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Communication

# Photochemical Synthesis of a Stable Terminal Uranium(VI) Nitride

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**ABSTRACT:** Terminal uranium nitrides have so far proven impossible to isolate by photolysis of azides. Here we report the second ever example of an isolated terminal uranium(VI) nitride. We show that the terminal nitride $[NBu_4][U(OSi(O^tBu)_3)_4(N)]$, **3**, can be prepared upon photolysis with UV light of the U(IV) azide analogue. This is achieved by careful tailoring of the azide precursor and of the reaction conditions. Complex **3** is stable under ambient conditions but reacts readily with electrophiles ($H^+$ and CO).

Terminal metal nitride complexes have been highly sought-after synthetic targets because of their key role in the catalytic $N_2$ hydrogenation for ammonia production and in N-transfer processes.[1] Terminal uranium nitride compounds provide molecular analogues of inorganic uranium nitride materials (UN) which are effective catalysts in the Haber–Bosch synthesis of ammonia.[2] In recent years, few examples of mononuclear borane-[3] or alkali-ion-capped[4] terminal nitrides and several multimetallic nitrides have been synthesized,[1g,5] which have demonstrated high reactivity toward small molecule activation and functionalization.[1g,6] However, the synthesis of *bona fide* terminal U(V) and U(VI) nitrides remains limited to a single polydentate ligand system ($Tren^{TIPS}$: $\{N(CH_2CH_2NSi^iPr_3)_3\}^{3-}$).[4b,7]

Photolysis of metal azide complexes has been the most effective route for the synthesis of metal nitrides. This route has allowed the synthesis of terminal metal nitrides in transition metal chemistry,[1c,h,8,9] but so far it has failed to yield a stable terminal uranium nitride complex. More generally, the photochemistry of organometallic actinide complexes remains limited to a small handful of studies, most of them going back to 40 years ago.[10]

Particularly relevant to the work here is the first report of a putative terminal U(VI) nitride intermediate that was generated in photolytic conditions but could not be isolated because it readily effected the C–H activation of the supporting cyclopentadienyl ligand.[11] Photolysis of uranium(IV) azide complexes with bulky amide supporting ligands[6h,7b] also failed to produce isolable terminal U(VI) nitrides, instead resulting in the intramolecular insertion of the nitride intermediate in the ligand framework. This led to the conclusion that it may not be possible to prepare terminal uranium nitrides by photolysis of azides due to the low stability of transient nitrides under the high-energy photolytic conditions.

Here we report the second example of a terminal U(VI) nitride $[U(OSi(O^tBu)_3)_4(N)]$, **3**, and show that by a careful tuning of the reaction conditions it is possible to prepare **3** by photolysis of the sterically demanding terminal U(IV) azide $[NBu_4][U(OSi(O^tBu)_3)_4(N_3)]$, **[NBu4]-2**. Notably, the fast conversion of **[NBu$_4$]-2** into nitride **3** under irradiation renders possible its isolation and suggests that previous attempts failed to produce isolable terminal U(VI) nitrides because the photolysis of the U(IV) azide precursor required longer times (24–80 h).[6h,11]

In order to investigate the photolysis of U(IV) azide complexes, we first pursued the synthesis of an anionic U(IV)-terminal azide supported by four alkoxy(siloxide) ligands $[U(N_3)(OSi(O^tBu)_3)_4]^-$ (Scheme S1). The bulky environment provided by the four siloxides was chosen for its ability to stabilize a terminal U(V) oxide by preventing the formation of oxide bridged multimetallic species.[12]

In previous studies, we isolated and crystallographically characterized the complex $[K(18c6)(\mu\text{-}N_3)U(OSi(O^tBu)_3)_4]$, **[K(18c6)]-2** (18c6 = 18-crown-6) which formed, together with a bis-nitride diuranium(V) complex and other products, from the reaction of the U(III) complex $[K(18c6)][U(OSi(O^tBu)_3)_4]$ with $CsN_3$.[5h] This reaction failed to yield a terminal nitride, and the U(IV) azide **[K(18c6)]-2** could not be reproducibly prepared from this route. Uranium(IV) azides were shown to provide a more reliable route to terminal uranium(V) nitrides for the $Tren^{TIPS}$ system.[4b] Therefore, we set out to prepare the U(IV) azide $[(N_3)U(OSi(O^tBu)_3)_4]^-$ by reacting the homoleptic U(IV) tetrasiloxide complex $[U(OSi(O^tBu)_3)_4]$,[5h] **1** with different azides.

The reaction of **1** with $KN_3$ resulted in intractable mixtures independent of the reaction temperature. In contrast, the addition of $NBu_4N_3$ to a solution of **1** in thf-$d_8$ at room temperature led to the formation of a single new species resonating at 0.33 ppm. Cooling down the reaction mixture in toluene at −80 °C afforded light blue single crystals of the ion pair complex $[NBu_4][U(OSi(O^tBu)_3)_4(N_3)]$, **[NBu$_4$]-2**, in 74% yield (Scheme S1). The synthesis of the K(18c6) analogue $[K(18c6)(\mu\text{-}N_3)U(OSi(O^tBu)_3)_4]$ **[K(18c6)]-2** in analytically pure form required performing the reaction

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between **1** and [K(18c6)]$N_3$ in thf at −80 °C for 5 h. Crystallization from toluene at −40 °C affords crystalline complex [**K(18c6)**]-**2** in 72% yield. Isolated complexes [$\mathbf{NBu_4}$]-**2** and [**K(18c6)**]-**2** are both stable in a thf or toluene solution at RT for at least 1 week or at 70 °C for at least 3 days. Moreover, $^1$H NMR studies of [**K(18c6)**]-**2** in thf-$d_8$ and toluene-$d_8$ showed that the $[K(18c6)]^+$ cation remains bound to the azide in both solvents. The 2.2.2.cryptand (crypt) analogue [K(crypt)($\mu$-$N_3$)U(OSi($O^tBu)_3)_4$], [**K(crypt)**]-**2**, could only be prepared *in situ* upon reaction of **1** with an excess (5 equiv) of [K(crypt)]$N_3$ in toluene or thf to avoid release of the bound azide. Light blue crystals of [**K(crypt)**]-**2** were obtained from a concentrated reaction mixture in hexane at −40 °C.

The molecular structures of complexes [**K(crypt)**]-**2** (Figure S55) and [$\mathbf{NBu_4}$]-**2** (Figure 1) all show a similar coordination environments and only differ in the nature of the counterion. Both $[K(crypt)]^+$ and $[K(18c6)]^+$ cations bind the azide ligand in an end-to-end fashion in [**K(crypt)**]-**2** and [**K(18c6)**]-**2**, while [$\mathbf{NBu_4}$]-**2** consists of a separated ion pair. The N1−K1 distance of 3.3(1) Å in [**K(crypt)**]-**2** is much longer than the one observed for [**K(18c6)**]-**2**[5h] (2.562(6) Å). This difference is in line with the cryptand being bulkier than the crown ether and is likely to be the origin of the different stability of the uranium-bound azides. The values of the U1−N1 in complexes [$\mathbf{NBu_4}$]-**2**, [**K(crypt)**]-**2**, and [**K(18c6)**]-**2**, of 2.375(4), 2.379(6), and 2.351(7) Å, respectively, are on the longer end of the range of values found in previously reported U(IV) azide complexes (2.142(5)−2.442(6), Å).[7b,11,13] The N−N bond distances are very close to each other in all the three complexes (1.187(5) and 1.165(6) Å for [$\mathbf{NBu_4}$]-**2**, 1.18(1) and 1.145(6) Å for [**K(crypt)**]-**2**, and 1.180(9) and 1.226(11) Å for [**K(18c6)**]-**2**).

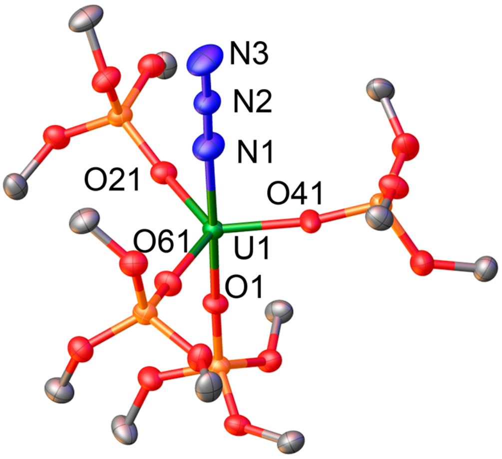


**Figure 1.** Thermal ellipsoid plot of the anion $[U(OSi(O^tBu)_3)_4(N_3)]^-$ in [$\mathbf{NBu_4}$]-**2** at 50% probability. The $^t$Bu moieties have been omitted for clarity in all figures.

These values do not necessarily suggest a low activation of the azide moiety. Notably, a similarly long U−N distance and similar equivalency in N−N distances were found in the terminal U(IV) azide supported by the bulky $Tren^{TIPS}$ ligand, which readily undergo photolysis to yield a cyclometalated amide trough a nitride intermediate.[7b] Moreover, the higher value found for $\nu_{as}(N_3)$ of [**K(18c6)**]-**2** (2096 $cm^{-1}$) compared to that of [$\mathbf{NBu_4}$]-**2** (2057 $cm^{-1}$) indicates a higher degree of activation.

The photolysis of thf-$d_8$ solutions of [$\mathbf{NBu_4}$]-**2** with a UV lamp (253.7 nm) for 30 min yielded an orange solution whose $^1$H NMR spectrum showed only one major species with a resonance at 1.44 ppm. Single crystals of the terminal nitride complex [$NBu_4$][U(OSi($O^tBu)_3)_4$(N)], **3** were obtained in 70% yield from a 1:1 toluene/hexane mixture at −25 °C. Longer irradiation times (8 h) resulted in the full transformation of **3** into unidentified products.

Complex **3** shows remarkable stability in thf and toluene under ambient light for up to 3 weeks. As a comparison, 1 week was indicated as the half-life of the only other reported terminal U(VI) nitride [U($Tren^{TIPS}$)N] in a toluene solution.[7b]

However, photolysis of thf and toluene solutions of **3** with a UV lamp (253.7 nm) resulted in the appearance of the same unidentified decomposition products after 5 h and 30 min, respectively, showing that the photolytic stability of **3** varies with the solvent nature.

Photolysis of toluene-$d_8$ solutions of [$\mathbf{NBu_4}$]-**2** with a UV lamp (253.7 nm) for 2 to 5 h showed the simultaneous progressive formation of **3** and other decomposition products, also formed by photolysis of **3** in toluene, rendering impossible the isolation of nitride **3** in these conditions. These results show that both the photochemical stability of nitride **3** and its rate of formation from the azide vary with the solvent, rendering its choice crucial for the isolation of the nitride. Notably, in thf the formation of the nitride from the azide is much faster than its decomposition, allowing its clean formation and isolation. We also became interested in investigating the potential effects of cations on the photochemical stability of the nitride and on the reactivity of the terminal azide.

$^1$H NMR studies showed that the addition of an excess (10 equiv) of [K(18c6)]I to complex **3** in toluene results in the formation of a capped nitride, [**K(18c6)**]-**3**, which is stable in toluene under irradiation (253.7 nm) for 5 h. These results indicate a significantly higher photochemical stability of the capped nitride compared to **3**. In contrast, the addition of an excess of [K(crypt)]I to **3** did not affect its decomposition rate under irradiation, suggesting that labile binding of $[K(crypt)]^+$ does not enhance the photochemical stability of the nitride.

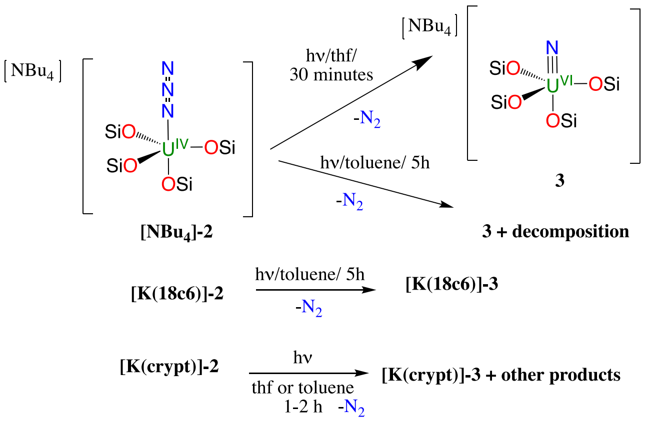
$^1$H NMR studies showed that the photolysis of toluene-$d_8$ solutions of [**K(18c6)**]-**2** with a UV lamp (253.7 nm) afforded the clean formation of [**K(18c6)**]-**3**, which is complete after 5 h (Scheme 1). Thus, although the formation of the nitride from the [K(18c6)]-capped azide is slow, as found for the uncapped [$\mathbf{NBu_4}$]-**2** azide in toluene, the increased stability of the [K(18c6)]-capped nitride compared to **3** renders possible its clean formation in toluene.

Photolysis of toluene-$d_8$ and thf-$d_8$ solutions of [**K(crypt)**]-**2** led in both cases to mixtures of [**K(crypt)**]-**2**, [**K(crypt)**]-**3**, and its decomposition products (Scheme 1). The presence of cryptand bound to the azide results in a slower $N_2$ elimination compared to uncapped azide [$\mathbf{NBu_4}$]-**2** rendering impossible the isolation of the nitride product in these conditions.

Thus, capping alkali ions can not only increase the stability of terminal nitride but also decrease the rate of the dinitrogen release. Thus, the counterion choice is key in the photochemical synthesis of terminal and capped nitrides.

Compound **3** represents the first example of an isolated terminal uranium nitride complex generated photochemically. The molecular structure of the $[U(OSi(O^tBu)_3)_4(N)]^-$ anion (Figure 2), presents the uranium in a slightly distorted trigonal

**Scheme 1. Synthesis of the Terminal Nitride Complex 3**[a]



[a]OSi = OSi(O$^t$Bu)$_3$.

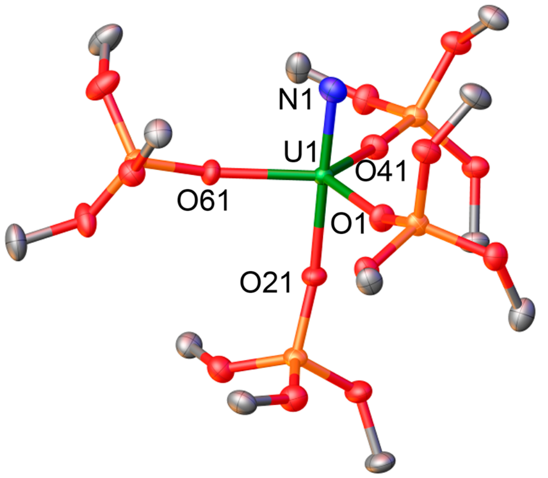
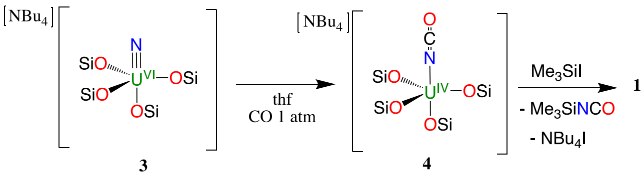


**Figure 2.** Thermal ellipsoid plot of the anion [U(OSi(O$^t$Bu)$_3$)$_4$(N)]$^-$ in **3** at 50% probability.

**Scheme 2. Reductive Carbonylation of 3 to Yield 4 and Formation of Me$_3$SiNCO**[a]



[a]OSi = OSi(O$^t$Bu)$_3$.

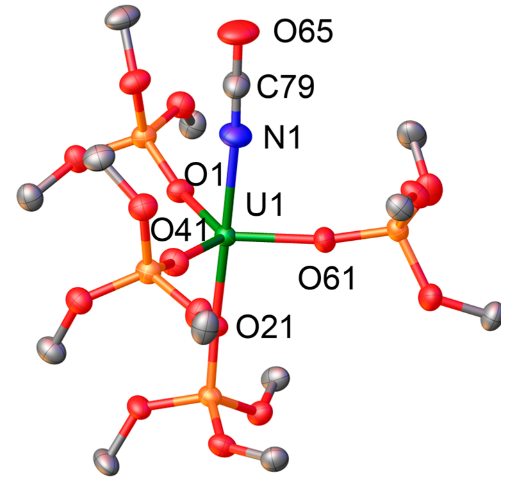


**Figure 3.** Thermal ellipsoid plot of the anion [U(OSi(O$^t$Bu)$_3$)$_4$(NCO)]$^-$ in **4** at 50% probability.

bipyramidal geometry, with three siloxides lying on the equatorial plane and the axial positions occupied by the nitride ligand and a fourth siloxide ligand. The U1–O21 distance at 2.073(1) Å is approximately 6% smaller compared to the mean value of the equatorial U–O$_{\text{siloxide}}$ bond distances (2.20(3) Å). This is indicative of an inverse trans influence (ITI), often manifested in high-valent f-element complexes.[14,7b] The U1–N1 bond distance (1.769 (2) Å) is slightly shorter than the U–nitride distance reported for [U(Tren$^{\text{TIPS}}$)-N] (1.799(7) Å)[7b] and compares well with the value calculated for the matrix-isolated terminal nitride complex [UNF$_3$] (1.76 Å).[15]

Complex **3** reacts with H$^+$ sources to afford ammonia. A 100% conversion to NH$_4$Cl was observed upon reaction of **3** with excess HCl. Using H$_2$O as the proton source yielded 20% conversion to NH$_3$. This value increased to 56% when the reaction was carried out in the presence of 3 equiv of CoCp*$_2$. Complex **3** was also found to react readily with 1 atm of CO in thf, yielding the reductive carbonylation product [NBu$_4$][U(OSi(O$^t$Bu)$_3$)$_4$(NCO)], **4**, in 80% yield (Scheme 2).

The solid-state structure of **4** (Figure 3), together with IR ($\nu_{\text{as}}$(NCO) 2162 cm$^{-1}$) and $^{13}$C NMR spectra (see Supporting Information), shows that the nitride group in **3** has been converted into an isocyanate ligand. The U1–N1 bond distance of 2.406(2) Å falls in the range of previously reported U(IV)-isocyanate complexes (2.270–2.559 Å).[6d,16]

A similar two-electrons reduction by CO was reported for U(V) and U(VI) terminal nitride species[6f] as well as for the U(V) bis-$\mu$-nitride complex [K$_2${U(OSi(O$^t$Bu)$_3$)$_2$($\mu$-N)}$_2$].[5a] However, the U(VI) terminal nitride complex, [U(Tren$^{\text{TIPS}}$)-N], reacts with CO over the course of 16 h, while complex **3** reacts immediately with CO. The addition of 1 equiv of SiMe$_3$I to [NBu$_4$][U(OSi(O$^t$Bu)$_3$)$_4$(NCO)], **4**, led to the formation of [U(OSi(O$^t$Bu)$_3$)$_4$], **1**, as the main U-containing species and of SiMe$_3$NCO as confirmed by $^1$H and $^{13}$C NMR spectroscopy. The formation of [U(OSi(O$^t$Bu)$_3$)$_4$], **1** closes the synthetic cycle for the formation of SiMe$_3$NCO from NBu$_4$N$_3$ and CO.

In summary, we have photochemically generated and characterized a terminal uranium(VI) nitride which is stable under ambient conditions but displays high reactivity toward electrophiles undergoing reductive carbonylation to yield cyanate. Photolysis studies of three sterically demanding anionic uranium azide complexes demonstrated that facile release of dinitrogen occurs in all conditions, but clean formation of the nitride requires a careful tailoring of the solvent and counterion. The use of an anionic azide precursor allows a fine-tuning of the photochemical generation of the terminal uranium nitride.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c09814.

Experimental procedures, NMR spectra, IR and UV spectroscopic data (PDF)

X-ray crystallographic data (CIF, CIF, CIF, CIF)

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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.

### Notes

The authors declare no competing financial interest.

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