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C−H Bond Addition across a Transient Uranium−Nitrido Moiety and Formation of a Parent Uranium Imido Complex

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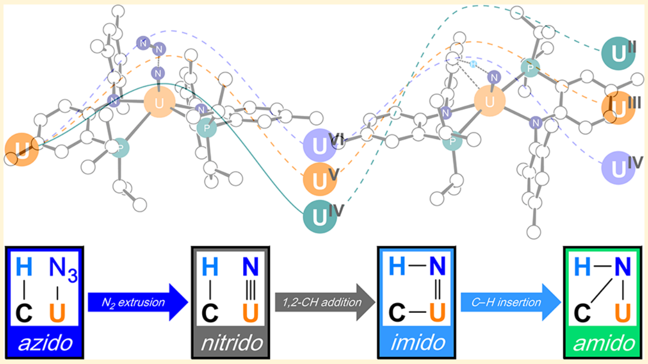
Supporting Information

ABSTRACT: Uranium complexes in the +3 and +4 oxidation states were prepared using the anionic PN^- (PN^- = (*N*-(2-(diisopropylphosphino)-4-methylphenyl)-2,4,6-trimethylanilide) ligand framework. New complexes include the halide starting materials, $(PN)_2U^{III}I$ (**1**) and $(PN)_2U^{IV}Cl_2$ (**2**), which both yield $(PN)_2U^{IV}(N_3)_2$ (**3**) by reaction with NaN_3. Compound **3** was reduced with potassium graphite to produce a putative, transient uranium−nitrido moiety that underwent an intramolecular C−H activation to form a rare example of a parent imido complex, $[K(THF)_3][(PN)U^{IV}({=}NH)[{}^iPr_2P(C_6H_3Me)N(C_6H_2Me_2CH_2)]]$ (**4**). Calculated reaction energy profiles strongly suggest that a C−H insertion becomes unfavorable when a reductant is present, offering a distinctively different reaction pathway than previously observed for other uranium nitride complexes.

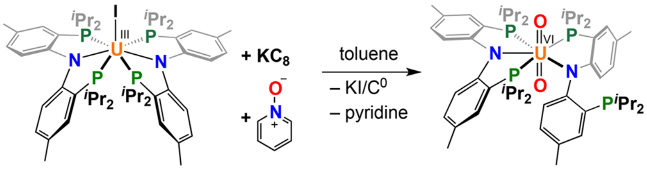


INTRODUCTION

Continued research on the chemistry of U−N multiple bonds is motivated in part by their strikingly different behavior when compared to analogous U═O bonds. For example, while *cis*-uranyl complexes have remained elusive, *cis*-bis(imido) complexes are common.[1−3] Recent advances in the field of uranium nitrogen multiple bonds include isolation of the first examples of a terminal, molecular uranium-nitride,[4−6] uranium tris- and tetrakis-imido moieties, and the complete scission and functionalization of N_2 with a molecular uranium cluster compound.[7−10] The single example of a uranium complex with a terminal parent imido U═NH moiety, $[K(15\text{-crown-}5)_2][U^{IV}(Tren^{TIPS})({=}NH)]$ ($Tren^{TIPS}$ = $N(CH_2CH_2NSi{}^iPr_3)_3$), has been reported by Liddle and coworkers.[11] Even in the d-block, where M−L multiple bonding is more prevalent, crystallographically characterized examples of parent imido complexes are rare.[12−35] The small number of these complexes is surprising because this functional group has been proposed as an intermediate in dinitrogen reduction to ammonia.[20,36,37] Indeed, uranium imido complexes are relevant in this context because of the high activity of uranium toward ammonia production reported in Haber's patent in 1909.[38]

We have developed a monoanionic and bidentate PN^- (PN^- = (*N*-(2-(diisopropylphosphino)-4-methylphenyl)-2,4,6-trimethylanilide) ligand for supporting M−L multiple bonds in first row transition metals.[35,39,40] Previously, Kiplinger reported several uranium complexes in a PNP^- (PNP^- = bis[2-(diisopropylphosphino)-4-methylphenyl]amido) pincer framework.[41,42] These complexes were noted to have steric and electronic profiles similar to uranium pentamethylcyclopentadienide ($C_5Me_5^-$) complexes but exhibited notable differences in their reactivity. For example, $(PNP)_2U^{III}I$ reacts with potassium graphite and pyridine-*N*-oxide to cleanly convert to $(PNP)_2U^{VI}O_2$, whereas the analogous reaction with $(C_5Me_5)_2U^{III}I(THF)$ resulted in decomposition to uranium oxides and formation of the $(C_5Me_5)_2$ dimer.[41] During this process, one phosphine arm of the PNP^- pincer ligand did not coordinate to the uranium center (Scheme 1). We hypothesized that the PN^- ligand framework would be well-matched to the uranium coordination sphere while also

Scheme 1. Hemilability of the PNP^- Ligand on Uranium Centers As Reported by Kiplinger and Co-workers[41]



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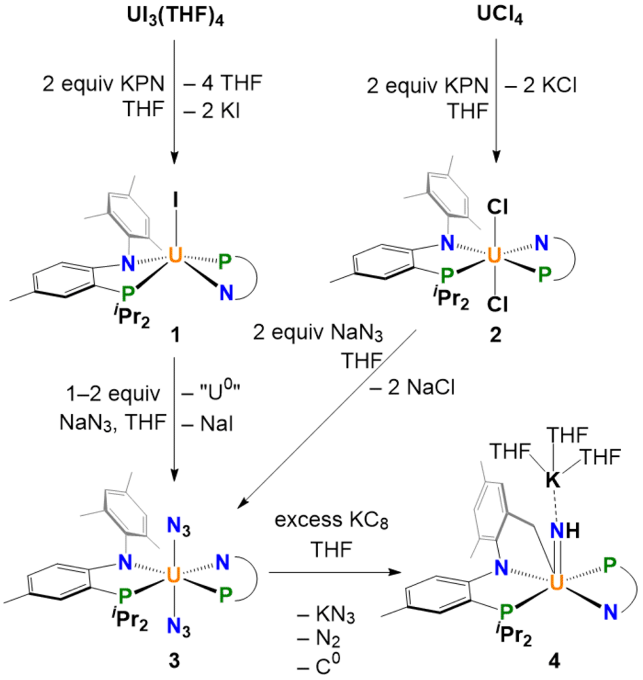
avoiding the dangling phosphine arm. Additionally, being a softer and less donating ligand than Tren^{TIPS}, PN^- may stabilize low- and mid-valent uranium oxidation states, while enforcing a pseudotetragonal and flexible ligand-binding environment that is ideal for metal−ligand multiple bonding.[35,40]

Herein we report the synthesis of uranium halide complexes supported by PN^- ligands, $(PN)_2U^{III}I$ (**1**) and $(PN)_2U^{IV}Cl_2$ (**2**). These compounds served as a new platform for exploring uranium−nitrogen multiple bond chemistry. Reaction of both **1** and **2** with sodium azide yielded the uranium(IV) product, $(PN)_2U^{IV}(N_3)_2$ (**3**). When treated with potassium graphite, complex **3** yielded a rare example of an f-block parent imido complex, $[K(THF)_3][(PN)U^{IV}({=}NH)[^iPr_2P(C_6H_3Me)N(C_6H_2Me_2CH_2)]]$ (**4**). We propose that this reaction proceeded through a transient uranium nitride intermediate, which added across the C−H bond of a proximate methyl group of the PN^- ligand, forming the parent imido metallacycle product. Theoretical studies have been used to probe the mechanism of uranium nitride formation and subsequent C−H bond activation involving the uranium−nitrogen multiple bond.

RESULTS AND DISCUSSION

Treatment of $UI_3(THF)_4$ and UCl_4 with 2 equiv K(PN) in THF solutions yielded **1** and **2**, respectively (Scheme 2). The salt metathesis reactions were completed in 2 h, and the products were isolated in crystalline yields of 48% and 62% for compounds **1** and **2**, respectively. In addition to ^1H NMR spectra, these compounds were characterized by single crystal X-ray diffraction (Figure 1). Notably, compounds **1** and **2** had differing coordination modes of the PN^- ligand, with transoid-(N,N) and cisoid-(N,N) geometries for **1** and **2**, respectively, which presumably coincide with their uranium(III) and uranium(IV) oxidation states. Similar isomerization processes have been observed in trivalent versus tetravalent group 4 transition metal complexes of the type $(PN)_2M^{III}Cl$ or $(PN)_2M^{IV}Cl_2$ (M = Ti, Zr, and Hf).[43] Isomerization between the two configurations was also observed upon electrochemical oxidation of **1** (see Electrochemical Data in Supporting Information).

Scheme 2. Synthesis of Complexes 1−4 from $UI_3(THF)_4$ or UCl_4 Precursors



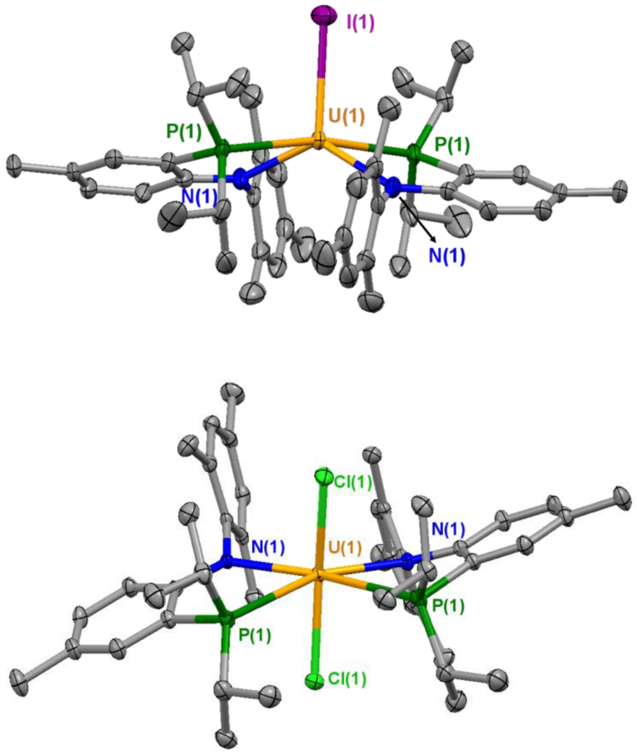


Figure 1. Thermal ellipsoid plots of **1** (top) and **2** (bottom) at 50% probability. Hydrogen atoms removed for clarity. Selected bond distances (Å) and angles (deg): **1**, U(1)−N(1) 2.337(4), U(1)−P(1) 3.0542(12), U(1)−I(1) 3.0633(4); **2**, U(1)−N(1) 2.2763(17), U(1)−P(1) 3.1495(6), U(1)−Cl(1) 2.6203(5), Cl(1)−U(1)−Cl(1) 166.58(3).

Compound **1** was treated with 1−2 equiv of sodium azide (NaN_3), and after 1.5 h the ^1H NMR spectrum revealed the formation of a uranium(IV) species, which corresponded to $(PN)_2U^{IV}(N_3)_2$ (**3**) on the basis of solid-state structural data (Scheme 2, Figure 2). The reaction mixture also contained free HPN presumably formed through the disproportionation of **1** or similarly through a disproportionation of the putative $(PN)_2U^{III}(N_3)$ to **3** and elemental uranium. This type of reaction has been previously observed for uranium(III) compounds; for example, reaction of $U^{III}[N(SiMe_3)_2]_3$ with MeLi results in $MeU^{IV}[N(SiMe_3)_2]_3$.[44] Given the low yield of **3** from **1** and NaN_3, we sought a more rational route involving salt metathesis of **2** with 2 equiv NaN_3. Accordingly, this reaction resulted in clean conversion to **3** in 94% isolated yield.

Extruding N_2 and forming the U−nitrido moiety is formally an oxidative process involving an increase of the oxidation state of the metal cation by +2. Thus, if **3** were to eject N_2, the resulting nitrido ligand in a hypothetical complex $(PN)_2U{\equiv}N(N_3)$ would be bound formally to a U(VI) center. The mechanism of N_2 extrusion is reminiscent of previous work on Mo-azides.[45] DFT-calculations estimate this process to be 24.1 kcal/mol downhill, due to the strong driving force provided by the liberation of N_2, but the barrier is estimated to be high at 30.3 kcal/mol. Unsurprisingly, we were unable to detect any

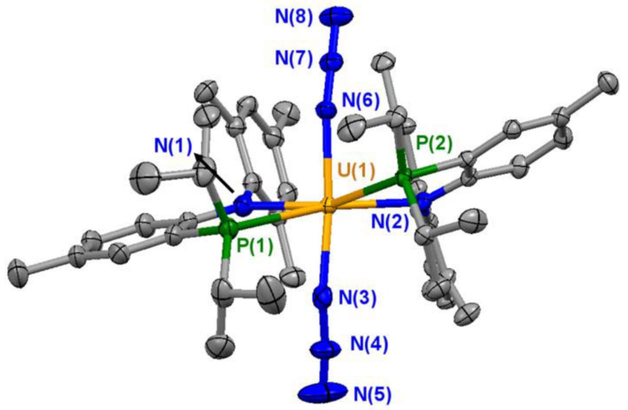


Figure 2. Thermal ellipsoid plot of **3** at 50% probability. Hydrogen atoms and azide disorder omitted in this figure for clarity. Selected bond distances (Å) and angles (deg): U(1)−N(1) 2.285(3), U(1)−N(2) 2.281(3), U(1)−P(1) 3.0544(10), U(1)−P(2) 3.0897(9), U(1)−N(3) 2.20(4), U(1)−N(6) 2.273(3), N(3)−N(4) 1.37(4), N(4)−N(5) 1.11(3), N(6)−N(7) 1.198(4), N(7)−N(8) 1.143(5), N(3)−U(1)−N(6) 170.6(8).

sign of such reaction from **3** experimentally. An obvious way of promoting N_2 extrusion is reducing the uranium center. Our DFT-calculations indicate that the reduction of the U(IV) center by a single electron to U(III) reduces the N_2 extrusion barrier by 9.3 kcal/mol to afford a $\Delta G^{\ddagger}$ of 21.0 kcal/mol. Additional reduction to U(II) lowers the free energy barrier further by 20.6 to 0.4 kcal/mol, rendering it a barrierless process. These computed barriers illustrate the general trend that the oxidative release of N_2 from the uranium center in lower oxidation states is more feasible. Realistically, U(III) is most likely the active species, as the barrier of 21.0 kcal/mol is reasonable and should result in rapid N_2 extrusion, while maintaining structural integrity. The over-reduction to U(II) is likely accompanied by degradation and decomposition of the metal-complex, initiated by loss of both azide ligands.

To test the simple notion that N_2 extrusion from a uranium center should become easier as the metal ion is reduced and made more electron-rich, we treated **3** with an excess of potassium graphite (KC_8) in a THF solution as shown in Scheme 2. The reaction mixture changed color immediately from pale orange to dark green concurrent with gas evolution, and within seconds the solution became dark red. Following workup of the reaction mixture, red crystals of a uranium(IV) parent imido complex having a metallacycle, namely, $[K(THF)_3][(PN)U^{IV}({=}NH)[{}^{i}Pr_2P(C_6H_3Me)N(C_6H_2Me_2CH_2)]]$ (**4**), were isolated from a saturated hexanes solution in 15% crystalline yield. The ^1H NMR spectrum of **4** was consistent with a highly desymmetrized system with multiple chemical environments ranging from 52.64 to −39.04 ppm (Figure S19). A ^1H NMR spectrum of the reaction mixture showed free HPN in addition to compound **4**, the latter of which was only stable at low temperatures for 48 h. Notably, reaction between KC_8, NaN_3, and **1** also formed **4** as detected in a ^1H NMR spectrum of the reaction mixture. However, isolation of **4** on a preparative scale returned higher yields from **3**, presumably due to deleterious side reactions on starting from **1** and NaN_3. An attempt to reduce **3** with $(C_5Me_5)_2Co$ showed no reaction. Efforts to trap the putative nitride intermediate (vide infra) using low temperatures or $B(C_6F_5)_3$ were not successful. Finally, attempts to deprotonate **4** with KBn or MeLi led to decomposition.

Figure 3 shows the computed reaction energy profile of the proposed mechanism, assuming that the putative monoazido

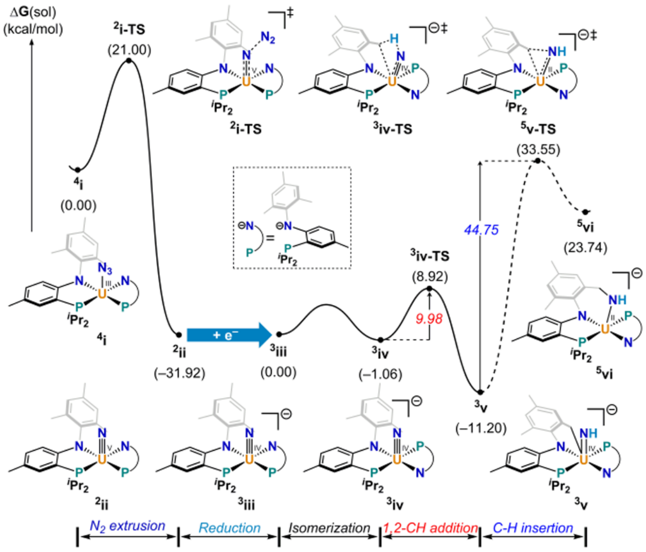


Figure 3. Computed energy profile of the most likely mechanism.

U(III)-intermediate $[(PN)_2U^{III}(N_3)]$, **i**, is the reactive complex. Reduction of **3** by one electron accompanied by loss of 1 equiv of the KN_3 is expected to afford ^{4}**i**. As mentioned above and illustrated in Figure 3, concerted loss of N_2 gives the U(V)−nitrido complex ^{2}**ii**, $(PN)_2U^{V}({\equiv}N)$, that we located at a relative energy of −31.9 kcal/mol in this highly exergonic step. The extrusion of N_2 is associated with an intersystem crossing from the quartet surface of ^{4}**i**, to the doublet surface, on which the intermediate ^{2}**ii** is located. Interestingly, the transition state connecting these two intermediates, ^{2}**i-TS**, is found on the doublet surface at an energy of 21.0 kcal/mol. Its structure, illustrated in Figure 4a, reveals a severely distorted square-pyramidal coordination motif and a N−(N_2) bond length of 1.419 Å. The formation of the N−N triple bond is nearly completed at a bond length of 1.186 Å in the transition state.

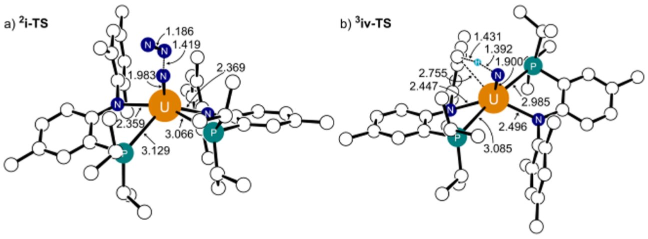
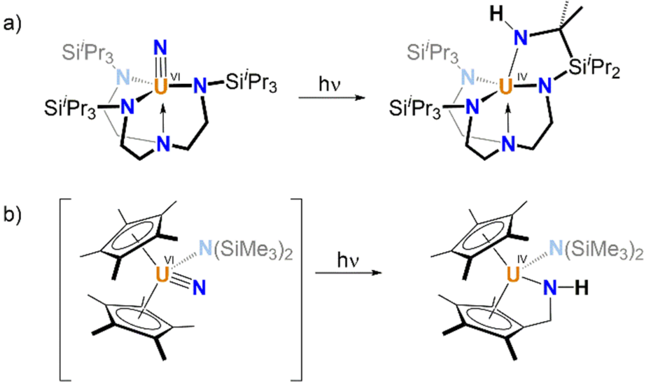


Figure 4. DFT-calculated geometries of the two important transition states (a) ^{2}**i-TS** and (b) ^{3}**iv-TS**. Hydrogen atoms, except for that on the imido nitrogen, were omitted for clarity.

We also considered an alternative mechanism where 1,2-addition of the C−H bond without N_2 extrusion and without the isomerization of the PN^- ligand. We observed that the product complex, ^{4}**xvii**, is ~50 kcal/mol higher in energy than ^{2}**ii**, as shown in Figure S24, indicating that this alternative intermediate is unstable because the nucleophilicity of the azide ligand and the electrophilicity of the U(III) center are not matched well enough to directly facilitate 1,2-CH addition without N_2 extrusion. The N_2 extrusion from the intermediate ^{4}**i** ($[(PN)_2U(N_3)]$) oxidizes the uranium center so that a methyl group from the PN^- ligand can readily coordinate to the uranium center. Unless the electrophilicity of the uranium is increased as the uranium is oxidized, the 1,2-CH addition does not occur.

The energies we found for the extrusion of N_2 suggest that the reaction should be feasible under mild conditions, which is in good agreement with the experimental observations but stands in contrast to where photochemical assistance was required to expel N_2.[6] Given the excess of reducing equivalents under our conditions, we expect that the high-valent U(V)−nitride complex will be reduced readily to afford $[K][(PN)_2U^{IV}(\equiv N)]$, ^{3}**iii**, which quickly isomerizes to ^{3}**iv** and performs a C−H activation on one of the proximal methyl groups of the anilido moieties to form the cyclometalated imido complex ^{3}**v** (i.e., **4**). This reactivity is consistent with Mazzanti's observation that addition of a reducing compound, $UI_3(THF)_4$, to the uranium azide complex, $Cs_3[U(N_3)_7]$, results in the release of nitrogen gas and formation of a tetranuclear azido/bridging nitride uranium(IV) cluster.[46] Our DFT-calculations show that with a barrier of 10.0 kcal/mol, the C−H activation from the uranium(IV) nitride complex ^{3}**iv** should be notably faster than from the corresponding uranium(V) nitride complex, where we found a barrier of 13.9 kcal/mol (see Figure S20). The calculated energy profiles of the 1,2-CH addition employing the oxidation states VI, V and IV are summarized in Figure S23 and show that the 1,2-CH addition becomes much easier as the uranium center is reduced. As the 5f orbital energies of the uranium move up in energy upon reduction, increasing the energy gap to the nitrido orbitals, the U≡N bond becomes weaker and the interaction between the uranium center and the nitrido ligand becomes more ionic. As a consequence, the nitrido ligand of the U(IV)≡N is much more basic and acts as a better nucleophile, which leads to a more facile 1,2-CH addition. Figure 4b depicts the transition state ^{3}**iv-TS** associated with the C−H activation step, where the nitride functionality virtually deprotonates the methyl group and the U−C bond is formed in the process. Formally a proton-transfer reaction, the C−H bond breaking and N−H forming is seen to have progressed to an equal extent in accord with a 1,2-CH addition pathway[47] and indicated by atomic distances of 1.43 and 1.39 Å, respectively.

Scheme 3. Previously Reported Insertion Reactions of Uranium(VI) Nitride Complexes into Nearby C−H Bonds[6,48]



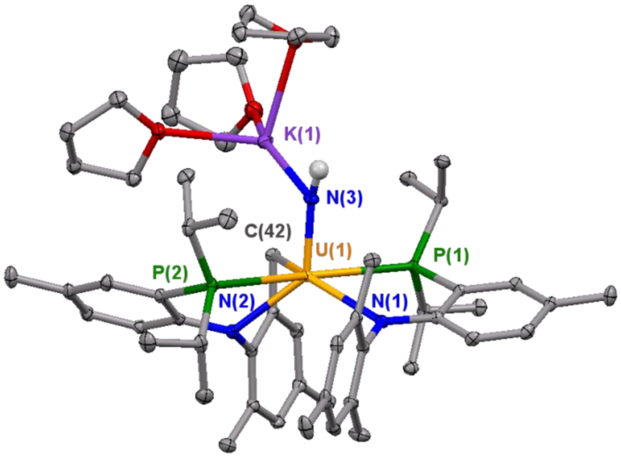


Figure 5. Thermal ellipsoid plot of **4** at 50% probability. Hydrogen atoms, except that on the imido ligand and hexane solvent, removed for clarity. Selected bond distances (Å): U(1)−N(1) 2.452(2), U(1)−N(2) 2.409(2), U(1)−N(3) 1.997(2), U(1)−P(1) 3.0106(8), U(1)−P(2) 3.0847(7), U(1)−C(42) 2.589(3), N(3)−K(1) 2.789(3), C(42)−K(1) 2.957(3).

The reactivity of the proposed uranium(IV) and (V) nitride intermediates is distinctively different from what was previously reported for uranium(VI) nitride complexes. The first isolated uranium(VI) nitride complex, $(Tren^{TIPS})U^{VI}(\equiv N)$, reported by Liddle and co-workers, inserted into a nearby C−H bond of the $Tren^{TIPS}$ ligand framework upon photolysis (Scheme 3a).[6] Kiplinger and co-worker's putative uranium(VI) nitride species, $(C_5Me_5)_2U^{VI}(\equiv N)[N(SiMe_3)_2]$, which was formed under photolytic conditions, also inserted intramolecularly into a nearby C−H bond of a C_5Me_5 ancillary ligand (Scheme 3b).[48] However, our system adds the C−H bond across the U≡N moiety to form **4** without undergoing insertion, as unequivocally shown by a solid-state structural analysis of **4** (Figure 5). The U(IV) center in **4** is six-coordinate and shows the cyclometalated anilido fragment with a characteristic U(1)−C(42) bond length of 2.589(3) Å, which is comparable to other uranium metallacycle complexes, such as $(C_5Me_5)_2U^{IV}[N(SiMe_3)SiMe_2CH_2]$ (U−C 2.52(2) Å).[48] The average $U-N_{amide}$ bond length in **4** (avg $U-N_{amide}$ 2.431(2) Å) was long when compared with those of **2** and **3** (avg $U-N_{amide}$ 2.2793(17) and 2.283(3) Å, respectively). The parent imido bond length (U(1)−N(3) 1.997(2) Å) in **4** was notably shorter than what was previously seen in other known uranium(IV) imido compounds, such as $[K(15\text{-crown-}5)_2][U(Tren^{TIPS})(NH)]$, which had a U═N bond length of 2.034(3) Å.[11] The K^+ countercation coordinated to the nucleophilic imido group exhibited a close contact to the alkyl moiety of 2.957(3) resulting from C−H activation.

To better understand why nitrogen insertion into the C−H bond is not observed in **4**, we calculated the required C−H insertion in complex **4**, as shown in broken lines in Figure 3. Our DFT model calculations suggest that the C−H insertion step, involving the transformation ^{3}**v** → ^{5}**vi** via ^{5}**v-TS** is extremely uphill energetically by 35.0 kcal/mol and is kinetically prohibitive with a calculated barrier of 44.8 kcal/mol. Fundamentally, this C−H insertion is accompanied by a formal reduction of the uranium center from U(IV) to U(II). Our calculations suggest that the ligand framework employed here is simply unable to accommodate such a low-valent uranium center.

Figure 6 summarizes the calculated changes of the energy profiles for the C−H insertion when different oxidation states are considered for the uranium center. If intermediate ^{3}**v** is oxidized to become ^{2}**vii** containing a U(V)-center, the reductive C−H insertion becomes much easier with a barrier of 29.6 kcal/mol and is endergonic by 16.3 kcal/mol. If another electron is removed to afford the U(VI) analogue, ^{1}**ix**, the C−H insertion is predicted to be downhill by 3.7 kcal/mol and shows a barrier of only 18.3 kcal/mol. Thus, the reductive C−H insertion is only predicted to be feasible for the U(VI) oxidation state, which allows us to relate our findings to Kiplinger's previous work.[48] The reason that we do not observe the insertion product is that the driving force for the formal reduction of U(IV) to U(II) is too low. To observe the reductive C−H insertion, the higher oxidation state U(VI) is required, as was also seen in the Kiplinger and Liddle systems.

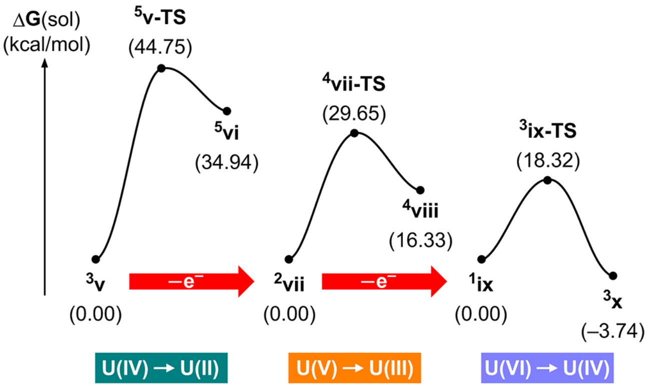


Figure 6. Energy profiles of the putative C−H insertion adopting different oxidation states at the uranium center.

CONCLUSIONS

The PN^{-} scaffold has allowed us to isolate and structurally characterize a rare example of a uranium(IV) imide. We also introduced a new route to a parent imido complex through reductive denitrogenation of a U(IV) bis-azide precursor. Our uranium imide **4** contains the shortest U=NH bond length known to date, at 1.997(2) Å, and is proposed to be formed via a C−H activation of a nearby methyl group from the putative U−nitride intermediate. Because the uranium center is in the U(IV) oxidation state, it engages in an unprecedented 1,2-CH addition instead of reductive C−H insertion. In other words, the nitrido ligand in putative ^{3}**iii** behaves more in accord with a nucleophilic nitride. Our combined experimental and computational study highlights the importance of the oxidation state of the uranium center, which is key to controlling both the thermodynamic and kinetic profiles of the chemical transformations. With the stable U(IV)−imido species at hand, we are presently exploring its reactivity and redox properties.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b06090.

X-ray data for **1**, **2**, **3**, and **4** (CIF)

Experimental procedures, spectra, electrochemical data, crystallographic details, and computational details and coordinates (PDF)

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[‖]K.C. and H.R. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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