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Facile Dinitrogen and Dioxygen Cleavage by a Uranium(III) Complex: Cooperativity Between the Non-innocent Ligand and the Uranium Center

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Dedicated to the 100th anniversary of the School of Chemistry and Chemical Engineering, Nanjing University

Abstract: Activation of dinitrogen (N₂, 78%) and dioxygen (O₂, 21%) has fascinated chemists and biochemists for decades. The industrial conversion of N₂ to ammonia requires extremely high temperatures and pressure. Here we report the first example of N₂ and O₂ cleavage by a uranium complex, [N(CH₂CH₂NPⁱPr₂)₃U]₂(TMEDA), under ambient conditions without an external reducing agent. The N₂ triple bond breaking implies a U(III)-P(III) six-electron reduction. The hydrolysis of the N₂ reduction product allows the formation of ammonia or nitrogen-containing organic compound. The interaction between U(III) and P(III) in this molecule allows an eight-electron reduction of two O₂ molecules. This study establishes that the combination of uranium and a low-valent nonmetal is a promising strategy to achieve a full N₂ and O₂ cleavage under ambient conditions, which may aid the design of new system for small molecules activation.

Introduction

The activation and cleavage of dinitrogen (N₂) remains a challenge due to its inert N≡N triple bond.^[1-5] Since the first N₂ complex of a transition metal was reported in 1965,^[6] chemists endeavor to explore molecular systems which can be utilized for fixation and activation of N₂ under mild conditions.^[7-14] In the past few decades, a series of significant advances in the N₂ fixation and activation have been demonstrated by transition metal complexes^[15-30] as well as by organoboron species.^[31-35] In addition, molecular uranium systems also exhibit attractive ability for N₂ binding, reduction, and activation.^[36-46] For instance, Mazzanti and co-workers reported that the multimetallic diuranium(III) complex [K_n{[U(OSi(O^tBu)₃)₃]₂(μ-E) (E = N, O) is capable of activating N₂ to N₂⁴⁻ via a four-electron reduction process.^[43,44] Arnold and co-workers found that the four-electron reduction of N₂ was also achieved by the thorium or uranium dinuclear metallacycles, M₂(mTP)₂ (mTP = [{2-(OC₆H₂-Bu-2,Me-4)₂CH}-C₆H₄-1,3]⁴⁻; M = U, Th) in the presence of a strong reductant (KC₈).^[46] Very recently, we reported an example of N₂ cleavage by a heterometallic uranium-rhodium cluster with

KC₈.^[47] However, the six-electron reduction of N₂ by a molecular uranium system without an external reducing agent has not been reported.

On the other hand, the binding and activation of O₂ is important for metabolism and synthetic oxidative catalysis.^[48-51] It is understood that the metal–oxygen species from the activation of O₂ is the key intermediates in enzymatic reactions.^[52] Thus, a number of high-valent bis(μ-oxo) bimetallic complexes have been synthesized by cleavage of O₂ in biomimetic studies.^[49,50] Here we report the first example of N₂ and O₂ cleavage under ambient temperature and pressure by a uranium complex via a metal-ligand cooperative strategy.

Results and Discussion

The diuranium(III) complex, [N(CH₂CH₂NPⁱPr₂)₃U]₂ (TMEDA) (**2**), was prepared by the reduction of the previously reported uranium(IV) complex [N(CH₂CH₂NPⁱPr₂)₃UCI] (**1**)^[53] with potassium-graphite (KC₈) in the presence of tetramethylethylenediamine (TMEDA) under argon (Scheme 1). Complex **2** was isolated as a dark purple solid in a 38% yield after recrystallization from hexane at -40 °C and was fully characterized by nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry (HRMS), elemental analysis, and single-crystal X-ray diffraction.^[54] The solid-state molecular structure of complex **2** features two U(III) which are bridged by a TMEDA molecule (Figure 1).

The assignment of the oxidation state of +III to the uranium ions was confirmed by the variable-temperature magnetic moment measured with a superconducting quantum interference device (SQUID). The magnetic moment of complex **2** at 5 K is 1.4 μ_B (per U), which gradually increases to 3.2 μ_B (per U) at 300 K (Figure S1). The measured magnetic moment at 300 K is lower than the theoretical value (3.6 μ_B) for free U(III) ion. However, the magnitude of μ_{eff} and temperature dependence of complex **2** are comparable to those of the other U(III) complexes.^[55-58]

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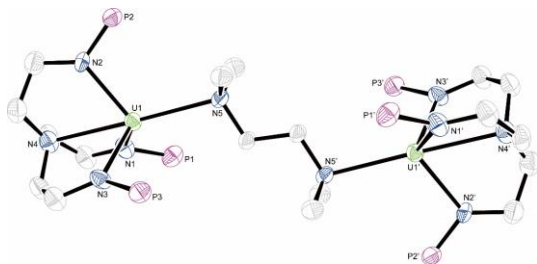
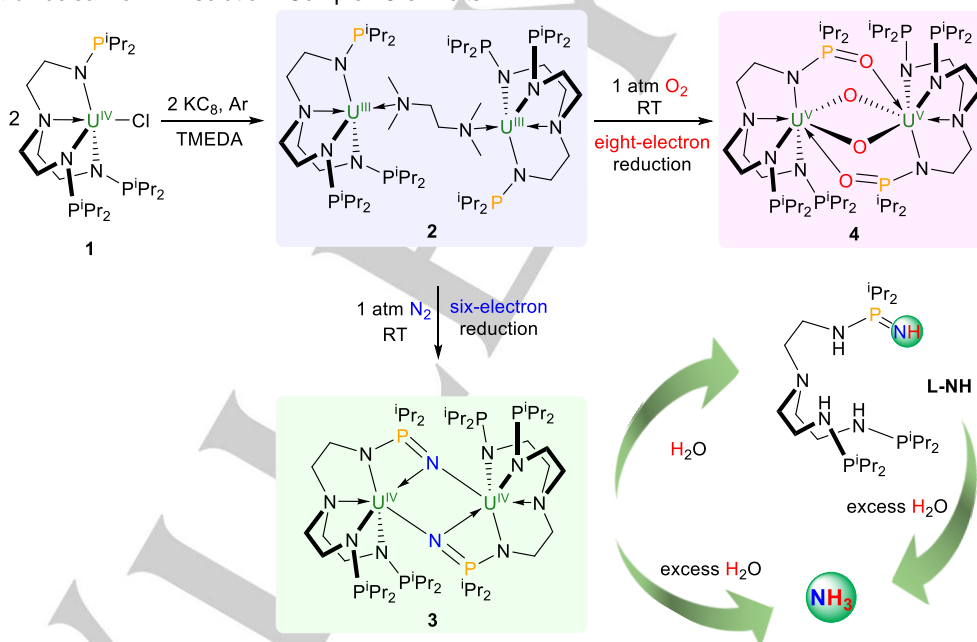


Figure 1. Solid-state structure of **2**. Thermal ellipsoids are depicted at 35% probability. Hydrogen atoms and isopropyl moieties in P^iPr_2 are omitted for clarity. Selected bond distances (Å): U1–N1 2.331(7), U1–N2 2.343(7), U1–N3 2.317(7), U1–N4 2.701(8), U1–N5 2.765(7).

Under argon, complex **2** appears to be stable both in solution and in the solid-state, while exposure of a solution of **2** in benzene to one atmosphere of N_2 at room temperature overnight resulted in a color change from dark purple to brown. A crystalline complex, $[\text{N}(\text{CH}_2\text{CH}_2\text{N}^i\text{Pr}_2)_2(\text{CH}_2\text{CH}_2\text{N}^i\text{Pr}_2\text{N})\text{U}]_2$ (**3**), was isolated from this reaction in 45% yield and determined to be the product of a six-electron reduction of N_2 (Scheme 1). Complex **3** shows two resonances in the ^{31}P NMR spectrum at +404.1 and -471.1 ppm, suggesting two inequivalent phosphine environments in solution. The ^1H NMR spectrum of complex **3** exhibits 15 paramagnetic resonances in a range from +141.44 to -31.48 ppm. The HRMS for complex **3** shows a molecular ion peak at 1525.7787, which corresponds to a dinuclear form in solution. Complex **3** exhibits

an intense absorption peaks at 288 nm in THF solution, which may be assigned to charge-transfer bands (Figure S8). In the NIR region, several weak absorptions ($\epsilon < 100 \text{ M}^{-1} \text{ cm}^{-1}$) at 955, 1016, 1075, 1118, 1460, and 1515 nm were observed (Figure S9), which may be attributed to $f-f$ transitions expected for U(IV) species. Complex **2** was demonstrated to be the first uranium complex capable of spontaneous N_2 cleavage in the absence of other reducing reagents such as KC_8 , Na/Hg , or Mg .

Complex **3** can be prepared independently by the reduction of complex **1** with KC_8 under N_2 at 1 atm and RT. In this case, crystalline complex **3** was isolated in 37% yield after recrystallization from benzene, and exhibits spectrographic features identical to those obtained from the reaction of N_2 with the TMEDA-bridged diuranium(III) complex (**2**). Ligand induced N_2 cleavage was already reported for group 4 metals.^[59] However, in these systems, an *in situ* reduction of the metal complexes under a N_2 atmosphere was needed and no intermediates were isolated. The formation of complex **3** from **1** or **2** is the first example of phosphine ligand induced N_2 cleavage with f -block elements. The reaction between uranium(III) complex $[\text{U}(\text{N}_3\text{N})]$ ($\text{N}_3\text{N} = \text{N}(\text{CH}_2\text{CH}_2\text{NSi}^i(\text{Bu})\text{Me}_2)_3$) with N_2 was reported by Scott and co-workers in 1998, which led to the formation of the first example of N_2 complex with an actinide element, $[\{\text{U}(\text{N}_3\text{N})\}_2(\mu^2-\eta^2:\eta^2-\text{N}_2)]$.^[36] The N–N bond distance in this species is 1.109(7) Å, which is identical with that found in free N_2 (1.0975 Å). This result further supports for the importance of the phosphine ligand in N_2 cleavage in complex **2**.



Scheme 1. Cleavage of N_2 and O_2 under ambient conditions by a uranium(III) species.

An X-ray diffraction analysis of complex **3** (Figure 2) shows a centrosymmetric structure in the solid state, which is consistent with its ^1H and ^{31}P NMR spectra in solution. The most salient structural feature of **3** is the diamond-shaped geometry of the U_2N_2 core that is formed from the N_2 cleavage. The bond length of U1–N5 (2.460(3) Å) is longer than that of the U1–N5' (2.241(3) Å), probably due to the steric reason. The P3–N5 distance (1.593(3) Å) is slightly shorter than that of N3–P3 (1.617(3) Å). In

addition, the U1...U1' separation in complex **3** (3.775(3) Å) is longer than the sum of the covalent single bond radii of U (3.40 Å), which suggests that there is no significant U–U interaction. Notably, the long N5–N5' distance (2.807(4) Å) corresponds to the complete cleavage of N_2 *via* a six-electron reduction. The magnetic moment of complex **3** declines slowly from 4.2 μ_B (per U) at 300 K to 3.2 μ_B at 50 K, and then drops sharply to 1.1 μ_B at 5 K with a trend to zero (Figure S2). These values and the

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temperature dependence are consistent with the reported U(IV) complexes.

Of the six electrons needed for the full N_2 reduction, two are derived from the one-electron oxidation of the two U(III) atoms. The four extra electrons come from the transformation of the two phosphine ligands into phosphinimides in this process (formal two electrons oxidation per phosphine). Thus, the formal oxidation state for the uranium ion in complex **3** is +IV and for the phosphorus in phosphinimide is +V. This results seems to indicate that cooperativity between the presence of U(III) and P(III) centers is responsible for the six-electron reduction of N_2 by complex **2**.

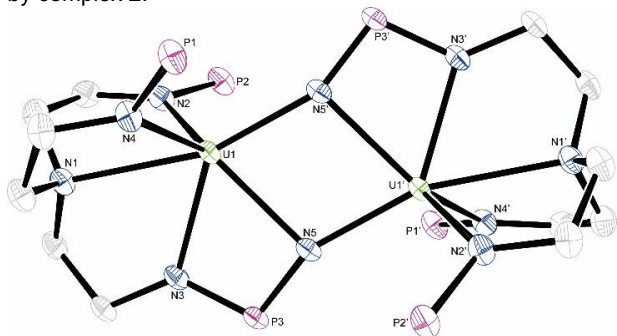


Figure 2. Solid-state structure of **3**. Thermal ellipsoids are depicted at 35% probability. Solvent molecules, hydrogen atoms, and isopropyl moieties in P^iPr_2 are omitted for clarity. Selected bond distances (Å) and angles (deg): U1–N1 2.685(3), U1–N2 2.335(3), U1–N3 2.393(3), U1–N4 2.350(3), U1–N5 2.460(3), U1–N5' 2.241(3), N3–P3 1.617(3), P3–N5 1.593(3), U1...U1' 3.775(3); U1–N5–U1' 106.76, N5–U1–N5' 73.18.

The possibility of generating ammonia (NH_3) or nitrogen-containing organic compounds from this N_2 activation product was investigated. Rather than using dihydrogen or acid as

sources of hydrogen for NH_3 production, the use of water as an alternative was considered. Treatment of a THF solution of **3** with 8 equivalents of degassed H_2O gave an organic species $[N(CH_2CH_2NP^iPr_2)_2(CH_2CH_2NP^iPr_2NH)]$ (**L-NH**) in 55% yield and an insoluble green precipitate (Scheme 1). The structure of **L-NH** was confirmed by NMR spectroscopy and HRMS. Compound **L-NH** can further react with excess H_2O to give ammonia *via* a similar process of Staudinger reaction.^[60] Ammonia could also be obtained directly by the addition of an excess of H_2O to a THF solution of complex **3**. Ammonia production was clearly identified by 1H NMR of the formation of NH_4Cl after treating the solution with an excess of ethereal HCl (Figure S19). Noted that no NH_4Cl was observed when a solution of ethereal HCl was added to a solution of either complex **3** or **L-NH** directly. Attempts to identify the possible products in these reactions were unsuccessful. Nevertheless, the nitrogen fixation and hydrolysis to organic species and ammonia have been accomplished under mild conditions through a well-defined U(III) complex and H_2O .

In order to further confirm that the two additional nitrogen atoms in complex **3** arose from the N_2 cleavage, the isotopically labelled species **3- ^{15}N** was synthesized in a similar manner to that used for **3** by the reaction of complex **2** with $^{15}N_2$ (98% isotopic purity) at RT. The IR spectra for **3** and **3- ^{15}N** were recorded on solid samples (KBr pellet), which exhibit isotope-sensitive bands in the range of 600–900 cm^{-1} (Figure S10). Purified **3- ^{15}N** reacts with 8 equivalents of H_2O to form **L- ^{15}NH** , which was confirmed by HRMS (Figure S21), showing a molecular ion signal at 511.3978 (510.3979 for **L- ^{14}NH**). In addition, $^{15}NH_3$ was formed by the reactions of **3- ^{15}N** or **L- ^{15}NH** with excess H_2O and was identified by the characteristic doublet signal of its conjugated acid ($^{15}NH_4Cl$) in the 1H NMR spectrum (Figure S20). These labeling studies confirm that the source of the nitrogen atoms in the phosphinimide units of **3** is N_2 .

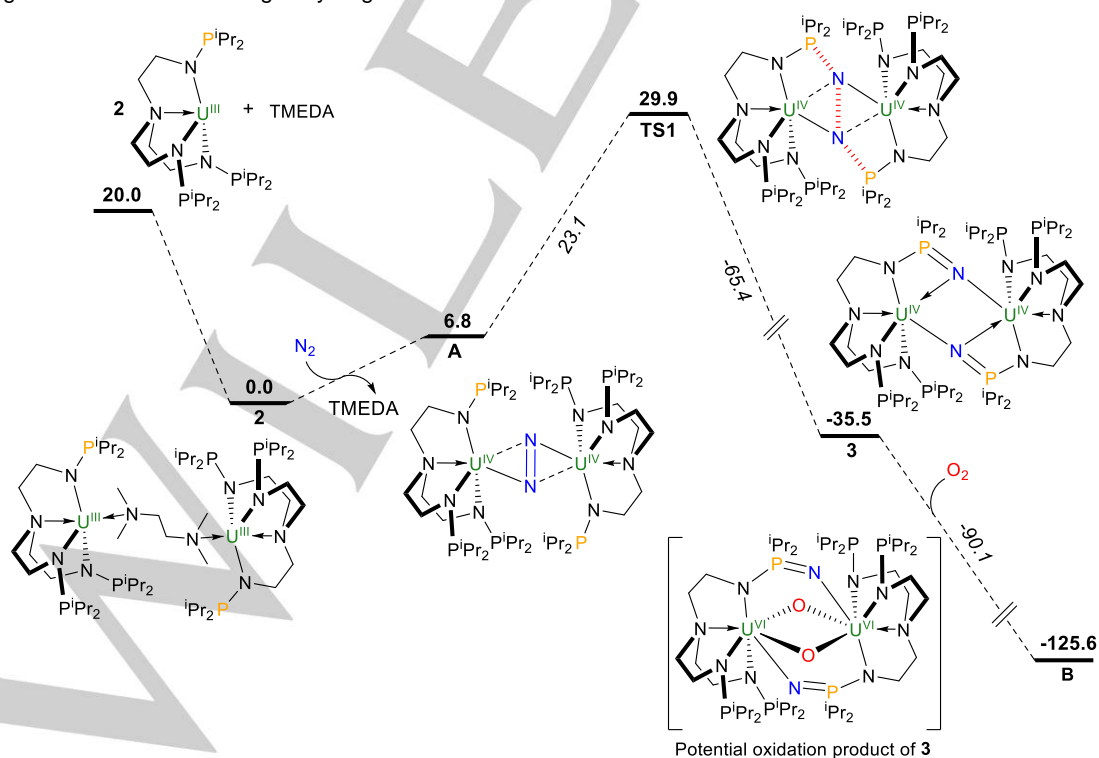


Figure 3. Computed enthalpy profile (in $kcal\ mol^{-1}$) for the formation of complex **3** by full reduction of N_2 .

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The formation of complex **3** was thus investigated by density functional theory (DFT) calculations at the B3PW91 level. The formation of a monomeric U(III) complex from complex **2** is endothermic by 20.0 kcal mol⁻¹. The uranium ions in complex **2** are being oxidized upon N₂ coordination, leading to the formation of a U(IV) complex **A** (Figure 3). Complex **A** may be regarded as a “key intermediate” in small molecule reduction by low valent *f* elements.^[61,62] In complex **A**, the N-N bond has been extended to 1.23 Å (vs. 1.0975 Å in free N₂) in line with the reduction of N₂ and the formation of complex **A** is endothermic by 6.8 kcal mol⁻¹. From complex **A**, the full reduction of N₂ occurs at the transition state (**TS1**) with a kinetically accessible barrier of 23.1 kcal mol⁻¹ from **A** (29.9 kcal mol⁻¹ from complex **2**). The lone pairs of electrons of the two phosphorus (one on each uranium unit) simultaneously attack the two nitrogens in a *trans* fashion, one above and one below the U₂N₂ plane. Therefore, the two lone pairs of the phosphorus are attacking the π* orbital of the N₂²⁻ moiety of complex **A** as evidenced by the depiction of the HOMO of **TS1** (Figure S22) as well as the HOMO (phosphorus lone pairs) and LUMO (π* orbital of the N₂²⁻) of intermediate **A** (Figure S23).

At **TS1**, the N-N bond is not yet fully broken (1.30 Å) which is consistent with the attack of only the π system of N₂²⁻ and the P-N bonds are not yet formed (2.18 and 2.20 Å). The two nitrogen atoms are bonded to the two uranium centers in a symmetrical way (U-N distances of 2.34–2.35 Å and 2.41 Å). Following the intrinsic reaction coordinate, the system evolves to the formation of complex **3**, which is exothermic by 35.5 kcal mol⁻¹ with respect to the reactants. The geometry of complex **3** compares well with the experimentally observed geometry as the N-N bond distance is 2.80 Å, in line with a full disruption of the N₂ triple bond.

Dioxygen is an abundant and environmentally benign oxidant. High-valent bis(μ-oxo) bimetallic species have been proposed as one of the important intermediates in O₂ activation. However, most of the reported examples of O₂ activation have been focused on transition metals and the controlled cleavage of O₂ by a molecular U(III) complex has not been reported.^[63-66] The addition of one atmosphere of O₂ gas to a solution of **2** in THF at ambient temperature resulted in the formation of dinuclear bis(μ-oxo) complex [N(CH₂CH₂NPⁱPr₂)₂(CH₂CH₂NPⁱPr₂O)U]₂(μ-O)₂ (**4**) (Scheme 1), which can be isolated in 43% yield after recrystallization from THF. The dark-red complex **4** shows broad absorption into the visible region below 600 nm (Figure S8). Generally, U(V) complexes with a 5*f*¹ configuration exhibit less complicated electronic absorption spectra than U(IV) species with a 5*f*² configuration in the NIR region. Compared with U(IV) complex **3**, complex **4** shows less absorption peaks in the range of 900 to 1600 nm (Figure S9), which may be suggested the presence of U(V) in complex **4**. NMR characterization of complex **4** was hampered by its poor solubility even in DMSO-*d*₆ and accordingly, single-crystal X-ray diffraction were used to verify its structure. The solid-state structure of complex **4** is centrosymmetric with the presence of two uranium centers and four oxygens (Figure 4). The distances of U1...U1' (3.417(6) Å) in complex **4** is shorter than that in complex **3** (3.775(3) Å), which compares well with the U...U distance of 3.4222(3) Å in the species of [({(n^{P,Me}ArO)₃tacn)U^V]₂(μ-O)₂] reported by Meyer and co-workers.^[66] Complex **4** has a slightly distorted [U(μ-O)₂U] core with two U-O distances of 2.030(6) Å (U1-O2) and 2.193(5) Å (U1'-O2). The angles of U1-O2-U1' and O2-U1-O2' were determined to be 107.98° and 72.02°, respectively. The two other

oxygens are clearly bonded to the phosphorus (P1-O1 and P1'-O1' distances of 1.432(6) Å) with a structure reminiscent of that of complex **3**. These data are therefore consistent with the eight-electron reduction of two molecules of O₂ by complex **2**. This reduction is possible because of the cooperative effect between U(III) and P(III) which was already observed in the reduction of N₂. However, since the formal oxidation state of uranium ions in complex **4** is +V, the implication is that the uranium centers act as a two electrons reductant, which is rather rare.^[67] Although the bis(μ-oxo) bridged dinuclear uranium species was previously reported,^[66] the formation of complex **4** with [U(μ-O)₂U] moiety represents the first example of controlled O₂ cleavage by a U(III) complex under ambient conditions.

The temperature-dependent SQUID magnetization data for complex **4** were very similar to the high-valent dinuclear bis(μ-oxo) complex [({(n^{P,Me}ArO)₃tacn)U^V]₂(μ-O)₂] reported by Meyer and co-workers.^[66] The magnetic moment of **4** at 300 K is 2.3 μ_B per U (Figure S5), which is comparable to those of the other U^V complexes.^[68] With decreasing temperatures, the magnetic moments of **4** persistently decline to 0.4 μ_B per U at 5 K, which suggests that the antiferromagnetic coupling was present in **4**. This antiferromagnetic coupling was probably due to the orbital overlap between the U ions *via* the bridging O-atoms. The χ versus T plot of **4** exhibits an antiferromagnetic coupling with a Néel temperature of approximately 44 K (Figure S6), which is close to that observed for the complex [({(n^{P,Me}ArO)₃tacn)U^V]₂(μ-O)₂] (70 K) reported by Meyer and co-workers.^[66] In addition, the χT versus T plot of complex **4** was also similar to Meyer's species (Figure S7).

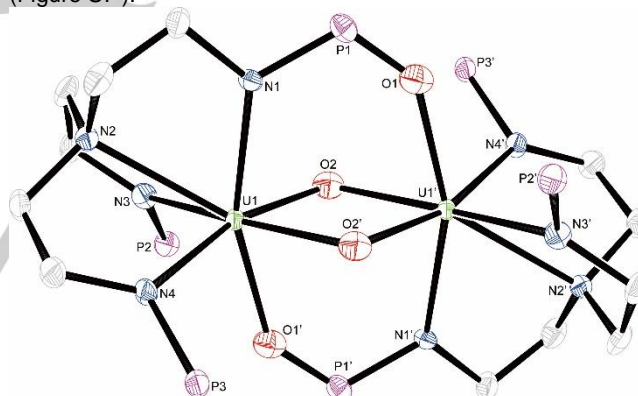


Figure 4. Solid-state structure of **4**. Thermal ellipsoids are depicted at 35% probability. Hydrogen atoms and isopropyl moieties in PⁱPr₂ are omitted for clarity. Selected bond distances (Å) and angles (deg): U1–N1 2.420(6), U1–N2 2.720(6), U1–N3 2.332(6), U1–N4 2.307(6), U1–O2 2.030(6), U1–O2' 2.193(5), U1–O1' 2.275(6), N1–P1 1.657(6), P1–O1 1.432(6), U1...U1' 3.417(6); U1–O2–U1' 107.98, O2–U1–O2' 72.02.

The formation of complex **4** was also investigated computationally (Figure 5). The direct oxidation of the phosphine by O₂ without uranium involvement was first considered and found not to be kinetically competitive (Figure S24). The reaction begins with the oxidation of uranium ions in complex **2** upon O₂ coordination, yielding the stable “key intermediate” **C** (-99.9 kcal mol⁻¹). Such a high stabilization has been found in the reaction of divalent samarium with O₂.^[69] In this intermediate (**C**), the O₂ molecule has been doubly reduced, as evidenced by the O-O bond distance of 1.51 Å (1.20 Å in free O₂), so that the two uranium centers are oxidized to the +IV state. The O-O bond is

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thus broken with a low barrier (13.9 kcal mol⁻¹) in the **TS2**, which is similar to the **TS1** found for the N-N bond breaking as it involves the two phosphorus atoms. Geometrically, the **TS2** appears to be symmetrical with the two P-O distances of 2.15 Å (vs. 2.18/2.20 Å for P-N bonds in **TS1**). The O-O bond is already broken (2.57 Å). Quite surprisingly, the U-O distances are not equivalent for the two oxygen atoms as one interacts strongly with one uranium atom (U-O distance of 2.06 Å and to a lower extent with the second one, U-O distance of 2.30 Å). For the second oxygen atom, the U-O distances are 2.24 and 2.50 Å, indicating a weaker interaction.

These geometrical features are explained by analyzing the frontier orbitals in the **TS2** (Figure S25). The HOMO of **TS2** is similar to the HOMO of **TS1** with the exception that only one phosphorus lone pair attacks one oxygen atom of O₂. The second phosphorus lone pair is involved in the HOMO-1 where there is an important contribution from *f* orbitals of the uranium centers (one of the uranium contributions is more important). The communication between the phosphorus lone pair and the uranium is ensured by the *p* orbitals of the two oxygen atoms. Indeed, the O-O bond breaking of complex **C** is formally a two-electron reduction process, while it is a four-electron reduction process for the N-N bond breaking in **TS1**. Thus, the O₂²⁻ two-electron reduction is ensured by one phosphorus lone pair as

highlighted in the HOMO, and the lone pair of the second phosphorus induces a two-electron reduction of the uranium centers, as can be derived from the HOMO-1.

The reduction of the uranium centers is further confirmed following the intrinsic reaction coordinates from **TS2**. This yields intermediate **D**, whose formation is strongly exothermic (33.2 kcal mol⁻¹ from **C** and 133.1 kcal mol⁻¹ from complex **2**). In intermediate **D**, unpaired spin density analysis indicates that the oxidation state of the two uranium center is +III. Interestingly, the presence of U(III) centers in intermediate **D** makes it prone to further substrate reduction. Complex **D** can then react with another O₂ molecule in a four-electron reduction process to yield complex **4** in a highly exothermal process (-148.6 kcal mol⁻¹ from intermediate **D**). In this reaction, each U(III) center acts as a two-electron reductant, which is quite unusual but has been reported by Liddle and co-workers.^[67] The driving force of the second reduction is the formation of very strong U-O bonds. Interestingly, the putative reduction of O₂ by complex **3**, bearing two U(IV) centers, is predicted to be highly favorable by 90.1 kcal mol⁻¹, forming **B** with two U(VI) centers (Figure 3). Experimentally, the reaction of complex **3** with 1 atm O₂ was found to occur, but no single-crystals suitable for X-ray crystallographic analysis were obtained. Spectroscopic data however are consistent with the formation of a diamagnetic U(VI) complex.

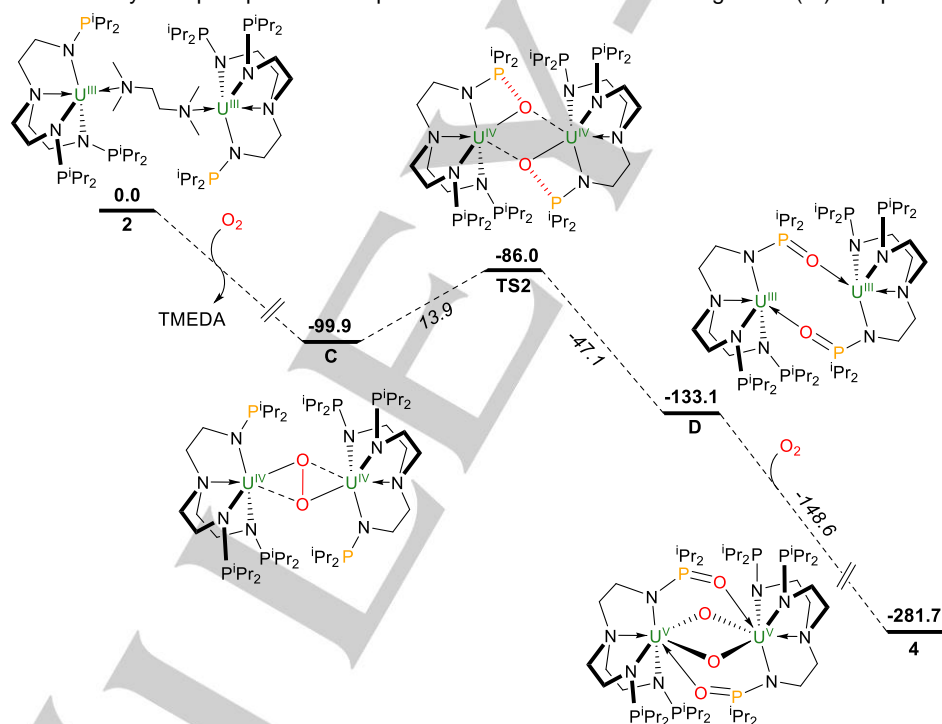


Figure 5. Computed enthalpy profile (in kcal mol⁻¹) for the formation of complex **4** by full reduction of two molecules of O₂.

Conclusion

The first full reductions of N₂ and O₂ were accomplished under ambient temperature and pressure by a well-defined U(III) complex. The electrons required for the reduction were stored in a dimeric U(III)-P(III) species, in which two U(III) and two P(III) atoms allow a facile six-electron reduction of N₂, and an eight-electron reduction of two molecules of O₂. The interaction between U(III) and P(III) has been demonstrated to play an

important role in the reduction of N₂ and O₂. This work represents an important step in increasing our understanding of the fundamental reactions of N₂ and O₂ activations. We envisage that the metal-ligand cooperativity shown in this study could be extended to other metals and low-valent main group elements (such as B, C, and P etc.), and thereby contribute to a rational design of new molecular systems for the activation of small molecules.

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Keywords: Uranium(III) • Dinitrogen cleavage • Dioxygen • DFT calculation • Phosphorus(III)

Conflict of interest

The authors declare no conflict of interest.

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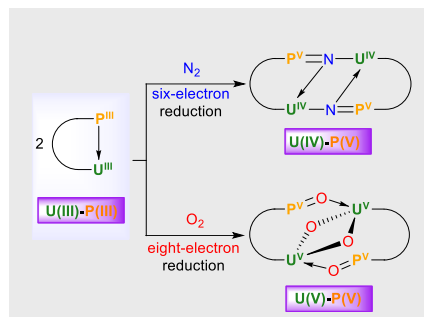
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N₂ and O₂ Cleavage: The example of N₂ and O₂ cleavage was achieved under ambient conditions *via* a cooperativity between U(III) and P(III). This study exhibited that the metal-ligand cooperation is a promising strategy for the activation of small molecules, which could be extended to other metals and low-valent main group elements.



Penglong Wang, Iskander Douair, Yue Zhao, Shuo Wang, Jun Zhu, Laurent Maron, * Congqing Zhu*

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