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Stepwise reduction of dinitrogen by a uranium-potassium complex yielding a U(VI)/U(IV) tetranitride cluster

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ABSTRACT: Multimetallic cooperativity is believed to play a key role in the cleavage of dinitrogen to nitrides (N³⁻), but the mechanism remains ambiguous due to the lack of isolated intermediates. Herein, we report the reduction of the complex [K₂{[U^V(OSi(O^tBu)₃)₃]₂(μ-O)(μ-η²:η²-N₂)}], **B**, with KC₈, yielding the tetranuclear tetranitride cluster [K₆{(OSi(O^tBu)₃)₂U^{IV}]₃{(OSi(O^tBu)₃)₂U^{VI}}(μ₄-N)₃(μ₃-N)(μ₃-O)₂], **1**, a novel example of N₂ cleavage to nitride by a diuranium complex. The structure of complex **1** is remarkable, as it contains a unique uranium center bound by four nitrides and provides the second example of a *trans*-N=U^{VI}=N core analogue of UO₂²⁺. Experimental and computational studies indicate that the formation of the U(IV)/U(VI) tetrauranium cluster occurs via successive one electron transfers from potassium to the bound N₂⁴⁻ ligand in complex **B** resulting in N₂ cleavage and the formation of the putative diuranium(V) bis-nitride [K₄{[U^V(OSi(O^tBu)₃)₃]₂(μ-O)(μ-N)₂}], **X**. Additionally, cooperative potassium binding to the U-bound N₂⁴⁻ ligand facilitates di-nitrogen cleavage during electron transfer. The nucleophilic nitrides in both complexes are easily functionalized by protons to yield ammonia in 93-97% yield and with excess ¹³CO to yield K¹³CN and KN¹³CO. The structure of two tetranuclear U(IV)/U(V) bis- and mono-nitride clusters isolated from the reaction with CO demonstrates that the nitride moieties are replaced by oxides without disrupting the tetranuclear structure, but ultimately leading to valence redistribution.

Introduction

Dinitrogen reduction and functionalization by molecular complexes under mild conditions remain a key challenge in current chemistry.¹ Although uranium-based inorganic materials were shown to be active catalysts of the Haber-Bosch process for the N₂ conversion to ammonia,² an iron-based catalyst was adopted for industrial production of ammonia. As a result, the dinitrogen chemistry of molecular uranium compounds is significantly less developed

than *d*-block metals and mostly involves labile N₂ binding or two electron N₂ reduction,³ with only three examples of four electron N₂ reduction reported recently (complexes **A-C** in Figure 1).⁴

In the industrial ammonia production process (Haber-Bosch), and biological enzymatic conversion of dinitrogen to ammonia by nitrogenase – which are both thought to involve metal-nitride intermediates – the reduction of dinitrogen occurs at multimetallic sites. Moreover, the secondary interactions of metal dinitrogen complexes with alkali ions are known to enhance the activity of the iron-

based Haber–Bosch catalysts.⁵ Molecular complexes capable of effecting the cleavage of dinitrogen to nitrides^{1a, 6, 7} are essentially limited to *d*-block metals^{1a, 6} and are all proposed to involve multimetallic intermediates^{6, 7} that have been isolated in a few instances.^{6c, 6d, 6o, 8} In particular, based on the structure of the final nitride complex, multimetallic cooperation of transition metals and Lewis acids, potassium in particular, has been suggested by several groups to be a crucial step in the six electron dinitrogen cleavage to nitride involving alkali ions as reducing agents.^{6j, 9, 6g, 6h, 6m} Similarly, multimetallic cooperativity between uranium and *s*- or *d*-block metals is thought to play an important role in the uranium mediated N₂ cleavage to nitride complexes, **D** and **E** (Figure 1),^{7a, 7b} which are unique examples of molecular complexes of *f*-block metals capable of splitting N₂ into nitrides in solution. However, the mechanism of this cooperative interaction remains unknown, due to the lack of isolated intermediates.

We previously reported^{4b} a well-defined multimetallic oxide bridged diuranium(III)-K complex [K₂{[U(OSi(O^{*i*}Bu)₃]₃]₂(μ-O)}] that effects the reduction of dinitrogen by transferring four electrons from the two uranium centers.

Figure 1. N₂ activation and N₂ cleavage by multimetallic uranium complexes. Reduction to N₂⁴⁻ by dinuclear U(III) complexes (**A** and **B**), and by a dinuclear U(IV) and K₂ (**C**). N₂ cleavage to nitride by U(III) (**D**) and U(IV) (**E**) complexes after addition of external reducing agent. The siloxide ligands OSi(O^{*i*}Bu)₃ are abbreviated as OSi(O^{*i*}Bu) in the complexes **A** and **B** for clarity. The phenol moieties in complex **C** are drawn as lines for clarity.

Functionalization of the resulting U(V) hydrazido complex [K₂{[U^V(OSi(O^{*i*}Bu)₃]₃]₂(μ-O)(μ-η²:η²-N₂)}], **B**, was also achieved by addition of CO to yield a cyanamido (NCN²⁻) analogue, but addition of H₂ or protons only resulted in N₂

release.^{4b} This system provides a unique candidate to investigate the stepwise reduction of dinitrogen at multimetallic centers.

Here we show that further reduction of the uranium-bound N₂ in **B** is achieved by addition of K₂C₈ yielding a tetranuclear tetranitride cluster *via* a putative dinuclear bis-nitride intermediate. The contribution of the potassium in the dinitrogen reduction is clearly identified as providing the two additional electrons required to cleave the single N-N bond in the hydrazido complex **B**, and contributing to the weakening of the N-N bond. The four bridging nitrides are readily functionalized by CO to yield NCO⁻ and CN⁻ and produce ammonia quantitatively upon acid addition.

Results and discussion

Synthesis and characterization of a nitride cluster derived from N₂ reduction

Complex [K₂{[U^V(OSi(O^{*i*}Bu)₃]₃]₂(μ-O)(μ-η²:η²-N₂)}], **B**, was synthesized as previously reported from the reaction of the diuranium(III) complex [K₂{[U^{III}(OSi(O^{*i*}Bu)₃]₃]₂(μ-O)}] with N₂.^{4b}

Complex **B** was reacted with 3-4 equivalents of K₂C₈ in toluene at -40 °C for 12 hours (Scheme 1, OL = OSi(O^{*i*}Bu)₃). The ¹H NMR spectrum of the resulting reaction mixtures (Figures S9 and S11) showed the signals of the product and of the ligand salt KOSi(O^{*i*}Bu)₃.

Scheme 1. Reduction of uranium bound N₂⁴⁻ (**B**) with K₂C₈ yielding the nitride cluster **1**.

The reaction mixture obtained after reacting **B** with 3 equiv of K₂C₈ in toluene at -40 °C for 12 hours, was left standing for a few days at -40 °C after graphite filtration. It afforded the tetranitride cluster [K₆{(OSi(O^{*i*}Bu)₃]₂U^{VI}}]₃·{(OSi(O^{*i*}Bu)₃]₂U^{VI}}(μ₄-N)₃(μ₃-N)(μ₃-O)₂], **1**, as a red-brown crystalline solid in 21% yield. The reduction of complex **B** in the presence of excess K₂C₈ (4 equiv) at -40 °C for 12 hours resulted in the isolation of complex **1** in higher yield (40%). The lower solubility of complex **1** compared to the ligand salt KOSi(O^{*i*}Bu)₃ allowed to isolate **1** in pure form.

The molecular structure of complex **1** (Figure 2a), Table 1) shows the presence of a tetrameric complex where four uranium ions and six potassium ions are bridged by four nitrides (the two μ₄-nitrides N1 and N2 bridge three U centers and one K, the μ₄-nitride N3 bridges two U and two K, and the μ₃-nitride N4 bridges two U and one K) and two oxide ligands. The four U centers are coplanar in a rhombohedral arrangement Figure 2b), with the longest distance between U1 and U3 of 5.8744(4) Å and other U–U

distances in the range 3.3774(4)-3.5329(6) Å. Each uranium center is bound by two siloxide ligands, confirming the loss of a $\text{KOSi}(\text{O}^t\text{Bu})_3$ fragment per uranium compared to complex **B**, as observed by ^1H NMR spectroscopy. The calculated Bond Valence Sum (BVS)¹⁰ (see SI, Table S2) for the uranium cations and the computational study (see below) show the presence of a mixed valence species with one U(VI) (U4) and three U(IV) ions and localized valence.

Figure 2. Molecular structure of $[\text{K}_6\{(\text{OSi}(\text{O}^t\text{Bu})_3)_2\text{U}^{\text{IV}}\}_3\{(\text{OSi}(\text{O}^t\text{Bu})_3)_2\text{U}^{\text{VI}}\}(\mu_4\text{-N})_3(\mu_3\text{-N})(\mu_3\text{-O})_2]$, **1**. (a) $\text{U}_4\text{N}_4\text{O}_2\text{K}_6$ core in **1**, with siloxide ligands depicted as wire frames for clarity. (b) $\text{U}_4\text{N}_4\text{O}_2$ core in **1**, with siloxide ligands depicted as tubes for clarity. Thermal ellipsoids are drawn at 50% probability. Solvent molecules, hydrogen, and carbon atoms are omitted for clarity.

The $\text{U}^{\text{IV}}\text{-N}$ bond distances (ranging from 2.183(7) Å to 2.319(78) Å) are comparable to those found in previously reported U(IV) μ_4 -nitride, (2.271(3)-2.399(5) Å),¹¹ U(IV) μ_3 -nitrides (2.154(7)-2.157(3) Å),^{7b,12} and U(IV)/U(VI) μ -nitride clusters (U(IV)-N 2.379-2.392 Å) and are consistent with the presence of a U-N single bond. The N- U^{IV} -N angles are all similar and range from 73.4(3) to 77.4(3)°.

The fourth uranium center (U4) provides the first molecular example of a uranium center coordinated by four nitride ligands. Two nitrides bind U4 in a *trans* mode with a nearly linear $\text{N}_4\text{-U}_4\text{-N}_3$ angle (178.7(3)°) and short $\text{U}^{\text{VI}}\text{-N}$ distances (1.963(8) and 1.902(8) Å) while two nitrides bind U4 in a *cis* mode ($\text{N}_1\text{-U}_4\text{-N}_2$: 79.8(2)°) at much longer $\text{U}^{\text{VI}}\text{-N}$ distances (2.256(6) and 2.265(7) Å) consistent with a single bond.

The short U-N distances in the *trans* bis-nitride $\text{N}=\text{U}(\text{VI})=\text{N}$ fragment are longer than those found in the first example of $\text{N}=\text{U}(\text{VI})=\text{N}$ bis-nitride recently identified in the cationic U(VI)/U(IV) complex $[(\text{NH}_3)_8\text{U}(\mu\text{-N})(\text{NH}_3)_5\text{U}(\mu\text{-N})\text{U}(\text{NH}_3)_8]\text{Br}_8$ (1.853(3) and 1.854(3) Å) reported by Kraus and coworkers.¹³ The increased U-N distance is likely to be the result of a more electron-rich uranium center due the presence of four additional anionic ligands in **1** compared to the neutral ammonia ligands found in the Kraus complex. The values of the $\text{U}^{\text{VI}}\text{-N}$ bond distances in **1** are also longer than those found in terminal U(VI) nitrides¹⁴ and in the *trans* U(VI)bis-imido complexes $[\text{U}(\text{N}^t\text{Bu})_2\text{I}_2(\text{THF})_2]$ (1.840(4), 1.848(4) Å) and $[\text{U}(\text{NPh})_2\text{I}_2(\text{THF})_3]$ (1.866(2), 1.859(2) Å)¹⁵ but close to those found in borane capped U(VI) nitrides (1.880(4)-1.916(4) Å)¹⁶ and slightly shorter than those found for

trans-imido groups in the tris-imido U(VI) complex $[\text{MesPDI}^{\text{Me}}\text{U}(\text{NMes})_3]$ (1.992(2) Å)¹⁷ and in tetrakis(imido) uranates (2.034-2.068 Å),¹⁸ consistently with the presence of U=N multiple bond. The lengthening of the U=NR bonds in the tris-imido complex $[\text{MesPDI}^{\text{Me}}\text{U}(\text{NMes})_3]$ compared to U(VI)bis-imido complexes $[\text{U}(\text{N}^t\text{Bu})_2\text{I}_2(\text{THF})_2]$ and $[\text{U}(\text{NPh})_2\text{I}_2(\text{THF})_3]$ was interpreted in term of equatorial ligands competing with axial ligands for uranium orbitals.

Complex **1** also exhibits a U(IV) *trans* bis-oxo motif with a $\text{O}_1\text{-U}_2\text{-O}_2$ angle of 174.5(2)° and U-O distances of 2.210(6) and 2.1816(6) Å. The two oxo groups bridge two U(IV) centers with U-O bond lengths ranging from 2.116(6) Å to 2.210(6) Å. These values are consistent with previously reported uranium complexes bridged by oxo linkers^{4b} and comparable to those previously reported for U(IV) *trans* bis-siloxide systems (2.065(6)-2.126(2) Å)¹⁹ formed upon functionalization of uranyl(VI) species.

The Fourier transform infrared (FTIR) spectrum of complex **1** shows a band at 954 cm^{-1} which can be assigned to the UN multiple bonds. In the FTIR spectrum of ^{15}N -labeled analogue $^{15}\text{N}\text{-1}$ the band is shifted at 931 cm^{-1} (Figures S45-47). This value is close to the isotopomer shift calculated from reduced mass considerations (923 cm^{-1}). These values are higher than those reported for the U(VI) terminal nitride complex $[\text{NU}(\text{Tren}^{\text{TIPS}})]^9$ (914 cm^{-1} and 883 cm^{-1} for ^{14}N and ^{15}N respectively) but lower than the value reported for the UN_2 formed in gas phase (1051.0 cm^{-1}).²⁰

Magnetic data were also measured for complex **1** both in solid state and in solution to further confirm the presence of three U(IV) centers. A magnetic moment of 4.33 μB was measured for **1** at 298 K in toluene solution using the Evans method.²¹ This value is consistent with the presence of a U(VI) and three U(IV) ions with a magnetic moment of 2.49 μB per uranium(IV) center. SQUID magnetization measurements from 2 to 300 K on solid samples of **1** (Figure 3) revealed a magnetic moment of 4.50 μB at 300 K which decreases with decreasing temperature to 1.26 μB at 2 K. The observed behavior is in agreement with the presence of three non-interacting U(IV) centers with a magnetic moment per U(IV) of 2.63 μB at 300 K and of 0.73 μB at 2 K.²²

Low temperature (10 K) X-band EPR measurements carried out on isolated complex **1** or on reaction mixtures obtained after addition of 4 equiv KC_8 to **B** did not reveal the presence of any signal. This is consistent with what previously reported for several complexes of U(IV) which is a non-Kramer ion.^{22e,22f}

Figure 3. Plots of the measured χ vs T for complex **1** (red) and μ_{eff} per U(IV) center vs T (blue) in complex **1**.

Uranium nitrides have recently been the subject of an increasing number of studies,^{4a, 4b, 11-14, 16b, 23} but in only two cases the uranium nitrides were obtained from dinitrogen reduction. In both cases, dinitrogen cleavage resulted in the bis-nitride complexes U(IV)/U(IV) $\text{U}_4\text{Rh}_2\text{N}_2$ **7b** (**E**) and U(IV)/U(V) $\text{U}_2\text{K}_2\text{N}_2$ **7a** (**D**) (Figure 1), presenting a similar diamond core arrangement of the two nitrides.

Complex **1** is the third example of uranium nitride isolated from dinitrogen reduction by a uranium complex. Moreover, complex **1** is the first example of a U(VI) nitride obtained from dinitrogen reduction and the second example of molecular uranium nitride featuring a linear $\text{N}=\text{U}=\text{N}$ core analogue to the uranyl cation UO_2^{2+} .

It should be noted that, although complex **B** is prepared by addition of N_2 to the diuranium(III) complex formed by reduction under argon of the diuranium(IV) complex $[\{\text{U}^{\text{IV}}(\text{OSi}(\text{O}^t\text{Bu})_3\}_2(\mu\text{-O})\}]$ in thf, the *in situ* reduction of this diuranium(IV) complex with excess KC_8 in toluene at -40°C carried out under N_2 , did not result in the formation of the N_2^{4-} complex **B**. In contrast, we observed that the reaction led to the formation of a complex mixture of products as indicated by the ^1H NMR spectrum (Figure S40). The reaction products could not be isolated from this complex mixture. However, the present study allowed the assignment of ^1H NMR signals of the major species to the tetranitride cluster **1** and to a reaction intermediate (see following section).

Characterization of the reaction intermediate

The evolution of the reaction mixture obtained after addition of 4 equiv of KC_8 to a toluene solution of **B** at -40°C was monitored over time by ^1H NMR spectroscopy (Figure S10). These studies show that the reduction proceeds through formation of an intermediate species, **X**, which is further reduced to complex **1** (Scheme 2).

The formation of the intermediate **X** was also observed after reacting 1-2 equiv of KC_8 with a toluene solution of **B** for 12 hours at -40°C . The ^1H NMR spectrum of the reaction mixture obtained after reacting **B** with 2 equiv of KC_8 for 12 hours at -40°C , showed full conversion of **B** into **X**.

Despite numerous attempts, we were unable to isolate intermediate **X**. Instead, further addition of 1 equiv of KC_8 to the reaction mixture resulted in full consumption of **X** after 5 days, yielding a mixture of $\text{KOSi}(\text{O}^t\text{Bu})_3$ and of complex **1**.

Two possible structures could be envisaged for the intermediate **X** depending on if the reduction occurs at the N_2^{4-} or at the metal center: a diuranium(IV) N_2^{4-} complex (Figure 4a) or a diuranium(V) bis-nitride complex (Figure 4b).

Figure 4. Possible structures of the intermediate **X**: a diuranium(IV) N_2^{4-} (a) or a diuranium(V) bis-nitride (b).

In order to further characterize the nature of the intermediate **X**, we investigated its *in situ* reactivity with protons and CO and compared it to the reactivity of the complex **B** (Scheme 2). The addition of excess acid to the complex **B** was previously reported to lead to the release of N_2 and formation of ammonium chloride was not observed.^{4b}

Scheme 2. Reactivity of the proposed intermediate **X**.

In contrast, addition of excess HCl to solutions of **X** obtained by reacting 2 equiv KC_8 with complex **B**, resulted in the formation of NH_4Cl in 93% yield (with respect to the amount of **B**) (Scheme 2). The quantitative formation of NH_4Cl is in agreement with the presence of two nitrides in complex **X**.

These results demonstrate that further reduction of the N-N bond in **B** allows the formation of ammonia upon H^+ addition, rather than the N_2 elimination observed for **B**. Therefore, further activation of the bound N_2^{4-} is required for its reaction with H^+ to occur and form ammonia.

The formulation of the intermediate as a diuranium(V) bis-nitride complex was confirmed by its reactivity with ^{13}CO . The addition of excess ^{13}CO (3 equiv) to intermediate

X resulted in the formation of the previously reported diuranium(IV) bis-oxo complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-O)_2\}]^{4b}$ (Scheme 2). Moreover, the ^{13}C NMR spectrum of the reaction mixture quenched in D_2O shows the presence of $K^{13}CN$ and $KN^{13}CO$ in 1:1 ratio (overall yield 94%).

The formation of the bis-oxo and $K^{13}CN$ indicates that one bridging nitride promotes the cleavage and deoxygenation of carbon monoxide to afford a N-C triple bond and a bridging oxo group. A second molecule of CO effects the reductive carbonylation of the second nitride to yield a diuranium(IV) isocyanate complex. Similar reactivity with CO was observed for the diamond core-shaped diuranium(V)nitride $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-N)_2\}]$ yielding the complex $[K_2\{[U^{IV}(OSi(O^tBu)_3)_3]_2(\mu-CN)(\mu-O)(\mu-NCO)\}]^{23r}$. In the current case, the presence of an additional oxo ligand in the core results in the release of KCN and KNCO upon reaction. These results indicate that the reduction intermediate should be formulated as a diuranium(V) bis-nitride.

In order to confirm the oxidation state of the uranium centers in **X**, solid state and solution measurements of the magnetic moment were performed. A magnetic moment of 1.41 μ_B per U center was measured at 298 K for *in situ* prepared toluene solutions of **X**. This value is comparable to the value measured at 298 K for the U ions in complex **B** (1.75 μ_B)^{4b} and is significantly lower compared to the value measured for the U(IV) centers in **1** (2.49 μ_B).

SQUID magnetization measurements from 2–300 K of *in situ* prepared oily residues of **X** revealed a magnetic moment per uranium of 1.51 μ_B at 300 K which decreases with decreasing temperature to 0.26 μ_B at 2 K. Overall, the magnetic data unambiguously confirm the presence of U(V) ions in **X**.

Isolation of the bis-oxo complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-O)_2\}]$ from reaction of **X** with CO, as well as the determined magnetic moment of the uranium centers in **X**, indicate that the structure of the intermediate consists of a dinuclear U(V) bisnitride.

Complex **X** is unstable in a toluene solution, converting to an unidentified species (**Y**) after 24 h at 25 °C or after 1 week at -40 °C. Complex **Y** is also the only species formed upon reduction of **B** with 2 equiv KC_8 at 25 °C. Further addition of KC_8 to a solution of **Y** did not result in the formation of **1** but lead to unidentified species. Solution measurements of the magnetic moment performed at 298 K for *in situ* prepared toluene solutions of **Y** yielded a magnetic moment of 1.45 μ_B per U center. This value is comparable to the value measured at 298 K for the U ions in complex **X** (1.41 μ_B). Moreover, the analysis of the headspace by GC/MS spectrometry performed after reacting ^{15}N -**B** with 2 equiv KC_8 at 25 °C overnight showed no presence of detectable $^{15}N_2$. These results indicate that no loss of N_2 occurs during the decomposition.

In order to gain more insight into the structure of **Y** we reacted this species with excess HCl and CO. The addition of excess ^{13}CO (3 equiv) to **Y** resulted in the formation of the diuranium(IV) bis-oxo complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu-O)_2\}]^{4b}$ and the ^{13}C NMR spectrum of the reaction mixture quenched in D_2O shows the presence of $K^{13}CN$ and $KN^{13}CO$ in 1:1 ratio but in lower yield compared to **X** (overall yield 59%).

The addition of excess HCl to **Y** still results in the formation of NH_4Cl but in lower yield (64% yield (2 equiv, 100%)), compared to complex **X**. Since we observed no change in magnetic moment or loss of N_2 during the decomposition of **X** to **Y**, the lower yield in NH_4Cl observed for **Y** could be explained by a structural rearrangement of the nitride groups that renders them less reactive.

Reactivity of the tetra-nitride complex

The reactivity of the isolated complex **1** with protons was explored (Scheme 3). Addition of excess HCl to the isolated nitride complex **1**, yielded NH_4Cl in 97% yield (Figure S14), confirming the presence of 4 nitrido-bridging ligands in **1**. Further, the reactivity of complex **1** with CO was investigated. The addition of 1 equiv of ^{13}CO to a toluene solution of **1** led to an immediate color change from red-brown to green and to the disappearance of the 1H NMR signal assigned to complex **1**. Green crystals of the cluster $[K_4\{[OSi(O^tBu)_3]_2U^{IV}\}_2\{[OSi(O^tBu)_3]_2U^{IV}\}_2(\mu_4-N)_2(\mu-O)_2(\mu_3-O)_2]$, **2**, precipitated out of the reaction mixture after 3 days together with $K^{13}CN$ (identified by ^{13}C NMR studies). Complex **2** results from the cleavage of two CO molecules by two nitride groups in **1** to yield two oxo ligands and two equivalents of KCN.

The isolation of crystals of **2** from the reaction of **1** with 1 equiv of CO suggest that selective addition of one equiv CO to **1** is not possible and indicate that multiple products are likely to be present in the reaction mixture. Complex **2** could not be isolated in pure form due to the presence of $K^{13}CN$.

The addition of 2 equiv of ^{13}CO to a toluene solution of **1** led to an immediate color change from red-brown to light green. A colorless solid precipitated from the mixture, and was identified as $K^{13}CN$ by ^{13}C NMR studies. A mixture of green crystals of **2**, and yellow crystals of the cluster $[K_3\{[OSi(O^tBu)_3]_2U^{IV}\}_2\{[OSi(O^tBu)_3]_2U^{IV}\}_2(\mu_3-N)(\mu-O)(\mu_3-O)_4]$, **3** (Scheme 3, OL = $OSi(O^tBu)_3$) were obtained from the reaction mixture after addition of hexane at -40 °C. The similar solubility of the complexes **2** and **3** prevented their isolation in pure form. The concomitant formation of these two species suggests that the successive addition of CO to the nitrides in complex **1** is immediate, and the formation of **2** cannot be controlled by stoichiometric addition of 2 equiv CO.

Since the complexes formed from the reaction of **1** with CO do not display a 1H NMR spectrum, we further investigated the reaction by performing the quantitative determinations of the amounts of $K^{13}CN$ formed in the reactions of **1** with 1, 3 and 8 equiv CO.

^{13}C NMR studies of the reaction mixtures obtained after addition of ^{13}CO were performed after quenching in basic (pD=13) D_2O . We found that $K^{13}CN$ is the only ^{13}C -containing product formed during the reaction of **1** with 1–3 equiv of CO. Addition of excess (8 equiv) ^{13}CO to a toluene solution of complex **1** resulted in the formation of both $K^{13}CN$ and $KN^{13}CO$. The ^{13}C NMR spectrum of the reaction mixture after quenching in basic (pD=13) D_2O revealed the presence of $^{13}CN^-$ and $N^{13}CO^-$ in a 3:1 ratio. This indicates that all four nitrides react with CO, but three of them effect the cleavage of CO to CN^- and oxide, while the remaining nitride is carbonylated to yield cyanate.

Quantitative ^{13}C NMR studies of reaction mixture after quenching in basic ($\text{pD}=13$) D_2O demonstrated that 1 equiv K^{13}CN is formed after reaction of **1** with 1 equiv ^{13}CO .

In order to investigate if, once formed, cluster **2** could be converted into cluster **3**, a solution of **1** was first reacted with 1 equiv of ^{13}CO and then 2 additional equivalents of ^{13}CO were added to the resulting reaction mixture. Quantitative ^{13}C NMR studies of the resulting reaction mixture after quenching in basic ($\text{pD}=13$) D_2O showed that the amount of K^{13}CN amounted to a total of 3 equiv indicating that three nitrides have reacted with CO to yield K^{13}CN .

Since **2** is present in the 1:1 reaction mixture of **1** and CO, further reaction of **2** with CO must occur upon addition of 2 equiv of CO to the 1:1 mixture in order to form 3 equiv KCN.

These results indicate that complex **3** could be obtained as the only reaction product upon addition of 3 equiv CO to **1** but the concomitant formation of KCN prevents its isolation in pure form.

Scheme 3. Reactivity of complex 1.

Complex **2** provides a snapshot of intermediates formed during the stepwise carbonylation of **1**, suggesting that the two *trans* U(VI) nitride react first.

The molecular structure of complex **2** (Figure 5, Table 1) shows the presence of a tetranuclear complex with four uranium centers bridged by four oxide and two nitride ligands. Four potassium cations are also present in the structure, two binding the nitride groups and two binding two oxides. The calculated Bond Valence Sum for the uranium cations (see Table S2) indicate the presence of localized valence with two U(V) (U1 and U1') and two U(IV) ions (U2 and U2'). This structure suggests that the two highly nucleophilic U(VI)-nitrides effect the cleavage of CO resulting in the elimination of KCN and formation of oxides. Furthermore, the replacement of nitride ligands by oxides results in a rearrangement of the valence of two U ions from U(VI)/U(IV) to U(V)/U(V).

The coplanar rhombohedral arrangement found in **1** remains primarily unchanged (Figure 5b), with the longest

distance found between U2 and U2' at 6.0079(7) Å and other U–U distances in the range 3.4749(1)–3.4759(2) Å.

Figure 5. Molecular structure of $[\text{K}_4\{(\text{OSi}(\text{O}^t\text{Bu})_3)_2\text{U}^{\text{IV}}\}_2\{(\text{OSi}(\text{O}^t\text{Bu})_3)_2\text{U}^{\text{V}}\}_2(\mu_4\text{-N})_2(\mu\text{-O})_2(\mu_3\text{-O})_2]$, **2**. (a) $\text{U}_4\text{N}_2\text{O}_4\text{K}_2$ core in **2** with the siloxide ligands depicted as wire frames for clarity. (b) $\text{U}_4\text{N}_2\text{O}_4$ core in **2** with siloxide ligands depicted as tubes for clarity. Thermal ellipsoids are drawn at 50% probability. Solvent molecules, hydrogen and carbon atoms are omitted for clarity.

The structure of **2** presents two U(V) *trans* bis-oxo motif with a O1–U1–O2 angles of 177.60(8). The U–O bond distances (2.157(2) and 2.089(2) Å) are shorter compared to those of the *trans*-oxo in **1** and slightly longer than those found in *trans* U(V) bis-siloxides (1.996(5) and 1.986(5) Å).²⁴ The two μ_4 -nitrido groups bridge one K^+ ion and three U centers. They bind the U(V) centers with a diamond type arrangement similar to those found in the previously reported dinuclear U(IV)/U(V)^{7a} (U–N: 2.076(6) and 2.099(5) Å) and U(V)/U(V)^{23g} (U–N: 2.022(5) and 2.101(6) Å) bis-nitride complexes but with longer U–N bond distances (2.203(8)–2.312(2) Å) probably due to the μ_4 bridging mode found in this tetranuclear cluster.

The molecular structure of complex **3** (Figure S41) shows the presence of two independent molecules with similar structural parameters in the unit cell. Each molecule consists of a tetranuclear cluster where one additional nitride has been replaced by an oxo ligand compared to **2**. Accordingly, only three potassium cations are now present in the structure, with all binding the oxide bridging groups. The position of the nitride cannot be unambiguously identified by crystallography; a position was chosen arbitrarily to draw the structure.

The calculated Bond Valence Sum for the uranium cations (see Table S2) shows the presence of localized valence with two U(V) (U1 and U3 in one molecule and U5 and U7 in a second molecule) and two U(IV) ions (U2 and U4 in one molecule and U6 and U8 in the other). The coplanar rhombohedral arrangement found in **1** and in **2** remains practically unchanged, with the longest distance found between U2 and U4 at 6.0028(11) Å. The μ_3 -nitrido ligand bridges 3 U centers with U–N bond distances ranging from 2.266 (14) Å to 2.316(14) Å.

	1	2	3
U-Nitride (Å)	2.183(7)- 2.319(7)	2.213(2)	2.266(14)
		2.203(2)	2.304(14)
		2.312(2)	2.316(14)
U(VI)- nitride (cis) (Å)	2.265(7)		
	2.256(6)		
U(VI)- nitride (trans) (Å)	1.963(8)-1.902(8)		-
U-μ-oxo (Å)	2.210(6) (trans)	2.157(2) (trans)	2.066(13)-2.284(13)
	2.181(6) (trans)	2.089(2) (trans)	
	2.117(6)	2.127(2)	
	2.116(6)	2.161(2)	
U-μ ₃ -oxo (Å)	-	-	2.230(12)-2.337(12)
U-U (Å)	3.3774(4)-5.8733(5)	3.4670(1)-6.0079(7)	3.5051(9)-6.0028(11)

Table 1. Selected bond distances for complexes 1, 2, and 3.

Computational studies

In order to gain more insight into the formation of complex **1**, calculations were conducted at the DFT level (B3PW91). Sequential addition of potassium was carried out computationally from **B** ultimately yielding **1** (Figure 6, OL = OSi(O^tBu)₃). In complex **B**, the two uranium ions are in the oxidation state +V with a N₂⁴⁺ ligand. This is corroborated by the N-N bond distance that is elongated to 1.41 Å, in line with a N-N single bond. The unpaired spin density is located on the two uranium centers with one electron each. The first reduction by potassium is predicted to be exothermic by 37.8 kcal mol⁻¹. In the first intermediate **K** the potassium is bridging a siloxide ligand and one nitrogen of N₂. The N-N bond distance in **K** is slightly elongated to 1.48 Å but the Natural Bonding Analysis (NBO) indicates the presence of a N-N σ bond so that the N₂ was not further reduced. On the other hand, the analysis of the unpaired spin density demonstrates that the reduction occurred at one uranium center that becomes U(IV) and that the intermediate **K** is a mixed-valence U(V)-U(IV) complex. The subsequent reduction by potassium is again an exothermic process and two different isomers could be identified (Isomer **I** in Figure S51 and **X**). The addition of the second potassium provides an additional electron and is accompanied by a one electron transfer from the uranium center resulting in the two electron reduction of N₂⁴⁺. The incorporated potassium adopts a symmetrical position with respect to the previous one, that is bridging the nitrogen and a siloxide ligand.

The potassium coordination allows the di-reduction of N₂ and therefore the formation of a bis-nitride complex, as evidenced by the K-N interaction found at the second order donor-acceptor level (25 kcal mol⁻¹). The formation of the less stable isomer **I** (a U(VI)/U(IV) bis-nitride) is exothermic by 16.9 kcal mol⁻¹ with respect to the mixed-valence complex U(V)/U(IV) species (see SI). However, the formation of the diuranium(V) bis-nitride **X** is favored by an extra 18.5 kcal mol⁻¹. The unpaired spin density in **X**

clearly indicates the presence of two U(V) and the NBO shows the formation of a U=N double bond and U-N single bond per uranium center. These bonds are still strongly polarized towards N as also found for the U(VI)-U(IV) complex. Further addition of a potassium to **X** promotes its dimerization accompanied by loss of a KOL per uranium center and results in the formation of complex **1** in an exothermic process. In this complex, three uranium centers are found to be at the +IV oxidation state while one is at the +VI, as shown by the unpaired spin densities. The geometry around the U(VI) center is interesting since a linear N=U=N moiety is observed, which is reminiscent of uranyl structure. The NBO gives indeed two sets of U=N double bonds around the U(VI) center, these bonds being polarized toward N(75%) and involving an hybrid *df* orbital at the uranium center (48%*d*-38%*f* in the σ and 40%*d*-57%*f* in the π).

This is in line with the U-N bond distances of 1.90 Å which are longer than the U-N triple bond distances found for Kraus U^{VI}N₂ core (1.82 Å) or those computed for the uranium dinitride NUN molecule formed by gas phase reaction of U atoms with dinitrogen (1.73 Å)^{20, 25} but quite similar to those reported by Bart et al. for tris and tetrakis U(VI)imido complexes (1.98-2.01 Å),¹⁷⁻¹⁸ where triple U-N bonds were identified computationally. The double bond character found here can be explained by the fact that the two nitrides of the N=U=N moiety strongly interacts with U(IV) centers (presence of polarized toward N (86%) single U-N bonds).

We also calculated the formation of the tetranitride **Z** from the bis-nitride **X** in the absence of added potassium and found the process to be endothermic by 40 kcal/mol. This observation suggests that the formation of the tetranitride cluster from the intermediate **X** is only favored by addition of potassium. Surprisingly we also find that dimerization and ligand loss result in a charge redistribution affording a U(VI)/U(IV) cluster rather than a U(V) core.

Therefore, the computational studies are in agreement with the experimental data indicating the formation of **1** proceeds through a diuranium(V) intermediate.

Figure 6. Computed enthalpy profile (in kcal · mol⁻¹) for the formation of **1** from **B** at room temperature, including an endo-energetic pathway calculated for the formation of **Z** from **X** without addition of potassium.

Conclusions

In conclusion, we have reported a novel example of six electron reduction of dinitrogen to nitride effected by a uranium complex, and the first one to generate a U(VI) nitride. The reduction of the diuranium(IV) oxide bridged complex $[\{U^{IV}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-O})]$ under nitrogen, or the reduction of the isolated (N_2^{4+})-diuranium(V) complex **B** with KC_8 , leads to the complete cleavage of N_2 and to the formation of a multimetallic tetranitride cluster (**1**) with a $\text{U}_4\text{N}_4\text{O}_2\text{K}_6$ core. The structure of complex **1** is remarkable as it contains a unique uranium center bound by four nitrides and provides the second example of a *trans*- $\text{N}=\text{U}^{\text{VI}}=\text{N}$ core analogue of UO_2^{2+} .

^1H NMR and computational studies of the reduction of **B** show that the reaction proceeds *via* successive one electron transfers from potassium first to the uranium center and then to the bound N_2^{4+} ligand in complex **B**, resulting in N_2 cleavage and the formation of the putative diuranium(V) bis-nitride intermediate $[\text{K}_4\{\text{U}^{\text{V}}(\text{OSi}(\text{O}^t\text{Bu})_3)_3\}_2(\mu\text{-O})(\mu\text{-N}_2)]$, **X**. Potassium binding

to the N_2^{4+} ligand facilitates dinitrogen cleavage during electron transfer. Further reduction of intermediate **X** results in the assembly of the multimetallic U(VI)/U(IV)₃ tetranitride **1**.

The nitrides in **1** react with H^+ to yield ammonia in quantitative yield and effect CO cleavage and CO nitrification to yield CN^- and NCO^- , respectively. The isolation of the clusters **2** and **3** provide snapshots of the reaction of **1** with CO showing that the nitrides are replaced by oxides without disrupting the structure, ultimately leading to valence redistribution. The combined experimental and computational study of the stepwise reduction of N_2 provides clear-cut evidence of a hydrazido intermediate in N_2 cleavage to nitride. Notably, the addition of an external reducing agent to the previously reported N_2^{4+} complex **B** (resulting from the four-electron reduction of N_2 by a diuranium(III) complex) leads to the cleavage of the N-N bond and nitride formation. Finally, these results highlight the important role of multimetallic cooperativity in dinitrogen reduction and functionalization.

ASSOCIATED CONTENT

Supporting Information

X-ray data for **1**, **2**, and **3** (CIF) and additional crystallographic details, experimental procedures, ^1H NMR spectra, FTIR spectra and computational details (PDF).

The Supporting Information is available free of charge on the ACS Publications website.

Accession Codes

CCDC : 2072137 (1), 2072138 (2) and 2073683 (3). contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

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