolysis of 4), with the N–H resonances falling between $\delta = -107$ and $-111$, which compares well to that seen for 5 ($\delta = -111.63$). Similarly, the methylene protons appear between $\delta = 41$ and 55, consistent with that seen for 5 ($\delta = 41.36$ and 52.36).

The observed C–H activation process can follow three different paths, all of which were investigated (Paths A, B, and C; Fig. 4): (i) direct single-insertion of the terminal nitride into the C–H bond of the cyclopentadienyl ligand to convert (C$_5$Me$_5$)$_2$(U=SiH$_3$)$_2$ ($9'$) to (C$_5$Me$_5$)(C$_5$Me$_5$Et)U[N(SiMe$_3$)$_2$]$\tilde{\nu}$ ($5'$) in one step (Path A); (ii) 1,2-addition of the C–H bond across the U=Si bond to form an imido-hydride intermediate (C$_5$Me$_5$)(C$_5$Me$_5$CH$_2$NH)U[N(SiH)$_2$]$\tilde{\nu}$ ($11'$), followed by 1,2-migration of the hydride ligand (Path B), and (iii) formal deprotonation/H-abstraction of the C–H bond followed by formation of the C–N bond (Path C). Considering the high-energy excitation required for the production of nitride $9'$, both spin states (singlet and triplet) are accessible and were computed; however, they do not differ significantly in reactivity, so spin interconversion was not studied. Although a pathway involving direct reaction of the C–H bond with the azide ligand cannot be ruled out, there is no precedent for such a reaction; however, there have been examples of N$_2$ loss from metal azides to generate nitride complexes$^{13,16}$.
Cytochrome P450

\[ \text{Fe}^{2+} + \text{R}_1\text{C}-\text{H} + \text{O}^2- \rightarrow \text{Fe}^{3+} + \text{R}_1\text{C}-\text{OH} + \text{O}_2 \]

Uranium nitride

\[ \text{N} \rightarrow \text{U} + \text{C} \rightarrow \text{N} \]

Figure 6 | Analogy between cytochrome P450 and uranium nitride C–H activation. Reaction of the U=N bond with a C–H bond occurs through the same basic steps of steps as the reaction of the Fe=O moiety with C–H bonds in cytochrome P450.

Although the addition of B–C bonds to osmium nitrides in a 1,1-fashion has been observed20, an analogous process involving direct addition of the C–H bond to the U=N fragment in a 1,1-fashion could not be computationally identified and converted instead to Path C. Addition of the C–H时尚 was also investigated, but the resulting imido-hydride complexes (11ija, 11jib) were too high in energy to be viable (11ija was found to be unstable, leading to cyclpentadienyl dissociation). The lowest-energy pathway was found to be deprotonation (singlet surface)/H- abstraction (triplet surface) of the methyl group by the nucleophilic nitride unit, which passes through an energetic transition state requiring ~20 (triplet)–36 (singlet) kcal mol\(^{-1}\) to generate an imido tuck-in complex (CMe\(_5\)C(=N)Me\(_5\)CH\(_3\)) (U=NH)\([\text{N}(\text{SiMe}_{3})]^{10} + \text{tuplet}\) being favoured by 8.8 kcal mol\(^{-1}\). This intermediate is plausible given the large number of uranium tuck-in complexes20,31 and high-valent uranium imido complexes that have been reported22,32. In contrast, high-valent uranium hydride species are currently unknown. Subsequent 1,2-migration (singlet surface)/radical recombinination (triplet surface) of the methylene group from the uranium centre to nitrogen requires ~14 kcal mol\(^{-1}\) on the singlet surface and essentially no energy on the triplet surface to traverse the transition state, with the final product 5T lying 36.2 kcal mol\(^{-1}\) below the azide starting material 3T, and 24.9 kcal mol\(^{-1}\) below the singlet nitride complex (9j). This mechanism is reminiscent of that proposed for the cytochrome P450 family of enzymes, which oxidize C–H bonds to alcohols (R–OH functionality) through formal 1,1-insertion of an iron–oxo (Fe=O) complex into a C–H bond23. By direct analogy, here we see that the uranium nitride (U=N) inserts into a C–H bond in a 1,1-fashion (Fig. 6).

In summary, we have shown that photolysis of a uranium azide complex can promote the release of N\(_2\) to generate a terminal oxo (Fe=O) complex. This unprecedented transformation illustrates that photochemistry can serve as a powerful tool for promoting new redox processes with organometallic uranium species, and may lead to the discovery of new photochemical reaction pathways for the actinides.

Methods

Preparation of (CMe\(_5\))\(_2\)C(N(SiMe\(_3\)))\(_2\)C(=N)Me\(_5\)CH\(_3\))(U=NH)(N\(_3\)). The syntheses of azidoborate complexes 6 and 7 are completely analogous, and the preparation of 7 is given as a representative example. A 20-ml scintillation vial equipped with a stir bar was charged with (CMe\(_5\))\(_2\)C(N(SiMe\(_3\)))\(_2\)C(=N)Me\(_5\)CH\(_3\))(U=NH)(N\(_3\))(1.17 mmol, 89% yield). X-ray-quality crystals of 7 were obtained from a saturated solution of (Me\(_3\)Si)\(_2\)O with minimal THF (0.825 g, 1.17 mmol, 89% yield). Sample 7.0 eV: m/z 710 M\(^{+}\). Analysis. Found: C, 44.42; H, 4.24; N, 4.19; U, Na, Si, U requires C, 43.93; H, 6.81; N, 7.88.

Preparation of (CMe\(_5\))\(_2\)C(N(SiMe\(_3\)))\(_2\)C(=N)Me\(_5\)CH\(_3\))(U=NH)(N\(_3\)). 5. A 20-ml thick-walled Schlenk tube equipped with a Teflon valve and a stir bar was charged with (CMe\(_5\))\(_2\)C(N(SiMe\(_3\)))\(_2\)C(=N)Me\(_5\)CH\(_3\))(U=NH)(N\(_3\))(3) (0.250 g, 0.352 mmol) and toluene (15 ml). The Teflon valve was wrapped with aluminium foil to prevent degradation. The reaction vessel was irradiated at room temperature using a water-cooled Hanovia 450 W medium-pressure Hg lamp filtered through a Pyrex cell at a distance of ~5 cm. After 80 h, the volatiles were removed from the reaction mixture under reduced pressure to yield a red-brown solid, which was dissolved in hexane (20 ml) and filtered through a Celite-padded coarse-porosity fritted filter. The Celite plug was washed with hexane (5 ml) until the washings became colourless. The filtrate was collected and volatiles were removed under reduced pressure to give 5 as a red-brown solid (0.200 g, 0.299 mmol, 85% yield). X-ray-quality crystals of 5 were obtained from saturated hexane or toluene solutions at ~30 °C. UV-NMR (300 MHz, benzene-d\(_6\), 25 °C): δ = −111.63 (1H, NH), −27.08 (3H, CH\(_3\)), −8.61 (3H, Si(CH\(_3\))\(_3\)), −2.57 (3H, CH\(_3\)), 1.04 (3H, CH\(_3\)), 1.19 (8H, C\(_5\)Me\(_4\)CH\(_3\)), 11.49 (3H, CH\(_3\)), 17.18 (3H, CH\(_3\)), 23.06 (3H, CH\(_3\)), 41.36 (6, 1H, CH\(_3\)), 52.36 (6, 1H, CH\(_3\)), 101.60 (3H, SiC\(_5\)Me\(_4\)), 183.08 (1H, Si-C\(_5\)Me\(_4\)). MS (EI, 70 eV): m/z 682 [M\(^{+}\)]. Analysis. Found: C, 45.17; H, 7.03; N, 4.32. C\(_{26}\)H\(_{48}\)N\(_2\)Si\(_2\)U requires C, 45.73; H, 7.08; N, 4.10.

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Author contributions

R.K.T. synthesized and characterized the compounds and wrote the manuscript. B.I.S. collected single-crystal X-ray crystallographic data and solved the structures. T.C. and E.R.B. performed DFT calculations. D.E.M. aided in the analysis and interpretation of UV–vis–NIR spectral data. J.L.K. generated and managed the project and helped write the manuscript.

Additional information

The authors declare no competing financial interests. Supplementary information and chemical compound information accompany this paper at www.nature.com/naturechemistry.