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Perspective

Dinitrogen Activation and Conversion by Actinide Complexes

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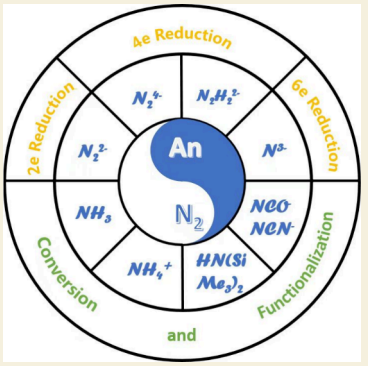
ABSTRACT: The efficient activation and conversion of dinitrogen (N_2) represent a significant challenge in sustainable chemistry, offering potential pathways for synthesizing valuable nitrogen-containing compounds while reducing the environmental impact of traditional nitrogen fixation processes. While transition metal catalysts have been extensively studied for this purpose, actinide complexes have been less explored but have recently emerged as promising candidates due to their unique electronic properties and reactivity. This Perspective systematically examines the recent advances in N_2 activation and conversion mediated by actinide complexes, with a particular focus on their synthesis, mechanistic insights, and catalytic capabilities.



KEYWORDS: *N_2 activation, actinide element, uranium, small-molecule activation*

1. INTRODUCTION

Nitrogen-containing organic compounds play a crucial role in pharmaceuticals, agriculture, and fine chemicals.[1−5] Despite the abundance of atmospheric nitrogen (N_2), its direct conversion into nitrogen-containing organic compounds remains a formidable challenge.[2,4,6] In nature, nitrogen fixation occurs primarily through high-energy processes, such as lightning, and biologically through nitrogenase enzymes in microorganisms.[7−13] However, these natural processes are insufficient to meet the demands of modern society.

Since Haber's patent for ammonia (NH_3) synthesis in 1909,[14] and the subsequent operation of the first commercial plant in 1913, there have been significant advancements in agriculture and industry. It is estimated that approximately 80% of the ammonia produced by the Haber-Bosch process is used in fertilizers, supporting food production for over half of the global population, which quadrupled during the 20th century.[4] However, this process requires harsh conditions, particularly high pressure (150−350 atm), which necessitates expensive materials and large-scale plants for economical production. Additionally, the steam reforming part for H_2 production contributes to 1.4% of global CO_2 emissions and roughly 2% of the world's total energy consumption.[15−17] Therefore, the activation and conversion of N_2 to nitrogen-containing compounds under milder conditions are critical research focuses in modern chemistry.[18−32]

Historically, uranium and uranium nitride materials were used as heterogeneous catalysts for ammonia production before iron-based catalysts were adopted for the Haber−Bosch process.[14] However, the limited availability of uranium resources and its complex chemistry have constrained further developments in uranium-based N_2 fixation. Dinitrogen, with its strong triple bond (154.2 kcal mol^{-1}), presents a significant challenge for bond cleavage due to its poor σ-donating and π-accepting abilities and its large HOMO−LUMO gap, which resists electron transfer.[33−35] Therefore, an electron-rich and highly reducing metal center, ideally in a medium-to-low oxidation state, is essential for effective N_2 activation, suggesting the potential of actinide elements.

Encouragingly, an increasing number of low-valent actinide complexes have been reported in recent years,[36−48] and some of them capable of binding and activating N_2. The actinide elements, particularly uranium, with its 5f, 6d, and 7s orbitals, can participate in bonding, offering multiple oxidation states.[49,50] Theoretically, multiple electron reductions of N_2

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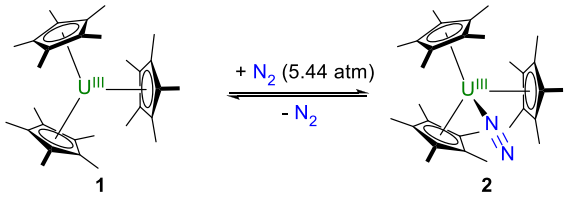
can be achieved through the transformation of low-valent to high-valent actinide complexes via electron transfer.[51]

In this review, we systematically summarize the research on N_2 activation and conversion by actinide complexes over the past 30 years. Given the limited reports on thorium−nitrogen complexes, this review primarily focuses on uranium complexes, detailing nitrogen coordination, two-electron, four-electron, and six-electron reduction and conversion.

2. DINITROGEN FIXATION BY ACTINIDE COMPLEXES

Coordinating N_2 to a metal center is a crucial initial step in N_2 activation. In 2003, Evans and co-workers reported an N_2-coordinated complex, $[(C_5Me_5)_3U(\eta^1\text{-}N_2)]$ (**2**), which was synthesized by exposing a solution of the sterically crowded trivalent uranium complex $[(C_5Me_5)_3U]$ (**1**) to N_2 at 5.44 atm (Scheme 1).[52] The solid-state structure of complex **2** revealed

Scheme 1. Synthesis of a Cp*-Supported Mononuclear U(III)−N_2 Complex



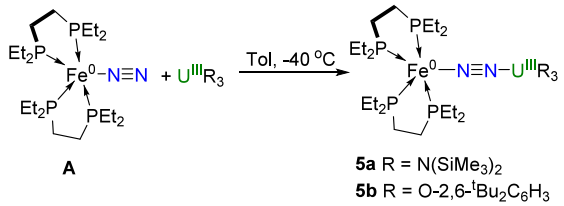
that the N_2 ligand adopts a mononuclear end-on (η^1-N_2) binding mode with the uranium center. The N−N bond length in complex **2** (1.120(14) Å) is slightly longer than that in free N_2 (1.0975 Å).[53] Additionally, complex **2** readily releases N_2 when the pressure is reduced to 1 atm, indicating a weak interaction between the U center and the N_2 ligand.

N_2 is known to be a weak σ-donor and moderate π-acceptor ligand, making it an unfavorable candidate for coordination with electron-deficient metal centers. However, in 2019, Liddle and colleagues successfully achieved N_2 fixation using a high-valent uranium complex with an electron-poor U(V) metal center.[54] The U(IV) carbene complex $[U\{C(SiMe_3)(PPh_2)\}(BIPM^{TMS})(Cl)][Li(2,2,2\text{-cryptand})]$ (**3**, $BIPM^{TMS}$ = $C(PPh_2NSiMe_3)_2$) was treated with 2 equiv of AdN_3, resulting in the formation of a N_2-bridged dinuclear end-on (μ-η^1:η^1-N_2) complex $[U(BIPM^{TMS})(NAd)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_2)(Li\text{-}2,2,2\text{-cryptand})]$ (**4**) (Scheme 2). Notably, the N_2 in complex **4** originates from the azide precursor, and the N_2 unit remains electrically neutral. The oxidation state of uranium in complex **4** was confirmed as + V through superconducting quantum interference device (SQUID) magnetometry. The N−N bond length in complex **4** (1.139(9) Å) is slightly elongated compared to free N_2, and the Raman spectrum exhibits a broad $\upsilon(N_2)$ absorption at approximately 1940 cm^{-1}.

The U ion in complex **4**, being electron-deficient and in a high oxidation state, demonstrates an unusual occurrence of back-bonding with N_2. The authors proposed two possible explanations for this phenomenon.[54] First, the heterobimetallic uranium−lithium combination may synergistically facilitate N_2 capture, resembling both heterogeneous Haber-Bosch chemistry and homogeneous molecular analogues. Second, the presence of two bonded imido ligands and the tridentate $BIPM^{TMS}$ carbene ligand, acting as π-donors, creates an electron-rich environment around the uranium center, which enhances its ability to engage in π back-bonding with N_2.

Recently, Mazzanti and co-workers used the Fe−N_2 complex $[Fe(depe)_2(N_2)]$ (**A**) (depe = 1,2-bis(diethylphosphino)-ethane) to react with trivalent U precursors $[U^{III}R_3]$ (R = $N(SiMe_3)_2$ or O-2,6-^{t}Bu$_2$C$_6$H$_3$), resulting in the formation of two instances of end-on N_2 bridging U/Fe heterobimetallic complexes **5a** and **5b** (Scheme 3).[55] The N−N bond lengths in

Scheme 3. Synthesis of N_2-Bridged Fe/U Bimetal Complexes

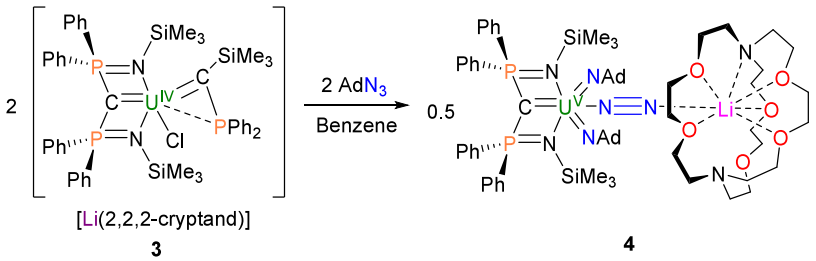


5a (1.150(7) Å) and **5b** (1.169(7) Å) are slightly longer than that in **A** (1.139(2) Å), and the solid-state IR spectra of **5a** and **5b** exhibit the N≡N triple bond bands at 1833 and 1820 cm^{-1}, respectively. These findings suggest that upon coordination to the U atom, the N_2 ligand is more highly activated compared to **A** (1955 cm^{-1}). Computational studies have revealed a back-bonding covalent contribution to the U(III)−N_2Fe bond, and also indicate that end-on binding of N_2 to U(III) complexes is preferred for the iron-bound N_2 compared to free N_2, likely due to higher polarization.

3. TWO-ELECTRON REDUCTION OF N_2 BY ACTINIDE COMPLEXES

The cleavage of the N_2 into reactive intermediates is a challenging process, with the breaking of the first bond being the most critical step. This requires more than 100 kcal mol^{-1}, which accounts for nearly half of the total energy needed to cleave the N≡N triple bond.[33] Since the Scott group first reported a uranium−N_2 complex in 1998,[56] researchers have increasingly recognized the importance of low-valent uranium

Scheme 2. Synthesis of U(V)−N_2 Complex



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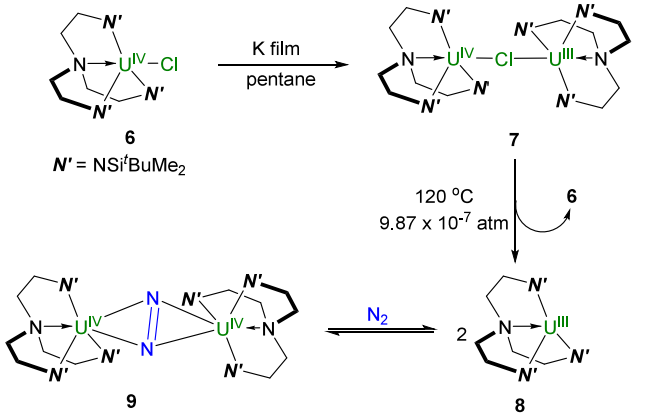
in N_2 activation. The abundant electrons and π-donor capabilities of low-valent U centers, combined with their strong reducing properties, make them particularly effective for this purpose. As a result, the activation of N_2 by low-valent U has become a key focus in actinide chemistry.[57]

In 1998, Scott and co-workers synthesized the species $[\{U(NN'_3)\}_2$-μ-Cl] (NN'_3 = $N(CH_2CH_2NSi^tBuMe_2)_3$) (**7**) by treating the uranium(IV) chloride precursor $[U(NN'_3)Cl]$ (**6**) with potassium film.[56] When the purple pentane solution of **7** was exposed to N_2, it underwent a significant color change to dark red. However, the red material was unstable and could not be isolated for extended study. Inspired by the N_2 activation chemistry observed in zirconium complexes by the Fryzuk group,[58] the authors carefully sublimated **7** at 120 °C and 9.87 × 10^{-7} atm to synthesize the trivalent U complex $[U^{III}(NN'_3)]$ (**8**). When a saturated pentane solution of **8** was exposed to N_2 and cooled to −20 °C, the first example of a uranium N_2 complex $[\{U(NN'_3)\}_2(\mu$-η^2:η^2-$N_2)]$ (**9**) was obtained (Scheme 4).

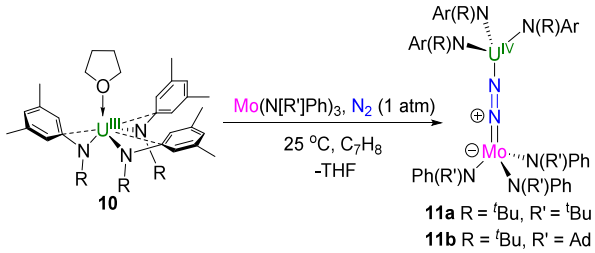
Scheme 4. Synthetic Route to the First Uranium−N_2 Complex



The crystal structure of complex **9** revealed that the N_2 ligand adopts a side-on bridging mode between the two U atoms, with a bond length of 1.109(7) Å between the two N atoms, slightly longer than that in free N_2 (1.0975 Å). This suggests a weak interaction between N_2 and the U centers, consistent with the observation that the N_2 ligand readily decoordinates under vacuum. The UV/visible spectrum and magnetic susceptibility of complexes **8** and **9** were similar, leading the authors to conclude that the coordination of N_2 did not alter the oxidation state of the U centers.[59] However, subsequent density functional theory (DFT) calculations suggest that complex **9** is best represented as $U(IV)_2N_2^{2-}$, where the N_2 molecule is reduced by two electrons and the U centers are oxidized.[60−62]

In 1998, Cummins and co-workers reported a U−Mo heterodinuclear complex featuring a U−N_2 interaction (Scheme 5).[63] They synthesized the trivalent uranium complex by reducing the U(IV) precursor $[U(N[R]Ar)_3I]$ (R = ^{t}Bu, Ar = 3,5-dimethylphenyl) with 1% Na/Hg. The resulting complex (**10**) showed no reactivity toward N_2 until 1 equiv of $Mo(N[R']Ph)_3$ (R′ = ^{t}Bu or Ad)[64] was added in toluene under a N_2 atmosphere. This led to the formation of a thermally stable U−Mo heterodinuclear N_2 activation complex $[U(\mu$-$N_2)Mo]$ (**11**). In this complex, the N_2^{2-} (d_{NN} = 1.232(11) Å, υ_{NN} = 1568 cm^{-1}) unit adopts an end-on, linear

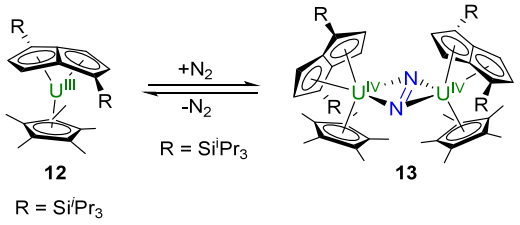
Scheme 5. Synthesis of the U−N_2−Mo Complex



bonding mode, bridging the U^{IV} and Mo^{IV} centers. Based on the crystal structure data, the authors proposed that Mo serves as the more effective π-donor to the complexed N_2 ligand, as depicted in the valence-bond resonance structure in Scheme 5.

Cyclopentadiene ligands are commonly used to stabilize low-valent actinide compounds.[65−67] The Cloke group utilized $[Cp^*]^-$ (Cp^* = pentamethylcyclopentadiene) and a silylated pentalene dianion $[C_8H_4\{Si^iPr_3$-1,4$\}_2]^{2-}$ as ligands to synthesize a mixed-sandwich U(III) complex $[U^{III}(\eta^5$-$Cp^*)(\eta^8$-$C_8H_4\{Si^iPr_3$-1,4$\}_2)]$ (**12**) through a salt elimination reaction in toluene under an argon atmosphere. Exposure of complex **12** to atmospheric pressure N_2 resulted in the formation of a green-black complex $[U^{IV}(\eta^5$-$Cp^*)(\eta^8$-$C_8H_4\{Si^iPr_3$-1,4$\}]_2(\mu$-η^2:η^2-$N_2)$ (**13**) (Scheme 6).[68] Despite the reduction of the

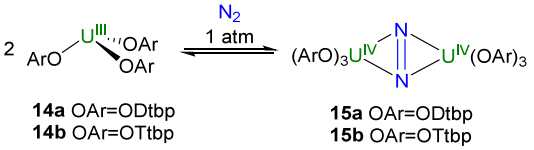
Scheme 6. Synthesis of Complex 13



N_2 molecule in complex **12** to a bridging N_2^{2-} (d_{NN} = 1.232(10) Å) motif between two U(IV) centers, the complex exhibited high susceptibility to decomposition in both solution and solid states.

The above-discussed N_2 bonding complexes, with the exception of complex **11**, generally exhibit instability, often existing in equilibrium between N_2-bound and non-N_2-bound species. In 2011, Arnold group reported a uranium N_2 complex that demonstrates significant stability in both solid-state and solution phases (Scheme 7).[69] Treatment of $[U^{III}N''_3]$ (N″ =

Scheme 7. Synthesis of Complex 15



$N(SiMe_3)_2$) with 3 equiv of HODtbp or HODipp (OTtbp = 2,4,6-tri-*tert*-butylphenoxide, ODipp = 2,6-diisopropylphenoxide) in hexane under argon respectively yielded two U(III) complexes supported by aryloxide ligands, $[U^{III}(ODtbp)_3]$ (**14a**) and $[U^{III}(OTtbp)_3]$ (**14b**). Subsequent exposure to N_2 resulted in the formation of a dimeric species $[U^{IV}(OAr)_3]_2(\mu$-η^2:η^2-$N_2)$ (**15**). In this complex, N_2 was reduced to N_2^{2-} and coordinated in a side-on fashion between two U centers. The

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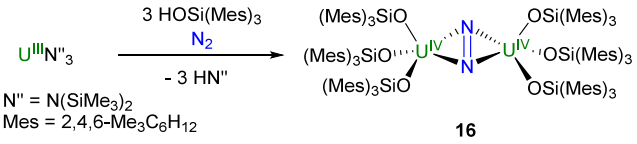
bond lengths of N═N in complex **15a** were reported as 1.163(19) Å, 1.204(17) Å, and 1.201(19) Å from three sets of crystal structure data, respectively. The distances of N−N in **15b** were 1.190(18) Å (crystallized from *n*-hexane) and 1.236(5) Å (from toluene). Raman spectroscopy revealed a N_2 stretching vibration at 1451 cm^{-1} for complex **15b**. DFT calculations by Kaltsoyannis confirmed the formulation of complex **15**, demonstrating strong overall polarity in U−N_2 binding, with a covalent U−N_2 π back-bonding interaction that results in the elongation and weakening of the N_2 bond.

Two years later, the Arnold group reported a similar result. They synthesized a uranium N_2 complex $[U^{IV}\{OSi(Mes)_3\}_3]_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)$ (**16**) using bulky trimesitylsiloxide ligands, following a method similar to that used for complex **15** (Scheme 8).[70] The crystal structure of complex **16** closely

Scheme 8. Synthesis of Complex 16

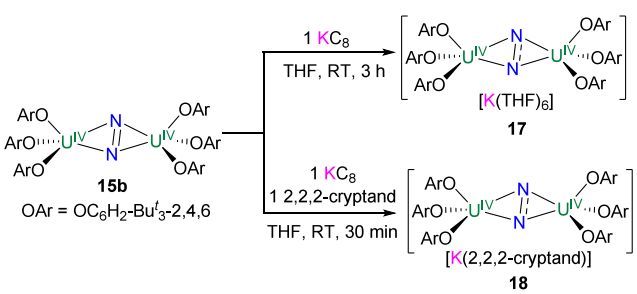


resembles that of **15**, with N_2 reduced to N_2^{2-} and bonding side-on with two $[U^{IV}(OSi(Mes)_3)_3]$ fragments. In comparison to complex **15**, complex **16** exhibited remarkable thermodynamic stability, showing minimal decomposition even when the toluene solution was heated to 100 °C. This underscores the critical role of bulky ligands in enhancing the stability of such compounds.

4. THREE-ELECTRON REDUCTION OF N_2 BY ACTINIDE COMPLEXES

Recently, a three-electron reduction of N_2 was reported by Mazzanti and co-workers.[71] They found that by reducing complex **15b** with 1 equiv of KC_8 or 1 equiv of KC_8 and 1 equiv of 2.2.2-cryptand, the $N_2^{\bullet 3-}$-bridged diuranium complex $[K(THF)_6][\{(ArO)_3U\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ (**17**) or $[K(2.2.2\text{-cryptand})][\{(ArO)_3U\}_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)]$ (**18**) was generated, respectively (Scheme 9). The N−N bond distances in **17**

Scheme 9. Synthesis of $N_2^{\bullet 3-}$-Bridged Diuranium Complexes



and **18** are comparable to that of complex **15b**. The magnetic susceptibility data confirm the three-electron reduction of N_2 to $N_2^{\bullet 3-}$. This represents the only known example of a three-electron reduction of N_2 by an actinide complex, which shows significant potential in the design of molecular magnets.

5. FOUR-ELECTRON REDUCTION OF N_2 BY ACTINIDE COMPLEXES

Over the past decade, the Mazzanti group has made significant contributions to the field of N_2 activation, particularly through the use of siloxide-ligand-stabilized multinuclear uranium-alkali metal clusters. In 2017, they reported the first example of a four-electron reduction product of N_2, $[K_3\{[U^{IV}(OR)_3]_2(\mu\text{-}N)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)\}]$ (R = $Si(O^tBu)_3$) (**21**), achieved by exposing the siloxide-stabilized multinuclear U(III)−K cluster $[K_3\{[U(OR)_3]_2(\mu\text{-}N)\}]$ (**20**) in a nitrogen atmosphere. Complex **20** was prepared from $[Cs\{[U(OR)_3]_2(\mu\text{-}N)\}]$ (**19**)[72] and KC_8 (Scheme 10).[73] In complex **21**, the coordinated N_2 was highly activated and reduced to a N_2^{4-} species (d_{NN} = 1.521(18) Å). In subsequent studies, they explored functionalization reactions of the N_2^{4-} group. The reaction of complex **21** with excess acid ($HBAr^F$, PyHCl or HCl) produced NH_4Cl with yields ranging from 25% to 42%. Interestingly, when HCl in ether was added to the reaction mixture of complex **21** and H_2, the yield of ammonia increased to 77%. Additionally, treatment of complex **21** with 10 equiv of CO in THF or benzene at room temperature resulted in the isolation of the oxo/cyanate diuranium complex $[K_2\{[U(OR)_3]_2(\mu\text{-}O)(\mu\text{-}NCO)_2\}]$ (**22**) in 68% yield, with the formation of CN^- confirmed by ^{13}C NMR spectroscopy.

Two years later, they reduced an oxo-bridged complex, $[\{U^{IV}(OSi(O^tBu)_3)_3\}_2(\mu\text{-}O)]$ (**23**) with KC_8 at −80 °C, leading to the formation of a U^{III}−K heteronuclear cluster $[K_2\{[U^{III}(OSi(O^tBu)_3)_3]_2(\mu\text{-}O)\}]$ (**24a**) (Scheme 11).[74] Subsequent reaction with N_2 in solution generated the U^{IV}−K heteronuclear N_2-bound complex $[K_2\{[U^{V}(OSi(OtBu)_3)_3]_2(\mu\text{-}O)(\mu\text{-}\eta^2\text{:}\eta^2\text{-}N_2)\}]$ (**25a**). Similar to complex **21**, the N_2^{4-} ligand in complex **25a** adopts a side-on bridging mode between two U(V) centers, with a N−N bond length of 1.40(1) Å, which is slightly shorter than that observed in complex **21**. Complex **25a** exhibited exceptional stability in both the solid state and in toluene solution, with no loss of N_2 observed after three cycles of freeze−pump−thaw degassing under argon.

In a subsequent study, they attempted to synthesize heavier analogs (M = Rb, Cs). However, **25b** (M = Rb) showed poor stability, and the Cs analog could not be afforded due to large cation size and low Lewis acidity.[75] The toluene solution of complex **25a** is exposed to 3 equiv of CO yielding a cyanamido-bridged complex $[K_2\{[U(OSi(O^tBu)_3)_3]_2(\mu\text{-}O)_2(\mu\text{-}NCN)\}]$ (**26**) in 68% yield. Further conversion of **26** with excess CO to N-containing product could not be identified. The addition of excess $HCl(Et_2O)$ to complex **25a** in the presence of 2.1 equiv of 2.2.2-cryptand in THF generated NH_4Cl in 74% yield.[76]

In 2020, Arnold and co-workers carried out the reaction of uranium/thorium complexes (**27**), supported by a phenyl-bridged phenoxide ligand, with potassium graphite under N_2 atmosphere, leading to the formation of N_2 four-electron reduction products (Scheme 12).[77] In this reaction, complex $K_4[U_2(\mu\text{-}N_2H_2)(mTP^{4-})_2]$ (mTP^{4-} = $[\{2\text{-}(OC_6H_2\text{-}^tBu\text{-}2,Me\text{-}4)_2CH\}\text{-}C_6H_4\text{-}1,3]^{4-}$) (**28a**) was characterized by X-ray diffraction. During the formation of **28**, hydrogen atoms at the benzyl C-position were abstracted, and the N_2 was reduced, resulting in the formation of an $N_2H_2^{2-}$ motif (d_{NN} = 1.491(5) Å in **28a**). However, the Th analogue, **28b**, was not characterized by X-ray diffraction.

Complex **28a** reacted with strong acid pyridinium chloride or weaker acid $[HNEt_3][BPh_4]$ to produce NH_4Cl. The N_2-

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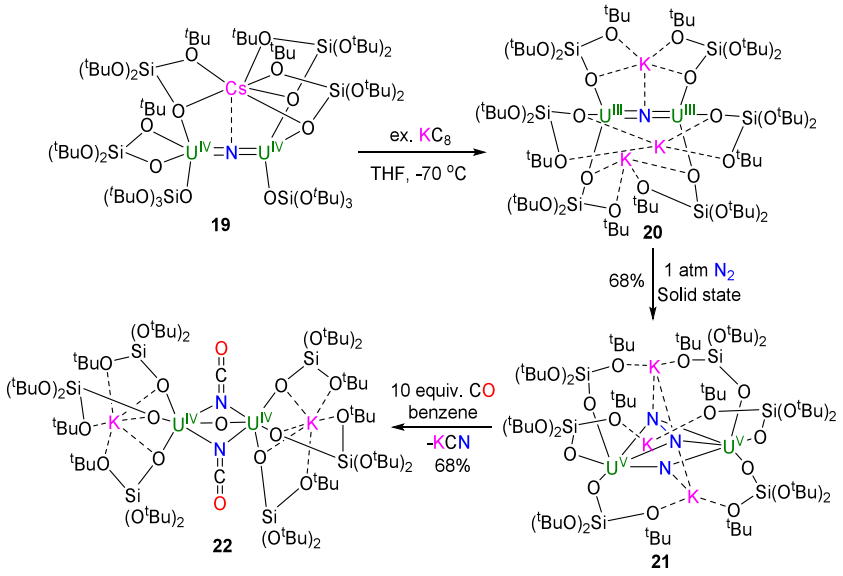
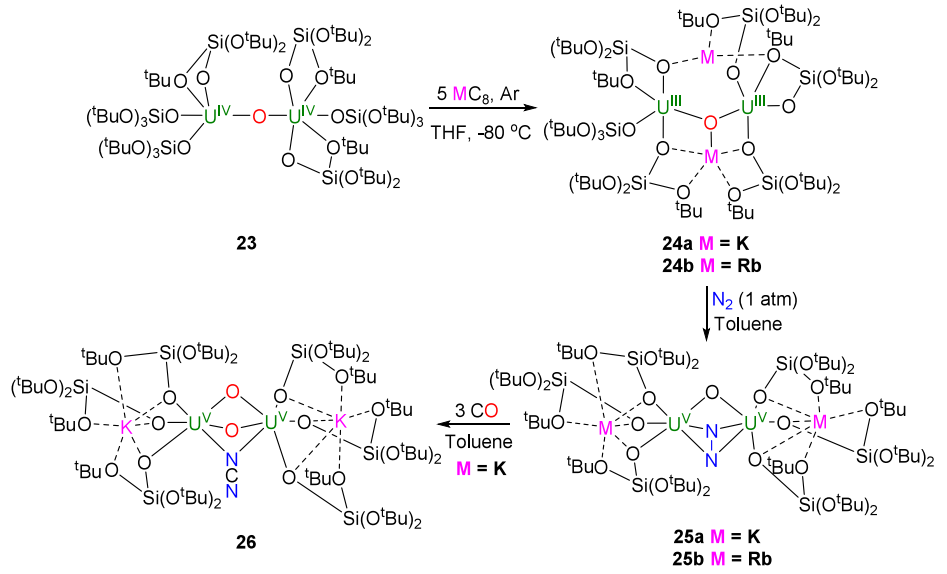
Scheme 10. N_2 Reduction and Functionalization Mediated by 20



Scheme 11. N_2 Reduction and Functionalization Mediated by 24



activated complex (**28a**) was capable of catalytically converting molecular N_2 to the secondary silylamine hexamethyldisilazane ($(Me_3Si)_2NH$) in yields of up to 6.4 equiv per molecule in the presence of excess reductant, weak acid, and chlorosilane at ambient temperature and pressure. NMR spectroscopy and gas chromatography−mass spectrometry (GC-MS) analysis of the nitrogen-containing products confirmed the formation of $(Me_3Si)_2NH$ with high selectivity. Recently, they reported a THF-solvated metallacyclic U(IV) complex with a larger cavity (**29**), prepared from complex **27a** (R = Me) in THF, which can catalyze the conversion of N_2 to $(SiMe_3)_2NH$ and $N(Me_3Si)_3$ (20.5 ± 1.7 combined equivalents of amine) with excess potassium metal, Me_3SiCl, and weak acid $[HNEt_3][BPh_4]$, and to $N(Me_3Si)_3$ (10.1 ± 1.5 equiv) in the absence of acid.[78] The release of silylamine did not lead to decomposition of the reaction precursors, which are stabilized by two rigid arene-bridged aryloxide ligands.

6. DINITROGEN CLEAVAGE BY ACTINIDE COMPLEXES

The cleavage of the N≡N bond is significant challenging due to its exceptionally high bond dissociation energy, necessitating a theoretical six-electron reduction for complete cleavage. This demanding process typically requires the involvement of multiple metal centers, in contrast to N_2 cleavage by single U atoms observed in matrix isolation studies.[79−84] Gambarotta and colleagues reported the first example of N_2 cleavage in the formation of a uranium nitride complex.[85] They reduced the U−K heterobimetallic complex [(Et$_8$-calix[4]tetrapyrrole)-U^{III}(dme)][K(dme)] (**30**) with [K(naphthalenide)] in the presence of N_2 in DME, leading to the formation of the anionic μ-nitrido U^V/U^{IV} mixed-valent complex, [{K(dme)(calix[4]-tetrapyrrole)U}$_2$[K(dme)$_4$] (**31**) (Scheme 13). In this complex, each nitride bridges two U atoms and a K atom. The U(V) center was confirmed by a characteristic absorption at 1247 nm in the near-IR spectrum. These results suggest that

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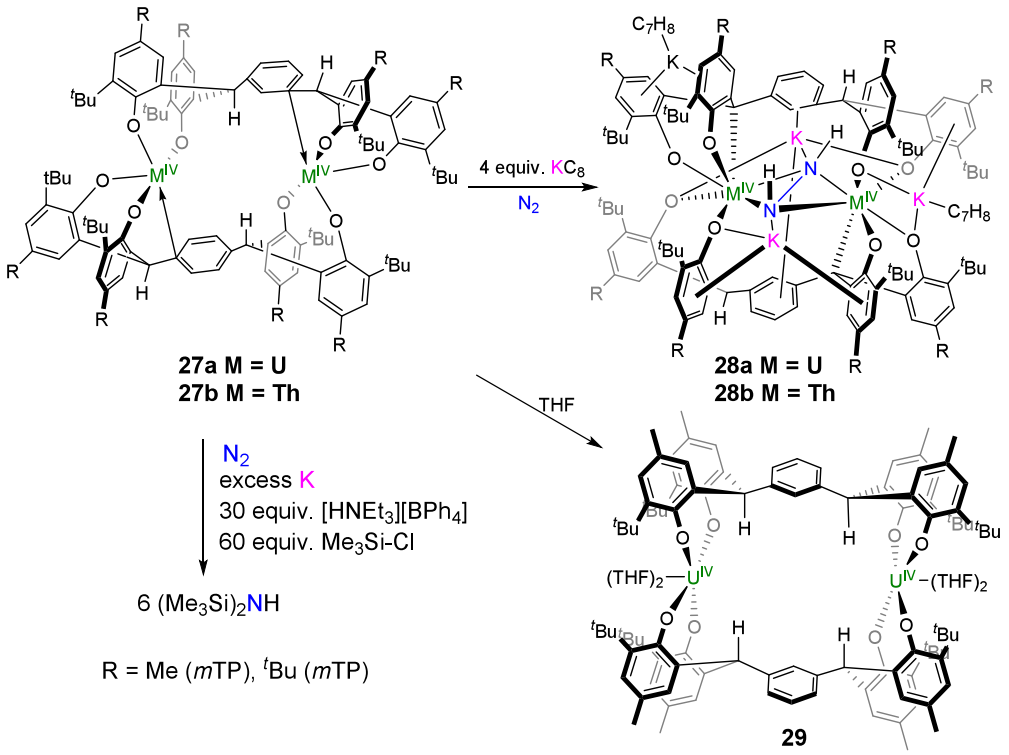
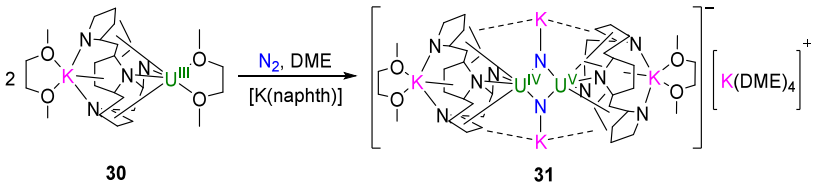
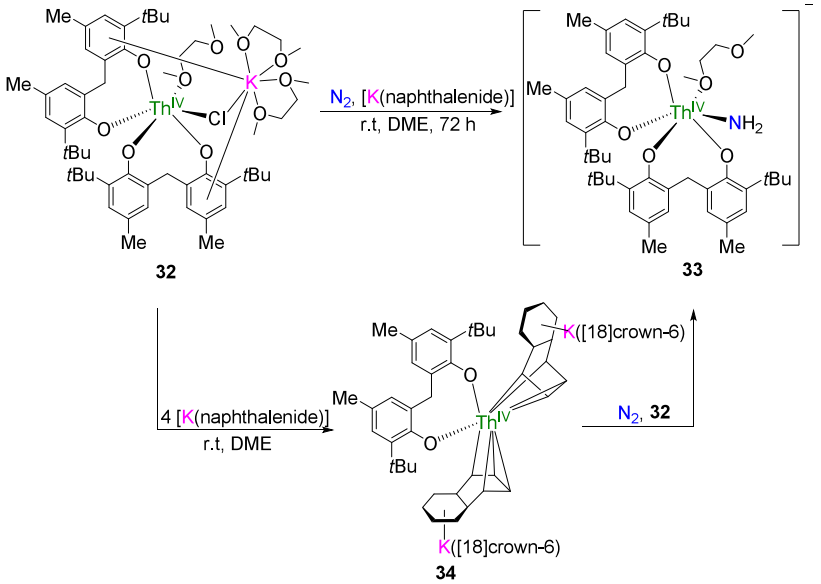
Scheme 12. Binuclear U and Binuclear Th Complex-Promoted N_2 Activation



Scheme 13. Synthesis of Complex 31



Scheme 14. Synthesis of N_2 Cleavage Product 33



the two U centers contribute three electrons, while the three K ions provide the remaining three electrons necessary for the six-electron reduction of N_2, highlighting the essential role of K ions in this process.

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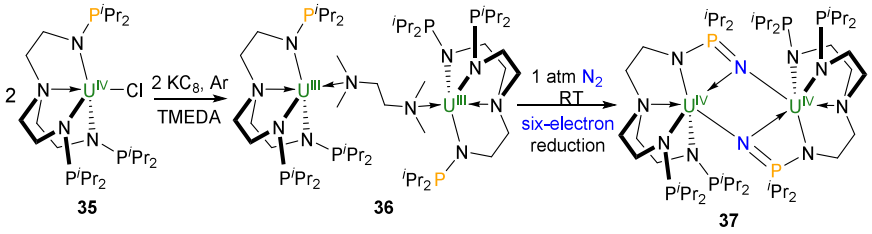
Scheme 15. Cleavage of N_2 though U(III)−P(III) Synergetic Strategy



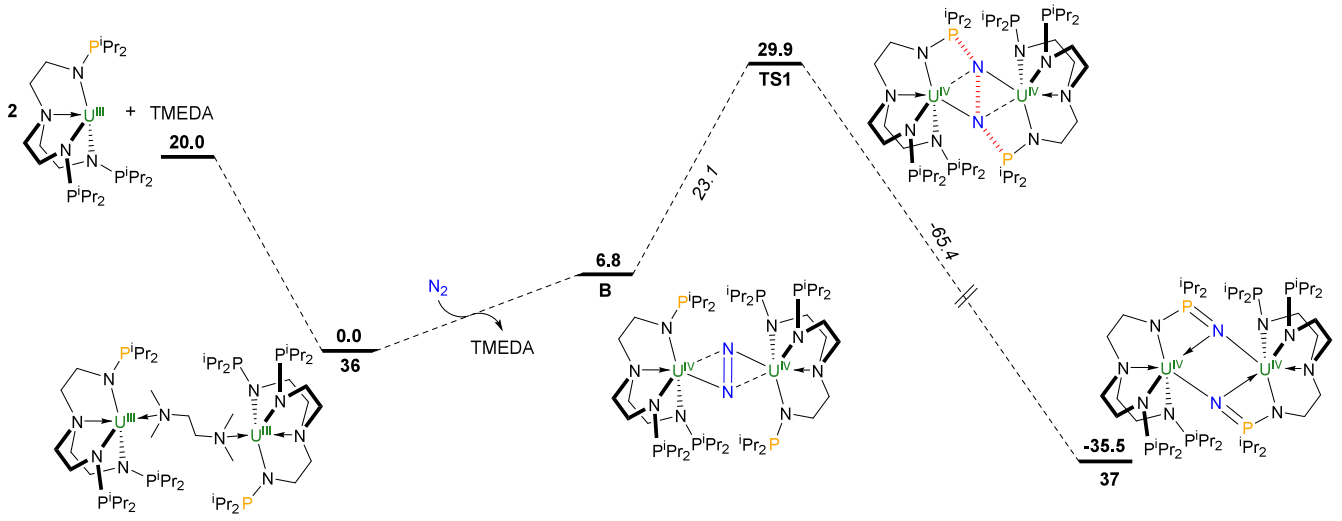


Figure 1. Computed enthalpy profile (in kcal mol^{-1}) for the formation of complex **37**.

The first instance of N_2 cleavage by a thorium complex was also reported by Gambarotta's group (Scheme 14).[86] They reduced a Th(IV) complex **32** supported by a diphenol ligand with 1 equiv of [K(naphthalenide)] in DME under N_2, resulting in the formation of a thorium amide complex **33**. In this complex, N_2 was transferred to the NH_2^- group. The ^{15}N NMR spectrum of compound **33** confirmed that the N atom in the amino group originated from N_2, evidenced by a sharp triplet peak at 155.01 ppm. The authors proposed that the two hydrogen atoms on the amino group may originate from the solvent through a radical-type hydrogen abstraction process. Additionally, when complex **32** was reacted with 4 equiv of [K(naphthalenide)] in the presence of [18]-crown-6, complex **34** was produced. Complex **34** could be considered a zerovalent synthon or a tetravalent species, though it does not react with N_2 on its own. The authors suggested that interaction between **32** and **34** under N_2 conditions could initiate a process in which N_2 is cleaved and partially hydrogenated to yield complex **33**. Arnold and co-workers attempted to reproduce this reaction with a wide variety of conditions, however, no evidence of N_2 binding, reduction, or activation or of ligand deprotonation was observed.[77]

Ligands can assist in the cleavage of N_2 by U centers. In 2020, Zhu group successfully cleaved the N≡N triple bond using a double-layer nitrogen−phosphorus ligand-supported trivalent uranium complex $[N(CH_2CH_2NP^iPr_2)_3U]_2(TMEDA)$ (**36**) (Scheme 15).[87] This complex was synthesized by reducing the uranium(IV) complex $[N(CH_2CH_2NP^iPr_2)_3UCl]$ (**35**) with KC_8. Complex **36** could react with N_2, leading to the formation of product $[N(CH_2CH_2NP^iPr_2)_2(CH_2CH_2NP^iPr_2N)U]_2$ (**37**) via phosphorus-assisted N_2 cleavage (Scheme 15). In complex **37**, a N═P double bond was formed (d_{NP} = 1.617(3) and 1.593(3) Å), indicating that the P atoms in the phosphinimide are in the +V oxidation state, each providing two electrons to the N_2 reduction. Reacting complex **37** with 8 equiv of degassed H_2O yielded a nitrogen-containing organic species $[N(CH_2CH_2NP^iPr_2)_2(CH_2CH_2NP^iPr_2NH)]$ (**L-NH**) in 55% yield, which could be further hydrolyzed to NH_3 with excess H_2O. The facile two-electron process that oxidizes P(III) to P(V) presents an innovative approach for N_2 reduction and functionalization, although similar processes have been observed in transition metal systems.[88,89]

A distinct outcome was observed when the silyl group in the triamidoamine ligand was replaced with a trivalent phosphorus group. Unlike in complex **9**,[56] where N_2 was only weakly activated. DFT calculations suggest that the U ions in complex **36** undergo oxidation upon coordination with N_2, resulting in the formation of a U(IV) complex **B** (Figure 1). At the transition state (**TS1**), complete reduction of N_2 occurs, followed by a simultaneous trans-attack of the two nitrogen atoms by lone pairs of electrons from the P atoms (one on each uranium unit) positioned above and below the U_2N_2 plane. At **TS1**, although the N−N bond is not fully broken, both nitrogen atoms are symmetrically bonded to their respective uranium centers.

Previous examples have demonstrated that nitrogen cleavage often requires the collaborative action of multiple metal centers, a condition well-suited to metal clusters. The nitrogen−phosphorus ligands developed by Zhu group were found to be particularly effective in constructing multiple clusters with metal−metal bonds.[90−96] These multiple metal systems may be used to activate N_2 due to the synergistic coordination effect of the metals. In 2020, they found that the

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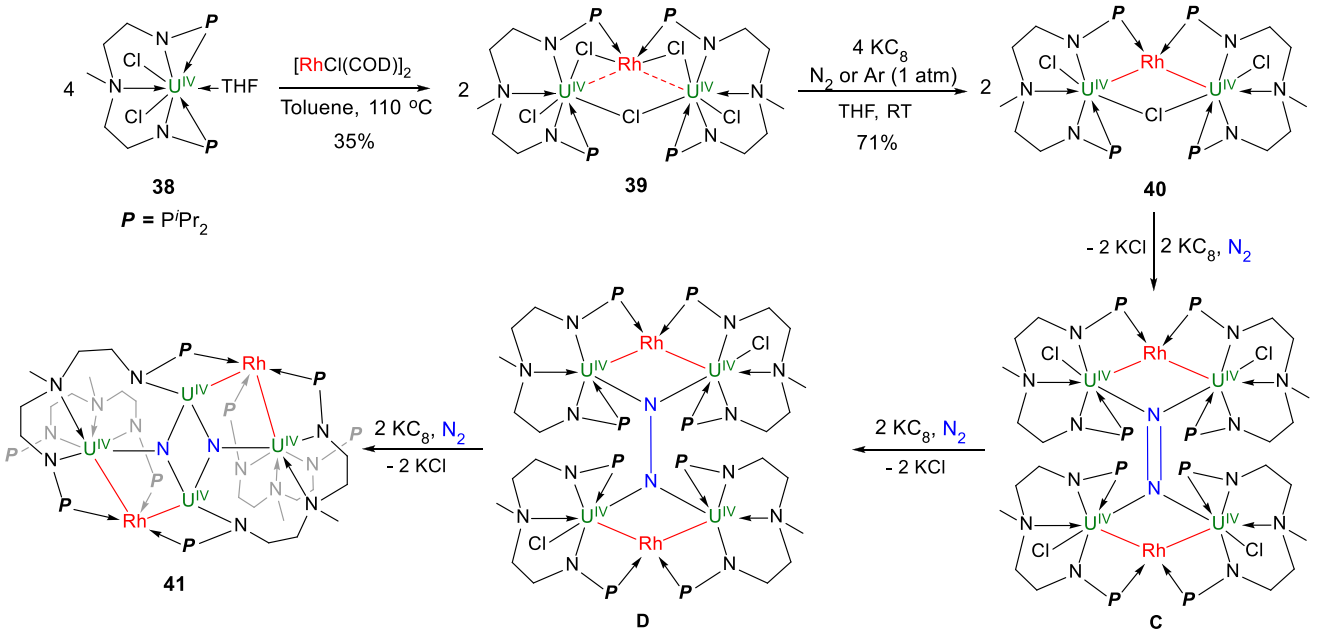
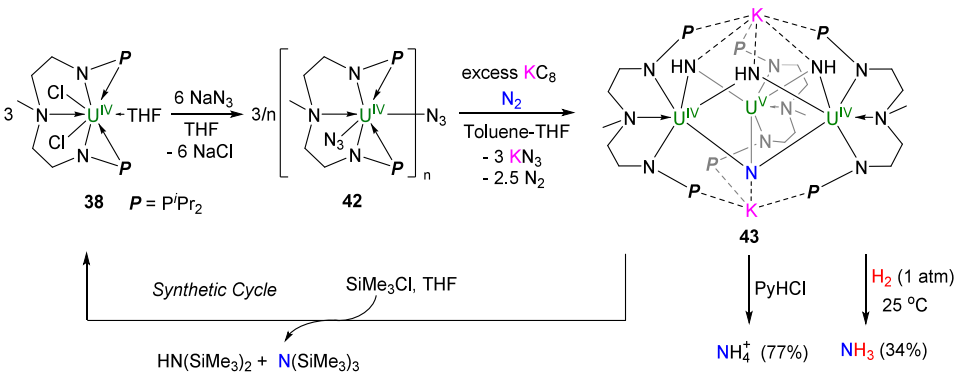
Scheme 16. N_2 Cleavage Mediated by the Cluster with U−Rh Bonds



Scheme 17. N_2 Cleavage by Uranium Azide Complex 43



N−P ligand-supported uranium−rhodium cluster could be used to cleave N_2 (Scheme 16). By reacting the uranium precursor $\{U[N(CH_3)(CH_2CH_2NP^iPr_2)_2](Cl)_2(THF)\}$ (**38**) with $[RhCl(COD)]_2$, a trinuclear cluster $[\{U[N(CH_3)(CH_2CH_2NP^iPr_2)_2](Cl_2)\}_2(\mu\text{-}Cl)(\mu\text{-}Rh)]$ (**39**) was obtained (Scheme 16).[97] Subsequent reduction with excess equivalents of KC_8 resulted in a six-electron N_2 reduction complex $[\{U_2[N(CH_3)(CH_2CH_2NP^iPr_2)_2]_2(Rh)(\mu\text{-}N)\}_2]$ (**41**). By controlling the amounts of KC_8, the intermediate $[\{U[N(CH_3)(CH_2CH_2NP^iPr_2)_2](Cl)\}_2(\mu\text{-}Cl)(\mu\text{-}Rh)]$ (**40**) was isolated, which could be further reacted with KC_8 to generate the N_2 cleavage product **41**. In complex **41**, the N−N distance is 2.780 Å, indicating complete cleavage of the N≡N bond. The N_2-cleaved uranium−rhodium cluster **41** was protonated with an excess of acid, generating substantial yields of ammonium. The ^{15}N-labeled product confirmed that the two nitride ligands in complex **41** originated from N_2.

Computational analysis indicates that the overall reduction of N_2 from **40** to **41** is exothermic by 40.0 kcal mol^{-1}, with each step of the reduction being thermodynamically favored (Scheme 16). The initial step in the formation of complex **41** from **40** involves a two-electron reduction of N_2 through coordination to the U centers, resulting in the proposed intermediate **C** with the release of energy of 23.4 kcal mol^{-1}. The N=N bond is further broken to generate intermediate **D** (6.3 kcal mol^{-1} from **C**) through reaction with 2 equiv of KC_8. Further reduction of **D** with an additional 2 equiv of KC_8 leads to the formation of complex **41**, which is exothermic by 10.3 kcal mol^{-1}. This study demonstrates the capability of a multimetallic uranium cluster to effectively facilitate N_2 fixation and reduction, serving as a promising platform for further research in this area.

Zhu and co-workers found that treatment of complex **38** with 3 equiv of NaN_3 resulted in the formation of a one-dimensional chain uranium azide complex **42**. Reduction of complex **42** with excess KC_8 in a toluene/THF mixed solvent under an N_2 atmosphere yielded a U−K nitride/imido complex $[\{[U\{N(CH_3)(CH_2CH_2NP^iPr_2)_2\}(\mu\text{-}NH)]_3(\mu\text{-}N)\}K_2]$ (**43**) (Scheme 17).[98] In this complex, the nitrogen atom of the N^{3-} ligand is derived from N_2, and the protons on the imido motifs are derived from the solvent. The hydrogenation of complex **43** with H_2 at atmospheric pressure and room temperature produced NH_3, which could be captured by excess PyHCl to form NH_4Cl.

Treatment of **43** with excess protonic acid also yielded substantial NH_4Cl. The N_2-cleaved product **43** reacted with

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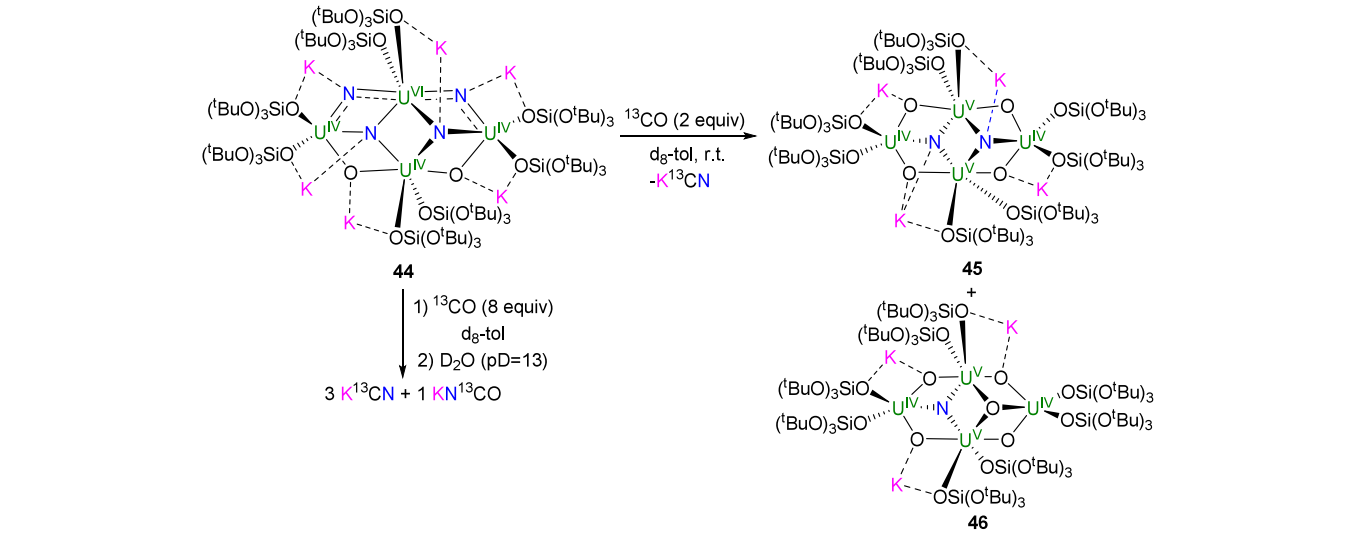
Scheme 18. Functionalization of N_2 Cleavage Product 44



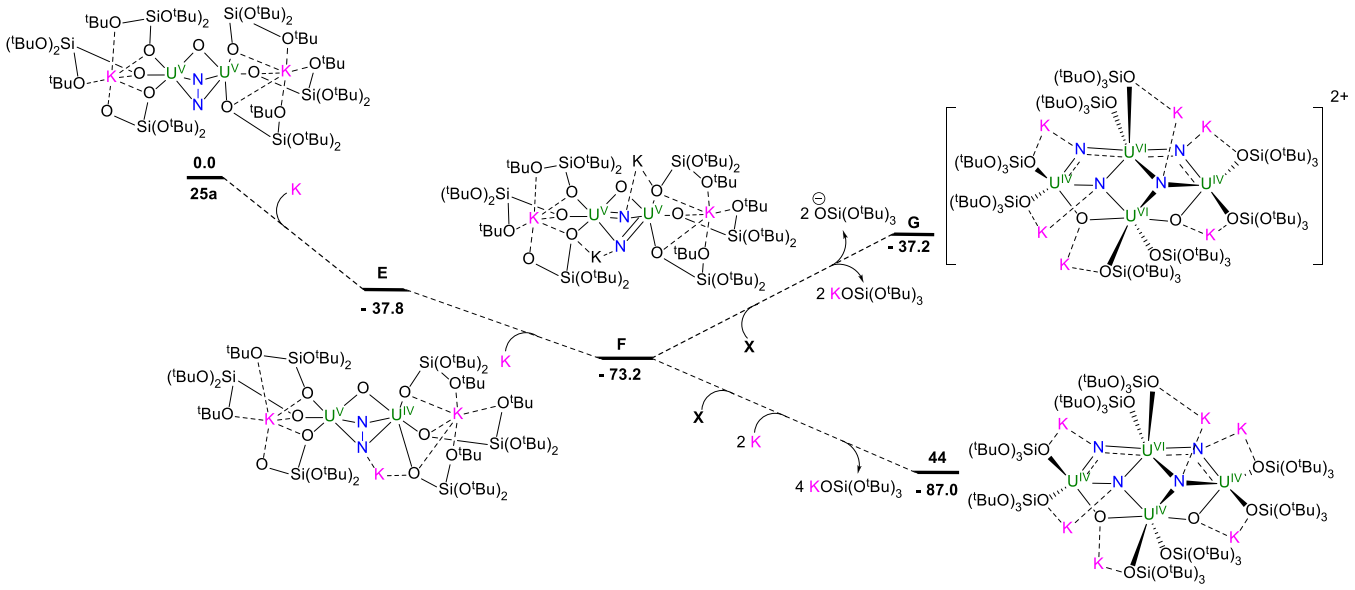


Figure 2. Computed enthalpy profile (in kcal mol^{-1}) for the formation of **44** from **25a**.

excess trimethylsilyl chloride ($SiMe_3Cl$) to generate silylamines ($HN(SiMe_3)_2$ and $N(SiMe_3)_3$) and the uranium precursor **38**, thereby completing a synthetic cycle. The formation of **43** has been elucidated through DFT calculations, which suggest that the synergetic effect between three U centers is important in the N≡N broken.

By adding 2−4 equiv of KC_8 to a toluene solution of the previously mentioned **25a** under N_2 at −40 °C, Mazzanti and co-workers successfully synthesized a tetranitride cluster with four uranium centers, $[K_6\{(OSi(OtBu)_3)_2U^{IV}\}_3\{(OSi(O^tBu)_3)_2U^{VI}\}(\mu^4\text{-}N)_3(\mu^3\text{-}N)(\mu^3\text{-}O)_2]$ (**44**).[99] In this reaction, the N_2^{4-} unit was cleaved into nitride ligands, resulting in a complex (**44**) containing three U(IV) and one U(VI) ions, as shown in Scheme 18. Complex **44** reacted with excess HCl to yield NH_4Cl in a quantitative yield of 97%, confirming the presence of four nitride ligands. Additionally, the reactivity of complex **44** with ^{13}CO was investigated. Reaction with 2 equiv of ^{13}CO led to the formation of a mixture of complexes **45** and **46**, along with $K^{13}CN$, as identified by ^{13}C NMR spectroscopy. The structures of **45** and **46** resemble that of complex **44**, where the nitride ligands have been replaced by oxygen ligands with valence redistribution. Further reaction of complex **44** with excess (8 equiv) ^{13}CO yielded $K^{13}CN$ and $KN^{13}CO$ in a 3:1 ratio.

DFT calculations illustrate the formation of compound **44** from **25a** (Figure 2). The first step by potassium reduction is predicted to be exothermic by 37.8 kcal mol^{-1}, resulting in a mixed-valence U(V)−U(IV) intermediate **E**, where K bridges a siloxide ligand and one N atom of the N_2 unit. The N−N bond distance in **E** is slightly elongated to 1.48 Å, longer than that in **25a** (1.40 Å). Subsequent reduction of **E** with K yields the diuranium(V) bis-nitride **F**, where natural bond orbital analysis reveals the formation of U═N double bonds and U−N single bonds at each U center. Further addition of K promotes the dimerization of **F**, accompanied by the loss of a $KOSi(O^tBu)_3$ per U center, resulting in the exothermic formation of complex **44**. These results indicate that only one U(V) ion was oxidized to U(VI), while the remaining three U(V) ions were reduced to U(IV). KC_8 acts as the electron donor in this process. According to ^1H NMR and computational studies, the authors

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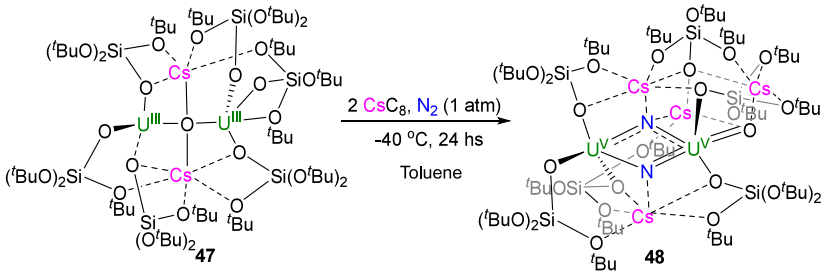
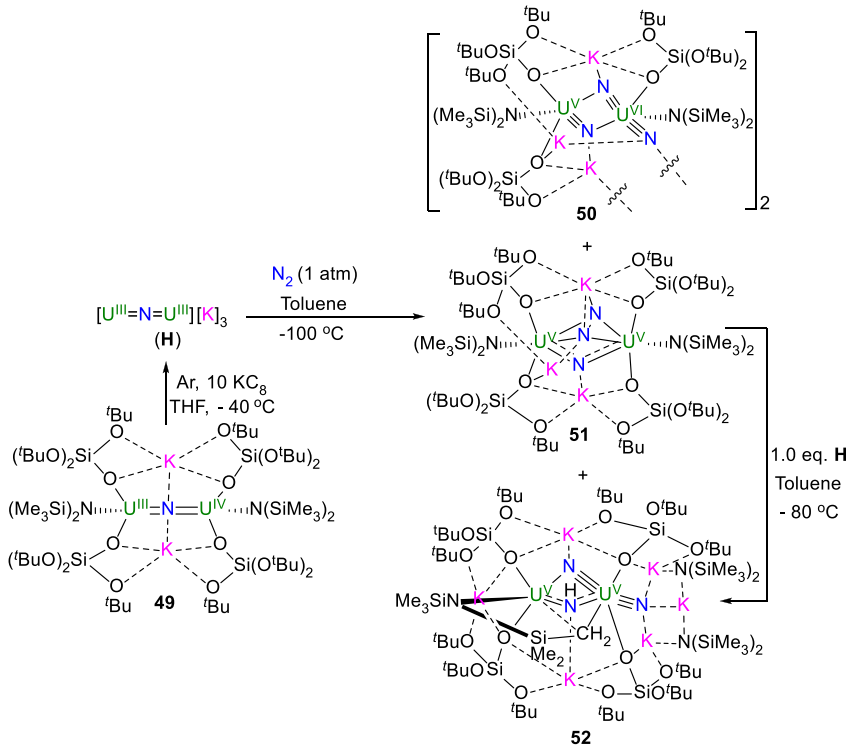
Scheme 19. Synthesis of N_2 Cleavage Product 48



Scheme 20. N_2 Cleavage by the Reduction of 49



proposed that the reaction proceeds via successive one-electron transfers from potassium first to the U center and then to the bound N_2^{4-} ligand in complex **25a**. This electron transfer induces N−N bond cleavage, suggesting that potassium binding to the N_2^{4-} ligand facilitates this cleavage.

As shown in Scheme 11, complex **23** can react with MC_8 (M = K, Rb) under N_2 atmosphere to produce a four-electron reduction product. Mazzanti and co-workers reported the formation of an oxide-bridged dinuclear multimetallic U(III) complex, $[Cs_2\{U^{III}(OSi(O^tBu)_3)_3\}_2(\mu\text{-}O)]$ (**47**), via the reaction of **23** with 5 equiv of CsC_8 under argon at −80 °C. This complex was then treated with an additional 2 equiv of CsC_8 under a N_2 atmosphere at −40 °C for 1 day, yielding a N_2 cleavage complex, $[Cs_3\{U^V(OSi(O^tBu)_3)_3\}(\mu\text{-}N)_2\{U^V(OSi(O^tBu)_3)_2(\kappa\text{-}O)\}][CsOSi(O^tBu)_3]$ (**48**) (Scheme 19). In complex **48**, two U atoms underwent oxidation to a + V state from + III and were bridged by two μ_3-/μ_4-nitride ligands. Consequently, two additional electrons were provided by Cs during the N_2 cleavage process. This highlights the crucial role of alkaline earth metal cations in the activation of N_2. By the addition of excess $HCl(Et_2O)$ to the complex **48**, 100% yield of NH_4Cl was formed. The reaction of **48** with excess ^{13}CO quenched in D_2O led to the formation of $Cs^{13}CN$ and $CsN^{13}CO$ in a 1:1 ratio as determined by the ^{13}C NMR spectrum.

Using mixed ligands of $OSi(O^tBu)_3^-$ and $N(SiMe_3)_2^-$, Mazzanti and co-workers synthesized a nitride-bridged mixed-valence U−K cluster $[K_2\{U^{IV/III}(OSi(O^tBu)_3)_2(N(SiMe_3)_2)\}_2(\mu\text{-}N)]$ (**49**). Subsequent reduction of **49** with 10 equiv of KC_8 under argon at −40 °C yielded a putative U(III) nitride species (**H**). However, the crystal structure of **H** remains unknown. When exposed to an N_2 atmosphere at −100 °C, the authors successfully isolated a U(VI)/U(V) tris-nitride complex, $[K_3\{U^{VI}(OSi(O^tBu)_3)_2(N(SiMe_3)_2)(\equiv N)\}(\mu\text{-}N)_2\{U^V(OSi(O^tBu)_3)_2(N(SiMe_3)_2)\}]_2$ (**50**), as well as (**51**), and a U(V)/U(V) bis-nitride imido cyclometalated product, $[K_4\{((OSi(O^tBu)_3)_2U^V)(\equiv N)\}(\mu\text{-}NH)(\mu\text{-}\kappa^2\text{:}C,N\text{-}CH_2SiMe_2NSiMe_3)\{U^V(OSi(O^tBu)_3)_2][K(N(SiMe_3)_2]_2$ (**52**), respectively (Scheme 20).[100] It is noteworthy that complexes **51** and **52** cannot always be isolated using this method. However, the addition of 1 equiv of *in situ* generated **H** to the toluene-d_8 solution of **51** afforded **52** in 51% NMR yield. In complexes **50** and **52**, N_2 was cleaved to nitride, forming U≡N bonds. Adding $HCl(Et_2O)$ to complex **51** or the reaction mixture of complex **51** and **H** did not result in the formation of NH_4Cl.

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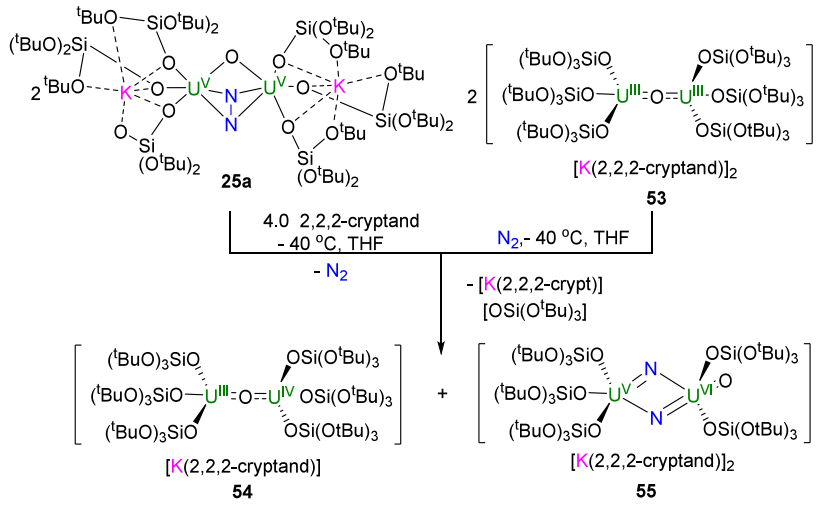
Scheme 21. N_2 Cleavage and Functionalization by 25a and 53



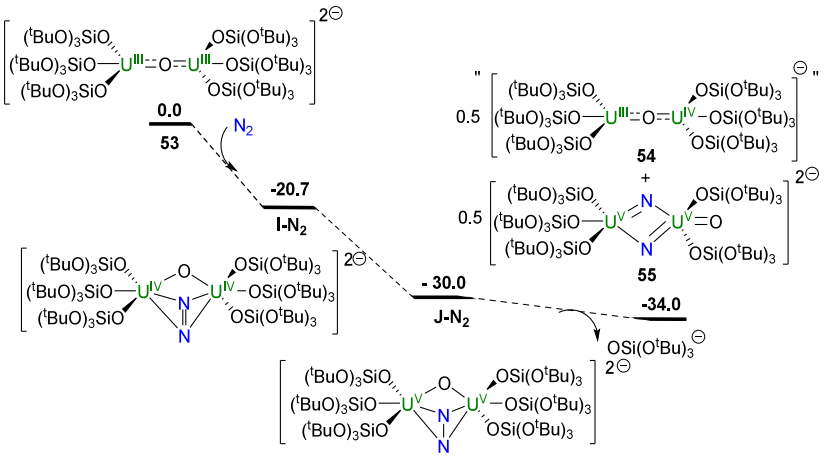


Figure 3. Computed enthalpy (in kcal mol^{-1}) profiles for the formation of **54** and **55**.

To explore N_2 activation solely by U centers, Mazzanti et al. exposed the alkali metal ion-sequestered oxide-bridged dinuclear U^{III} complex $[K(2.2.2\text{-cryptand})]_2[\{U^{III}(OSi(O^tBu)_3)_3\}_2(\mu\text{-}O)]$ (**53**) to N_2 at −40 °C. This reaction yielded an oxide-bridged U^{III}/U^{IV} dinuclear complex, $[K(2.2.2\text{-cryptand})][\{U^{III}(OSi(O^tBu)_3)_3\}(\mu\text{-}O)\{U^{IV}(OSi(O^tBu)_3)_3\}]$ (**54**) and a bis-nitride, terminal-oxo complex $[K(2.2.2\text{-cryptand})]_2[\{U^{V}(OSi(O^tBu)_3)_3\}(\mu\text{-}N)_2\{U^{VI}(OSi(O^tBu)_3)_2(\kappa\text{-}O)\}]$ (**55**) (Scheme 21).[76] The U−N distances in complex **55** are 1.950(7) and 1.892(8) Å for the U═N double bond, and 2.315(8) and 2.251(7) Å for the U−N single bond, respectively. The molecular structure of complex **55** is similar to that of **48**, and the reduction potential measured for complex **53** is greater than that of **24a** but similar to **47**, although an additional 2 equiv of reducing agent was required. This suggests that alkali ions hinder N_2 binding and further activation. Removing K^+ from complex **25a** through the addition of 2 equiv of 2,2,2-cryptand under N_2 atmosphere at −40 °C produced complexes **54** and **55**, similar to the reaction of **53** with N_2. These results suggest that complete sequestration of K^+ cations could enhance the reducing ability of uranium complexes. The addition of excess HCl to the reaction mixture of complex **53** and N_2 resulted in substantial NH_4Cl formation, as confirmed by $^{15}N_2$-labeling experiments. The addition of ^{13}CO to the reaction mixture, followed by quenching with D_2O yielded $N^{13}CO^-$ and $^{13}CN^-$ as evidenced by ^{13}C NMR spectroscopy. The reaction of complex **55** with excess HCl/Et_2O yielded NH_4Cl in 92% yield.

DFT calculations were conducted to elucidate the N_2 reduction pathways facilitated by complex **53** (Figure 3). The results reveal that N_2 undergoes three consecutive two-electron reductions, leading to the formation of intermediates **I−N_2** and **J-N_2**, ultimately yielding complexes **54** and **55**. Importantly, each step of this reduction process is thermodynamically favorable.

Recently, Mazzanti group further investigated the reactivity of a uranium−nitrogen complex **15b**, previously reported by Arnold group.[69] Treatment of **15b** with 4 equiv of KC_8 in diethyl ether or toluene solution at −40 °C under N_2 yielded a tetranitride cluster $[\{(Et_2O)K\}_2(Et_2O)U^{IV}_4(\mu\text{-}N)_4(OAr)_6]$ (**56**) and it can also be synthesized by reacting **17** with 3 equiv of KC_8 in a toluene solution.[71] When the reaction was conducted in *n*-hexane, a hexanitride cluster $[K_2\{U^{IV}_6(\mu\text{-}N)_6(OAr)_8\}]$ (**57**) was formed (Scheme 22). In both complexes **56** and **57**, the N−N double bonds were cleaved, resulting in nitride ligands. The U_4N_4 cubane cluster **56** and the U_6N_6 edge-shared cubane cluster **57** reacted with excess HCl/Et_2O to yield quantitative amounts of ammonia. Additionally, the addition of ^{13}CO to **56** in toluene-d_8 resulted in quantitative conversion of nitrides to cyanides. The authors

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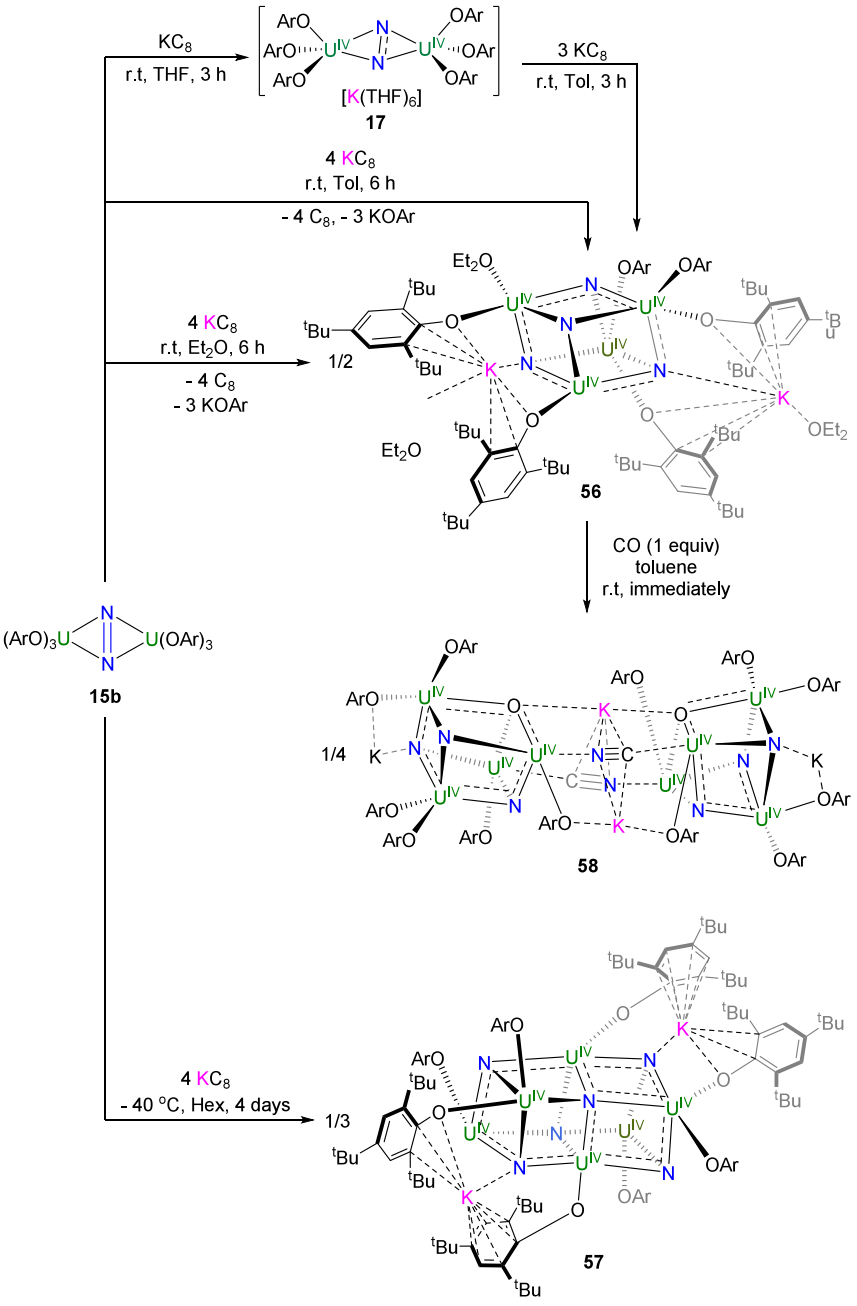
Scheme 22. Synthesis of the Tetranitride (56) and Hexanitride (57) Clusters



also isolated a CN-bridged cluster aggregate with the formula $[\{K\{U^{IV}_4(\mu\text{-}N)_3(\mu\text{-}O)\}(OAr)_6\}_2(\mu\text{-}K)_2(\mu\text{-}\eta^1\text{:}\eta^1\text{-}CN)_2]$ (**58**), which was produced by the reaction of complex **56** with 1 equiv of ^{13}CO. A protonation experiment of **58** with HCl and D_2O resulted in the formation of NH_4Cl (94%) and $^{13}CN^-$ (2 equiv), respectively.

7. CONCLUSION AND FUTURE PERSPECTIVE

Nitrogen-containing compounds are pivotal in fields such as agriculture, biology, pharmacology, and materials science. However, the conversion of N_2 into more valuable N-containing products remains a significant challenge in both chemistry and industry. Although actinide complexes have demonstrated substantial potential in N_2 activation, only a limited number of these complexes have successfully converted N_2 into N-containing compounds. These complexes are capable of activating N_2 into N_2^{2-}, N_2^{3-}, N_2^{4-}, N^{3-}, and $(N_2H_2)^{2-}$ species, which can then be further transformed by specific electrophiles such as protons, CO, and silyl reagents to produce NH_3, CN^-, cyanate, and silylamines. However, direct functionalization of N_2 into N-containing organic compounds has yet to be accomplished. Therefore, a significant challenge is to deepen our understanding of N_2 fixation mechanisms and the N-atom transfer process, which could help in controlling the formation of N-containing products.

Ligands play a crucial role in modifying the steric and electronic properties of metal complexes, which is essential for understanding their structure−reactivity relationships. The ligands employed in the construction of actinide complexes for N_2 activation can be categorized into cyclopentadienyl-type ligands, triamidoamines, amide-type ligands, aryloxides, tetrapyrrole, siloxides, nitrogen−phosphorus ligands, and silyl

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phosphino-carbene ligands. These ligands stabilize low- or high-valent actinide complexes, facilitating N_2 activation and adopting varied coordination modes. Rational design of these ligands is crucial to stabilize the low-valent actinide complexes for N_2 activation.

Uranium complexes, in particular low-valent uranium species, have shown exceptional performance in N_2 binding, activation, and cleavage. However, their catalytic potential is limited by the inherent instability of these complexes. To address this, there is a need to explore new systems with strong reducing capabilities that can activate bound N_2 and facilitate N-atom transfer without requiring additional reducing agents under mild conditions. Particularly, multimetallic systems offer diverse coordination modes and synergistic effects for N_2 activation. Moreover, other actinide metals in the tetravalent oxidation state struggle to reduce or form stable reduced intermediates capable of reacting with inert N_2. In this regard, metal−ligand cooperativity should be a central consideration in ligand design. Despite significant advancements in uranium's N_2 chemistry over the past three decades, future research in this area should focus on several key aspects:

Only uranium complexes have been extensively explored in the context of N_2 activation and conversion. Extending N_2 chemistry to thorium and other transuranium elements is crucial for the broader field of actinide chemistry.

Biological nitrogenase metalloenzymes achieve this challenging conversion at ambient temperature and pressure, suggesting that multimetallic cooperativity warrants further investigation in N_2 activation and functionalization.

While numerous activated N_2 metal complexes have been reported, the functionalization of N_2 into N-containing products remains limited. The transfer of nitrogen atoms from these complexes may benefit from photochemical and electrochemical approaches.

Mechanistic studies of N_2 activation and transformation processes are vital for enhancing the selectivity and diversity of N-containing products. Direct catalytic conversion of N_2 into N-containing organic compounds (beyond NH_3 and amines) under mild conditions may become achievable in the future.

The research discussed demonstrates the capability of uranium complexes to facilitate the cleavage and functionalization of N_2 under relatively mild conditions. These breakthroughs point toward a future where actinide metals could play a crucial role in N_2 fixation processes. While significant challenges remain, the potential of actinide metals in the activation and conversion of N_2 is undeniably promising. Continued research in this area is essential and will likely lead to significant advancements, ultimately making the mild conditions for N_2 activation and conversion a realizable goal.

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Author Contributions

[§]Y.L. and X.X. contributed equally. CRediT: **Yafei Li** data curation, formal analysis, writing - original draft; **Xiaoqing Xin** data curation, formal analysis, writing - original draft; **Qin Zhu** conceptualization, formal analysis, writing - original draft, writing - review & editing; **Congqing Zhu** conceptualization, funding acquisition, project administration, supervision, writing - review & editing.

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Notes

The authors declare no competing financial interest.

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