Photochemical Synthesis of Transition Metal-Capped Uranium(VI) Nitride Complexes

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Abstract: Uranium nitrides play important roles in dinitrogen activation and functionalization and in nuclear power chemistry, but the synthesis and isolation of mono-uranium molecular nitrides remains a challenge due to their high reactivity. Here, we report the first example of transition metal (TM)-capped mono-U(VI) nitride complexes, which was generated by the photolysis of azide-bridged U(IV)-TM (TM = Rh, Ir) precursors. The U(V) nitride intermediates with bridged azide ligands were isolated successfully by careful control of the irradiation time, suggesting that the photolysis of azide-bridged U(IV)-TM precursors is a stepwise process. The presence of two U(VI) nitrides capped by three TMs was clearly demonstrated by an X-ray crystallographic study. These TM-capped mono-U(V) nitride intermediates and mono-U(VI) nitride products exhibit excellent stability both in the solid-state and in THF solution under ambient light. Density functional theory calculations show that the photolysis was necessary to break the N-N bond of the azide ligands, as suggested by the antibonding N-N interaction in their lowest unoccupied molecular orbitals.

Metal nitride complexes were proposed as a key intermediate in N₂ activation and functionalization.^{1,2} Uranium nitride complexes have attracted significant attention due to their potential applications in N₂ fixation,³⁻⁵ small molecule activation⁶⁻¹¹ and utility as next-generation nuclear fuels.¹²⁻¹⁵ Since uranium nitride materials have been considered to be effective catalysts for the Haber–Bosch synthesis of NH₃ from N₂,¹⁶ a series of molecular uranium nitride complexes have been synthesized by N₂

cleavage or azide reduction, which generally leads to bi- and polymetallic uranium nitride complexes containing U(IV) centers and a few examples with U(III), U(V) or U(VI) centers.^{17- 29} However, the synthesis of mono-uranium nitrides lags far behind, largely due to the limited synthetic methods and high chemical reactivity of mono-uranium nitrides.³⁰⁻³²

Although several examples of mono-U(V) nitrides have been reported,^{33- 39} mono-U(VI) nitrides are extremely rare.^{37- 40} For instance, the Cummins group reported a borane-capped U(V) nitridoborate complex $[\text{N}(\text{n-Bu})_4][(\text{C}_6\text{F}_5)_3\text{BNU}(\text{N}[\text{t-Bu}]\text{Ar})_3]$ ($\text{Ar} = 3,5\text{-Me}_2\text{C}_6\text{H}_3$), which could be converted to a U(VI) nitride complex $[(\text{C}_6\text{F}_5)_3\text{BNU}(\text{N}[\text{t-Bu}]\text{Ar})_3]$ by chemical oxidation.³⁷ Liddle and co-workers reported that a U(III) complex $[\text{U}(\text{Tren}^{\text{TIPS}})]$ $\{\text{Tren}^{\text{TIPS}} = [\text{N}(\text{CH}_2\text{CH}_2\text{NSi}^i\text{Pr}_3)_3]^{3-}\}$ could react with NaN_3 , leading to a terminal U(V) nitride complex $[\text{UN}(\text{Tren}^{\text{TIPS}})][\text{Na}(12\text{-crown-}4)_2]$, which could be further oxidized to the U(VI) nitride complex $[\text{U}(\text{N})(\text{Tren}^{\text{TIPS}})]$ by iodine.³⁸ However, this U(VI) nitride species is unstable and decomposes to a U(IV) amide through C–H activation under photolytic conditions, which is consistent with the direct photolysis of U(IV) azide species.

Photolysis of metal azides is a typical route to metal nitrides in transition metal chemistry.^{41- 47} However, despite continuous efforts, this method is less successful in the synthesis of actinide nitride complexes. For example, Kiplinger and co-workers attempted to isolate a U(VI) nitride complex (**I** in Fig. 1) by the photolysis of $(\text{C}_5\text{Me}_5)_2\text{U}[\text{N}(\text{SiMe}_3)_2](\text{N}_3)$, but only the intramolecular C–H activated product $(\text{C}_5\text{Me}_5)(\text{C}_5\text{Me}_4\text{CH}_2\text{NH})\text{U}[\text{N}(\text{SiMe}_3)_2]$ was isolated.⁴⁸ Fortier and co-workers proposed

that a U(VI) nitride (**II** in Fig. 1) was formed as a transient intermediate by the photolysis of the corresponding U(IV) azide complex, but the U(VI) nitride also could not be isolated.⁴⁹ Recently, Mazzanti and co-workers reported a stable U(VI) nitride [NBu₄][U(OSi(O^tBu)₃)₄(N)] (**III** in Fig. 1) by the photolysis of an anionic U(IV) azide analogue.⁴⁰ This remains the only example of the successful isolation of a mono-U(VI) nitride complex *via* a photolysis route. These results demonstrate that U(VI) nitrides are accessible under photochemical conditions but require an appropriate ligand framework and specific reaction conditions to capture this transient mono-U(VI) nitride intermediate.

Figure 1. Mono-U(VI) nitrides generated by the photolysis of uranium azides.

Our group successfully isolated a multimetallic U(IV) nitride supported by a multidentate N-P ligand (N(CH₃)(CH₂CH₂NHP^{*i*}Pr₂)₂) *via* U-Rh synergistic N₂ cleavage.²⁹ Thus we attempt to access mono-U(VI) nitride with the aid of transition metals by this platform. Herein, we report the synthesis of the first example of transition-metal-

capped mono-U(VI) nitride (**IV** in Fig. 1) via photolysis of U(IV)-azide precursors. The mono-U(V) nitride intermediates were also successfully isolated by careful control of the irradiation time.

Results

Synthesis and structural characterization. By treatment of complex **1**²⁹ with 1 equiv. of [RhCl(COD)]₂ in tetrahydrofuran (THF) at room temperature (RT) overnight, the complex [{U{N(CH₃)(CH₂CH₂NPⁱPr₂)₂}(Cl)₂[(μ-Cl)Rh(COD)]₂}] (**2a**) was formed and was isolated as green crystals in 81% yield after recrystallization from toluene at -30 °C (Fig. 2). Its iridium analogue, [{U{N(CH₃)(CH₂CH₂NPⁱPr₂)₂}(Cl)₂[(μ-Cl)Ir(COD)]₂}] (**2b**), could also be prepared by the reaction of **1** with 1 equiv. of [IrCl(COD)]₂ following the same procedure, which was isolated as orange crystals in 74% yield. The formation of complexes **2a** and **2b** is analogous to the FLP-type reactivity observed previously in rare-earth organometallic chemistry.⁵⁰⁻⁵² Both **2a** and **2b** were fully characterized by nuclear magnetic resonance (NMR) spectroscopy, elemental analysis, and single-crystal X-ray diffraction.

Treatment of **2a** with 4 equiv. of NaN₃ in THF at RT overnight led to the formation of a uranium azide complex [{U{N(CH₃)(CH₂CH₂NPⁱPr₂)₂}(N₃)₂[(μ-N₃)Rh(COD)]₂}] (**3a**) as brown crystals in 70% yield by generating crystals from the concentrated reaction mixture (Fig. 2). The complex **2b** could also react with 4 equiv. of NaN₃ affording the corresponding complex [{U{N(CH₃)(CH₂CH₂NPⁱPr₂)₂}(N₃)₂[(μ-N₃)Ir(COD)]₂}] (**3b**) as red crystals in 65% yield. The ¹H NMR spectra of complexes **3a** and **3b** exhibit a broad range of peaks from +67.46 to -50.01 ppm and +70.12 to -52.63 ppm, respectively,

103 consistent with the paramagnetic U(IV) species (Figs. S3 and S4).

104
105 **Figure 2. Synthesis and reactivity of complexes 2, 3, 4 and 5.** Complexes **3a** and **3b**
106 with four azides were prepared by the reaction of complexes **2** with NaN_3 . By careful
107 control of the irradiation time of complexes **3**, the mono-U(VI) nitrides **5** were formed
108 via the mono-U(VI) nitride intermediates **4**. The nitride groups in complexes **5** could
109 react with acid or H_2 /acid to form NH_4^+ in good yield.

110
111 The asymmetric structures of **2a** and **2b** feature one U atom and two Rh or Ir
112 atoms, which are bridged by two Cl ligands (Fig. 3). The U–N_{amido} and U–N_{amine} bond
113 lengths are comparable to those observed in precursor **1**. The bridged U–Cl distances
114 are approximately 0.2 Å longer than the terminal U–Cl bonds, which reveals a weak
115 interaction between the U center and the bridged Cl atoms.

The molecular structures of complexes **3a** and **3b** were also confirmed by X-ray crystallography (Fig. 3). The salient features of complexes **3a** and **3b** are the two terminal uranium azide ligands and two sideways-bound azide units bridging Rh or Ir atoms. The distances of two terminal U–N_{azide} bonds in complexes **3a** (2.307(5) and 2.304(5) Å) and **3b** (2.295(8) and 2.311(8) Å) are significantly shorter than the bridged U–N_{azide} bond lengths (2.515(5) and 2.453(5) Å for **3a**, 2.533(8) and 2.475(7) Å for **3b**), but these all fall in the range of previously reported U(IV) azide species (2.20(4)–2.564(12) Å).^{22,30,48,53–55} The terminal azides of N10–N11–N12 in **3a** (1.140(7) Å for N10–N11 and 1.147(8) Å for N11–N12) and **3b** (1.148(11) Å for N10–N11, 1.157(12) Å for N11–N12) present delocalized forms and are consistent with a typical U–N=N=N pattern, whereas the terminal azides of N13–N14–N15 in **3a** (1.179(7) Å for N13–N14, 1.138(8) Å for N14–N15) and **3b** (1.168(11) Å for N13–N14, 1.126(12) Å for N14–N15) show more localized structures.

The distances of Rh–N_{azide} (2.091(5) and 2.103(5) Å) in **3a** are consistent with the values found in previously reported rhodium complexes with side-on bridged azide ligands (2.076(10)–2.28(9) Å).^{56,57} The corresponding N–N bond distances of bridged azides in **3a** (1.197(7) and 1.159(7) Å for N4–N5 and N5–N6, 1.228(7) and 1.144(7) Å for N7–N8 and N8–N9) are very close to those observed in **3b** (1.244(11) and 1.137(11) Å for N4–N5 and N5–N6, 1.229(10) and 1.117(10) Å for N7–N8 and N8–N9). Therefore, the bridged azide groups are liable to shift toward a more localized U=N–N≡N bonding interaction due to their coordination with the uranium center, which suggests that the elimination of N₂ from the bridged azides is possible.

Figure 3. Molecular structures of 2 and 3. a–d, Solid-state structures of 2a (a), 2b (b), 3a (c) and 3b (d) by X-ray crystallography with 50% probability ellipsoids. Solvent molecules, hydrogen atoms and the isopropyl moieties in P^iPr_2 are omitted for clarity.

The reduction, photolysis, and thermolysis of uranium azide complexes are known to be effective methods for the synthesis of uranium nitrides with the release of N_2 .^{8,20,35,38,40,48} Thus, we attempted to synthesize uranium nitride complexes by these routes. Only unidentified products were formed by the reduction of **3** with KC_8

or thermolysis of **3** at 70 °C for 2 days as suggested by the *in-situ* ^1H NMR spectra. Fortunately, the photolysis of complex **3a** in THF under UV light irradiation for 2 days resulted in the formation of $[\{\text{U}\{\text{N}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{NP}^i\text{Pr}_2)_2\}(\text{N}_3)[(\mu\text{-N}_3)\text{Rh}(\text{COD})]_2[(\mu\text{-N})\text{Rh}(\text{COD})]\}]$ (**4a**), which was isolated as brown crystals in 54% yield from toluene at RT (Fig. 2). In comparison with **3a**, the ^1H NMR spectrum of **4a** exhibits a narrow spectral range of +23.37 ppm to -12.46 pm, which was consistent with a previously reported U(V) complex $[\{\text{U}(\text{Tren}^{\text{DMBS}})_2(\mu\text{-N})\}]$ (from +24.86 to -13.31 ppm) and reflects the $5f^1$ nature of these species (Fig. S5).²⁰

After further photolysis of complex **4a** under UV light for 2 days, a diamagnetic U(VI) species $[\{\text{U}\{\text{N}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{NP}^i\text{Pr}_2)_2\}(\text{N}_3)\{[(\mu\text{-N})\text{Rh}(\text{COD})]_2[\text{Rh}(\text{COD})]\}]\}$ (**5a**) was isolated in 65% yield after recrystallization (Fig. 2). The ^1H NMR study shows that exposing complex **3b** to UV light for 1 day resulted in the disappearance of **3b**, and formation of complex $[\{\text{U}\{\text{N}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{NP}^i\text{Pr}_2)_2\}(\text{N}_3)[(\mu\text{-N}_3)\text{Rh}(\text{COD})]_2[(\mu\text{-N})\text{Rh}(\text{COD})]\}]$ (**4b**) as brown crystals in 52% yield after recrystallization (Fig. 2). Similar to the Rh analogues, complex **4b** could be further photolysis under UV light for 1 day, leading to the formation of complex $[\{\text{U}\{\text{N}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{NP}^i\text{Pr}_2)_2\}(\text{N}_3)\{[(\mu\text{-N})\text{Ir}(\text{COD})]_2[\text{Ir}(\text{COD})]\}]\}$ (**5b**) as brown crystals in 58% yield. Both **5a** and **5b** could be obtained by the photolysis of **3a** and **3b** under UV light for 4 and 2 days, respectively. These results suggest that the photolysis of **3** is controllable and that complexes **4a** and **4b** can be viewed as the intermediates in these processes.

The solid-state structures of **4** and **5** were determined by single-crystal X-ray diffraction. The U centers in **4a** and **4b** are coordinated with a tridentate

[N(CH₃)(CH₂CH₂NPⁱPr₂)₂]²⁻ ligand, three azide ligands and a nitride ligand and in a distorted pentagonal bipyramidal geometry (Fig. 4). The nitride atom (N4) is bonded to one U atom and two Rh atoms. The U1-N4 distances are 1.963(5) Å in **4a** and 2.011(4) Å in **4b**, which are shorter than U–N multiple bond lengths (2.0470(3) and 2.0511(3) Å) in a U(V) nitride complex with a U(V)=N=U(V) unit.²¹ However, the U–N bond length is slightly longer than the U≡N bond length (1.916(4) Å) in the borane-capped uranium(V) species.³⁷ The Rh/Ir–N4 bond lengths in **4a** and **4b** are close to the Rh/Ir–N_{azide} bond lengths, and are comparable to those observed in **3a** and **3b**, respectively. The bridged U–N_{azide} bond lengths in complexes **4** are comparable to those found in complexes **3**. The U(V) azide units in complexes **4** could be further photolyzed to generate U(VI) nitride complexes **5**.

The centrosymmetric structures of **5** feature two bridged nitride atoms, which are capped by three Rh or Ir atoms (Fig. 4). The bond lengths of U1–N3 in **5a** and **5b** are 1.975(5) Å and 2.005(6) Å, which are comparable with the U–N_{nitride} bond lengths found in complexes **4a** and **4b**, respectively. These results indicate that **5a** and **5b** have two U–N multiple bonds. Therefore, complexes **5** represent the first example of a transition metal capped U(VI) nitride species. It is also the rare U(VI) nitride complex generated by the photolysis of uranium azide species. The distances of Rh–N3 (2.082(4) Å and 2.067(4) Å) and Ir–N3 (2.059(6) Å and 2.047(6) Å) are comparable to the Rh/Ir–N4 bond distances observed in **4a** and **4b**, respectively. The bond lengths of N4–N5 and N5–N6 in **5a** and **5b** are comparable, and are consistent with the delocalized N–N distances in complexes **3** with a U–N=N=N form.

Figure 4. Molecular structures of 4 and 5. a–d, Solid-state structures of **4a** (a), **4b** (b), **5a** (c) and **5b** (d) by X-ray crystallography with 50% probability ellipsoids. Solvent molecules, hydrogen atoms and the isopropyl moieties in P^iPr_2 are omitted for clarity.

Stability and reactivity of uranium-nitride complexes. It is known that high oxidation state uranium nitride complexes are extremely unstable and consequently, the stabilities of the newly synthesized U(V) and U(VI) nitrides **4** and **5** were investigated.

Both **4** and **5** exhibit remarkable stability in the solid-state or in THF solution for at least 2 weeks under a N₂ atmosphere, which is probably because the active nitrides are capped/stabilized by transition metals. Irradiation of U(V)-nitride-azide complexes **4a** and **4b** for 2 and 1 days resulted in the formation of rare U(VI)-nitride complexes **5a** and **5b**, respectively (Fig. 2). However, further extending the irradiation time leads to the decomposition of **5a** and **5b** to unidentified products.

The protonation of metal nitrides to produce NH₃ is a critical step in N₂ reduction and conversion. Thus, we examined the reactivity of **4** and **5** toward acid and H₂ (Fig. 2). We found that substantial NH₄Cl (in 68%-82% yields) was formed by the reactions of uranium nitride complexes **4** and **5** with excess PyHCl in THF solution (Figs. S9-S12). The addition of 1 atm H₂ to the crystalline solids or to the degassed THF solution of **4** and **5**, led to a gentle color change from brown to red. Unfortunately, attempts to isolate the single crystals of the resulting products were unsuccessful. However, addition of excess PyHCl to the reaction mixtures of **4** and **5** with H₂ in THF solution led to the formation of NH₄Cl in 41%-67% yields, respectively (Figs. S13-S16). In comparison, no NH₄⁺ was observed from the reactions of uranium azide complexes **3** with excess PyHCl (Fig. S17). These results suggest that the nitride units in complexes **4** and **5** are the sources of the NH₄⁺.

Magnetic studies and electronic absorption spectra. The variable-temperature magnetic data of complexes **3** and **4** in the solid-state were measured by a superconducting quantum interference device (SQUID) magnetometry (Fig. 5). The magnetic moments of **3a** and **3b** at 300 K are 3.90 μ_B and 3.54 μ_B, respectively, which

are close to the theoretical value ($3.58 \mu_B$) for the $5f^2$ uranium ion in the 3H_4 ground state. With decreasing temperatures, the magnetic moments of **3a** and **3b** decrease persistently to $0.43 \mu_B$ and $0.47 \mu_B$ at 1.8 K, respectively, and with a trend to zero, which is characteristic of U(IV) complexes.^{58,59} The effective magnetic moments of **4a** and **4b** at 300 K are $2.76 \mu_B$ and $2.30 \mu_B$, respectively, which are very close to the theoretical value of $2.54 \mu_B$ for one U(V) ion. The magnetic moments of **4a** and **4b** decrease smoothly to $0.91 \mu_B$ and $1.03 \mu_B$ at 1.8 K, respectively, with decreasing temperature. The temperature dependence and the magnitude of μ_{eff} values of complexes **4a** and **4b** are consistent with reported U(V) complexes.^{34,59} These results suggest that the oxidation states of uranium centers in complexes **3** and **4** were U(IV) and U(V), respectively.

Figure 5. Variable-temperature effective magnetic moment data of **3** and **4**.

The ultraviolet/visible/near-infrared (UV/Vis/NIR) electronic absorption spectra of complexes **3-5** were recorded in THF at RT (Figs. S22-S27). These complexes exhibit similar absorption profiles with gradually increasing molar absorption at high energy in the UV–Visible region but show different fingerprint features in the NIR region. Here, both **3a** and **3b** display broad bands approximately from 975 nm to 1200 nm with a

series of weak absorptions ($\epsilon < 100 \text{ M}^{-1} \text{ cm}^{-1}$), which is in agreement with those observed for previously reported U(IV) complexes.^{60,61} Generally, species with $5f^1$ configured U(V) centers exhibit less complicated absorption spectra than species with $5f^2$ configured U(IV) centers in the NIR region. Consistently, the spectra for **4a** and **4b** show a weak and sharp $5f-5f$ transition at $\lambda = 1631$ and 1634 nm , which are characteristic of the U^{V} -centered $5f^1$ electronic configuration.^{62,63} As expected for U(VI) species with a $5f^0$ electronic configuration, the spectra of **5a** and **5b** show no characteristic absorption peak in the NIR region ($900-1700 \text{ nm}$), consistent with previously reported U(VI) complexes $[\text{U}(\text{N})(\text{Tren}^{\text{TIPS}})]^{38}$ and $[\text{NBu}_4][\text{U}(\text{OSi}(\text{O}^t\text{Bu})_3)_4(\text{N})]$.⁴⁰

Theoretical studies. DFT calculations (B3PW91) were used to describe the bonding properties of these complexes, in particular complexes **4** and **5**. To probe the validity of the computational approach, the geometries of complexes **3a/3b** are compared with the experimental geometries. The two terminal $\text{U}-\text{N}_{\text{azide}}$ bonds are well reproduced ($2.27/2.30 \text{ \AA}$ in **3a** and $2.27/2.30 \text{ \AA}$ in **3b**). The same is true for the two bridged $\text{U}-\text{N}_{\text{azide}}$ bonds ($2.49/2.54 \text{ \AA}$ in **3a** and $2.51/2.55 \text{ \AA}$ in **3b**). In the same way, the $\text{Rh}-\text{N}_{\text{azide}}$ bonds are correctly described ($2.11 \text{ \AA}$) indicating that the computational method is appropriate to describe such complexes. The LUMOs of complexes **3a/3b** (see SI) clearly display some antibonding π interactions in the azide ligands so that populating such orbital would result in N-N bond breaking. According to the orbital energies, this would imply an energy of $78.0 \text{ kcal mol}^{-1}$ which is consistent with the need for photolysis to form complexes **4a/4b**. Moreover, it is interesting to note that

the formation of the two latter complexes from **3a/3b** is thermodynamically favorable (by 17.6 kcal mol⁻¹ for **4a** and 18.2 kcal mol⁻¹ for **4b**). The bonding situation was thus analyzed for complexes **4a** and **4b** and the bond lengths are well reproduced.

Analysis of the unpaired spin densities (1.23 in **4a** and 1.24 in **4b**), clearly indicates the presence of a U(V) metal center in these two complexes. At the NBO level, the U1-N4 bond is found to be a double bond with polarized bonds toward N (68% for σ and 72% for π in **4a** and 72%/75% in **4b**, Table S10). These bonds involve *fd* hybrid orbitals on uranium (78% 5f-20% 6d for σ and 59% 5f-39% 6d for π in **4a** but 59% 5f-33% 6d and 57% 5f-33% 6d in **4b**). Although polarized, these bonds appear to be quite covalent as demonstrated by the U1-N4 Wiberg Bond Index (WBI) of 1.96 in **4a** (1.83 in **4b**). The associated Rh1-N4 bond was only observed at the second order donor-acceptor and the associated WBI was 0.45. On the other hand, the Ir1-N4 bond is 0.49 in **4b**. Therefore, as found by scrutinizing the molecular orbitals (MO, Fig. 6), the U1-N4-Rh(Ir) bonds in **4a** and **4b** are 3c-2e bonds. Similar to complexes **3a/3b**, the LUMOs of complexes **4a** and **4b** (see SI) also display some antibonding interactions in the azide ligands so that populating this orbital would allow the N-N bond breaking. According to the orbital energy, this process would imply an energy of 80.0 kcal mol⁻¹ in line with photolysis. For the transformation of **4a/4b** onto complexes **5a/5b**, the reaction is thermodynamically favored by 43.5 kcal mol⁻¹ (**5a**) and 49.6 kcal mol⁻¹ (**5b**).

Finally, the bonding in complexes **5a/5b** was analyzed. The optimized geometries compare well with the experimental geometries. In both complexes, the uranium centers are at the oxidation state +VI and have no residual unpaired spin densities.

The two double U-N bonds are similar to the those found in complexes **4** with a WBI of 1.91 for **5a** (1.80 for **5b**), and the MO clearly displays 3c-2e U-N-Rh(Ir) bonds (Fig. 6). At the NBO level, the U1-N3 and U1-N3' bonds are found to be U-N double bonds polarized toward N and these bonds also involve *fd* hybrid orbitals on uranium (Table S10).

Figure 6. U-N-Rh(Ir) bonding molecular orbitals of complexes **4a/4b** and **5a/5b**.

Conclusion

In summary, we have synthesized the first example of transition metal capped-U(VI) nitride complexes **5a** and **5b**. These are the second examples of U(VI) nitride

species generated by photolysis of U(IV) azide precursors, **3a** and **3b**. The mono-U(V) nitride intermediates **4a** and **4b** were successfully isolated by controlling the duration of the irradiation. They were sufficiently stable to be fully characterized and could be further photolyzed to mono-U(VI) nitrides **5** under UV irradiation conditions. Therefore, the photolysis of the azide units in complexes **3a** and **3b** was controllable and is a stepwise process. The excellent stabilities of both the U(V) nitride intermediates **4** and the U(VI) nitride products **5** are probably due to the active nitrides being capped/stabilized by transition metals. DFT study allowed us to analyze the bonding of these complexes, indicating the presence of U-N multiple bonds and U-N-Rh(Ir) 3c-2e interactions. Moreover, the DFT calculations showed that the photolysis was necessary to break the N-N bond of the azide ligands by populating the LUMOs of complexes **3** and **4** and this displays an antibonding N-N interaction. This study implies that a multiple N-P ligand is an effective platform to capture unstable U(VI) nitrides with the aid of transition metals.

Methods

General considerations. Experiments were performed under an Ar atmosphere using standard Schlenk-line or glove-box techniques. Solvents were dried and degassed with a solvent purification system before use. See the Supplementary Information for detailed experimental procedures, crystallographic, and computational details.

Data Availability. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC),

under deposition numbers CCDC-2104709 (**2a**), 2104710 (**2b**), 2104711 (**3a**), 2104712 (**3b**), 2104713 (**4a**), 2104714 (**4b**), 2104715 (**5a**) and 2104716 (**5b**). These data can be obtained free of charge from the CCDC *via* www.ccdc.cam.ac.uk/data_request/cif. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

C.Z. conceived this project. X.X. performed the experiments and solved all the X-ray structures with support from Y.Z.. C.Z. and X.X. analyzed the experimental data. I.D. and L.M. conducted the theoretical calculations. L.M. analyzed the theoretical results. C.Z. and L.M. drafted the paper with support from others. All authors discussed the results and contributed to the preparation of the final manuscript.

Additional information

Supplementary Information accompanies this paper at <http://www.nature.com/naturecommunications>

337 **Competing interests:** The authors declare no competing interests.

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