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A DISSERTATION
in
Chemistry
Presented to the Faculties of the University of Pennsylvania
in
Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

2017

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REACTIVITY AND ELECTRONIC STRUCTURES OF URANIUM COMPLEXES WITH NITROGEN AND OXYGEN DONORS IN AXIAL SYMMETRIES

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## Acknowledgements

I would like to acknowledge my advisor, Professor Eric Schelter, for supporting the research presented here. He set high expectations for the quality of research, presentations, and publications I produced, while giving me the freedom to approach all three with my own interests and voice. He also worked with Professor Sally Mallory to come up with creative funding solutions for me that enabled me to remain in the graduate program at the University of Pennsylvania, for which I will always be grateful. I would like to acknowledge the members of my dissertation committee - Professors Bill Dailey, Gary Molander, Pat Walsh, and Dan Mindiola - for their guidance and feedback; Drs. Pat Carroll and Brian Manor for their time spent solving my crystal structures, even on weekends; Drs. George Furst and Jun Gu for their work in NMR facility, including their advice concerning the work described in Chapter 6; Judith Currano for facilitating access to library resources and even writing to Reaxys when we found that there was not a comprehensive way to search for compounds with radicals; Professor Eiko Nakamaru-Ogiso for her work in collecting EPR spectra of my compounds; Professor Jay Kikkawa for training me to collect magnetic data and maintaining the SQUID; the members of the Schelter research group that I have worked with - especially Drs. Andrew Lewis, Haolin Yin, and Thibault Cheisson who have contributed to the chemistry presented here; to the undergraduate and visiting researchers that I have worked closely with in the Schelter lab - Professor Benny Chan, Jerry Hertzog, and Kyle Kersey; to the members of the Walsh, Tomson, and Mindiola groups for sharing resources and advice; Professors Pat Walsh and Sally Mallory, who supervised my teaching assignments and will be role models for me for the rest of my career; Professors Chris Graves, Ursula Williams, and Walter Dorfner for their help and advice as I applied for academic jobs; the undergraduates I have taught for reminding me how fun chemistry can be; and my friends and family for their support and encouragement. I would especially like to thank my undergraduate research mentors, Professors Frank and Sally Mallory, who I think of as equal parts family and career/life role models. I cannot overstate how supportive they have been during my time at Bryn Mawr and beyond.

# ABSTRACT <br> REACTIVITY AND ELECTRONIC STRUCTURES OF URANIUM COMPLEXES WITH NITROGEN AND OXYGEN DONORS IN AXIAL SYMMETRIES 

Kimberly C. Mullane

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The effects of the ligand field are generally on the same order of magnitude as spin-orbit coupling for uranium complexes. However, significant impacts on the electronic structure, reactivity, and stability of uranium complexes have been observed as a result of changing the ligand framework. In the work presented here, uranium complexes in a variety of ligand frameworks are synthesized, and their unique electronic structures and reactivities are studied. Uranium imido complexes with varying substitution at the imido nitrogen are contrasted with uranium oxo complexes, showing that their ability to impart an inverse trans influence, a thermodynamic phenomenon in which strong donor ligands gain stability from trans axial geometries, was comparable. We also synthesized uranium complexes with a weakly donating phosphino-anilide ancillary ligand. This ligand stabilized the uranium(III/IV) couple and allowed the synthesis of a rare uranium(IV) parent imido moiety. In contrast, the bis(trimethysilyl)amide ligand framework resulted in more reducing complexes and afforded reactivity in which reactive amide radical anions could be stabilized, and other carbonyl functional groups were reduced. In this same ancillary ligand framework, we synthesized uranium( VI ) oxo phenyl(acetylide) complexes and observed that distal para aryl substituents could affect covalency in $U-C$ bonding.

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## Chapter 1:

## Introduction and Outline of the Dissertation

### 1.1 Uranium.

Uranium has been of interest since the Manhattan project in the 1940s, when volatile uranium complexes were investigated for isotope separation purposes. ${ }^{1}$ Since that time, uranium has remained relevant in the contexts of nuclear fuels and waste processing ${ }^{2}$ and environmental waste remediation cleanup projects. ${ }^{3}$ As an academic pursuit, uranium is a challenging and unique metal to work with; owing to relativistic effects, uranium has available oxidation states ranging from +2 to +6 , differentiating it from much of the $f$-block. ${ }^{4-9}$ Despite relativistic effects, $f$ orbitals are contracted by nature, and covalency in uranium-ligand bonding is more limited than in the d-block. ${ }^{10,11}$ This dichotomy results in interesting reactivity and electronic structure observed nowhere else in the periodic table.

### 1.2 Recent Advances.

Recently, non-aqueous uranium chemistry has enjoyed developments in new ligand frameworks, ${ }^{12-15}$ metal-ligand multiple bonds, ${ }^{16-20}$ and even oxidation states. ${ }^{4,5}$ While some challenges remain, such as the synthesis of uranium-alkylidene complexes, the recent accomplishments in synthetic actinide chemistry are numerous.

### 1.2.1 Inverse Trans Influence.

The inverse trans influence, which is discussed in more detail in Chapter 2, is the thermodynamic explanation for the stability of the uranyl dication $\left(\mathrm{UO}_{2}{ }^{2+}\right)$, the most prevalent form of uranium in the environment. The uranyl dication is infamous for its role in the contamination of groundwater in Washington state. The DOE had estimated that the cost to complete this large scale cleanup project would be $\$ 113.6$ billion over the next thirty years. Accordingly,
understanding the inverse trans influence and its role in the stability of the uranyl dication are active areas of research. ${ }^{9,21}$ In contrast with the trans influence in transition metal complexes, where strong donor ligands weaken the bonding between the metal center and trans ligand, in the inverse trans influence strong donor ligands strengthen the bonding between the metal center and trans ligand. This phenomenon has been studied historically in high-valent actinyl and [UOX $\left.{ }_{5}\right]^{-}$complexes. ${ }^{22-24}$ Recently, the inverse trans influence was observed in the chemistry of a uranium imido complex, $\left[\left(\left({ }^{\mathrm{Ad}} \mathrm{ArO}\right)_{3} \mathrm{~N}\right) \mathrm{U}^{\mathrm{V}}(=\mathrm{NMes})\right]\left(\left({ }^{\mathrm{Ad}} \mathrm{ArO}\right)_{3} \mathrm{~N}^{3-}=\right.$ trianion of tris(2-hydroxy-3-adamantyl-5-methylbenzyl)amine). In this complex the U-O bond trans to the imido ligand was $2.145(2) \AA$ A , which was shorter in comparison to the cis U-O bonds, at 2.177(2) and 2.173(2) $\AA .{ }^{25}$ This expanded the study of the inverse trans influence to strong donor ligands apart from the ubiquitous oxo ligand.


Scheme 1.2.1 The uranium $(\mathrm{V})$ imido complex, $\left[\left(\left({ }^{\mathrm{Ad}} \mathrm{ArO}\right)_{3} \mathrm{~N}\right) \mathrm{U}^{\mathrm{V}}(=\mathrm{NMes})\right]$, in which a short $\mathrm{U}-\mathrm{O}$ bond trans to the imido ligand was observed. ${ }^{25}$

Additionally, work from our group has used experimental and computational metrics to develop an inverse trans influence ligand series by examining compounds of the general formula $\mathrm{U}^{\mathrm{V1}}(=\mathrm{O}) \mathrm{R}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} .{ }^{9}$ One metric that was used was the equatorial $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond lengths, since it was shown that equatorial bonding is weakened and lengthened, as a consequence of the strong axial bonding in compounds with an inverse trans influence. Additionally, $\mathrm{E}_{1 / 2}$ values for uranium $(\mathrm{V} / \mathrm{VI})$ couple were compared, as a metric of the stability of the uranium +6 oxidation state. Last, a correlation was observed in the energies of $\pi^{*} U=O$ and $\sigma^{*} O-U-R$ anti-bonding
orbitals in which electron-donating ligands had higher energy anti-bonding orbitals. In examining the trends from each of these metrics, the following ligand series was constructed: $\mathrm{CN}^{-}<\mathrm{I}^{-} \approx \mathrm{Br}^{-}<$ $\mathrm{Cl}^{-} \approx \mathrm{PhS}^{-}<\mathrm{PhCC}^{-} \approx \mathrm{F}^{-}<\mathrm{MeO}^{-}<\mathrm{NMe}_{2}^{-}<\mathrm{Me}^{-}<\mathrm{H}^{-}$.

### 1.2.2 Uranium-Ligand Multiple Bonds.

Compared with lanthanide ions, uranium has more accessible $f$ and $d$ valence orbitals for bonding with ligands due to relativistic effects (Figure 1.2.1). However, while the valence orbitals of uranium ions are more available than those of lanthanides, they are still contracted when compared with the valence orbitals of transition metals. The contracted valence orbitals present challenges for covalency in metal-ligand multiple bonding; while atoms with a high charge density such as $\mathrm{O}^{2-}$ oxo ligands are well matched to have a strong ionic interaction with uranium $(\mathrm{VI})$ ions, as seen in uranyl complexes, other U-L multiple bonds are more challenging to isolate.


Figure 1.2.1 Radial distribution plot for a uranium(III) ion compared with a neodymium(III) ion, showing the increased accessibility $f$ orbitals in the uranium ion for bonding. Reproduced from reference 26 with permission from Elsevier. ${ }^{26}$

However, the field of uranium-ligand multiple bonding has recently achieved many milestone discoveries. Ephritikhine and coworkers synthesized the first uranium sulfide complex by cleavage of a thiolate $\mathrm{C}-\mathrm{S}$ bond in $\mathrm{U}^{\mathrm{IV}}\left(\mathrm{Cp}^{*}\right)_{2}\left(\mathrm{~S}^{t} \mathrm{Bu}\right)_{2}$ to yield $[\mathrm{Na}(18-c r o w n-$ 6) $]\left[U^{\mathrm{IV}}\left(\mathrm{Cp}^{*}\right)_{2}\left(S^{t} \mathrm{Bu}\right)(\mathrm{S})\right] .^{27}$ Since that time, the Hayton group has expanded the chemistry of uranium-chalcogen multiple bonds, by reacting the uranium(III) adduct of methylene triphenylphosphorane, $\mathrm{U}^{\text {III }}\left(\mathrm{H}_{2} \mathrm{C}=\mathrm{PPh}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, with elemental sulfur, selenium, and tellurium to yield the uranium $(\mathrm{IV})$ complexes, $\left[\mathrm{Ph}_{3} \mathrm{PCH}_{3}\right]\left[\mathrm{U}^{\mathrm{IV}}(=\mathrm{E})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right](\mathrm{E}=\mathrm{S}, \mathrm{Se}, \mathrm{Te})$. It was proposed that the formation of these multiply bonded products was accompanied by the formation of the uranium(IV) metallacycle complex, $\mathrm{U}^{\mathrm{IV}}\left(\mathrm{CH}_{2} \mathrm{SIMe}_{2} \mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{2} \cdot{ }^{28}$ Subsequently, the Hayton group illustrated a more straightforward reaction pathway to uranium-oxo and -sulfido complexes. They synthesized complexes, $[K(L)]\left[U^{\text {IV }}(=E)\left[N\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(E=O, S)(L=\right.$ 18-crown-6, 2,2,2-cryptand), by cleavage of a trityl protecting group from $\mathrm{K}\left[\mathrm{U}^{\text {III }}\left(\mathrm{ECPh}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ complexes upon encapsulation of the potassium counter-ion by 18-crown-6 or 2,2,2-cryptand (Scheme 1.2.2, bottom). ${ }^{29}$ This method was also used with thorium to synthesize thorium oxo and sulfido complexes, $[\mathrm{K}(18-$ crown- 6$)]\left[\mathrm{Th}^{\mathrm{IV}}(=\mathrm{E})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(\mathrm{E}=\mathrm{O}, \mathrm{S}) .{ }^{30}\right.$


1) $\mathrm{MC}_{8}$
2) $N_{3} \mathrm{DIPP}$
3) $\mathrm{MC}_{8} \longrightarrow$

$\mathrm{M}=\mathrm{K}, \mathrm{Rb}, \mathrm{Cs}$


$x_{2}$

$\mathbf{N}^{*}=\mathbf{N}\left(\mathrm{SiMe}_{3}\right)_{2}$

$$
+0.5
$$



Scheme 1.2.2 Examples of recent advances in the chemistry of uranium-ligand multiple bonds, including the first example of a uranium tris(imido) complex (top), the first example of a uranium tetrakis(imido) complex (middle), and reductive cleavage of a trityl group to install a $\mathrm{U}=\mathrm{S}$ bond. ${ }^{18,19,29}$

Uranium-pnictogen multiple bonds have also seen many recent successes. Starting with the synthesis of the first uranium trans bis(imido) complexes, $\mathrm{U}^{\mathrm{VI}}\left(=\mathrm{NR}_{2}\right) \mathrm{I}_{2}(\mathrm{THF})_{3}\left(\mathrm{R}={ }^{t} \mathrm{Bu}, \mathrm{Ph}\right)$, which are isoelectronic to uranyl complexes, there have been many important developments in uranium imido complexes. ${ }^{31}$ The Bart group synthesized the first uranium tris(imido) complex,
$\left(^{\text {Mes }} \mathrm{PDI}^{\mathrm{Me}}\right) \mathrm{U}^{\mathrm{Vl}}(=\mathrm{NMes})_{3}\left({ }^{\text {Mes }} \mathrm{PDI}^{\mathrm{Me}}=2,6-\left(2,4,6-\mathrm{Me}_{3}-\mathrm{C}_{6} \mathrm{H}_{2}-\mathrm{N}=\mathrm{CMe}\right)_{2} \mathrm{C}_{5} \mathrm{H}_{3} \mathrm{~N}\right)$, through an elegant synthesis using redox-active ${ }^{\text {Mes }} \mathrm{PDI}^{\text {Me }}$ ligands to facilitate the two-electron reduction of mesityl azide (Scheme 1.2.2, top). ${ }^{18}$ Subsequently, the Bart group found that uranium tris(imido) and even tetrakis(imido) complexes, $\mathrm{U}^{\mathrm{V1}}(=\mathrm{NDIPP})_{3}(\mathrm{THF})_{4}$ and $\mathrm{M}_{2}\left[\mathrm{U}^{\mathrm{V}}(=\mathrm{NDIPP})_{4}\right](\mathrm{M}=\mathrm{K}, \mathrm{Rb}, \mathrm{Cs})$, could be synthesized by reaction of uranium with $\mathrm{N}_{3}$ DIPP and external $\mathrm{MC}_{8}$ reductants (Scheme 1.2.2, middle). ${ }^{19,32} \mathrm{~A}$ single example of a uranium(IV) parent imido complex, $\left[U^{\text {IV }}\left(\operatorname{Tren}^{\text {TIPS }}\right)(=\mathrm{NH})\right]\left[\mathrm{K}(15-\text { crown- } 5)_{2}\right] \quad\left(\operatorname{Tren}^{\text {TIPS }}=\mathrm{N}-\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NSiPr}_{3}^{i}\right)_{3}\right)$, has been reported by Liddle and coworkers. ${ }^{33}$ The Liddle group has also synthesized the first examples of a terminal molecular uranium-nitride, phosphide, and phosphinidene complexes. ${ }^{16,17,34-37}$

Uranium-alkylidene complexes remain elusive; however, nucleophlic carbene ${ }^{14,38-42}$ and $N$-heterocyclic carbene complexes ${ }^{43-45}$ of uranium have now been reported. In the case of $(B I P M) \mathrm{U}^{\mathrm{VI}}(=\mathrm{O}) \mathrm{Cl}_{2}\left(\mathrm{BIPM}=\mathrm{C}\left(\mathrm{PPh}_{2} \mathrm{NSiMe}_{3}\right)_{2}\right)$, the carbene ligand is positioned trans to a strong oxo donor. Through the inverse trans influence, the U-C bond is shortened, with a bond length of 2.183(3) $\AA .{ }^{39}$ In comparison, uranium $(\mathrm{VI})$-carbon single bonds range from 2.319(2)-2.707(4) $\AA$ for $U^{\mathrm{VI}}(=\mathrm{O})\left[\mathrm{CH}_{2} \mathrm{SIMe}_{2} \mathrm{NSiMe}_{3}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ and $U^{\mathrm{VI}}(=\mathrm{O})_{2} \mathrm{Cl}\left[\mathrm{HC}\left(\mathrm{PPh}_{2} \mathrm{NMes}\right)_{2}\right](\mathrm{THF})\left(\mathrm{Mes}=\mathrm{C}_{6} \mathrm{H}_{2^{-}}\right.$ $2,4,6-\mathrm{Me}_{3}$ ), respectively. These advances indicate that true uranium-carbon multiple bonds are likely to be isolable if given an appropriate ligand environment. ${ }^{46}$

### 1.2.3 A New Divalent Oxidation State.

Recently, the first examples of divalent uranium complexes have been reported. The first example, reported by Evans and coworkers, was synthesized by the reduction of $\mathrm{U}^{\prime \prime \prime}\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{SIMe}_{3}\right)_{3}$ with potassium graphite in the presence of 2,2,2-cryptand, yielding [K(2,2,2cryptand) $]\left[U^{\prime \prime}\left(\mathrm{C}_{5} \mathrm{H}_{4} \mathrm{SIMe}_{3}\right)_{3}\right]$ (Scheme 1.2.3, left). ${ }^{5}$ Density functional theory calculations and electronic absorption spectroscopy indicated that the electronic configuration is $5 f^{3} 6 d^{1}$ for this compound. The Meyer group has synthesized the only other molecular example of a uranium(II) complex (Scheme 1.2.3, right). The synthesis of this compound was also accomplished by the
 $2,2,2$-cryptand. The resulting divalent complex, $[\mathrm{K}(2,2,2-$ cryptand $)]\left[U^{11}\left[\left({ }^{\mathrm{Ad}, \mathrm{Me}} \mathrm{ArO}\right)_{3} \mathrm{Mes}\right]\right]$,
remarkably had a ground state electronic configuration of $5 f^{4}$, rather than $5 f^{3} 6 d^{1}$ as had been observed for the complex reported by Evans. This result showed that the electronic structure of a uranium complex can be drastically impacted by the ligand environment, which is surprising given that ligand field effects are generally on the same order of magnitude as spin-orbit coupling, due to the contracted nature of the valence orbitals. ${ }^{47}$


Scheme 1.2.3 The two reported examples of divalent uranium complexes and their ground state electronic configurations. The $[\mathrm{K}(2,2,2 \text {-cryptand })]^{+}$counter-ions are omitted for clarity. ${ }^{4,5}$

### 1.3 Outline and Goal of Dissertation.

From these three areas of development in synthetic uranium chemistry, it has become clear that the ligand environment has substantial effects on the electronic structure, reactivity, and stability of uranium complexes. The main goals of the research presented in this dissertation were to study the effects of the inverse trans influence, as imparted by nitrogen-donors, on the electronic structure of high-valent uranium complexes and to utilize ligand frameworks with varying donating ability to exploit the rich uranium-based redox-chemistry and stabilize rare or unknown moieties. Chapters 2 and 3 will concentrate on this first goal of studying the inverse trans influence as imparted by imido ligands. Chapters 4-6 will utilize various ligand frameworks to alter the electronic structure of the uranium ion for purposes of reactivity and stabilizing unique structures. Chapter 7 will conclude with our attempts to synthesize a uranium-alkylidene complex. Additionally, miscellaneous results with novel ancillary amide ligands and our synthesis of a tetra-
nuclear uranium complex with bridging nitride and azide ligands are described. More detail on the contents of the chapters are as follows:

In Chapter 2, the trimethylsilyl(imido) ligand was directly compared with the oxo ligand for effectiveness in stabilizing the +6 oxidation state of uranium and imparting an inverse trans influence. We found this ligand to be on par with the oxo ligand in imparting this stability, presumably due to the electron-donating trimethylsilyl group of the imido ligand. In Chapter 3 redox-active naphthalene-based groups were used to substitute the imido ligand. In contrast with oxo-ligands, imido ligands can be electronically and sterically varied, allowing more varied electronic structures.

In Chapter 4, a weakly donating PN equatorial ligand is used. In contrast with the bis(trimethylsilyl)amide ligands used in much of this work, the PN ligand stabilized the low-valent $(+3$ and +4$)$ oxidation states of uranium. Because the (III/IV) couple was stabilized, and high oxidation states were disfavored, we were able to add reductants to synthesize a rare example of a uranium(IV) parent imido ( $\mathrm{U}=\mathrm{NH}$ ) complex. In contrast, in Chapter 5 we used the donating bis(trimethylsilyl)amide ligands, which have a reducing (III/IV) couple, to stabilize the first example of an amide radical anion. In this chapter we also reacted $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with other carbonyl functional groups and accessed different reactivity for ketone, amide, and ester functional groups. In Chapter 6, para substituents in uranium phenyl(acetylide) complexes were varied. With more electron-donating groups, the +6 oxidation state of uranium and the axial bonding were stabilized. We were able to detect experimentally the phenyl(acetylide) ligand interaction with the weakly paramagnetic uranium(VI) ion by ${ }^{13} \mathrm{C}$ NMR.

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## Chapter 2: <br> Uranium(VI) trimethyl silyl imido complexes: donors comparable with the oxo ligand in the inverse trans influence

### 2.1 Introduction.

The uranyl cation $\left(\mathrm{UO}_{2}^{2+}\right)$ is a thermodynamic sink in uranium chemistry and is formed by exposure of uranium complexes to air or moisture. Additionally, uranyl complexes have high solubility in water and a number of organic solvents. ${ }^{1}$ To date, eight billion gallons of contaminated groundwater at the Hanford site, which has suffered contamination of groundwater from legacy waste, have been treated to remove this environmentally mobile form of uranium. Over the next thirty years the DOE plans to spend $\$ 113.6$ billion to complete this large scale cleanup project. ${ }^{2}$ Accordingly, functionalization of the uranyl ion and understanding its electronic structure are active areas of research. ${ }^{3,4}$ Interestingly, while the $[\mathrm{O}=\mathrm{U}=\mathrm{O}]^{2+}$ moiety is stable and formed in ambient aqueous conditions, the first example of the isoelectronic bis-imido complex was not isolated until $2005 .{ }^{5}$ Accounting for the differences between uranium oxo and imido functional groups may be critical to understanding the stability of the uranyl moiety.

### 2.2 The Inverse Trans Influence.

The inverse trans influence (ITI) can be contrasted with the trans influence, which is a well understood thermodynamic property of transition metal complexes in square planar geometries. In complexes with a trans influence, two trans ligands share bonding molecular orbitals with $p_{x}$ and $d_{x 2-y_{2}}$ metal orbitals. When one M-L bond is strong, the orbital overlap is maximized with that ligand at the expense of bonding with the trans ligand. ${ }^{6}$

[^0]In contrast, axially symmetric high-valent uranium complexes exhibit an inverse trans influence, in which trans axial ligands mutually strengthen their bonding with the metal center, and equatorial bonding is weakened. This phenomenon is responsible for the stability and trans orientation of oxo ligands of the uranyl dication. Previous work in this field attributed $6 p_{z}$ mixing with the $5 f_{z 3}$ orbital to form a stabilized bonding molecular orbital with the axial ligands. ${ }^{7,8}$ However, later computational work showed that when 6 p orbitals were treated as part of a frozen core, a significant inverse trans influence was nevertheless observed. ${ }^{9}$ Work from our group has developed a ligand series for compounds of the general form $\mathrm{U}^{\mathrm{Vl}} \mathrm{O}(\mathrm{R})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, in which a correlation between the inverse trans influencing donation of the ligand and energy of axially antibonding complex $\sigma^{*}$ and $\pi^{*}$ molecular orbitals was observed. ${ }^{4}$ However, a single clear electronic explanation for the inverse trans influence remains elusive.

Compounds exhibiting an inverse trans influence can be synthesized and studied using a combination of experimental and computational techniques. The most important and clear metric is to examine the bond lengths of X -ray structures for differences in equatorial and axial metalligand bond lengths, when those ligands are identical. This has most effectively been illustrated in $\left[\mathrm{UOX}_{5}\right]^{-}(\mathrm{X}=\mathrm{F}, \mathrm{Cl}, \mathrm{Br})$ complexes, which show that the $\mathrm{U}-\mathrm{X}$ bond trans to the $\mathrm{U}=\mathrm{O}$ bond are shorter by $2-3 \mathrm{pm}$. These subtle differences in bond metrics can be supported by computed bond distances. ${ }^{4,8,9}$ O'Grady and Kaltsoyannis used these metrics to describe the inverse trans influence as a percentage by using the formula $\mathrm{ITI}=\left[r\left(\mathrm{An}-\mathrm{X}_{\text {trans }}\right) / \mathrm{r}\left(\mathrm{An}-\mathrm{X}_{\text {cis }}\right) \times 100 \%\right.$ in their work with uranium(VI) oxo pentahalide complexes. ${ }^{9}$ Additionally, since the inverse trans influence has a stabilizing effect on the complex (Figure 2.2.1), solution electrochemistry can be used to determine the stability imparted to the +6 or +5 oxidation state, and thus the extent to which a ligand imparts an inverse trans influence. ${ }^{4,10}$ Lastly, computational methods can be used to determine the energy cost from forcing strong trans donors into cis positions. ${ }^{7,11}$

### 2.3 Previous Reports of Uranium-Nitrogen Multiple Bonds.

Uranium-ligand multiple bonding is a topic of significant current interest, ${ }^{12,13}$ with recent landmark discoveries in uranium-nitrogen multiple bonding including the isolation of the first
examples of a terminal molecular uranium-nitride. ${ }^{14-18}$ There are now a number of examples of high valent uranium bis-imido complexes, ${ }^{5,19-34}$ and several examples of uranium(VI) oxo imido complexes. ${ }^{24,35,36}$ The synthesis of uranium(IV) mono-imido complexes has been successful with a variety of supporting ligands, ${ }^{35,37-41}$ whereas uranium(VI) mono-imido complexes were limited to two structurally related examples $\mathrm{U}^{\mathrm{V1}}(=\mathrm{NR}) \mathrm{F}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(\mathrm{R}=-\mathrm{SiMe}_{3}\right.$, Ph$)$ prior to this work. ${ }^{42}$ Subsequently, Meyer and coworkers published the uranium(VI) mono-imido complex, $\left[\left(\left({ }^{\mathrm{nP}, \mathrm{Me}} \mathrm{ArO}\right)_{3}\right.\right.$ tacn $\left.) \mathrm{U}^{\mathrm{Vl}}\left(=\mathrm{NCPh}_{3}\right)\right]\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{4}\right]$ by oxidation of $\left(\left({ }^{\mathrm{nP}, \mathrm{Me}} \mathrm{ArO}\right)_{3} \mathrm{tacn}\right) \mathrm{U}^{\mathrm{V}}\left(=\mathrm{NCPh}_{3}\right)$ with $\mathrm{Ag}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)\right]_{]}{ }^{43}$

As part of our studies of the inverse trans influence (ITI) in high-valent uranium complexes with axial symmetry, ${ }^{4,44,45}$ we demonstrated that reactive uranium(VI)-carbon bonds could be stabilized through coordination trans to a strong uranium-oxo multiple bond. ${ }^{4}$ As a step toward engendering the stabilization of uranium-ligand bonds through ITI stabilization with the imido ligand, we sought to explore the influence of the imido substituent on the reactivity of the imido ligand itself, the relative donating ability of various imido ligands toward high-valent uranium, and the extent of ITI stabilization relative to the oxo ligand.

The imido ligand is known to impart an ITI stabilization. ${ }^{46}$ Uranium bis(imido) complexes exhibit electronic structures similar to that of uranyl, with a larger degree of 5f-ligand covalency in the $U=N R$ bond relative to the $U=O$ bond. ${ }^{5}$ Recent work from Meyer and coworkers has alluded to the ability for the imido ligand to engage in varying degrees of ITI stabilization depending on the imido substituent. ${ }^{47}$ In this context, we turned our attention to mono-imido complexes to explore their electronic structures with variable ligands trans to the imido group. Synthetic pathways for formation of uranium imido linkages have primarily included the two-electron reduction of organoazides, ${ }^{19,21,28,41,48-55}$ as well as deprotonation of primary amides. ${ }^{14,24,32,38,50,56,57}$ In this work, we present the synthesis of the complex $\mathrm{U}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, which is oxidized to uranium $(\mathrm{VI})$ imido complexes for comparison with uranium $(\mathrm{VI})$ oxo and uranyl complexes.

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### 2.4 Results and discussion.

### 2.4.1. Synthesis and structural characterization.

Our group has described methods for the synthesis of uranium(VI) mono-oxo complexes, including the direct, one electron oxidation of a uranium $(\mathrm{V})$ oxo precursor, $\mathrm{U}^{\vee} \mathrm{O}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, with $\mathrm{Cu}(I I)$ salts. ${ }^{45}$ Encouraged by the reported synthesis of $\mathrm{U}^{\mathrm{VI}}\left(=\mathrm{NSiMe}_{3}\right) \mathrm{F}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ by Burns et al. using $\mathrm{AgPF}_{6},{ }^{42}$ we attempted the analogous oxidation reactions of the uranium $(\mathrm{V})$ imido precursor, $\mathrm{U}^{\vee}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (2.1) (Scheme 2.4.1), through divalent copper reagents. Complex 2.1 was conveniently obtained by the reported procedure, through addition of $\mathrm{Me}_{3} \mathrm{SiN}_{3}$ to $\mathrm{U}^{\mathrm{II}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} \cdot{ }^{49,58}$ Addition of either $\mathrm{CuBr}_{2}$ or $\mathrm{CuCl}_{2}$ to $\mathbf{2 . 1}$ led to the immediate formation of the corresponding uranium $(\mathrm{VI})$ products $\quad \mathrm{U}^{\mathrm{VI}}\left(=\mathrm{NSiMe}_{3}\right) \mathrm{Br}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} \quad$ (2.1-Br) and $\mathrm{U}^{\mathrm{V} 1}\left(=\mathrm{NSiMe}_{3}\right) \mathrm{Cl}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(2.1-\mathrm{Cl})$, respectively. Though the oxidation of uranium(IV) imido complexes with copper-based oxidants proved to be a broadly successful strategy in the synthesis of $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{U}^{\vee} \mathrm{X}(=\mathrm{NAr})\left(\mathrm{Ar}=2,6-{ }^{-} \mathrm{Pr}_{2} \mathrm{C}_{6} \mathrm{H}_{3}, \mathrm{X}=-\mathrm{F},-\mathrm{Cl},-\mathrm{Br},-\mathrm{I},-\mathrm{OTf},-\mathrm{SPh},-\mathrm{CCPh}\right)$ complexes, ${ }^{59-61}$ this reactivity had not been extended to the preparation of uranium(VI) imido complexes. The ${ }^{1} \mathrm{H}$ NMR spectra of $\mathbf{2 . 1 - B r}$ and $\mathbf{2 . 1 - C l}$ both exhibited two resonances for the bis(trimethylsilylamide) ligands in a $1: 1$ ratio, with one very broad resonance and one sharp resonance. The difference in the peak widths was attributed to steric clash between the bulky $\mathrm{SiMe}_{3}$ groups of the imido and amide ligands causing hindered rotation. ${ }^{4,42,44,45}$


Scheme 2.4.1 Synthesis of compounds 2.1, 2.1-CI, 2.1-Br, 2.1-O.
Having established the reactivity of the uranium $(\mathrm{V})$ mono-imido complex 2.1 toward copper oxidants, we turned to the one-electron reduction of nitrite, a protocol that we previously reported in the synthesis of uranium $(\mathrm{VI})$ mono-oxo complexes. ${ }^{45}$ Replacement of a uranium(IV)or uranium(V)-halide bond with nitrite led to spontaneous formation of the uranium(V)- or uranium $(\mathrm{VI})$-oxo product through loss of nitric oxide. Recent work from Cantat and coworkers showed that the use of $\left[\mathrm{Ph}_{4} \mathrm{P}\right]\left[\mathrm{NO}_{2}\right]$ rather than $\mathrm{NaNO}_{2}$ or $\mathrm{AgNO}_{2}$ allowed installation of the nitrite ion into an open coordination site, rather than through displacement of a halide. ${ }^{62}$ Addition of $\left[\mathrm{Ph}_{4} \mathrm{P}\right]\left[\mathrm{NO}_{2}\right]$ to 2.1 led to formation of the orange-red uranium(VI) oxo imido complex $\left[\mathrm{Ph}_{4} \mathrm{P}\right]\left[\mathrm{U}^{\mathrm{V}} \mathrm{O}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right](\mathbf{2 . 1} \mathbf{- O})$, in $69 \%$ yield (Scheme 2.4.1). In contrast to the oneelectron reduction of nitrite, the two other reported preparations of uranium mono-oxo/mono-imido
complexes were through hydrolysis of uranium(VI) bis-imido complexes, ${ }^{24}$ and through oxygen atom transfer to uranium(IV) mono-imido complexes. ${ }^{35,50}$

X-Ray structural analysis of $\mathbf{2 . 1} \mathbf{- B r}, \mathbf{2 . 1 - C I}$, and 2.1-O (Figures 2.4.1, 2.4.2, and 2.4.3) allowed comparison of the bond metrics with the structurally related oxo-halides $\mathrm{U}^{\mathrm{Vl}} \mathrm{OBr}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ and $\mathrm{U}^{\mathrm{Vl}} \mathrm{OCl}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3},{ }^{45}$ as well as the uranyl complex $\left[\mathrm{Na}(\mathrm{THF})_{2}\left[\mathrm{UO}_{2}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]{ }^{63}\right.$ In each case, the 2.1-X complex exhibited longer equatorial U-N bond lengths relative to the corresponding uranium oxo complexes, indicative of greater destabilization of the U-N bonds (Table 2.4.1). To support that these small differences in U-N bond lengths were not an artifact of crystal packing forces, we ran DFT calculations on $2.1-\mathrm{Br}$, 2.1-CI, and 2.1-O using a 60 electron core incorporating quasi-relativistic effects for uranium and $6-31 \mathrm{G}^{*}$ basis set for all other atoms. Though the differences in the bond lengths were small, they were well reproduced in the calculated geometries. Greater destabilization of the cis metal-ligand bonds relative to the strong trans-axial donor ligands is indicative of a more significant ITI, ${ }^{4,8,9,64,65}$ suggesting, surprisingly, that the electron-rich trimethylsilylimido donor ability is comparable to the oxo ligand.


Figure 2.4.1 Thermal ellipsoid plot of $2.1-\mathrm{Br}$ at $30 \%$ probability. Bond lengths ( A ) and angles ( ${ }^{\circ}$ ): $\mathrm{U}(1)-\mathrm{Br}(1) 2.7675(11), \mathrm{U}(1)-\mathrm{N}(1) 2.222(10), \mathrm{U}(1)-\mathrm{N}(2) 2.191(9), \mathrm{U}(1)-\mathrm{N}(3) 2.215(10), \mathrm{U}(1)-\mathrm{N}(4)$ 1.907(9), $\operatorname{Br}(1)-\mathrm{U}(1)-\mathrm{N}(4) 179.5(2), \mathrm{U}(1)-\mathrm{N}(4)-\mathrm{Si}(1) 177.2(5)$.


Figure 2.4.2 Thermal ellipsoid plot of 2.1-CI at $30 \%$ probability. Bond lengths ( $\AA$ ) and angles ( ${ }^{\circ}$ ): $\mathrm{U}(1)-\mathrm{Cl}(1) 2.593(4), \mathrm{U}(1)-\mathrm{N}(1) 2.184(11), \mathrm{U}(1)-\mathrm{N}(2) 2.197(13), \mathrm{U}(1)-\mathrm{N}(3) 2.197(13), \mathrm{U}(1)-\mathrm{N}(4)$ 1.922(11), $\mathrm{Cl}(1)-\mathrm{U}(1)-\mathrm{N}(4) 179.7(3), \mathrm{U}(1)-\mathrm{N}(4)-\mathrm{Si}(7)$ 178.6(7).


Figure 2.4.3 Thermal ellipsoid plot of 2.1-O at $30 \%$ probability. Hydrogen atoms, disorder of the methyl substituents of the imido ligand, and the $\left[\mathrm{Ph}_{4} \mathrm{P}\right]^{+}$ion are omitted for clarity. Bond lengths $(\AA)$ and angles ( ${ }^{\circ}$ : $\mathrm{U}(1)-\mathrm{N}(1) 2.348(3), \mathrm{U}(1)-\mathrm{N}(2) 2.347(3), \mathrm{U}(1)-\mathrm{N}(3) 2.346(3), \mathrm{U}(1)-\mathrm{N}(4)$ $1.980(3), \mathrm{U}(1)-\mathrm{O}(1) 1.805(2), \mathrm{O}(1)-\mathrm{U}(1)-\mathrm{N}(4) 179.82(12), \mathrm{U}(1)-\mathrm{N}(4)-\mathrm{Si}(1) 176.15(18)$.

Table 2.4.1 Experimental and calculated equatorial $\mathrm{U}-\mathrm{N}$ bond lengths in the 2.1-X and $\mathrm{U}^{\mathrm{VI}} \mathrm{OX}\left(\mathrm{N}^{*}\right)_{3}$ complexes $(\mathrm{X}=\mathrm{Br}, \mathrm{Cl}, \mathrm{O})$.

|  | $\begin{aligned} & \mathrm{U}-\mathrm{N}_{\text {eq }} \\ & \text { Exp. } \\ & \hline \end{aligned}$ | Calc. |
| :---: | :---: | :---: |
| 2.1-Br |  |  |
| $\mathrm{U}^{\mathrm{Vl} 1}\left(=\mathrm{NSiMe}_{3}\right) \mathrm{Br}\left(\mathrm{N}^{*}\right)_{3}{ }^{\text {a }}$ | 2.209(11) | 2.235 |
| $\mathrm{U}^{\mathrm{v}} \mathrm{OBr}\left(\mathrm{N}^{*}\right)_{3}^{\text {a }}$ as ${ }^{\text {a }}$ | 2.200 (3) | 2.219 |
| 2.1-CI |  |  |
| $\mathrm{U}^{\mathrm{Vl}}\left(=\mathrm{NSiMe}_{3}\right) \mathrm{Cl}\left(\mathrm{N}^{*}\right)_{3}{ }^{\text {a }}$ | 2.205(15) | 2.235 |
| $\mathrm{U}^{\mathrm{V}} \mathrm{OCl}\left(\mathrm{N}^{*}\right)_{3}{ }^{\text {a }}$ ab | 2.193 (2) | 2.221 |
| 2.1-O |  |  |
| $\left[\mathrm{Ph}_{4} \mathrm{P}\right]\left[\mathrm{U}^{\mathrm{Vl}}\left(=\mathrm{NSiMe}_{3}\right) \mathrm{O}\left(\mathrm{N}^{*}\right)_{3}\right]^{\text {a }}$ | 2.347 (4) | 2.389 |
| $\left[\mathrm{Na}(\mathrm{THF})_{2}\right]\left[\mathrm{U}^{\mathrm{V} 1} \mathrm{O}_{2}\left(\mathrm{~N}^{*}\right)_{3}\right]^{\text {a63 }}$ | 2.310 (5) | 2.350 |

The accessibility of the 5 -coordinate complexes $\mathbf{2 . 1} \mathbf{- C I}, \mathbf{2 . 1 - B r}$, and $\mathbf{2 . 1 - O}$ suggested that the coordination sphere in 2.1 was not completely saturated. We anticipated that a larger uranium(IV) ion in this coordination environment would prove susceptible to further reactivity. Treatment of 2.1 with excess $\mathrm{KC}_{8}$ led to smooth conversion to the expected reduction product, $\mathrm{K}\left[\mathrm{U}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right](\mathbf{2 . 1 - K})$, isolated as a pink solid in $87 \%$ yield (Scheme 2.4.2). The ${ }^{1} \mathrm{H}$ NMR spectrum of 2.1-K exhibited an extremely broad resonance at -7.9 ppm , corresponding to the $-\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}$ ligands and a sharp resonance at 34.6 ppm , corresponding to the $=\mathrm{NSiMe}_{3}$ ligand.

(2.1-K)
(2.2)


Scheme 2.4.2 Synthesis of compounds 2.1-K, 2.2, 2.3, and 2.3-K.

The X-ray crystal structure of 2.1-K was obtained as the benzene- $d_{6}$ solvate, following suspension in benzene- $d_{6}$, removal of the volatiles, and crystallization from pentane (Figure 2.4.4). The $\mathrm{K}^{+}$ion closely associated with the imido ligand at a $\mathrm{K}-\mathrm{N}$ distance of 2.957 (3) $\AA$, analogous to the structure of the reported anilide complex $\left[\mathrm{Li}\left(\mathrm{OEt}_{2}\right)\right]\left[\mathrm{U}\left(=\mathrm{NSiMe}_{3}\right)(\mathrm{NAdAr})_{3}\right](\mathrm{Ar}=$ 3,5 -dimethylphenyl), ${ }^{41}$ which also exhibited close association of the alkali metal to the nitrogen atom of the imido ligand. The U-N bond length of the imido ligand in 2.1-K was 2.010(3) $\AA$, and the average $\mathrm{U}-\mathrm{N}$ bond length of the amido ligands was $2.378(4) \AA$, lengthened relative to the
corresponding metrics of 2.1 at $1.910(6)$ and $2.295(10) \AA$, respectively, ${ }^{49}$ due to the larger ionic radius of the uranium(IV) cation. ${ }^{66}$


Figure 2.4.4. Thermal ellipsoid plot of 2.1-K at $30 \%$ probability. Hydrogen atoms are omitted for clarity. Bond lengths ( $\AA$ ) and angles $\left({ }^{\circ}\right)$ : $1-\mathrm{K}-\mathrm{U}(1)-\mathrm{N}(1) 2.368(3), \mathrm{U}(1)-\mathrm{N}(2) 2.352(3), \mathrm{U}(1)-\mathrm{N}(3)$ $2.415(3), \mathrm{U}(1)-\mathrm{N}(4) 2.010(3), \mathrm{U}(1)-\mathrm{N}(4)-\mathrm{Si}(1)$ 156.90(16).

The trityl analog, $\mathrm{U}\left(=\mathrm{NCPh}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (2.3), could be prepared by the room temperature addition of $\mathrm{Ph}_{3} \mathrm{CN}_{3}$ to $\mathrm{U}^{1 I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ in $\mathrm{Et}_{2} \mathrm{O}$ to generate 2.3. Treatment of 2.3 with excess $\mathrm{KC}_{8}$ gave the analogous uranium(IV) compound, $\mathrm{K}\left[\mathrm{U}\left(=\mathrm{NCPh}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ (2.3-K), which crystallized from toluene as a pale orange solid in $50 \%$ yield. The ${ }^{1} \mathrm{H}$ NMR spectrum for 2.3-K showed a broad resonance at -8.9 ppm , corresponding to the $-\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}$ ligand protons, and three resonances at 41.1, 13.8, and 12.0 ppm, corresponding to the aryl resonances from the $=\mathrm{NCPh}_{3}$ ligand. X-Ray quality crystals were obtained by crystallization from toluene, following the reaction conducted in THF, filtration over Celite, and removal of the volatiles (Figure 2.4.5). In contrast to $2.1-\mathrm{K}$, the $\mathrm{K}^{+}$ion is neither coordinated to an aryl solvent nor to the imido ligand, but instead interacts with two of the phenyl rings of the trityl group and is solvated by three THF molecules. The U-N bond length of the imido ligand in $2.3-\mathrm{K}$ was slightly shorter than in 2.1-K at $1.9926(14) \AA$, and the average $U-N$ bond length of the amido ligands was comparable to those in 2.1-K at $2.3870(18) \AA$. Similar to $2.1-\mathrm{K}$, the U-N bonds in $\mathbf{2 . 3}$-K are lengthened with respect to its
parent uranium $(\mathrm{V})$ complex 2.3, which exhibited $\mathrm{U}-\mathrm{N}$ imido and average amido bond lengths of 1.959(5) and 2.264(3) Å respectively.


Figure 2.4.5. Thermal ellipsoid plot of $\mathbf{2 . 3} \mathbf{- K}$ at $30 \%$ probability. Hydrogen atoms are omitted for clarity. Bond lengths $(\AA \AA)$ and angles $\left({ }^{\circ}\right): ~ \mathrm{U}(1)-\mathrm{N}(1) 2.3870(14), \mathrm{U}(1)-\mathrm{N}(2) 2.3763(15), \mathrm{U}(1)-\mathrm{N}(3)$ $2.3978(14), \mathrm{U}(1)-\mathrm{N}(4) 1.9926(14), \mathrm{U}(1)-\mathrm{N}(4)-\mathrm{C}(19) 169.82$ (12).

Noting the evidently high charge density at the nitrogen atom of the imido ligands in 2.1-K as judged by the close association of the $\mathrm{K}^{+}$ions in the crystal structures, we investigated the reactivity of these complexes with electrophiles. Additionally, 2.3-K was reacted with electrophiles for comparison. To the best of our knowledge there are no examples of direct addition of an electrophile to a uranium imido complex, though the multiple-bond metathesis reactivity has been noted previously, ${ }^{51}$ and similar reactivity was observed by Liddle and coworkers in the silylation of the uranium $(\mathrm{V})$ nitride, $\left[\mathrm{Na}(12-\text { crown }-4)_{2}\right]\left[\mathrm{U}^{\mathrm{V}}(\equiv \mathrm{N})\left(\right.\right.$ Tren $\left.\left.^{\mathrm{TIPS}}\right)\right]$, to form $\mathrm{U}^{\mathrm{V}}\left(=\mathrm{NSiMe}_{3}\right)\left(\right.$ Tren $\left.^{\text {TIPS }}\right) .{ }^{16}$ Silylation of an imido was also implicated in the formation of an unusual uranium(IV) azido amide complex, $[\mathrm{K}(18$-crown- 6$)]\left[\mathrm{U}\left(\mathrm{N}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]\left[\mathrm{OSi}\left(\mathrm{O}^{t} \mathrm{Bu}\right)_{3}\right]_{3}\right]$, obtained from the reaction of $[\mathrm{K}(18$ -crown-6) $]\left[\mathrm{U}\left[\mathrm{OSi}\left(\mathrm{O}^{t} \mathrm{Bu}\right)_{3}\right]_{4}\right]$ with $\mathrm{Me}_{3} \mathrm{SiN}_{3}$, though only as a minor side product. ${ }^{19}$ The methylation of 2.1-K with MeOTf was carried out successfully, which cleanly produced $U^{I V}\left[N\left(S_{i M e}^{3}\right) \mathrm{Me}\right][\mathrm{N}(\mathrm{SiMe}-$
$\left.\left.{ }_{3}\right)_{2}\right]_{3}$ (2.2) in $68 \%$ yield (Scheme 2.4.2). In contrast, addition of $\mathrm{Me}_{3} \mathrm{SiOTf}$ to $\mathbf{2 . 1}$-K led to formation of a complex mixture of products that did not include the known complex $\mathrm{U}^{1 \mathrm{~V}}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{4} .{ }^{67}$

The ${ }^{1} \mathrm{H}$ NMR of 2.2 displayed a single, broad resonance for the three bis(trimethylsilyl)amide ligands at -4.6 ppm and two sharp resonances for the methyl(trimethylsilyl)amide ligand at 76.9 and -3.3 ppm , indicating that the trimethylsilyl groups freely rotated at room temperature. The X-ray structure of 2.2 (Figure 2.4.6) exhibited close contact of the added methyl group with the uranium center, with a U-C distance of $2.869 \AA$. The close contact of the methyl group with the uranium ion is nearly in the range of some uraniumcarbon single bonds. ${ }^{68,69}$ This structural perturbation is also evident in the acute $\mathrm{U}-\mathrm{N}-\mathrm{C}$ bond angle, at $99.79^{\circ}$. The $\mathrm{U}-\mathrm{N}$ bond lengths of the $-\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}$ ligands were on average 2.2888(19) $\AA$, similar to those of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{4}$ at $2.297(2) \AA \AA^{67}$ Reaction of 2.3-K with $\mathrm{Me}_{3} \mathrm{SiOTf}$ or Mel resulted in oxidation of 2.3-K to yield $\mathbf{2 . 3}$ and unidentified side products (Scheme 2.4.2). This reactivity differed from that of 2.1-K possibly due to the decrease in charge density at the imido nitrogen atom in $2.3-\mathrm{K}$, as evidenced by the coordination of the $\mathrm{K}^{+}$ion with the trityl aryl groups instead of the imido nitrogen atom in its solid state structure. Reaction of $2.3-\mathrm{K}$ with MeOTf resulted in a mixture of as yet unidentified products.


Figure 2.4.6. Thermal ellipsoid plot of 2.2 at $30 \%$ probability. Hydrogen atoms are omitted for clarity. Bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right): ~ \mathrm{U}(1)-\mathrm{N}(1) 2.290(2), \mathrm{U}(1)-\mathrm{N}(2) 2.2978(19), \mathrm{U}(1)-\mathrm{N}(3)$ 2.2786(17), U(1)-N(4) 2.2168(19), U(1)-N(4)-C(1) 99.79(13).

After observing the reactivity of 2.1-K with electrophiles, we reacted 2.1 - K with $\mathrm{Ph}_{2} \mathrm{CN}_{2}$ with the hypothesis that two-electron reduction of $\mathrm{Ph}_{2} \mathrm{CN}_{2}$ would occur to release $\mathrm{N}_{2}$ gas and install a $\left[\mathrm{Ph}_{2} \mathrm{C}\right]^{2-}$ ligand at the uranium center. However, none of the desired product $\mathrm{K}\left[\mathrm{U}^{\mathrm{VI}}\left(=\mathrm{NSiMe}_{3}\right)\left(=\mathrm{CPh}_{2}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ was observed after one day. Over the course of several days 2.1-K began to decompose, and a peak corresponding to $\mathrm{HN}\left(\mathrm{SiMe}_{3}\right)_{2}$ appeared in ${ }^{1} \mathrm{H}$ NMR aliquots of the reaction mixture. We hypothesized that 2.1-K was not a powerful enough reductant to react with $\mathrm{Ph}_{2} \mathrm{CN}_{2}$, and that coordination of an external reductant, such as potassium naphthalenide, to $2.1-\mathrm{K}$ would allow the reduction of $\mathrm{Ph}_{2} \mathrm{CN}_{2}$. We attempted to synthesize $[\mathrm{K}($ naphthalene $)]\left[\mathrm{U}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ by reduction of 2.1 by potassium graphite in the presence of naphthalene and by addition of potassium naphthalenide to 2.1-K. However, in all cases we observed the formation of a uranium(IV) dimer bridged by a single naphthalene moiety, $\left[\mathrm{K}\left[\mathrm{U}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]_{2}(\mu\right.$-naphthalene) (2.1-Knaph) (Scheme 2.4.3). Reaction of 2.1Knaph with additional equivalents of potassium graphite resulted in formation of the cyclometalated complex, $\mathrm{U}^{\mathrm{IV}}\left[\mathrm{CH}_{2} \mathrm{SiMe}_{2} \mathrm{~N}\left(\mathrm{SiMe}_{3}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} .{ }^{70,71}$ The ${ }^{1} \mathrm{H}$ NMR of 2.1-Knaph contains a sharp peak at 34.36 ppm , corresponding to the $\left[=\mathrm{NSiMe}_{3}\right.$ ] ligand and an extremely broad peak centered at -1.22 ppm , corresponding to the trimethylsilyl amide ligands. Additionally, two multiplets were centered at 7.65 and 7.26 ppm in the ${ }^{1} \mathrm{H}$ NMR spectrum, corresponding to the bridging naphthalene moiety.


Scheme 2.4.3 Synthesis of 2.1-Knaph.

The X-ray structure of 2.1-Knaph revealed a similar structure to 2.1-K (Figure 2.4.7). The U-N bond length of the imido ligand in 2.1-Knaph was 2.0198(16) Å, which was comparable to
that in 2.1-K at $2.010(3) \AA$. The $U(1)-N(1)$ and $U(1)-N(2)$ amide bond lengths were also similar between the two compounds and averaged 2.3520(16) Å in 2.1-Knaph compared to 2.360(3) $\AA$ in 2.1-K. Notably, in 2.1-Knaph the potassium ion was slightly removed from its coordination to the amide and imido ligands, resulting in a shortening of the $\mathrm{U}(1)-\mathrm{N}(3)$ bond length to 2.3947(16) $\AA$ when compared to 2.415(3) $\AA$ in 2.1-K.


Figure 2.4.7. Thermal ellipsoid plot of 2.1-Knaph at $30 \%$ probability. Bond lengths ( $\AA$ ) and angles $\left({ }^{\circ}\right): ~ \mathrm{U}(1)-\mathrm{N}(1) 2.3480(15), \mathrm{U}(1)-\mathrm{N}(2) 2.3561(16), \mathrm{U}(1)-\mathrm{N}(3) 2.3947(16), \mathrm{U}(1)-\mathrm{N}(4) 2.0198(16)$, $\mathrm{N}(3)-\mathrm{K}(1)$ 2.9688(17), $\mathrm{N}(4)-\mathrm{K}(1)$ 2.8793(17), U(1)-N(4)-Si(7) 162.16(10).

### 2.2.2. Electronic characterization of uranium imido complexes

Electrochemical analysis yielded insight into the different imido complexes (Table 2.4.2). In the previous report of the cyclic voltammetry of $\mathbf{2 . 1}$, a reversible oxidation feature at -0.41 V versus ferrocene was observed in THF, with [ ${ }^{n} \mathrm{Bu}_{4} \mathrm{~N}^{\mathrm{N}}\left[\mathrm{BF} F_{4}\right]$ serving as the electrolyte. ${ }^{42}$ The cyclic voltammograms of $\mathbf{2 . 1}$ and $\mathbf{2 . 3}$ were collected in dichloromethane with [ $\left.{ }^{n} \mathrm{Bu}_{4} N\right]\left[P F_{6}\right.$ ] electrolyte (Figure 2.4.9). An irreversible $\mathrm{U}(\mathrm{VI} / \mathrm{V})$ couple was observed in 2.1, with an $E_{\mathrm{pa}}$ of +0.21 V and an $E_{\mathrm{pc}}$ of -0.79 V . The $\mathrm{E}_{1 / 2}$ of this couple was obtained from the differential pulse voltammogram, which revealed a reversible potential of +0.26 V . Therefore, the apparent irreversibility of this couple is attributed to a large shift in the cathodic wave. By comparison, the $\mathrm{U}(\mathrm{VI} / \mathrm{V})$ couple in $\mathbf{2 . 3}$ was reversible under all conditions, at a potential of +0.38 V . The higher potential $\mathrm{U}(\mathrm{VI} / \mathrm{V})$ couple in $\mathbf{2 . 3}$ relative to $\mathbf{2 . 1}$ indicates that the trimethylsilylimido ligand more significantly stabilizes the 6+ oxidation state than the electron deficient tritylimido ligand. The $\mathrm{U}(\mathrm{V} / \mathrm{IV})$ couple was reversible in both complexes, appearing at -1.35 V in 2.1 and -1.31 V in 2.3.


Figure 2.4.8. Cyclic voltammogram of 2.1 (top) and 2.3 (bottom) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, at a scan rate of 250 $\mathrm{mV} / \mathrm{s}$ with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ electrolyte.

Table 2.4.2. Reduction potentials of the imido complexes determined by DPV measurements, compared to the previously reported mono-oxo complexes. ${ }^{4,45}$

|  | $E_{1 / 2}(\mathrm{~V})$ |  |
| :---: | :---: | :---: |
|  | $\mathrm{U}(\mathrm{VI} / \mathrm{V})$ | U(V/IV) |
| 2.1 | +0.26 | -1.35 |
| $\mathrm{U}^{\mathrm{V}}\left(=\mathrm{NSiMe}_{3}\right)\left(\mathrm{N}^{*}\right)_{3}{ }^{\text {a }}$ |  |  |
| 2.3 | +0.38 | -1.31 |
| $\mathrm{U}^{\mathrm{V}}\left(=\mathrm{NCPh}_{3}\right)\left(\mathrm{N}^{*}\right)_{3}{ }^{\text {a }}$ |  |  |
| 2.1-Br | -0.40 | -1.28 |
| $\mathrm{U}^{\mathrm{Vl}}\left(=\mathrm{NSiMe}_{3}\right) \mathrm{Br}\left(\mathrm{N}^{*}\right)_{3}{ }^{\text {a }}$ |  |  |
| 2.1-CI | -0.47 | -1.25 |
| $\mathrm{U}^{\mathrm{Vl}}\left(=\mathrm{NSiMe}_{3}\right) \mathrm{Cl}\left(\mathrm{N}^{*}\right)_{3}{ }^{\text {a }}$ |  |  |
| 2.1-O | -2.34 | - |
| $\left[\mathrm{Ph}_{4} \mathrm{P}\right]\left[\mathrm{U}^{\mathrm{V1}}\left(=\mathrm{NSiMe}_{3}\right) \mathrm{O}\left(\mathrm{N}^{*}\right)_{3}\right]^{\text {a }}$ |  |  |
| $\mathrm{U}^{\mathrm{V} 1} \mathrm{OBr}\left(\mathrm{N}^{*}\right)_{3}{ }^{\text {a,4b }}$ | -0.21 | - |
| $\mathrm{U}^{\mathrm{Vl}} \mathrm{OCl}\left(\mathrm{N}^{*}\right)_{3}{ }^{\text {a4,4b }}$ | -0.43 | - |

The strong donating ability of the trimethylsilylimido ligand in $\mathbf{2 . 1}$ led us to consider its ability to stabilize the $\mathrm{U}(\mathrm{VI})$ oxidation state relative to the oxo ligand. Cyclic voltammetry was
collected on 2.1-Br and 2.1-Cl for comparison to the corresponding oxo-halides. ${ }^{68,69}$ The cyclic voltammogram of $\mathbf{2 . 1 - B r}$ displayed two redox features (Figure 2.4.10), assigned as a quasireversible $\mathrm{U}(\mathrm{VI} / \mathrm{V})$ couple centered at -0.40 V and a reversible $\mathrm{U}(\mathrm{V} / \mathrm{IV})$ couple at -1.28 V . The poor reversibility of the first reduction feature is due to a large shift in the return oxidation wave, with low current intensity. This behavior is attributed to chemical loss of the bromide ligand upon reduction. In contrast, the two redox couples were reversible in $\mathbf{2 . 1} \mathbf{- C l}$, centered at -0.47 V and 1.25 V , respectively. Surprisingly, in both $\mathbf{2 . 1}-\mathrm{Br}$ and $\mathbf{2 . 1} \mathbf{- C I}$ the $\mathrm{U}(\mathrm{VI} / \mathrm{V})$ couple were measured at more reducing potentials than the analogous features in $U^{V I}(\mathrm{O}) \operatorname{Br}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ and $\mathrm{U}^{\mathrm{VI}}(\mathrm{O}) \mathrm{Cl}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, which appear at -0.21 V and -0.43 V , respectively, indicating that the stabilization of the $6+$ oxidation state is comparable in the presence of either the trimethylsilylimido ligand or the oxo ligand. The cyclic voltammogram of 2.1-0 revealed a significant shift in the $\mathrm{U}(\mathrm{VI} / \mathrm{V})$ couple, exhibiting an irreversible reduction identified from differential pulse voltammetry (DPV) at -2.34 V . The strong stabilization of the 6+ oxidation state in 2.1-O is reminiscent of complexes of $\mathrm{U}^{\mathrm{VI}} \mathrm{O}_{2}{ }^{2+}$.


Figure 2.4.9. Cyclic voltammetry of $\mathbf{2 . 1}-\mathrm{Br}$ (top), 2.1- Cl (middle), and 2.1-O (bottom) at a scan rate of $250 \mathrm{mV} / \mathrm{s}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, with 0.1 M [ $\left.{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ supporting electrolyte.

### 2.5 Summary.

The reactivity and increase in donating ability, with respect to analogous uranium(VI) oxo complexes, of the uranium imido complexes shown here demonstrates that there is still much to learn about the behavior of complexes bearing uranium-nitrogen multiple bonds. In this work, we observed the unexpected one-electron transfer reactions involved in the preparation of uranium mono-imido complexes in the $4+$, $5+$, and $6+$ oxidation states. Among these was the first direct synthesis of a uranium oxo/imido complex through one-electron oxidation and first instance of uranium-imido complexes reacting with electrophiles.

### 2.6 Experimental.

### 2.6.1 Methods.

All reactions and manipulations were performed under an inert atmosphere $\left(\mathrm{N}_{2}\right)$ using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at $150^{\circ} \mathrm{C}$ prior to use. Unless otherwise noted, reactions were conducted in 20 mL scintillation vials in approximately $5-10 \mathrm{~mL}$ of solvent. ${ }^{1} \mathrm{H}$ NMR were obtained on a Bruker DMX300 Fourier transform NMR spectrometer at 300 MHz . Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks. Elemental analyses were performed at the University of California, Berkeley Microanalytical Facility using a Perkin-Elmer Series II 2400 CHNS analyzer. The infrared spectra were obtained from $400-4000 \mathrm{~cm}^{-1}$ using a Perkin Elmer 1600 series infrared spectrometer.

### 2.6.2 Materials.

Tetrahydrofuran, $\mathrm{Et}_{2} \mathrm{O}, \mathrm{CH}_{2} \mathrm{Cl}_{2}$, hexanes, pentane, and toluene were purchased from Fisher Scientific. These solvents were sparged for 20 min with dry argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina, respectively (for hexanes and pentane), or two columns of neutral alumina (for THF, $\mathrm{Et}_{2} \mathrm{O}$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ). All solvents were stored over $3 \AA$ molecular sieves. Deuterated
solvents were purchased from Cambridge Isotope Laboratories, Inc. and stored over potassium mirror overnight prior to use. Starting materials: $\mathrm{Ul}_{3}(\mathrm{THF})_{4},{ }^{72} \mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3},{ }^{73} 2.1,{ }^{49}$ and $2 . \mathbf{3}^{11}$ were prepared according to the reported procedures.

### 2.6.3 Synthesis of $\mathrm{U}(=\mathrm{NSiMe} 3) \mathrm{Br}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(2.1-\mathrm{Br})$.

To a stirred solution of $\mathrm{U}\left[\left(\mathrm{NSiMe}_{3}\right)_{2}\right]_{3}(150 \mathrm{mg}, 0.20 \mathrm{mmol}, 1.00$ equiv $)$ in hexanes, was added trimethylsilyl azide ( $23 \mathrm{mg}, 0.20 \mathrm{mmol}, 1.00$ equiv). After stirring for 10 min , the volatiles were removed under reduced pressure. The crude reaction mixture was dissolved in THF, and $\mathrm{CuBr}_{2}$ (228 mg, $1.02 \mathrm{mmol}, 5.00$ equiv) was added. After stirring for 1 h the reaction mixture was filtered over Celite suspended in a glass pipet, and the volatiles were removed under reduced pressure. The resulting residue was extracted with hexanes, filtered over Celite, and recrystallized from minimal hexanes to yield 2.1-Br as a dark red solid. Yield: $130 \mathrm{mg}, 0.15 \mathrm{mmol}$, $79 \%$. ${ }^{1}$ H NMR (benzene- $d_{6}$ ): $0.84(27 \mathrm{H}), 0.71(27 \mathrm{H}),-0.05(9 \mathrm{H})$. IR (Nujol mull): 1302 ( vw ), 1249 (s), 1170 (vw), 1109 (vw), 982 ( vw ), 922 (m), 848 (vs), 773 (m), 722 (vw), 654 (s), 621 (m), 566 (vw) $\mathrm{cm}^{-1}$. Elemental analysis found (calculated) for $\mathrm{C}_{21} \mathrm{H}_{63} \mathrm{BrN}_{4} \mathrm{Si}_{7} \mathrm{U}: \mathrm{C}, 28.32$ (28.46); H 6.96 (7.17); N 6.16 (6.32).

### 2.6.4 Synthesis of $\mathrm{U}\left(=\mathrm{NSiMe}_{3}\right) \mathrm{Cl}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(2.1-\mathrm{Cl})$.

To a stirred solution of $\mathrm{U}\left[\left(\mathrm{NSiMe}_{3}\right)_{2}\right]_{3}(150 \mathrm{mg}, 0.20 \mathrm{mmol}, 1.00$ equiv) in hexanes, was added trimethylsilyl azide ( $23 \mathrm{mg}, 0.20 \mathrm{mmol}, 1.00$ equiv). After stirring for 10 min , the volatiles were removed under reduced pressure. The crude reaction mixture was dissolved in THF and $\mathrm{CuCl}_{2}$ ( $137 \mathrm{mg}, 1.02 \mathrm{mmol}, 5.00$ equiv) was added. After stirring for 1 h , the reaction mixture was filtered over Celite suspended in a glass pipet, and the volatiles were removed under reduced pressure. The resulting residue was extracted with hexanes, filtered over Celite, and recrystallized from minimal hexanes to yield $\mathbf{2 . 1} \mathbf{- C l}$ as a dark red solid. Yield: $70 \mathrm{mg}, 0.08 \mathrm{mmol}$, $45 \%$. ${ }^{1}$ H NMR (benzene- $d_{6}$ ): $0.84(27 \mathrm{H}), 0.62(27 \mathrm{H}), 0.00(9 \mathrm{H})$. IR (Nujol mull): 1303 (vw), 1261 (m), 1248 (s), 1152 (vw), 1085 (vw), 922 (m), 848 (vs), 774 (m), 722 (w), $698(\mathrm{vw}), 681(\mathrm{vw}), 654$ (s), 621 (m). Elemental analysis found (calculated) for $\mathrm{C}_{21} \mathrm{H}_{63} \mathrm{ClN}_{4} \mathrm{Si}_{7} \mathrm{U}: \mathrm{C}, 29.89$ (29.96); H 7.59 (7.54); N 6.48 (6.66).

### 2.6.5 Synthesis of $\mathrm{Ph}_{4} \mathrm{P}\left[\mathrm{U}\left(=\mathrm{NSiMe}_{3}\right) \mathrm{O}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right](2.1-\mathrm{O})$.

To a stirred solution of $\mathrm{U}\left[\left(\mathrm{NSiMe}_{3}\right)_{2}\right]_{3}(100 \mathrm{mg}, 0.14 \mathrm{mmol}, 1.00$ equiv) in hexanes was added trimethylsilyl azide ( $16 \mathrm{mg}, 0.14 \mathrm{mmol}, 1.00$ equiv). The crude reaction mixture was dissolved in THF, and tetraphenylphosphonium nitrite ( $61 \mathrm{mg}, 0.16 \mathrm{mmol}, 1.1$ equiv) was added. After stirring for 10 minutes, the mixture was filtered over Celite suspended in a glass pipet, and the volatiles were removed under reduced pressure. The product was then dissolved in toluene and layered with pentane to yield $\mathbf{2 . 1 - O}$ as a dark orange solid. Yield: $99 \mathrm{mg}, 0.09 \mathrm{mmol}, 69 \% .{ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $8.19(8 \mathrm{H}), 8.09(4 \mathrm{H}), 7.83(8 \mathrm{H}), 0.91(54 \mathrm{H}), 0.09(9 \mathrm{H})$. IR (Nujol mull): 2187 (w), 2081 (w), 1241 (m), 1109 (m), 1026 (w), 999 (w), 951 (s), 838 (s), 774 (w), 754 (w), 723 (m), 689 (m), 662 (m), 607 (w), 526 (m). Elemental analysis found (calculated) for $\mathrm{C}_{45} \mathrm{H}_{83} \mathrm{~N}_{4} \mathrm{OPSi}_{7} \mathrm{U}: \mathrm{C}, 46.36$ (46.52); H 7.09 (7.20); N 4.69 (4.82).

### 2.6.6 Synthesis of $\mathrm{K}\left[\mathrm{U}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ (2.1-K).

To a stirred solution of $\mathrm{U}\left[\left(\mathrm{NSiMe}_{3}\right)_{2}\right]_{3}(100 \mathrm{mg}, 0.14 \mathrm{mmol}, 1.00$ equiv) in hexanes was added trimethylsilyl azide ( $16 \mathrm{mg}, 0.14 \mathrm{mmol}, 1.00$ equiv). The crude reaction mixture was dissolved in THF and cooled to $-21^{\circ} \mathrm{C}$ before adding $\mathrm{KC}_{8}$ ( $28 \mathrm{mg}, 0.20 \mathrm{mmol}, 1.5$ equiv) and stirring for 10 minutes. The mixture was then filtered over Celite suspended in a glass pipet, and the volatiles were removed under reduced pressure. The resulting residue was extracted with pentane, filtered over Celite, and the volatiles were removed under reduced pressure. The residue was dissolved in benzene, and the volatiles were removed under reduced pressure before crystallizing the product from a small volume of pentane to yield $\mathbf{2 . 1} \mathbf{- K}$ as a light pink solid. X-ray structural analysis of a sample prepared with benzene- $d_{6}$ indicated that $\mathbf{2 . 1 - K}$ crystallized as $\left[K\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)\right]\left[\mathrm{U}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right.$, though desolvation was confirmed by elemental analysis. Yield: $112 \mathrm{mg}, 0.12 \mathrm{mmol}, 87 \%{ }^{1} \mathrm{H}$ NMR (benzene- $\mathrm{d}_{6}$ ): $34.63(9 \mathrm{H}),-7.87$ ( 54 H ). IR (Nujol mull): 2205 (w), 2101 (w), 1249 (s), 1180 (w), 1012 (s), 944 (s), 840 (s), 770 (m), 663 (m), 601 (m), 511 (w). Elemental analysis found (calculated) for $\mathrm{C}_{21} \mathrm{H}_{63} \mathrm{KN}_{4} \mathrm{Si}_{7} \mathrm{U}: \mathrm{C}, 29.52$ (29.83); H 7.49 (7.51); N 6.32 (6.63).

### 2.6.7 Synthesis of $\left[\mathrm{K}\left[\mathrm{U}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]\right]_{2}$ ( $\mu$-naphthalene) (2.1-Knaph).

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To a solution of 2.1 ( $100 \mathrm{mg}, 0.124 \mathrm{mmol}$ ) in hexanes was added potassium graphite (17 $\mathrm{mg}, 0.124 \mathrm{mmol})$. The reaction mixture was filtered over Celite suspended in a glass pipet, and naphthalene ( $16 \mathrm{mg}, 0.124 \mathrm{mmol}$ ) was added to the reaction mixture. Crystallization from minimal hexanes at $-21^{\circ} \mathrm{C}$ gave light pink crystals of 2.1-Knaph. ${ }^{1} \mathrm{H}$ NMR (benzene-d6): $34.36(18 \mathrm{H})$, $7.65(4 \mathrm{H}), 7.26(4 \mathrm{H}),-1.22(108 \mathrm{H})$.

### 2.6.8 Synthesis of $\mathrm{U}\left[\mathrm{NMe}\left(\mathrm{SiMe}_{3}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(2.2)$.

To a stirred solution of 2.1-K ( $239 \mathrm{mg}, 0.26 \mathrm{mmol}$, 1 equiv) in hexanes was added methyl triflate ( $63 \mathrm{mg}, 0.386 \mathrm{mmol}, 1.5$ equiv). The reaction mixture was stirred for 10 minutes, filtered over Celite suspended in a glass pipet, and the volatiles were removed under reduced pressure. Recrystallization from minimal $\left(\mathrm{SiMe}_{3}\right)_{2} \mathrm{O}$ at $-21^{\circ} \mathrm{C}$ gave light brown crystals of 2.2. Yield: 144 $\mathrm{mg}, 0.18 \mathrm{mmol}, 68 \% .{ }^{1} \mathrm{H}$ NMR (benzene- $\mathrm{d}_{6}$ ): $76.93(3 \mathrm{H}),-3.21(9 \mathrm{H}),-4.63(54 \mathrm{H})$. IR (Nujol mull): 1250 (m), 904 (s), 848 (s), 772 (m), 722 (m), 666 (w), 612 (w). Elemental analysis found (calculated) for $\mathrm{C}_{22} \mathrm{H}_{66} \mathrm{~N}_{4} \mathrm{Si}_{7} \mathrm{U}: \mathrm{C}, 31.78$ (32.17); H, 7.99 (8.10); N, 6.54 (6.82).

### 2.6.9 Synthesis of $\mathrm{K}\left[\mathrm{U}\left(=\mathrm{NCPh}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3]}(2.3-\mathrm{K})\right.$.

To a solution of $2.3(58 \mathrm{mg}, 0.06 \mathrm{mmol})$ in 4 mL of THF, $\mathrm{KC}_{8}(8 \mathrm{mg}, 0.06 \mathrm{mmol}, 1.00$ equiv) was added. After stirring for 10 minutes, the reaction mixture was filtered over Celite, and the volatiles were removed under reduced pressure. The crude material was recrystallized from minimal toluene at $-21^{\circ} \mathrm{C}$ to yield pale orange crystals of $2.3-\mathrm{K}$. Yield: $30 \mathrm{mg}, 0.03 \mathrm{mmol}, 50 \%$. ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $41.10(6 \mathrm{H}), 13.79(6 \mathrm{H}), 11.98(3 \mathrm{H}),-8.92(54 \mathrm{H})$. Compound 2.3-K was chemically unstable toward evacuation; it decomposed to an insoluble, as yet uncharacterized gray solid upon exposure to vacuum. Elemental analysis was attempted for 2.3-K, but was unobtainable due to its instability.

### 2.7 Crystallographic Analysis.

X-Ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Ka radiation ( $\lambda=0.71073 \AA$ ) at a temperature of $143(1) \mathrm{K}$. In all cases, rotation frames were integrated using SAINT, ${ }^{74}$ producing a listing of unaveraged $\mathrm{F}^{2}$ and $\sigma\left(\mathrm{F}^{2}\right)$ values, which were then passed to the SHELXTL ${ }^{75}$ program package for further processing

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and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS ${ }^{76}$ or SADABS. ${ }^{77}$ The structures were solved by direct methods (SHELXS-97). ${ }^{78}$ Refinement was by full-matrix least squares based on $\mathrm{F}^{2}$ using SHELXL-97. ${ }^{78}$ All reflections were used during refinements. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

### 2.8 Spectroscopic Analysis.

${ }^{1} \mathrm{H}$ NMR spectra were obtained on a Bruker DMX-300 Fourier transform NMR spectrometer at 300 MHz . Chemical shifts were recorded in units of parts per million referenced to residual solvent peaks ( ${ }^{1} \mathrm{H}$ ). The UV-Visible absorption spectra were obtained from 2000-290 nm using a Perkin Elmer 950 UV-Vis/NIR Spectrophotometer, and all samples were prepared under an $\mathrm{N}_{2}$ environment. 1 mm pathlength screw cap quartz cells were used with a blank measured before each run.


Figure 2.8.1. ${ }^{1} \mathrm{H}$ NMR of 2.1 in benzene $-d_{6}$.


Figure 2.8.2. ${ }^{1} \mathrm{H}$ NMR of $2.1-\mathrm{Br}$ in benzene $-d_{6}$.


Figure 2.8.3. ${ }^{1} \mathrm{H}$ NMR of $2.1-\mathrm{Cl}$ in benzene- $d_{6}$.



Figure 2.8.5. ${ }^{1} \mathrm{H}$ NMR of $2.1-\mathrm{K}$ in benzene- $d_{6}$.



Figure 2.8.6. ${ }^{1} \mathrm{H}$ NMR of 2.1-Knaph in benzene- $d_{6}$.

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- 77.03


(2.2)


Figure 2.8.7. ${ }^{1} \mathrm{H}$ NMR of 2.2 in benzene- $d_{6}$.
N


(2.3)

Figure 2.8.8. ${ }^{1} \mathrm{H}$ NMR of 2.3 in benzene- $d_{6}$.

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Figure 2.8.9. ${ }^{1} \mathrm{H}$ NMR of $2.3-\mathrm{K}$ benzene- $d_{6}$.


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Figure 2.8.10. Electronic absorption spectrum of $\mathbf{2 . 3}$ in toluene, in the UV-Vis (top) and near-IR (bottom).



Figure 2.8.11. Electronic absorption spectrum of 2.1-K in toluene, in the UV-Vis (top) and near-IR (bottom).

### 2.9 Electrochemical Analysis.

Voltammetry experiments (CV, DPV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation, and the data were processed using CHI software v9.24. All experiments were performed in an $N_{2}$ atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The quasi-reference electrode was prepared by dipping a length of silver wire in concentrated hydrochloric acid. The working electrode surfaces were polished prior to each set of experiments. Potentials were reported versus ferrocene, which was added as an internal standard for calibration at the end of each run. Solutions employed during these studies were $\sim 3 \mathrm{mM}$ in analyte and 100 mM in $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ in 2 mL of dichloromethane. All data were collected in a positive-feedback IR compensation mode.
a)

b)


c)


d)


Figure 2.9.1. a) Full scan cyclic voltammetry of compound 2.1 in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$; [analyte] = ca. $1 \mathrm{mM} ; \mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec} . \mathrm{b}$ ) Left: Isolated uranium(IV/V) redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(IV/V) couple. c) Left: Isolated uranium(V/VI) redox couple at varying scan rates. Right: Current versus $v^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(V/VI) couple. d) Differential pulse voltammetry.
a)

b)

c)

d)


Figure 2.9.2. a) Full scan cyclic voltammetry of compound $2.1-\mathrm{Br}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with 0.1 M [ $\left.{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right.$ ]; [analyte] = ca. 1 mM ; v = $0.25 \mathrm{~V} / \mathrm{sec} . \mathrm{b}$ ) Left: Isolated uranium(IV/V) redox couple at varying scan rates. Right: Current versus $v^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(IV/V) couple. c) Left: Isolated uranium(V/VI) redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium $(\mathrm{V} / \mathrm{VI})$ couple. d ) Differential pulse voltammetry.
a)

b)


c)

d)


Figure 2.9.3. a) Full scan cyclic voltammetry of compound $2.1-\mathbf{C l}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with 0.1 M $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[P F_{6}\right.$ ]; [analyte] $=$ ca. 1 mM ; $\mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$. b) Left: Isolated uranium $(\mathrm{IV} / \mathrm{V})$ redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(IV/V) couple. c) Left: Isolated uranium(V/VI) redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium $(\mathrm{V} / \mathrm{VI})$ couple. d ) Differential pulse voltammetry.
a)

b)

c)


Figure 2.9.4. a) Full scan cyclic voltammetry of compound $2.1-\mathrm{O}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with 0.1 M $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$; [analyte] $=$ ca. 1 mM ; v $=0.25 \mathrm{~V} /$ sec. b) Isolated uranium(V/VI) redox couple at varying scan rates. c) Differential pulse voltammetry.
a)

b)

c)


Figure 2.9.5. a) Full scan cyclic voltammetry of compound $2.1-\mathrm{K}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with 0.1 M ["Bu4N][PF ${ }_{6}$ ]; [analyte] = ca. 1 mM ; v = $0.25 \mathrm{~V} / \mathrm{sec}$. b) Left: Isolated uranium(IV/V) redox couple at varying scan rates. Right: Current versus $v^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(IV/V) couple. c) Differential pulse voltammetry.
a)

b)

c)


d)


Figure 2.9.6. a) Full scan cyclic voltammetry of compound 2.3 in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$; [analyte] = ca. $1 \mathrm{mM} ; \mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$. b) Left: Isolated uranium(IV/V) redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(IV/V) couple. c) Left: Isolated uranium(V/VI) redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(V/VI) couple. d) Differential pulse voltammetry.
a)

b)


c)


Figure 2.9.7. a) Full scan cyclic voltammetry of compound $2.3-\mathrm{K}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with 0.1 M $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[P F_{6}\right]$; [analyte] $=$ ca. 1 mM ; $\mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$. b) Left: Isolated uranium(IV/V) redox couple at varying scan rates. Right: Current versus $v^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(IV/V) couple. c) Left: Isolated uranium(V/VI) redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium $(\mathrm{V} / \mathrm{VI})$ couple. d ) Differential pulse voltammetry.

### 2.10 Computational Details.

All calculations were performed with Gaussian 09 Revision D.01, ${ }^{79}$ with the B3LYP hybrid DFT method. An effective core potential incorporating quasi-relativistic effects were applied to uranium, with a 60 electron core and the corresponding segmented natural orbital basis set. ${ }^{80,81}$ The $6-31 \mathrm{G}^{*}$ basis set was used for all small molecules. ${ }^{82}$ Geometry optimizations were carried out in $C_{1}$ symmetry for all uranium complexes and all small molecules, as higher symmetry solutions were either higher in energy or were not successfully converged. Default settings were used for the integration grid, SCF, and geometry convergence criteria. All frequency calculations found no imaginary frequencies, confirming that the optimized structures are minima.

Table 2.10.1. Geometry optimized coordinates of compound 2.1-Br.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -0.00251649 | -0.000150542 | -0.051913681 |
| Si | 1.940345707 | 2.789551851 | 0.80269802 |
| Si | -3.40314417 | 0.287615035 | 0.759251722 |
| Si | -0.149013151 | 3.312130249 | -1.343487048 |
| C | 1.270797695 | 3.706413952 | 2.321977549 |
| C | -3.878045915 | -0.746815311 | 2.275405686 |
| C | -1.81488143 | 2.002281417 | 1.32494037 |
| C | -.295171514 | 1.214319099 | 4.33656039 |
| C | 3.11770086 | 1.411089685 | 1.369066201 |

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| C | 1.648579815 | 0.45912123 | 4.362384737 |
| :---: | :---: | :---: | :---: |
| Si | -2.782304335 | -1.791857 | -1.36895954 |
| C | 2.565518572 | -2.956756272 | 2.315384609 |
| C | 1.956492604 | -4.660107583 | -0.137712953 |
| C | -1.846660553 | 2.751977769 | -2.005414411 |
| C | -3.604023864 | -1.030653863 | -2.896922132 |
| N | 1.557388059 | -1.592813179 | -0.21599083 |
| H | 0.563319707 | 3.098597551 | 2.891870527 |
| H | 2.098116676 | 3.97563001 | 2.991711245 |
| H | -4.401764018 | -1.664397574 | 1.990423973 |
| H | 3.891257592 | 4.281368357 | 0.572955167 |
| H | 3.54187034 | 3.542625804 | -0.994606716 |
| H | -2.954090124 | 2.73998393 | 0.528978536 |
| H | 4.357264148 | 0.534603803 | -1.722380504 |
| H | 3.232808363 | 0.26780295 | -3.066253004 |
| H | -1.106350044 | 2.24666534 | 4.025850232 |
| H | 0.391508037 | 4.292690347 | -3.551233518 |
| H | 1.184533236 | 2.720022062 | -3.376918738 |
| H | 3.832991489 | 1.165986774 | 0.578100109 |
| H | -5.664126632 | 1.234405339 | 0.504063645 |
| H | -5.576639134 | -0.222101182 | -0.489022644 |
| H | 1.934853049 | 1.485205647 | 4.115138172 |
| H | -0.527574579 | -1.640756522 | 5.422203093 |
| H | 0.282022405 | -2.474891925 | 4.090344794 |
| H | -0.931153226 | -2.549117549 | 1.56631683 |
| H | 2.391152414 | -3.820608069 | 2.970290737 |
| H | 3.626648409 | -2.955106647 | 2.047193547 |
| H | -4.966521055 | -2.411166041 | -0.191167424 |
| H | 1.345529037 | -4.823822737 | -1.031966545 |
| H | 1.776334215 | -5.505769282 | 0.540096599 |
| H | -1.150480315 | 4.854868815 | 0.382678983 |
| H | -1.794832002 | 2.662436713 | -3.095934599 |
| H | -2.207047876 | 1.791719583 | -1.633252794 |
| H | 2.722560975 | -3.67758174 | -2.615065544 |
| H | -2.907766673 | -0.373267468 | -3.426976556 |
| H | -3.887677316 | -1.83857872 | -3.584774984 |
| H | 4.577397698 | -3.075940203 | -0.126781631 |
| H | 4.781666069 | -1.400112231 | 0.411880448 |
| H | -1.375833775 | -2.91822829 | -3.088391653 |
| Br | 0.019054005 | -0.002180421 | -2.833328785 |
| Si | -0.035125792 | -0.01560953 | 3.634257883 |
| Si | 1.454811622 | -3.074490236 | 0.782560238 |
| N | -0.017565968 | -0.008245831 | 1.850287196 |
| N | -2.165705867 | -0.536146307 | -0.237748718 |
| N | 0.615464267 | 2.1411169 | -0.211555527 |
| C | 3.080488777 | 4.00302959 | -0.114018508 |
| C | 3.326148642 | 0.256464704 | -1.974978644 |
| C | 0.943987134 | 3.650161384 | -2.852575856 |
| C | -5.015886275 | 0.663390215 | -0.174768476 |
| C | -0.475381445 | -1.722524069 | 4.32828455 |
| C | -0.33171436 | -3.430129965 | 1.324785511 |
| C | -4.054493851 | -2.919641511 | -0.518110069 |
| C | -0.488857454 | 4.97428145 | -0.483344502 |


| C | 2.734166737 | -2.610525383 | -2.853154342 |
| :---: | :---: | :---: | :---: |
| Si | 2.965202994 | -1.501842334 | -1.333359881 |
| C | -1.432988696 | -2.982628796 | -1.996375497 |
| H | 0.759425096 | 4.632546387 | 2.042025216 |
| H | -4.549272769 | -0.170556983 | 2.925719783 |
| H | -3.006329348 | -1.035642285 | 2.868882035 |
| H | 2.591783851 | 4.929147255 | -0.431891572 |
| H | -3.434672174 | 2.3167007 | 2.174055739 |
| H | -1.772860224 | 2.050171238 | 1.651589648 |
| H | 2.666939149 | 1.041032198 | -1.599400452 |
| H | -2.324919838 | 0.965438599 | 4.066534088 |
| H | -1.222610111 | 1.182894866 | 5.43193969 |
| H | 1.879867606 | 4.157643498 | -2.604101176 |
| H | 3.69368399 | 1.781281022 | 2.227486109 |
| H | 2.628719243 | 0.486273039 | 1.683536438 |
| H | -4.84154084 | 1.286873771 | -1.058584616 |
| H | 1.573408578 | 0.390540274 | 5.455967512 |
| H | 2.461967559 | -0.201697692 | 4.048032104 |
| H | -1.443070486 | -2.09694983 | 3.980367876 |
| H | -0.858173312 | -3.999695938 | 0.552381518 |
| H | -0.301217169 | -4.055960963 | 2.225769765 |
| H | 2.370796924 | -2.051884518 | 2.897088013 |
| H | -3.622737001 | -3.432898176 | 0.349342118 |
| H | -4.355001265 | -3.692087859 | -1.238887026 |
| H | 3.009308918 | -4.700074859 | -0.432822256 |
| H | -1.003653123 | 5.62812009 | -1.200313873 |
| H | 0.410294864 | 5.502247502 | -0.151480542 |
| H | -2.602613855 | 3.510479202 | -1.764967556 |
| H | 1.806400849 | -2.364742808 | -3.378600294 |
| H | 3.565734932 | -2.434145224 | -3.548582065 |
| H | -4.507580311 | -0.460527662 | -2.665068465 |
| C | 4.567838958 | -2.033042475 | -0.457389229 |
| H | 5.398749904 | -1.908722027 | -1.164779218 |
| H | -1.705522493 | -4.011784188 | -1.732494663 |
| H | -0.424387297 | -2.799606034 | -1.62210177 |

Table 2.10.2. Geometry optimized coordinates of compound 2.1-CI.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | 0.000695204 | -0.00494565 | -0.1664621 |
| Si | 0.97882921 | 3.25332438 | 0.670000824 |
| Si | -3.331524537 | -0.756802313 | 0.657785196 |
| N | $9.09713 \mathrm{E}-05$ | -0.007513019 | 1.736248419 |
| N | -1.90344168 | -1.164470189 | -0.3380284 |
| N | -0.064787439 | 2.221831073 | -0.334042615 |
| C | 1.704574631 | 4.756961128 | -0.253841732 |
| C | 3.026992514 | 1.22899741 | -2.151088859 |
| C | -0.185779616 | 3.724125049 | -2.995083025 |
| C | -4.981931749 | -0.887926366 | -0.276513569 |
| C | 0.101137471 | -1.765523124 | 4.222532948 |
| C | 0.740249718 | -3.373293032 | 1.214167072 |
| C | -2.987412934 | -3.998169373 | -0.665459531 |


| C | -1.988887591 | 4.566399881 | -0.643018627 |
| :---: | :---: | :---: | :---: |
| C | 3.313915794 | -1.682509337 | -3.009330757 |
| Si | 3.24620757 | -0.547767457 | -1.494929237 |
| C | -0.457894367 | -3.235835426 | -2.120104187 |
| H | -0.719238121 | 4.611511326 | 1.905962426 |
| H | -4.276409945 | -1.54945665 | 2.8279518 |
| H | -2.541175038 | -1.89346671 | 2.762478985 |
| H | 0.957193631 | 5.489379869 | -0.572655849 |
| H | -3.979877975 | 1.178280922 | 2.060538614 |
| H | -2.307683033 | 1.410743905 | 1.552640064 |
| H | 2.195740544 | 1.793182837 | -1.724844755 |
| H | -2.474454401 | 0.220616049 | 3.967667046 |
| H | -1.48562511 | 0.780818541 | 5.322566796 |
| H | 0.553860272 | 4.492631128 | -2.753518696 |
| H | 3.003241118 | 2.849528261 | 2.0652567 |
| H | 2.372970371 | 1.284560071 | 1.554114045 |
| H | -5.007167921 | -0.230551468 | -1.152535676 |
| H | 1.424124273 | 0.885071794 | 5.323608322 |
| H | 2.437892376 | 0.562815951 | 3.912471139 |
| H | -0.718891341 | -2.409582933 | 3.890551548 |
| H | 0.397999518 | -4.069447489 | 0.441992202 |
| H | 0.961663977 | -3.966390739 | 2.110624987 |
| H | 2.889084832 | -1.227477647 | 2.762309288 |
| H | -2.423309711 | -4.364123614 | 0.200413281 |
| H | -3.038130779 | -4.818636588 | -1.393690432 |
| H | 4.289891148 | -3.559350139 | -0.592738348 |
| H | -2.664080756 | 5.036292599 | -1.370549733 |
| H | -1.301935389 | 5.34139905 | -0.290105265 |
| H | -2.651903837 | 1.021133155 | -1.717469644 |
| H | 2.341664001 | -1.715382521 | -3.511740289 |
| H | 4.043459388 | -1.277758625 | -3.723416788 |
| H | -4.151295176 | -1.774785646 | -2.793816761 |
| C | 4.956889732 | -0.550051217 | -0.662271106 |
| H | 5.694141196 | -0.192018231 | -1.393115312 |
| H | -0.410277854 | -4.30926647 | -1.89904853 |
| H | 0.440339432 | -2.773363854 | -1.707212289 |
| Si | -0.000463609 | -0.008891737 | 3.520654846 |
| Si | 2.331741595 | -2.493485679 | 0.660489588 |
| Cl | 0.001580606 | -0.000103372 | -2.78033152 |
| Si | -1.138516617 | 3.088461759 | -1.486694154 |
| C | 0.081780538 | 3.921339366 | 2.189131136 |
| C | -3.462411937 | -1.887809673 | 2.173733295 |
| C | -3.28579776 | 1.056969419 | 1.218699983 |
| c | -1.571724492 | 0.780106105 | 4.227857117 |
| C | 2.550899368 | 2.310014656 | 1.223035447 |
| C | 1.467392451 | 0.957620629 | 4.22865427 |
| Si | -2.109768842 | -2.527282637 | -1.492105468 |
| C | 3.361258674 | -2.023337644 | 2.180586955 |
| C | 3.289098455 | -3.852462883 | -0.262077705 |
| C | -2.565807974 | 2.017245502 | -2.155178737 |
| C | -3.109211926 | -2.01917703 | -3.019061358 |
| N | 1.964753394 | -1.056867732 | -0.341221918 |
| H | -0.368475231 | 3.121572654 | 2.782921467 |


| H | 0.77753252 | 4.468979911 | 2.838185754 |
| :---: | :---: | :---: | :---: |
| H | -3.677802661 | -2.922385702 | 1.887331291 |
| H | 2.393234753 | 5.271440659 | 0.430230871 |
| H | 2.284706887 | 4.459150396 | -1.13408389 |
| H | -3.63079048 | 1.716458164 | 0.416041387 |
| H | 3.946262625 | 1.799624888 | -1.968027906 |
| H | 2.858678556 | 1.19693469 | -3.232865424 |
| H | -1.715579444 | 1.81723878 | 3.909669283 |
| H | -0.900086626 | 4.161238903 | -3.705621784 |
| H | 0.325771177 | 2.901137854 | -3.504839993 |
| H | 3.291618524 | 2.283800718 | 0.417699628 |
| H | -5.776613629 | -0.553895722 | 0.40430403 |
| H | -5.23951041 | -1.899627063 | -0.603935744 |
| H | 1.435275604 | 2.01845328 | 3.965744566 |
| H | 0.045826015 | -1.698865343 | 5.317185751 |
| H | 1.042157197 | -2.260992644 | 3.968685087 |
| H | -0.092052095 | -2.711598566 | 1.466663271 |
| H | 3.48479687 | -2.893090899 | 2.838879553 |
| H | 4.360700117 | -1.678296975 | 1.898489628 |
| H | -4.010699946 | -3.791212267 | -0.338657297 |
| H | 2.737981708 | -4.219761605 | -1.134782113 |
| H | 3.40960745 | -4.700077468 | 0.426262654 |
| H | -2.598740722 | 4.242161455 | 0.208563622 |
| H | -3.51842112 | 2.537934525 | -1.993762161 |
| H | -2.437676826 | 1.873490253 | -3.233330968 |
| H | 3.613534185 | -2.707129484 | -2.773410003 |
| H | -2.653044748 | -1.156388393 | -3.515011737 |
| H | -3.111200108 | -2.851279293 | -3.735538011 |
| H | 5.291940874 | -1.534046829 | -0.320343421 |
| H | 4.987720927 | 0.133447743 | 0.194412641 |
| H | -0.397390122 | -3.113333227 | -3.206946693 |

Table 2.10.3. Geometry optimized coordinates of compound 2.1-0.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -0.005928879 | -0.002115526 | 0.21447308 |
| Si | 0.930891394 | 3.388670632 | -0.640198773 |
| Si | 2.483384559 | -2.479859862 | -0.649324657 |
| Si | 2.457634931 | 2.185563005 | 1.64660601 |
| C | 2.060294124 | 3.452699301 | -2.17635785 |
| C | 1.97271295 | -3.455419579 | -2.20380638 |
| C | 3.44207683 | -0.917335789 | -1.166247923 |
| C | 1.768131216 | -0.135648899 | -4.148908893 |
| C | -0.890188848 | 3.440446117 | -1.195700347 |
| C | -0.717118698 | 1.601789909 | -4.168653248 |
| Si | 0.668039868 | -3.242330775 | 1.620595694 |
| C | -4.007702231 | 0.064930696 | -2.201708827 |
| C | -5.004803367 | -1.555191482 | 0.146655241 |

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| C | 2.974703255 | 0.54582135 | 2.463008393 |
| :---: | :---: | :---: | :---: |
| C | 1.891432029 | -3.344006236 | 3.082125115 |
| N | -2.389028281 | 0.070238895 | 0.37792074 |
| H | 2.011866727 | 2.526517082 | -2.75706067 |
| H | 1.786823841 | 4.283166929 | -2.841747493 |
| H | 1.570249876 | -4.436500049 | -1.923088364 |
| H | 2.178231857 | 5.304081629 | 0.526557355 |
| H | 0.894682716 | 5.881363207 | -0.542965089 |
| H | 4.05515964 | -0.559348295 | -0.330593227 |
| H | -1.373844703 | 2.866168298 | 1.746513738 |
| H | -2.608628494 | 3.029169083 | 3.003307545 |
| H | 2.428551302 | 0.670744059 | -3.813134599 |
| H | 2.680514578 | 3.251768408 | 3.904843154 |
| H | 0.978346052 | 2.931982157 | 3.527047652 |
| H | -1.527398457 | 3.779512666 | -0.369952683 |
| H | 4.657959494 | -3.696651204 | -0.572484866 |
| H | 3.517876793 | -4.535788179 | 0.486386592 |
| H | -0.15109731 | 2.490095849 | -3.872944942 |
| H | -0.897405957 | -1.367339273 | -5.277701572 |
| H | -2.048724166 | -1.35352572 | -3.931215941 |
| H | -1.500712017 | -2.340864711 | -1.540500177 |
| H | -4.572900787 | -0.587053243 | -2.88183494 |
| H | -4.666151137 | 0.891173874 | -1.90720603 |
| H | 1.406591218 | -5.413490613 | 0.478884215 |
| H | -4.778864187 | -2.205837886 | 0.999945866 |
| H | -5.544769751 | -2.162286419 | -0.593972749 |
| H | 4.503629622 | 2.241336895 | 0.183489383 |
| H | 3.93147038 | 0.699045003 | 2.982189219 |
| H | 2.234224494 | 0.219511936 | 3.198796866 |
| H | -4.666949443 | -0.640118471 | 2.803659764 |
| H | 2.060347708 | -2.347031875 | 3.50589767 |
| H | 1.477648647 | -3.979025348 | 3.877807743 |
| H | -5.392270076 | 1.489999549 | 0.502404407 |
| H | -4.225637483 | 2.780426899 | 0.185010765 |
| H | -1.361678929 | -3.801623502 | 2.935609159 |
| 0 | -0.015207298 | -0.014163304 | 1.994745176 |
| Si | 0.014773292 | 0.010135556 | -3.427188984 |
| Si | -3.402757611 | -0.886214086 | -0.664313899 |
| N | -0.000708164 | -0.001451858 | -1.674660702 |
| N | 1.133950516 | -2.095206117 | 0.382897094 |
| N | 1.248159593 | 2.023911479 | 0.392407447 |
| C | 1.155906011 | 5.102482666 | 0.187321905 |

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| C | -1.990923384 | 2.304160607 | 2.454427106 |
| :---: | :---: | :---: | :---: |
| C | 1.92552077 | 3.29046803 | 3.107011358 |
| C | 3.853375312 | -3.54490986 | 0.161209134 |
| C | -0.985950715 | -1.417511955 | -4.183550291 |
| C | -2.536747882 | -2.486840874 | -1.22356962 |
| C | 0.485223388 | -5.014873742 | 0.918637829 |
| C | 4.095001946 | 2.901772147 | 0.959416112 |
| C | -3.824226583 | -2.09788E-05 | 3.086995202 |
| Si | -3.141591509 | 1.02984102 | 1.632993079 |
| C | -1.016335052 | -2.891198461 | 2.425843841 |
| H | 3.106528457 | 3.59654678 | -1.878366817 |
| H | 2.822096295 | -3.624742233 | -2.879733825 |
| H | 1.193422366 | -2.932430322 | -2.764537002 |
| H | 0.489034855 | 5.225365661 | 1.049198467 |
| H | 4.122417217 | -1.146377371 | -1.99796876 |
| H | 2.799558429 | -0.090981224 | -1.48111858 |
| H | -1.310790731 | 1.825091157 | 3.1642237 |
| H | 2.246105698 | -1.084802279 | -3.88991799 |
| H | 1.704204858 | -0.07872844 | -5.244542055 |
| H | 1.789285537 | 4.34070787 | 2.827181577 |
| H | -1.014088964 | 4.154356249 | -2.021351568 |
| H | -1.273745567 | 2.473775949 | -1.532284843 |
| H | 4.293454696 | -3.040201857 | 1.029514835 |
| H | -0.678884324 | 1.528806873 | -5.264624602 |
| H | -1.762328523 | 1.764964265 | -3.885310963 |
| H | -0.627342634 | -2.402485602 | -3.867794153 |
| H | -2.533776219 | -3.21721451 | -0.405682217 |
| H | -3.079721116 | -2.938439141 | -2.065202825 |
| H | -3.175559285 | 0.498136366 | -2.764579808 |
| H | -0.288437794 | -5.042007565 | 0.14083215 |
| H | 0.175704607 | -5.704821368 | 1.716165047 |
| H | -5.692412162 | -0.777019282 | 0.494105565 |
| H | 4.8438646 | 2.974350781 | 1.760435905 |
| H | 3.98922153 | 3.89891748 | 0.518306322 |
| H | 3.108410762 | -0.278551412 | 1.756739765 |
| H | -3.037032625 | -0.646848928 | 3.49219309 |
| H | -4.162917771 | 0.662147035 | 3.895870737 |
| H | 2.86727104 | -3.755491417 | 2.801991036 |
| C | -4.588595454 | 2.084185916 | 0.952285903 |
| H | -5.035528197 | 2.6842807 | 1.756972651 |
| H | -1.792664836 | -2.595063972 | 1.71365852 |
| H | -0.937955334 | -2.091401121 | 3.167274211 |

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## Chapter 3:

## Synthesis and Reduction of Uranium(V) Imido Complexes with Redox-Active Substituents

### 3.1 Introduction.

The uranyl dication $\left(\mathrm{UO}_{2}{ }^{2+}\right)$, an environmentally mobile form of uranium, gains thermodynamic stability from the inverse trans influence, as described in Sections 2.1 and 2.2. ${ }^{1}$ In the work described in Chapter 2 we observed a strong inverse trans influence in our $U^{V 1}\left(=\mathrm{NSiMe}_{3}\right) \mathrm{X}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(\mathrm{X}=\mathrm{Cl}, \mathrm{Br})$ and $\left[\mathrm{Ph}_{4} \mathrm{P}\right]\left[\mathrm{U}^{\mathrm{VI}} \mathrm{O}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ complexes. ${ }^{2}$ Surprisingly, this was comparable to that observed in the oxo complexes, $\mathrm{U}^{\mathrm{VI}} \mathrm{OX}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(\mathrm{X}=$ $\mathrm{Cl}, \mathrm{Br})^{3}$ and $\left[\mathrm{Na}(\mathrm{THF})_{2}\right]\left[\mathrm{U}^{\mathrm{V}} \mathrm{O}_{2}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right.$ as judged by bond metrics, electrochemical analysis, and computational methods. ${ }^{4}$ However, when $\left.\mathrm{K}\left[\mathrm{U}^{\mathrm{IV}}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{NSiMe}_{3}\right)_{2}\right]_{3}\right]$ was reacted with methyl triflate, methylation did not occur at the uranium center. Rather, a reaction occurred at the nucleophilic imido ligand to yield $\mathrm{U}^{\mathrm{lV}}\left[\mathrm{NMe}\left(\mathrm{SiMe}_{3}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}{ }^{2}$. We considered that a more reducing uranium center may be required to facilitate the installation of new moieties trans to the imido ligand at a high valent uranium center by two electron chemistry.

### 3.2 Previous Reports of Uranium Complexes with Redox-Active Ligands.

Considering that there are, to date, no reported examples of uranium(III) imido complexes, we evaluated the use of a redox-active imido ligand to introduce the capability of reducing equivalents to uranium(IV) mono(imido) complexes. The resulting complexes would have the potential to act as uranium(III) imido synthons. Redox-active ligands have been used extensively by the Bart group and others in uranium organometallic chemistry to promote multielectron reactivity. ${ }^{5-7}$ Most notably, this approach has resulted in the first example of a uranium tris(imido) complex. Redox-active ligands also allowed formal reductive elimination and oxidative addition

Portions of this chapter are adapted from "Synthesis and Reduction of Uranium(V) Imido Complexes with Redox Active Substituents" Mullane, K. C.; Carroll, P. J.; Schelter, E. J. Chem., Eur. J., 2017, 23, 5748-5757. Copyright 2017 Wiley-VCH Verlag GmbH \& Co. KGaA, Weinheim.
mechanistic steps (Scheme 3.2.1). ${ }^{5,7-10}$ In this work, we present the synthesis of uranium naphthyl-imido complexes in the +5 and +4 oxidation states for comparison with previously reported $\mathrm{U}^{\mathrm{V}}\left[=\mathrm{NCPh}_{3}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(2.3),{ }^{2}$ which contains a redox-innocent triphenylmethyl-imido ligand. The electronic structures of these compounds are investigated using a combination of electrochemistry and DFT analysis, and the uranium(IV) counterparts were isolated.

First example of uranium tris(imido):



Formal Reductive elimination:




Scheme 3.2.1. Examples of notable uses of redox-active ligands, resulting in the formation of the first example of a uranium tris(imido) complex and a formal reductive elimination mechanistic steps. ${ }^{5,7}$

### 3.3 Results and Discussion.

### 3.3.1 Synthesis and Structural Characterization.

The organic azides 2-(azidodiphenymethyl)naphthalene, 2,2',2"(azidomethane)trinaphthalene, and 2-(2-azidopropan)naphthalene were synthesized from alcohol precursors (Scheme 3.3.1). The alcohols, $\alpha, \alpha$-diphenyl-2-naphthalene methanol, tri(2naphthalene)methanol, and 2-(naphthalene)propanol were prepared by syntheses adapted from

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the literature, by reaction of 2-bromonaphthalene with benzophenone, 2-naphthoyl chloride, and acetone, respectively, with the exception that $n$-butyllithium was used instead of magnesium or lithium metal. ${ }^{11-13}$ This approach resulted in moderate to good yields of $88 \%, 97 \%$, and $60 \%$ for a, $\alpha$-diphenyl-2-naphthalene methanol, tri(2-naphthalene)methanol, and 2-(naphthalene)propanol, respectively. These alcohols were then reacted with sodium azide in a chloroform/water biphasic mixture with a catalytic amount of sulfuric acid, which was based on a reported synthesis of triaryl methyl azides. ${ }^{14}$ This procedure gave the novel compounds 2-(azidodiphenymethyl)naphthalene (3.1) and 2,2',2"-(azidomethane)trinaphthalene (3.2) in 68\% and 88\% yield as white powders and the previously reported compound 2-(azidopropan)naphthalene (3.3) in $72 \%$ yield as a colorless oil. ${ }^{15}$

(3.1)

(3.2)

(3.3)

Scheme 3.3.1 Synthesis of organic azides.

The synthesis of $U^{\vee}\left[=N C(2-n a p h) \mathrm{Ph}_{2}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (3.4), $\mathrm{U}^{\mathrm{V}}\left[=\mathrm{NC}(2 \text {-naph })_{3}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (3.5), $\quad \mathrm{U}^{\mathrm{V}}\left[=\mathrm{NC}(2-n a p h) \mathrm{Me}_{2}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} \quad$ (3.6), and $\quad \mathrm{U}^{\mathrm{V}}[=\mathrm{N}(2$-naph $)]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} \quad$ (3.7) were accomplished by reduction of the organic azides with $\mathrm{U}^{\prime \prime \prime}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (Scheme 3.3.2) in an analogous route to the reported procedures for the syntheses of $\mathrm{U}^{\vee}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}{ }^{16}$ and 2.3. ${ }^{2}$ The preparations of $3.4-3.7$ proved to be strongly solvent dependent. Compound 3.4 was synthesized by dissolving $\mathrm{U}^{\mathrm{II}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ in hexanes and adding a THF solution of 2(azidodiphenylmethyl)naphthalene to afford a dark green crystalline solid after workup in $63 \%$

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yield. If prepared without the mixed solvent conditions, multiple paramagnetic species were observed by ${ }^{1} \mathrm{H}$ NMR spectroscopy, including small amounts of the bridging nitride complex $\left[\left(\mathrm{Me}_{3} \mathrm{Si}_{2}\right)_{2} \mathrm{~N}_{3} \mathrm{U}^{\mathrm{V}}(\mathrm{N}) \mathrm{U}^{1 \mathrm{~V}}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right.$ (Figure 3.3.1). The formation of actinide ligand multiple bonds by trityl deprotection has been established by the Hayton group to yield $\left[\mathrm{An}^{\mathrm{IV}}(=\mathrm{S})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]^{-}$ $\left[\mathrm{An}^{\mathrm{IV}}(=\mathrm{O})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]^{-} \quad\left(\mathrm{An}=\mathrm{U}\right.$, Th) complexes. ${ }^{17,18}$ It is feasible that $\left[\left(\mathrm{Me}_{3} \mathrm{Si}_{2}\right)_{2} \mathrm{~N}_{3} \mathrm{U}^{\mathrm{V}}(\mathrm{N}) \mathrm{U}^{1 \mathrm{~V}}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right.$ was produced from a similar reaction pathway. In the preparation of 3.5, a THF solution of 2,2',2"-(azidomethane)trinaphthalene was added to $U^{\prime \prime \prime}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ in THF, resulting in the targeted dark green product obtained in $55 \%$ isolated yield. If other solvents were present during the synthesis, $2,2^{\prime}$-binaphthalene was observed as a product, with only minimal 3.5 present in the resulting mixture. The synthesis of 3.6 was accomplished in pentane, which showed a cleaner crude reaction mixture than that from hexanes.


Scheme 3.3.2 Synthesis of 2.3, 3.4, 3.5, 3.6, 3.7, and 3.8.


Figure 3.3.1 Thermal ellipsoid plot of $\left[\left(\mathrm{Me}_{3} \mathrm{Si}_{2} \mathrm{~N}_{2} \mathrm{~N}_{3} \mathrm{U}^{\mathrm{V}}(\mathrm{N}) \mathrm{U}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right.\right.$ at $50 \%$ probability. Bond lengths (A): $\mathrm{U}(1)-\mathrm{N}(1) 2.288(9), \mathrm{U}(1)-\mathrm{N}(2) 2.291(9), 2.281(10), \mathrm{U}(1)-\mathrm{N}(7) 2.091(10), \mathrm{U}(2)-$ $\mathrm{N}(7) 2.133(10), \mathrm{U}(2)-\mathrm{N}(6) 2.265(10), \mathrm{U}(2)-\mathrm{N}(5)$ 2.278(8), U(2)-N(4) 2.293(9).

Compound 3.7 was synthesized for comparison with the triaryl imido ligand framework, because the triaryl frameworks are subject to reductive deprotection ${ }^{17,18}$ and other one electron processes. ${ }^{2}$ Compound 3.7 , in contrast, bears a simple naphthyl moiety bound directly to the imido nitrogen that was expected to show relatively better stability than 2.3 and 3.4-3.6. The preparation of 3.7 was performed in hexanes, as the reaction in THF yielded a mixture of unidentified paramagnetic compounds and none of the desired product. The synthesis of 3.7 was further complicated by the presence of $U^{I V}\left[(2\right.$-naph $\left.) \mathrm{NNNCH}_{2} \mathrm{SiMe}_{2} \mathrm{NSiMe}_{3}-\mathrm{K}^{3} N^{1,3,6}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{2}$ (3.8), a persistent side product in the crude reaction mixtures. Fortunately, 3.7 was isolable by selective crystallization from hexanes to obtain a $70 \%$ yield of dark brown crystals. The side product (3.8) was likely formed by reaction of 2-azidonaphthalene with the in situ generated cyclometalated compound, $\mathrm{U}^{\mathrm{IV}}\left[\mathrm{CH}_{2} \mathrm{SiMe}_{2} \mathrm{NSiMe}_{3}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{2}$, a common byproduct of the chemistry of $\mathrm{U}^{\mathrm{II}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} .{ }^{19,20}$

Similar compounds to 3.8 have been synthesized by insertion of organic azides into U-C bonds by the Evans ${ }^{21-23}$ and Bart groups. ${ }^{24}$ The precedent for azides inserting into U-C bonds
further supports the proposal that 2-azidonaphthalene inserts into the U-C bond of $\mathrm{U}^{\mathrm{IV}}\left[\mathrm{CH}_{2} \mathrm{SiMe}_{2} \mathrm{~N}\left(\mathrm{SiMe}_{3}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$. An X-ray structure of 3.8 was obtained (Figure 3.3.2) which showed that the $\mathrm{U}(1)-\mathrm{N}(4)$ and $\mathrm{U}(1)-\mathrm{N}(6)$ distances were 2.408(2) and 2.453(2) $\AA$, respectively. The similar bond lengths implied that the negative charge was delocalized across the triazenido moiety. The average $U-N_{\text {amide }}$ bond length was 2.2771 (16) $\AA$, which was similar to those in previously reported uranium(IV) metallacycle complexes. ${ }^{25}$


Figure 3.3.2 Thermal ellipsoid plot of 3.8 at $50 \%$ probability. Hydrogen atoms removed for clarity. Bond lengths ( $\AA$ ) and angles $\left({ }^{\circ}\right): \mathrm{U}(1)-\mathrm{N}(1)$ 2.2878(19), $\mathrm{U}(1)-\mathrm{N}(2) 2.250(2), \mathrm{U}(1)-\mathrm{N}(3)$ $2.2936(19), \mathrm{U}(1)-\mathrm{N}(4) 2.408(2), \mathrm{U}(1)-\mathrm{N}(6) 2.453(2), \mathrm{N}(4)-\mathrm{C}(18) 1.450(3), \mathrm{N}(4)-\mathrm{N}(5)-\mathrm{N}(6)$ 108.0(2).

The ${ }^{1} \mathrm{H}$ NMR spectra of 3.4 and 3.5 were similar and exhibited broad peaks at -3.39 , 3.64 corresponding to the $-\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}$ ligands. In contrast, the $-\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}$ ligands were split into two peaks centered at -2.30 and -4.35 ppm for compound 3.6 , presumably due to hindered rotation about the U-N bond. For 3.4-3.6 the majority of the aryl resonances of the imido ligand ranged from 7.08-11.89 ppm with the exception of the ortho proton of the naphthyl group closest to the uranium center, which appeared as a broad singlet at approximately 22 ppm for all three complexes. Additionally, 3.6 exhibited a peak at 1.38 ppm corresponding to the methyl substituents in the imido ligand. The ${ }^{1} \mathrm{H}$ NMR spectra of 3.7 differed slightly, as the $-\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}$ protons gave a sharp peak at -2.01 ppm . Three of the aryl protons for 3.7 were shifted downfield at $21.41,13.99$, and 12.20 ppm , similar to those in compounds $3.4-3.6$. However, four of the aryl
protons were shifted upfield to give a coincident peak at -5.42 ppm . Electronic absorption spectra of compounds 3.4 and 3.5 showed absorption maxima in the UV and visible region between 343 and 426 nm , which were tentatively assigned to $\pi-\pi^{*}$ transitions and compare well with our previously reported data for compound 2.3. ${ }^{26}$ Compound 3.7 showed a broad absorption throughout the visible and UV regions.

X-Ray crystal structures of 3.4, 3.5, and 3.7 allowed structural analysis within the series of compounds (Figures 3.3.3, 3.3.4, 3.3.5, and Table 3.3.1). The methyl substituents installed in the imido ligand of compound 3.6 resulted in high solubility in organic solvents, which prevented crystallization. In these compounds the steric properties of the amide and imido ligands determined the overall geometry of the compounds. In 3.4 and 3.5 the imido ligand was the most sterically demanding, which caused the $\mathrm{N}=\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond angle to be large at the expense of decreasing the $\mathrm{N}_{\text {amide }}-\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond angles and lengthening the $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bonds. To illustrate, the average $\mathrm{N}=\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond angles in 3.4 and 3.5 were $113.98(18)^{\circ}$ and $115.23(15)^{\circ}$, respectively. Because these bond angles are larger than those in an idealized tetrahedral geometry, the $\mathrm{N}_{\text {amide }}-\mathrm{U}-\mathrm{N}_{\text {amide }}$ angles were compressed, and averaged 104.61(17) ${ }^{\circ}$ and $103.15(18)^{\circ}$ for 3.4 and 3.5 , respectively. Conversely, in compound 3.7 the steric bulk of the supporting amide ligands dominated the coordination sphere; in this case the $\mathrm{N}_{\text {amide }}-\mathrm{U}-\mathrm{N}_{\text {amide }}$ angles were larger than an idealized tetrahedral geometry with an average of $116.85(5)^{\circ}$. These large uranium-amide bond angles caused a compression of the average $\mathrm{N}=\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond angle to 100.21 (6) ${ }^{\circ}$. An additional consequence of the large strain imposed by the imido ligand in compounds 3.4 and 3.5 was observed in the average $U-N_{\text {amide }}$ bond lengths of $2.271(5) \AA$ and $2.269(6) \AA$, which were lengthened with respect to 3.7 with average bond lengths of $2.2437(14) \AA$. The differences in geometry for 3.4 and 3.5 versus 3.7 were consistent with the computed bond metrics (Table 3.3.1).


Figure 3.3.3 Thermal ellipsoid plot of 3.4 at $50 \%$ probability. Hydrogen atoms and solvent were omitted for clarity. Bond lengths (Å) and angles ( ${ }^{\circ}$ : $2-\mathrm{U}(1)-\mathrm{N}(1) 2.271(5), \mathrm{U}(1)-\mathrm{N}(2) 2.270(5)$, $\mathrm{U}(1)-\mathrm{N}(3) 2.271(5), \mathrm{U}(1)-\mathrm{N}(4) 1.960(5), \mathrm{N}(4)-\mathrm{C}(19) 1.486(7), \mathrm{C}(19)-\mathrm{N}(4)-\mathrm{U}(1) 179.3(4), \mathrm{N}(4)-$ $\mathrm{U}(1)-\mathrm{N}(1) 113.13(19), \mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(2)$ 105.33(17).


Figure 3.3.4 Thermal ellipsoid plot of 3.5 at $50 \%$ probability. Hydrogen atoms and solvent were omitted for clarity. Bond lengths ( A ) and angles ( ${ }^{\circ}$ : : $\mathrm{U}(1)-\mathrm{N}(1)$ 2.269(6), $\mathrm{U}(1)-\mathrm{N}(2) 1.956(9), \mathrm{N}(2)-$ $\mathrm{C}(7) \quad 1.502(14), \quad \mathrm{C}(7)-\mathrm{N}(2)-\mathrm{U}(1) \quad 180.000(2), \quad \mathrm{N}(2)-\mathrm{U}(1)-\mathrm{N}(1) \quad 115.23(15), \quad \mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(1)$ 103.15(18).


Figure 3.3.5 Thermal ellipsoid plot of 3.7 at $50 \%$ probability. Hydrogen atoms and solvent were omitted for clarity. Bond lengths ( $(\AA)$ and angles $\left({ }^{\circ}\right): ~ U(1)-N(1) 1.9503(14), U(1)-N(2) 2.2313(14)$, $\mathrm{U}(1)-\mathrm{N}(3) 2.2529(14), \mathrm{U}(1)-\mathrm{N}(4) 2.2469(14), \mathrm{N}(1)-\mathrm{C}(1) 1.387(2), \mathrm{C}(1)-\mathrm{N}(1)-\mathrm{U}(1) 172.32(13)$, $\mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(2) 99.51, \mathrm{~N}(2)-\mathrm{U}(1)-\mathrm{N}(3) 115.42$ (5).

Table 3.3.1 Experimental and calculated $U-N_{\text {amide }}$ bond lengths in complexes $3.4-3.7$ in $\AA$.

| $\mathrm{U}^{\mathrm{V}}[=\mathrm{NR}]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ Derivative | $\mathrm{U}=\mathrm{N}$ |  | Avg. U- Namide |  |
| :---: | :---: | :---: | :---: | :---: |
|  | exptl. | calcd. | exptl. | calcd. |
| 3.4, $\mathrm{R}=\mathrm{C}(2-\mathrm{naph}) \mathrm{Ph}_{2}$ | 1.960(5) | 1.960 | 2.271 (5) | 2.294 |
| 3.5, $\mathrm{R}=\mathrm{C}(2-\mathrm{naph})_{3}$ | 1.956(9) | 1.961 | 2.269(6) | 2.295 |
| 3.6, $\mathrm{R}=\mathrm{C}(2-$ naph $) \mathrm{Me}_{2}$ | -- | 1.957 | -- | 2.289 |
| 3.7, $\mathrm{R}=2$-naph | 1.9503(14) | 1.956 | $2.2437(14)$ | 2.271 |

Previously the Meyer group, ${ }^{27}$ Walter group ${ }^{28}$, and our group ${ }^{2}$ have reported actinide 'trityl imido' complexes. In compounds 3.4 and 3.5 the $\mathrm{U}=\mathrm{N}-\mathrm{C}$ bond angle was very close to linear at
$179.3(4)^{\circ}$ and $180.000(2)^{\text {o }}$. The linear bond angle was also observed in our previously reported compound 2.3. However, the other known uranium(V) trityl imido complex, $\left.\left[{ }^{\mathrm{RP}, \mathrm{Me}} \mathrm{ArO}\right)_{3} \operatorname{tacn}\right] \mathrm{U}^{\mathrm{V}}\left[=\mathrm{NCPh}_{3}\right]$ had a more bent $\mathrm{U}=\mathrm{N}-\mathrm{C}$ bond angle of $165.2(2)^{\circ}{ }^{27}$ This compound also featured a shorter $U=N$ bond length of 1.939(3) Å when compared with compounds 2.3-3.5, which average $1.958(7) \AA$. The thorium(IV) trityl imido complex reported by Walter and coworkers, $\left[\left(\mathrm{Me}_{3} \mathrm{C}\right)_{3} \mathrm{C}_{5} \mathrm{H}_{2}\right]_{2} \mathrm{Th}^{\mathrm{V}}\left[=\mathrm{NCPh}_{3}\right]$, also exhibited a more bent angle of $168.3(2){ }^{2} .^{28}$

Actinide mono(imido) complexes with aryl-imido functional groups are more common. Compound 3.7 had a U=N-C bond angle 172.32(13)ㅇ. This was very similar to the thorium imido complex in the bis(trimethylsilyl) amide ligand framework, $[\mathrm{K}(18-\mathrm{c}-6)]\left[\mathrm{Th}(=\mathrm{NDipp})\left[\left(\mathrm{NSiMe}_{3}\right)_{2}\right]_{3}\right.$, which had a $\mathrm{Th}=\mathrm{N}-\mathrm{C}$ bond angle of $172.0(3)^{\circ}{ }^{29}$ Uranium(V) complexes with aryl imido ligands also exhibited similar $\mathrm{U}=\mathrm{N}-\mathrm{C}$ bond angles; a series of uranium( V ) imido complexes reported by Kiplinger, Graves, and co-workers, $\left.\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{U}^{\mathrm{V}}[=\mathrm{NDipp})\right] \mathrm{X}\left(\mathrm{X}=\mathrm{Cl}, \mathrm{Br}, \mathrm{I}, \mathrm{OTf}, \mathrm{SPh}, \mathrm{NPh}_{2}\right)$, had $\mathrm{U}=\mathrm{N}-\mathrm{C}$ bond angles ranging from $169.6(4)^{\circ}$ when $\mathrm{X}=\mathrm{Cl}$ to $174.0(3)$ when $\mathrm{X}=\mathrm{NPh}_{2}{ }^{30}$ Compound 3.7 had a short $U=N$ bond of $1.9503(14) \AA$ when compared with this series which range between $1.9575(5) \AA$ Å when $\mathrm{X}=\mathrm{OTf}$ to 1.984 (4) $\AA$ A when $\mathrm{X}=\mathrm{NPh}_{2}$.

We then pursued reduction of the uranium $(\mathrm{V})$ imido complexes. Reduction of compound 3.4 with one equivalent of potassium graphite at $-21{ }^{\circ} \mathrm{C}$ yielded a pink solution after filtration. Impurities were removed by extraction with pentane to give $\mathrm{K}\left[\mathrm{U}^{\mathrm{IV}}\left[=\mathrm{NC}(2\right.\right.$-naph $\left.\left.) \mathrm{Ph}_{2}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ (3.4-K) in $50 \%$ yield (Scheme 3.3.3). The ${ }^{1} \mathrm{H}$ NMR spectrum of compound $3.4-\mathrm{K}$ revealed a broad peak centered at -8.77 ppm , corresponding to the silyl amide ligands. This peak was shifted upfield in comparison with the silyl amide peak for compound 3.4, which was centered at -3.93 ppm. The seventeen aryl protons in this uranium(IV) complex were shifted further downfield in comparison with 3.4 and exhibited shifts from 8.68 ppm to 47.54 ppm . Similarly, conversion of $\mathbf{3 . 5}$ to $\mathrm{K}\left[\mathrm{U}^{\mathrm{IV}}\left[=\mathrm{NC}(2-\mathrm{naph})_{3}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ (3.5-K) was accomplished by addition of potassium graphite to a solution of 3.5 in toluene at $-2{ }^{\circ} \mathrm{C}$. Solid was precipitated by the addition of pentane to give 3.5-K as a dark pink solid in a $49 \%$ yield. The ${ }^{1} \mathrm{H}$ NMR of this compound was similar to $3.4-\mathrm{K}$,
with the bis(trimethylsilyl)amide peak at -8.85 ppm and twenty-one aryl protons between 8.42 and 49.29 ppm . Compound 3.6 was reduced in a THF solution with two equivalents of potassium graphite. Crystallization at $-21{ }^{\circ} \mathrm{C}$ from a concentrated THF solution afforded orange crystals of 3.6-K. The ${ }^{1} \mathrm{H}$ NMR of $\mathbf{3 . 6 - K}$ was similar to $\mathbf{3 . 4 - \mathrm { K }}$ and $\mathbf{3 . 5 - \mathrm { K }}$ and exhibited a broad peak at -7.81 ppm. The seven naphthalene protons were shifted downfield between 12.48 and 58.35 ppm , and the methyl protons were shifted to 46.26 ppm. Compound 3.7 was reduced by an identical procedure to that of 3.4 and crystallized from a concentrated solution of pentane to yield $\mathrm{K}\left[\mathrm{U}^{\mathrm{IV}}[=\mathrm{N}(2-\mathrm{naph})]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right](3.7-\mathrm{K})$ as pink crystals in $46 \%$ yield. Similar to compounds 3.4-K and $3.5-\mathrm{K}$, the ${ }^{1} \mathrm{H}$ NMR of $3.7-\mathrm{K}$ exhibited a silylamide peak that was shifted upfield, at -4.77 ppm , in relation to its uranium $(\mathrm{V})$ counterpart, 3.7, which was centered at -2.01 ppm . Additionally, the seven aryl protons were shifted downfield, with respect to 3.7 , between 10.57 and 32.02 ppm .

3.4, $R=P h$
3.5, R=2-naph
3.6, R=Me

3.7

$$
\mathbf{N}^{*}=\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}
$$

3.4-K, R=Ph
3.5-K, R=2-naph
3.6-K, R=Me

## 3.7-K

Scheme 3.3.3 Synthesis of compounds 3.4-K, 3.5-K, 3.6-K, and 3.7-K.

The electronic absorption spectra for 3.4-K and 3.5-K exhibited broad absorption bands in the visible region between 390 and 690 nm . Compound $3.5-\mathrm{K}$ was more intensely colored, which is reflected in the higher molar absorptivity of this compound. In contrast, 3.7-K absorbed most strongly in the UV region at 323 nm with a low intensity broad absorption in the visible region between 366 and 490 nm and was the least intensely colored compound of the three. These absorptions are tentatively assigned to $\pi$ to $\pi^{*}$ transitions, which are red shifted in comparison to the analogous transitions in the uranium( V ) electronic absorption spectra. The shift of the $\pi$ to $\pi^{*}$ transitions to lower energy may imply that subsequent reduction would occur at the naphthalene moieties. This data agrees well with the electrochemical data, which shows that 3.7 has the most negative naph/naph ${ }^{-1}$ couple and the highest energy $\pi$ to $\pi^{*}$ transition. These low intensity features along with the numerous features in the near-IR spectra support the +4 oxidation state assignment and compare well with spectra for previously reported uranium(IV) imido complexes. ${ }^{2}$

X-Ray structural analysis allowed comparison of bond metrics of compounds $3.5-\mathrm{K}-3.7-\mathrm{K}$ (Figures 3.3.6, 3.3.7, 3.3.8, and Table 3.3.2). When compared with compounds 3.5 and 3.7, the $\mathrm{U}=\mathrm{N}$ and average $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond lengths were slightly longer, which is expected due to the larger radius of the uranium(IV) ion. Specifically, the $\mathrm{U}=\mathrm{N}$ bond length increased by 0.045 and $0.082 \AA$ for $3.5-\mathrm{K}$ and $3.7-\mathrm{K}$ in comparison with 3.5 and 3.7 , respectively. Likewise, the $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond length increased by 0.119 and $0.076 \AA$ for $3.5-\mathrm{K}$ and $3.7-\mathrm{K}$ in comparison with 3.5 and 3.7 . The difference in distortion from the idealized tetrahedral geometry observed for 3.5 and 3.7 were not maintained in the uranium(IV) counterparts, 3.5-K and 3.7-K. Upon coordination of a potassium ion to the naphthyl imido ligand of $\mathbf{3 . 5 - K}$, the geometry was altered such that for both $3.5-\mathrm{K}$ and 3.7-K repulsive interactions between the silyl amide ligands dominated the coordination sphere. This can be seen in the large average $\mathrm{N}_{\text {amide }}-\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond angles of $113.1(3)^{\circ}$ and $116.67(15)^{\circ}$, which resulted in compression of the average $\mathrm{N}=\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond angles to $105.5(3)^{\circ}$ and $100.59(13)^{\circ}$, for $3.5-\mathrm{K}$ and $3.7-\mathrm{K}$, respectively. Also, $3.5-\mathrm{K}$ and $3.7-\mathrm{K}$ have bent $\mathrm{U}=\mathrm{N}-\mathrm{C}$ bond
angles of $168.5(8)^{-}$and $165.8(5)^{-0}$ in comparison to the near linearity of their uranium(V) counterparts, 3.5 and 3.7.


Figure 3.3.6 Thermal ellipsoid plot of $3.5-\mathrm{K}$ at $50 \%$ probability. Hydrogen atoms are omitted for clarity. Bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right): ~ U(1)-N(1) 2.366(10), \mathrm{U}(1)-\mathrm{N}(2) 2.393(10), \mathrm{U}(1)-\mathrm{N}(3)$ $2.406(10), \mathrm{U}(1)-\mathrm{N}(4)$ 2.001(9), $\mathrm{N}(4)-\mathrm{C}(19) 1.447(14), \mathrm{U}(1)-\mathrm{N}(4)-\mathrm{C}(19) 168.5(8), \mathrm{N}(4)-\mathrm{U}(1)-\mathrm{N}(1)$ 109.2, $\mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(2) 117.1$ (3).


Figure 3.3.7 Thermal ellipsoid plot of $\mathbf{3 . 6 - K}$ at $50 \%$ probability. Hydrogen atoms are omitted for clarity. Bond lengths ( $(\AA)$ and angles $\left({ }^{\circ}\right): ~ U(1)-N(1) 2.389(3), \mathrm{U}(1)-N(2) 2.360(3), \mathrm{U}(1)-\mathrm{N}(3)$
2.433(3), $\mathrm{U}(1)-\mathrm{N}(4) 2.004(3), \mathrm{N}(4)-\mathrm{C}(19) 1.480(5), \mathrm{U}(1)-\mathrm{N}(4)-\mathrm{C}(19) 165.7(3), \mathrm{N}(4)-\mathrm{U}(1)-\mathrm{N}(1)$ 114.58(12), $\mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(2) 110.29(12)$.


Figure 3.3.8 Thermal ellipsoid plot of 3.7-K at $50 \%$ probability. Hydrogen atoms are omitted for clarity. Bond lengths ( $\AA$ ) and angles $\left({ }^{\circ}\right): ~ U(1)-N(1) 2.032(3), \mathrm{U}(1)-\mathrm{N}(2) 2.301(4), \mathrm{U}(1)-\mathrm{N}(3)$ $2.337(3), \quad \mathrm{U}(1)-\mathrm{N}(4) \quad 2.321(4), \quad \mathrm{N}(1)-\mathrm{C}(1) \quad 1.330(12), \quad \mathrm{N}(1)-\mathrm{C}(1)^{\prime} \quad 1.465(19), \quad \mathrm{U}(1)-\mathrm{N}(1)-$ $\mathrm{C}(1) 165.8(5), \mathrm{U}(1)-\mathrm{N}(1)-\mathrm{C}(1){ }^{\prime} 170.8(7), \mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(3) 98.91(12), \mathrm{N}(2)-\mathrm{U}(1)-\mathrm{N}(3) 113.07(17)$.

Table 3.3.2 Experimental and calculated $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond lengths in complexes $3.4-\mathrm{K}-3.7-\mathrm{K}$ in $\AA$.

|  | $\mathrm{U}=\mathrm{N}$ |  | Avg. U-N $\mathrm{N}_{\text {amide }}$ |  |
| :--- | :--- | :--- | :--- | :--- |
| $\mathrm{K}\left[\mathrm{U}^{\mathrm{V} \mathrm{V}}[=\mathrm{NR}]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ Derivative | exptl. | calcd. | exptl. | calcd. |
| $3.4-\mathrm{K}, \mathrm{R}=\mathrm{C}(2-$ naph $) \mathrm{Ph}_{2}$ | -- | 1.991 | -- | 2.418 |
| $3.5-\mathrm{K}, \mathrm{R}=\mathrm{C}(2-\text { naph })_{3}$ | $2.001(9)$ | 1.971 | $2.388(10)$ | 2.413 |
| $3.6-\mathrm{K}, \mathrm{R}=\mathrm{C}(2$-naph $) \mathrm{Me}_{2}$ | $2.004(3)$ | 1.977 | $2.394(3)$ | 2.435 |
| $3.7-\mathrm{K}, \mathrm{R}=$ 2-naph | $2.032(3)$ | 2.002 | $2.320(4)$ | 2.390 |

The $\mathrm{U}=\mathrm{N}$ bond lengths of $3.5-\mathrm{K}, 3.6-\mathrm{K}$, and $3.7-\mathrm{K}$ of 2.001(9), 2.004(4), and 2.032(3) $\AA$, compared well with the uranium(IV) trityl imido compounds reported by the Meyer group ${ }^{27}$ and
our group $\left.{ }^{2}, \mathrm{~K}\left[\left({ }^{\mathrm{PP}, \mathrm{Me}} \mathrm{ArO}\right)_{3} \operatorname{tacn}\right) \mathrm{U}^{\mathrm{IV}}\left(=\mathrm{NCPh}_{3}\right)\right]$ and $\mathrm{K}\left[\mathrm{U}^{\mathrm{IV}}\left(=\mathrm{NCPh}_{3}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right.$, which had bond lengths of $2.036(2)$ and $1.9926(14) \AA$, respectively. In the case of the Meyer uranium(IV) trityl imido compound the $\mathrm{U}=\mathrm{N}-\mathrm{C}$ bond angle was more compressed, at $153.3(2)^{\circ}$, in comparison with the compounds we have reported in the bis(trimethylsilyl)amide ligand framework, which range from $165.7(3)^{\circ}$ for compound 3.6 -K to $169.82(12)^{\circ}$ for $\mathrm{K}\left[\mathrm{U}^{\mathrm{IV}}\left(=\mathrm{NCPh}_{3}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right.$. Uranium(IV) imido compounds that do not have close interactions with potassium ions, such as $\mathrm{U}^{\mathrm{IV}}(=\mathrm{NDipp}) \mathrm{Cl}_{2}(\mathrm{tppo})_{3}$ reported by Boncella and coworkers, have similar $\mathrm{U}=\mathrm{N}$ bond lengths (1.995(5) Å) but more linear U=N-C bond angles (177.7(4) $\left.{ }^{\mathrm{o}}\right)^{31}$

When compounds 3.4-3.6 were reacted with an excess of potassium graphite, the reaction mixtures became dark blue. ${ }^{1} \mathrm{H}$ NMR revealed many peaks between $8.04-6.88 \mathrm{ppm}$, a large amount of $\mathrm{HN}\left(\mathrm{SiMe}_{3}\right)_{2}$, and numerous paramagnetically shifted peaks between -1.66 to -28.87 ppm. Reaction conditions that afford clean reduced compound have yet to be identified. Surprisingly, when compound 3.7 was reacted with an excess of potassium graphite, 3.7-K was the only product of the reaction as judged by ${ }^{1} \mathrm{H}$ NMR spectroscopy. Although work toward isolation and application of the reduced species for reactivity studies is ongoing, our electrochemical and computational studies have yielded insight on the accessibility and electronic structure of the uranium(IV) naphthalene ${ }^{-1}$ species.

### 3.3.2. Electronic Characterization of Uranium Imido Complexes.

Electrochemical analysis provided insight into the possibility of accessing the different redox congeners of the naphthyl-imido uranium complexes versus $\mathrm{Fc}^{+/ 0}$ (Figure 3.3.9, Table 3.3.3). We previously reported the electrochemistry of $\mathbf{2 . 3}$, which featured reversible $\mathrm{U}(\mathrm{V} / \mathrm{VI})$ and $\mathrm{U}(\mathrm{IV} / \mathrm{V})$ couples at +0.38 and -1.31 V , respectively. ${ }^{2}$ Compounds 3.4 , 3.5 , and 3.7 exhibited reversible $\mathrm{U}(\mathrm{V} / \mathrm{VI})$ couples at $-0.17,+0.29$, and +0.12 V . The stability of the +6 oxidation state was correlated with the Mulliken charges of the uranium $(\mathrm{V})$ centers, as obtained by DFT analysis. For compounds 2.3 and 3.5 the Mulliken charges on the uranium center were similar at +1.15 and +1.17 , respectively, while for compound 3.4 the charge was less at +1.10 . Similarly, the $E_{1 / 2}$ of
the $\mathrm{U}(\mathrm{V} / \mathrm{VI})$ couple for compounds 2.3 and 3.5 were only 90 mV apart and at much higher potentials than the $\mathrm{U}(\mathrm{V} / \mathrm{VI})$ couple for $\mathbf{3 . 4}$, which was 550 mV shifted from compound 2.3. This significant shift of the $\mathrm{U}(\mathrm{V} / \mathrm{VI})$ couple in compound $\mathbf{3 . 4}$ implied that the +6 oxidation state was most stabilized by the [=NC(2-naph) $\mathrm{Ph}_{2}$ ] imido ligand, which is surprising due to the small structural and electronic differences between these compounds. Contrary to compounds 2.3, 3.4, and 3.5, compound 3.7 exhibited an irreversible $\mathrm{U}(\mathrm{V} / \mathrm{VI})$ couple with an $\mathrm{E}_{\mathrm{pa}}=-0.64$ and an $\mathrm{E}_{\mathrm{pc}}=$ +0.20 . The $E_{1 / 2}$ as obtained from differential pulse voltammetry exhibited a reversible $\mathrm{U}(\mathrm{V} / \mathrm{VI})$ couple at 0.12 V , implying that the apparent irreversibility in the cyclic voltammetry experiment was due to a large overpotential in the anodic wave. ${ }^{2,32}$


Figure 3.3.9. Cyclic voltammetry of 2.3 (red), $\mathbf{3 . 4}$ (orange), $\mathbf{3 . 5}$ (green), and 3.7 (blue) at a scan rate of $250 \mathrm{mV} / \mathrm{s}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, with 0.1 M [ $\left.{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right.$ ] supporting electrolyte. The data for compound $\mathbf{2 . 3}$ is previously reported and included for comparison. ${ }^{2}$

Table 3.3.3. Reduction potentials (vs. $\mathrm{Fc}^{+/ 0}$ ) of (naphthyl)imido complexes determined by DPV measurements, compared to the previously reported trityl(imido) complex. ${ }^{2}$

|  |  | $\mathrm{E}_{1 / 2}(\mathrm{~V})$ |  |
| :--- | :--- | :--- | :--- |
| $\mathrm{U}^{\vee}[=\mathrm{NR}]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ Derivative | $\mathrm{U}(\mathrm{VI} / \mathrm{V})$ | $\mathrm{U}(\mathrm{V} / \mathrm{IV})$ | naph $^{0} / \mathrm{naph}^{-1}$ |
| 2.3, $\mathrm{R}=\mathrm{CPh}_{3}$ | 0.38 | -1.31 | -- |
| 3.4-K, $\mathrm{R}=\mathrm{C}(2-$ naph $) \mathrm{Ph}_{2}$ | -0.17 | -1.32 | -1.71 |
| 3.5-K, $\mathrm{R}=\mathrm{C}(2-\text { naph })_{3}$ | 0.29 | -1.37 | -1.75 |
| 3.7-K, R = 2-naph | 0.12 | -1.25 | -2.27 |

The potential of the $\mathrm{U}(\mathrm{IV} / \mathrm{V})$ couple was similar across the series, ranging from -1.31 V to 1.37 V in the compounds with the triaryl moiety, and -1.25 V for compound 3.7 , with its simple naphthyl moiety. Because the $\mathrm{U}(\mathrm{VI} / \mathrm{V})$ couples span 550 mV across the series, while the $\mathrm{U}(\mathrm{V} / \mathrm{IV})$ couples only vary by 120 mV , the $\Delta \mathrm{E}_{1 / 2}$ varied substantially. Most interestingly for compounds 2.3, 3.4, and 3.5 , which are structurally similar, the $\Delta \mathrm{E}_{1 / 2}$ for 2.3 and 3.5 are 1.69 V and 1.66 V , respectively. However, for compound $\mathbf{3 . 4}$, the $\Delta \mathrm{E}_{1 / 2}$ is much smaller at 1.15 V . In contrast, the electrochemistry of uranium $(\mathrm{V})$ imido complexes $\left.\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{U}^{\mathrm{V}}[=\mathrm{NDipp})\right] \mathrm{X}(\mathrm{X}=\mathrm{Cl}, \mathrm{Br}, \mathrm{I}, \mathrm{OTf}$, SPh, $\mathrm{NPh}_{2}$, CCPh, OPh, Me, $\mathrm{N}=\mathrm{CPh}_{2}$ ), reported by Kiplinger, Graves, and coworkers, showed that despite their markedly different structures $\Delta \mathrm{E}_{1 / 2}$ remained relatively consistent across the series, at 1.52 V with a standard deviation of $\pm 0.03 \mathrm{~V} .{ }^{30}$

Following the $\mathrm{U}(\mathrm{IV} / \mathrm{V})$ feature was a second irreversible reduction feature that is only present in compounds 3.4, 3.5, and 3.7, which contained a naphthyl group in the imido ligand. This second reduction process was assigned to the naphthalene $0 /$ naphthalene $^{-1}$ couple. Under these electrochemical conditions, free naphthalene and 2-azidonaphthalene did not appear in the solvent window. However, in the series of complexes, the potential of the naphthalene ${ }^{0} /$ naphthalene $^{-1}$ process shifted to more negative potentials from compound 3.4 at 1.71 V , to compound 3.5 at -1.75 V , to compound 3.7 , which had the most shifted napthalene ${ }^{0}$ /naphthalene ${ }^{-1}$ couple, at -2.27 V . The poor reversibility of this feature in all of the complexes implied that complexes with reduced naphthalene moieties are reactive on the electrochemical timescale.

Based on comparing the electrochemical data for 2.3, 3.4, and 3.5, it is reasonable to conclude that the triaryl imido ligand is responsible for the third feature in the electrochemistry, which we have assigned as the naphthalene ${ }^{0} /$ naphthalene $^{-1}$ couple, since it is the only feature that does not appear in the electrochemistry of compound 2.3. To understand the electronic structure of the complexes with a reduced naphthalene moiety better we performed DFT calculations using a 60 electron core incorporating quasi-relativistic effects for uranium and 6$31 \mathrm{G}^{*}$ basis set for all other atoms. We calculated a putative dianionic compound, [U[=NC(2naph $\left.\left.) \mathrm{Ph}_{2}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]^{2-}(\mathbf{3 . 4 - 2 K})$ (Scheme 3.3.4), in the gas phase with and without potassium counterions present, and in a dichloromethane CPCM (conductor-like polarizable continuum model) solvent field with and without potassium counterions present (Figure 3.3.10). Additionally, we calculated $3.4-2 \mathrm{~K}$ in a dichloromethane CPCM solvent field with Grimme's dispersion corrections. However, the addition of dispersion correction resulted in little or no changes in molecular geometry or overall electronic structure between the calculations of $\mathbf{3 . 4 - 2 \mathrm { K }}$.


Scheme 3.3.4 Monoanionic (3.4-K) and computed dianionic (3.4-2K) naphthyl imido compounds.

The optimized geometries resulting from these calculations resulted in different bond lengths and angles depending on the conditions used in the calculation (Table 3.3.4). Both optimizations performed with potassium counterions included in the coordination sphere showed shorter average $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond lengths of 2.418 and $2.485 \AA$, for the gas phase and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ CPCM optimizations, respectively, compared with 2.577 and $2.620 \AA$ for those optimizations performed without cations. The $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond lengths with counterions ions present matched well with the experimental $\mathrm{U}^{\mathrm{IV}}-\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}$ bond lengths in imido complexes ${ }^{2}$. As yet, there are no U (III) imido complexes reported for comparison; however, the larger radius of a uranium(III) ion may be responsible for the longer calculated $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond lengths. Likewise, $\mathrm{U}=\mathrm{N}$ bond lengths for the optimizations with cations present were shorter at 2.018 and $1.999 \AA$ compared with bond lengths of 2.066 and $2.095 \AA$ for the optimized geometries without potassium ions present. The $\mathrm{U}=\mathrm{N}-\mathrm{C}$ bond angle is near linear in the gas phase optimized geometry with no counterions present (179.1 ${ }^{\circ}$ ), but bends by 6.9 degrees when counterions are added (172.2ㅇ). However, in a $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ CPCM solvent field, the $\mathrm{U}=\mathrm{N}-\mathrm{C}$ bond angle changes by less than a degree when counterions are included.

Table 3.3.4 Calculated bond lengths ( $\AA$ ) and angles (ㅇ) for $3.4-2 \mathrm{~K}$ in gas phase and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ CPCM (conductor-like polarizable continuum model) conditions with and without potassium counterions.

| Optimization Conditions | $\mathrm{U}-\mathrm{N}_{\text {avg }}$ | $\mathrm{U}=\mathrm{N}$ | $\mathrm{U}=\mathrm{N}-\mathrm{C}$ |
| :--- | :---: | :---: | :---: |
| Gas Phase, no cations | 2.577 | 2.066 | 179.1 |
| Gas Phase, K cations | 2.418 | 2.018 | 172.2 |
| $\mathrm{CH}_{2} \mathrm{Cl}_{2} \mathrm{CPCM}$, no cations | 2.620 | 2.095 | 177.0 |
| $\mathrm{CH}_{2} \mathrm{Cl}_{2} \mathrm{CPCM}, \mathrm{K}$ cations | 2.485 | 1.999 | 176.3 |

We projected spin density plots from the optimized geometries and found that when counterions were excluded from the computed dianionic structure, minimal spin density was located on the naphthalene moiety with +0.03 in the case of a $\mathrm{CH}_{2} \mathrm{Cl}_{2} \mathrm{CPCM}$ solvent field and +0.05 in the gas phase. In these cases spin densities of +3.07 and +3.08 were located on the uranium cation. However, with potassium counterions present significant spin density $(+0.95)$ is located on the naphthalene moiety in a $\mathrm{CH}_{2} \mathrm{Cl}_{2} \mathrm{CPCM}$ solvent field, with less in the gas phase optimization result (+0.30). In both of these cases similar spin densities reside on the uranium ion of +2.18 and +2.16 for the $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and gas phase calculations, respectively. The electrochemical data shows that a second reduction feature, ranging from -1.71 to -2.27 V , is present for compounds $3.4,3.5$, and 3.7 , but not for compound 2.3 with its redox innocent ligand $\left[=\mathrm{NCPh}_{3}\right]$. Since it is unlikely that the alteration of the imido ligand from [ $=\mathrm{NCPh}_{3}$ ] to $\left[=\mathrm{NC}(2-\mathrm{naph}) \mathrm{Ph}_{2}\right]$, [=NC(2-naph) $)_{3}$, or $[=\mathrm{N}(2-$ naph $)]$ would drastically shift the $\mathrm{U}(\mathrm{IV} / \mathrm{III})$ couple, it is reasonable to conclude that the calculations with the counterions present are more representative of the electronic structure of the dianions and that the second reduction feature is ligand-based. Additionally, we can conclude that the presence of the counterions as well as a dichloromethane CPCM solvent field is important for the most accurate electronic structure calculation results for these compounds. The presence of potassium counterions has been shown by Mazzanti and coworkers to affect the stability of reduced uranium complexes in some cases. ${ }^{33}$


Figure 3.3.10 Spin density plots of 3.4-2K with quartet multiplicity as the gas phase dianion (upper left), dianion in a $\mathrm{CH}_{2} \mathrm{Cl}_{2} \mathrm{CPCM}$ (conductor-like polarizable continuum model) solvent field (upper right), neutral gas phase compound with potassium counterions present (lower left), and
neutral compound with potassium counterions present in a $\mathrm{CH}_{2} \mathrm{Cl}_{2} \mathrm{CPCM}$ solvent field (lower right). Hydrogen atoms removed for clarity.

### 3.4 Summary.

In summary, we have synthesized and fully characterized a series of three uranium(V) imido compounds 3.4-3.7 bearing redox-active imido ligand fragments. Electrochemical analysis reveals accessible ligand reduction events and computational results indicate that, with close contacts to potassium counterions, reduced ligands can be stabilized. We have reduced the uranium $(\mathrm{V})$ compounds to their uranium(IV) counterparts $3.4-\mathrm{K}-3.7-\mathrm{K}$. Efforts to isolate and achieve two-electron reactivity from the compounds with reduced imido ligands are ongoing.

### 3.5 Experimental.

### 3.5.1 Methods.

All reactions and manipulations were performed under an inert atmosphere $\left(\mathrm{N}_{2}\right)$ using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at $150^{\circ} \mathrm{C}$ prior to use. Unless otherwise noted, reactions were conducted in 20 mL scintillation vials in approximately $5-10 \mathrm{~mL}$ of solvent. ${ }^{1} \mathrm{H}$ NMR were obtained on a Bruker DMX300 Fourier transform NMR spectrometer at 300 MHz . Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks. Elemental analyses were performed at Complete Analysis Laboratories, Inc., Parsippany, New Jersey. The infrared spectra were obtained from $400-4000 \mathrm{~cm}^{-1}$ using a Perkin Elmer 1600 series infrared spectrometer.

### 3.5.2 Materials.

Tetrahydrofuran, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, hexanes, pentane, and toluene were purchased from Fisher Scientific. These solvents were sparged for 20 min with dry argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina, respectively (for hexanes and pentane), or two columns of neutral alumina (for THF and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ). All solvents were stored over $3 \AA$ molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and stored over 3 Å molecular sieves overnight prior
to use. Starting materials: $\mathrm{Ul}_{3}(\mathrm{THF})_{4},{ }^{34} \mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3},{ }^{35} 2.3^{2}$, and 2-naphthyl azide ${ }^{36}$ were prepared according to the reported procedures.

### 3.5.3 Synthesis of $\alpha, \alpha$-diphenyl-2-naphthalene methanol.

To a flame-dried three-neck round-bottom flask equipped with an addition funnel and condenser was added 2-bromonaphthalene ( $3.01 \mathrm{~g}, 15 \mathrm{mmol}, 1.0$ equiv) in 40 mL of diethyl ether under inert atmosphere. To the solution was added $n$-butyllithium ( 1.6 M hexanes solution, 10 $\mathrm{mL}, 16 \mathrm{mmol}, 1.1$ equiv) dropwise at $0^{\circ} \mathrm{C}$. The reaction mixture was stirred at $0^{\circ} \mathrm{C}$ for 1 h , before adding a solution of benzophenone ( $2.00 \mathrm{~g}, 11 \mathrm{mmol}, 0.75$ equiv) in 50 mL of diethyl ether. The reaction mixture was warmed to room temperature and stirred for 30 min before being heated to reflux and stirred for an additional 1.5 h . The reaction mixture was cooled to $0^{\circ} \mathrm{C}$ and quenched with a saturated solution of ammonium chloride followed by extraction with three 75 mL portions of diethyl ether. The combined organics were washed with two 50 mL portions of water, and one 50 mL portion of brine. The solution was dried over sodium sulfate, decanted, and the volatiles were removed. The resulting oil was dissolved in minimal hexanes and stored in a freezer until a, a-diphenyl-2-naphthalene methanol precipitated as a white solid ( $3.01 \mathrm{~g}, 9.7 \mathrm{mmol}, 88 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 7.79-7.27 (m, 17 H ), 2.90 (s, 1 H ). Characterization matched previously reported data. ${ }^{37}$

### 3.5.4 Synthesis of tri(2-naphthalene)methanol.

To a flame-dried three-neck round-bottom flask equipped with an addition funnel and condenser was added 2-bromonaphthalene ( $8.03 \mathrm{~g}, 39 \mathrm{mmol}, 3.0$ equiv) in 50 mL of diethyl ether under an inert atmosphere. To the solution was added $n$-butyllithium ( 1.6 M hexanes solution, 27 $\mathrm{mL}, 42 \mathrm{mmol}, 3.3$ equiv) dropwise at $0^{\circ} \mathrm{C}$. The reaction mixture was stirred at $0^{\circ} \mathrm{C}$ for 1 h , before adding a solution of 2-naphthoyl chloride ( $2.50 \mathrm{~g}, 13 \mathrm{mmol}, 1.0$ equiv) in 50 mL of diethyl ether. The reaction mixture was allowed to warm to room temperature and stirred for 30 min before being heated to reflux and stirred for an additional 4 h . The reaction mixture was cooled to $0^{\circ} \mathrm{C}$ and quenched with a saturated solution of ammonium chloride and extracted with
dichloromethane three times. The combined organics were washed with two 50 mL portions of water, and one 50 mL portion of brine. The solution was dried over sodium sulfate, decanted, and the volatiles were removed. The resulting solid was collected and washed with 50 mL of hexanes to yield tri(2-naphthalene)methanol as a white solid ( $5.22 \mathrm{~g}, 13 \mathrm{mmol}, 97 \%$ yield). ${ }^{1} \mathrm{H}$ NMR (300 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.47-7.92(\mathrm{~m}, 21 \mathrm{H}), 2.91(\mathrm{~s}, 1 \mathrm{H})$. Characterization matched previously reported data. ${ }^{38}$

### 3.5.5 Synthesis of 2-(naphthalene)propan-2-ol.

To a flame-dried three-neck round-bottom flask equipped with an addition funnel and condenser was added 2-bromonaphthalene ( $8.00 \mathrm{~g}, 39 \mathrm{mmol}, 1.5$ equiv) in 30 mL of diethyl ether under an inert atmosphere. To the solution was added $n$-butyllithium ( 1.6 M hexanes solution, 18 $\mathrm{mL}, 28 \mathrm{mmol}, 1.1$ equiv) dropwise at $0^{\circ} \mathrm{C}$. The reaction mixture was stirred at $0^{\circ} \mathrm{C}$ for 1 h , before adding a solution of acetone ( $1.9 \mathrm{~mL}, 26 \mathrm{mmol}, 1$ equiv) in 25 mL of diethyl ether. The reaction mixture was allowed to warm to room temperature and stirred for 30 min before being heated to reflux and stirred for an additional 4 h . The reaction mixture was cooled to $0^{\circ} \mathrm{C}$ and quenched with a saturated solution of ammonium chloride and extracted with diethyl ether three times. The combined organics were washed with two 50 mL portions of water, and one 50 mL portion of brine. The solution was dried over sodium sulfate, decanted, and the volatiles were removed. The resulting solid was collected and washed with 50 mL of hexanes to yield a colorless oil ( $2.89 \mathrm{~g}, 16$ mmol, $60 \%$ yield). ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.96(1 \mathrm{H}, \mathrm{m}), 7.85(3 \mathrm{H}, \mathrm{m}), 7.64(1 \mathrm{H}, \mathrm{m}), 7.47$ $(2 \mathrm{H}, \mathrm{m}), 1.70(6 \mathrm{H}, \mathrm{s})$. Characterization matched previously reported data. ${ }^{39}$

### 3.5.6 Synthesis of 2-(azidodiphenymethyl)naphthalene (3.1).

(Caution: $\mathrm{HN}_{3}$ was generated in the course of this synthesis, which is an extremely toxic and volatile compound.) To a three-neck round-bottom flask equipped with an addition funnel, condenser, and gas inlet attached to an aqueous sodium hydroxide ( 3 M ) bubbler to quench $\mathrm{HN}_{3}$, was added sodium azide ( $2.51 \mathrm{~g}, 39 \mathrm{mmol}, 4.0$ equiv) in a solution of 15 mL water and 30 mL chloroform. To the solution of sodium azide was added $\alpha, \alpha$-diphenyl-2-naphthalene methanol (3.0
$\mathrm{g}, 10 \mathrm{mmol}, 1.0$ equiv) dissolved in chloroform. The reaction mixture was cooled to $0^{\circ} \mathrm{C}$ on an ice bath, and 6 mL of concentrated sulfuric acid was added dropwise. The reaction mixture was stirred at room temperature for 1 h and heated to reflux for 6 h . The reaction mixture was quenched with an aqueous sodium hydroxide solution $(3 \mathrm{M})$ at $0^{\circ} \mathrm{C}$ until basic, and extracted with three 50 mL portions of dichloromethane. The combined organics were washed with water and brine and dried over sodium sulfate. The solution was decanted, and the volatiles were removed. A small volume of hexanes ( 15 mL ) was added to the resulting oil, and the mixture was stored in a freezer until 2-(azidodiphenylmethyl)naphthalene precipitated as a white solid (2.21 g, 6.59 mmol, $68 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 7.83-7.77 ( $\mathrm{m}, 4 \mathrm{H}$ ), 7.51-7.48 (m, 3H), 7-36-7.34 ( $\mathrm{m}, 10 \mathrm{H}$ ). ${ }^{13} \mathrm{C}$ NMR ( $360 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 146.89, 144.37, 143.16, 132.98, 132.72, 128.78, 128.62, 128.45, 128.21, 128.00, 127.85, 127.66, 127.55, 126.73, 126.52, 126.38, 126.31, 82.38. HRMSESI ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{23} \mathrm{H}_{17} \mathrm{~N}_{3}\left[\mathrm{M}+\mathrm{H}-\mathrm{N}_{2}\right]^{+}, 308.1439$; found, 308.1429. IR (KBr plate): 3059 (m), 3034 (w), 2101 (s), 1599 (w), 1506 (w), 1491 (m), 1447 (m), 1384 (w), 1318 (w), 1272 (m), 1256 (m), 1214 (w), 1185 (w), 1146 (w), 1121 (w), 1082 (w), 1034 (w), 941 (w), 905 (w), 892 (m), 857 (m), 817 (m), 748 (s), 701 (s), 649 (w), 625 (w), $570(\mathrm{~m}), 478(\mathrm{~m}) \mathrm{cm}^{-1}$.

### 3.5.7 Synthesis of 2,2',2"-(azidomethane)trinaphthalene (3.2).

(Caution: $\mathrm{HN}_{3}$ was generated in the course of this synthesis, which is an extremely toxic and volatile compound.) To a three-neck round-bottom flask equipped with an addition funnel, condenser, and gas inlet attached to an aqueous sodium hydroxide $(3 \mathrm{M})$ bubbler to quench $\mathrm{HN}_{3}$, was added sodium azide ( $3.31 \mathrm{~g}, 51 \mathrm{mmol}, 4.0$ equiv) in a solution of 20 mL water and 35 mL chloroform. To the solution of sodium azide was added tri(naphthalene-2-yl)methanol ( $5.22 \mathrm{~g}, 13$ mmol, 1.0 equiv) dissolved in 75 mL of chloroform. The solution was cooled to $0^{\circ} \mathrm{C}$, and 10 mL of concentrated sulfuric acid was added dropwise. The solution was warmed to room temperature and stirred for 1 h before heating to reflux for an additional 6 h . The reaction mixture was quenched with an aqueous solution of sodium hydroxide (3M) at $0{ }^{\circ} \mathrm{C}$ until basic and extracted with three 50 mL portions of dichloromethane. The combined organics were washed with water

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and brine and dried over sodium sulfate. The solution was decanted, and the volatiles were removed to yield 2,2',2"-(azidomethanetriyl)trinaphthalene as a white solid ( $4.90 \mathrm{~g}, 11 \mathrm{mmol}, 88 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $360 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 7.86-7.67 (m, 12H), 7.45 (m, 8H). ${ }^{13} \mathrm{C}$ NMR ( 360 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 140.24,132.89,132.74,128.59,128.17,127.7,127.55,126.66,126.60,126.42$. HRMSESI ( $\mathrm{m} / \mathrm{z}$ ): calcd for $\mathrm{C}_{31} \mathrm{H}_{21} \mathrm{~N}_{3}\left[\mathrm{M}+\mathrm{H}-\mathrm{N}_{2}\right]^{+}$, 408.1752; found, 408.1746. IR (KBr plate): 3053 (m), 2101 (s), 1630 (w), 1594 (m), 1504 (m), 1427 (w), 1385 (m), 1274 (m), 1254 (w), 1178 (w), 1128 (w), 1019 (w), 965 (m), 951 (w), 905 (m), 882 (m), 853 (s), 817 (s), 747 (m), 737 (s), 626 (w), 477 (s), $469(\mathrm{~m}) \mathrm{cm}^{-1}$.

### 3.5.8 Synthesis of 2-(2-azidopropan)naphthalene (3.3).

(Caution: $\mathrm{HN}_{3}$ was generated in the course of this synthesis, which is an extremely toxic and volatile compound.) To a three-neck round-bottom flask equipped with an addition funnel, condenser, and gas inlet attached to an aqueous sodium hydroxide ( 3 M ) bubbler to quench $\mathrm{HN}_{3}$, was added sodium azide ( $4.06 \mathrm{~g}, 62 \mathrm{mmol}, 4.0$ equiv) in a solution of 20 mL water and 35 mL chloroform. To the solution of sodium azide was added 2-(naphthalene)propan-2-ol (2.89 g, 16 mmol, 1.0 equiv) dissolved in 75 mL of chloroform. The solution was cooled to $0^{\circ} \mathrm{C}$ and 10 mL of concentrated sulfuric acid was added dropwise. The solution was warmed to room temperature and stirred for 1 h before heating to reflux for an additional 6 h . The reaction mixture was quenched with an aqueous solution of sodium hydroxide $(3 \mathrm{M})$ at $0^{\circ} \mathrm{C}$ until basic and extracted with three 50 mL portions of dichloromethane. The combined organics were washed with water and brine and dried over sodium sulfate. The solution was decanted, and the volatiles were removed to yield 2-(2-azidopropan)naphthalene as a colorless oil. The crude oil was purified over a silica plug, which was first washed with petroleum ether, followed by dichloromethane to yield pure product ( $1.40 \mathrm{~g}, 6 \mathrm{mmol}, 42 \%$ yield). ${ }^{1} \mathrm{H}$ NMR ( $360 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.87(4 \mathrm{H}, \mathrm{m}), 7.60(1 \mathrm{H}$, dd, $J=8.7,1.9 \mathrm{MHz}), 7.49(2 \mathrm{H}, \mathrm{m}), 1.75(6 \mathrm{H}, \mathrm{s})$. IR (KBr plate): 3058 (m), 2973 (s), 2931 (m), 2865 (w), 2100 (s), 1631 (w), 1600 (m), 1505 (m). 1459 (m), 1385 (m), 1368 (m), 1275 (s), 1261
(s), 1198 (m), 1131 (s), 1090 (m), 1080 (m), 1019 (m), 951 (w), 892 (m), 856 (m), 817 (s), 747 (s), 714 (w), 680 (w), 661 (w), 627 (w), 602 (w), 565 (w), 477 (m).

### 3.5.9 Synthesis of $\mathrm{U}\left[=\mathrm{NC}(2-\mathrm{naph}) \mathrm{Ph}_{2}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (3.4).

To a stirred solution of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(600 \mathrm{mg}, 0.834 \mathrm{mmol})$ in hexanes was added a solution of 2-(azidodiphenymethyl)naphthalene ( $280 \mathrm{mg}, 0.834 \mathrm{mmol}$ ) in THF. The reaction mixture bubbled and turned brown, after which the volatiles were removed under reduced pressure. The residue was extracted with hexanes, filtered over Celite suspended in a glass pipet, and recrystallized at $-21^{\circ} \mathrm{C}$ from minimal hexanes $(2 \mathrm{~mL})$ to yield 3.4 as a green-brown solid ( $535 \mathrm{mg}, 0.52 \mathrm{mmol}, 63 \%$ yield). ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $22.22(3 \mathrm{H}), 10.19(4 \mathrm{H}), 9.72(1 \mathrm{H})$, $9.25(1 \mathrm{H}), 8.70(2 \mathrm{H}), 8.14-8.21(2 \mathrm{H}), 7.08-7.31(4 \mathrm{H}),-3.39(54 \mathrm{H})$. IR (KBr pellet): $3059(\mathrm{w}), 2955$ (m), 2900 (w), 1918 (vw), 1599 (w), 1491 (w), 1445 (w), 1250 (s), 1183 (m), 1117 (w), 1033 (w), 936 (s), 887 (s), 844 (s), 771 (s), 756 (s), 699 (m), 669 (m), 657 (m), 608 (m). Elemental analysis found (calculated) for $\mathrm{C}_{41} \mathrm{H}_{71} \mathrm{~N}_{4} \mathrm{Si}_{6} \mathrm{U}$ : C 47.80 (47.97), H 6.88 (6.97), N 5.34 (5.46).

### 3.5.10 Synthesis of $\mathrm{U}\left[=\mathrm{NC}(2-\mathrm{naph})_{3}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (3.5).

To a stirred solution of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(250 \mathrm{mg}, 0.35 \mathrm{mmol})$ in THF was added a solution of 2,2',2"-(azidomethanetriyl)trinaphthalene ( $151 \mathrm{mg}, 0.35 \mathrm{mmol}$ ) in THF. The reaction mixture bubbled and turned green-brown, after which it was reduced to a small volume under reduced pressure and crystallized at $-21^{\circ} \mathrm{C}$ to yield 3.5 as a dark green solid ( $217 \mathrm{mg}, 0.19 \mathrm{mmol}, 55 \%$ yield). ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $22.01(3 \mathrm{H}), 9.43(6 \mathrm{H}), 8.25(6 \mathrm{H}), 7.60(3 \mathrm{H}), 7.1-7.16(3 \mathrm{H}),-3.64$ (54H). IR (KBr pellet): 3057 (m), 2958 (m), 2900 (m), 1937 (w), 1792 (vw), 1580 (w), 1500 (w), 1433 (vw), 1351 (vw), 1248 (m), 1182 (vw), 1125 (vw), 1069 (w), 1019 (w), 895 (m), 852 (m), 750 (m), 658 (w), 609 (m). Elemental analysis found (calculated) for $\mathrm{C}_{49} \mathrm{H}_{75} \mathrm{~N}_{4} \mathrm{Si}_{6} \mathrm{U}: \mathrm{C} 52.31$ (52.24); H 6.59 (6.71); N 4.83 (4.97).

### 3.5.11 Synthesis of $\mathrm{U}\left[=\mathrm{NC}(2-\mathrm{naph}) \mathrm{Me}_{2}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (3.6).

To a solution of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(250 \mathrm{mg}, 0.348 \mathrm{mmol})$ in hexanes cooled to $-21^{\circ} \mathrm{C}$ was added a solution of 2-(2-azidopropane)naphthalene ( $73 \mathrm{mg}, 0.348 \mathrm{mmol}$ ) in pentane. The
reaction mixture bubbled and turned brown. Volatiles were evaporated, and crystallization from pentane, hexane and $\left(\mathrm{Me}_{3} \mathrm{Si}_{2}\right)_{2} \mathrm{O}$ were attempted at $-21{ }^{\circ} \mathrm{C}$, however, 3.6 was very soluble in organic solvents and never precipitated from these conditions. ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $22.50(2 \mathrm{H})$, 11.89 (1H), $9.22(1 \mathrm{H}), 7.98(1 \mathrm{H}), 7.67(2 \mathrm{H}), 1.38(6 \mathrm{H}),-2.31(18 \mathrm{H}),-4.38(36 \mathrm{H})$.

### 3.5.12 Synthesis of $\mathrm{U}[=\mathrm{N}(2-\mathrm{naph})]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (3.7).

To a solution of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(300 \mathrm{mg}, 0.417 \mathrm{mmol})$ in hexanes cooled to $-21^{\circ} \mathrm{C}$ was added a solution of 2-azidonaphthalene ( $71 \mathrm{mg}, 0.417 \mathrm{mmol}$ ) in hexanes cooled to $-21^{\circ} \mathrm{C}$. The reaction mixture bubbled and turned brown, yielding a mixture of 3.7 and 3.8. The solution was then reduced to a small volume under reduced pressure and crystallized at $-21^{\circ} \mathrm{C}$ to yield pure 3.7 as a brown solid ( $250 \mathrm{mg}, 0.29 \mathrm{mmol}, 70 \%$ yield). ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $21.40(1 \mathrm{H}), 13.96$ (1H), 12.19 (1H), -2.02 (54H), -5.43 (4H). IR (KBr pellet): 3054 (vw), 2958 (m), 2900 (w), 2190 (vw), 1917 ( vw ), 1814 ( vw ), 1621 (m), 1587 (m), 1432 (m), 1251 (s), 1182 (m), 875 (s), 843 (s), 752 (w), 690 (w), 653 (w), 619 (w). Elemental analysis found (calculated) for $\mathrm{C}_{28} \mathrm{H}_{61} \mathrm{~N}_{4} \mathrm{Si}_{6} \mathrm{U}$ : C 38.83 (39.09); H 7.00 (7.15); N 6.39 (6.51).

### 3.5.13 Synthesis of $\mathrm{K}\left[\mathrm{U}\left[=\mathrm{NC}(2-\mathrm{naph}) \mathrm{Ph}_{2}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ (3.4-K).

To a solution of compound $3.4(260 \mathrm{mg}, 0.244 \mathrm{mmol})$ in toluene cooled to $-21^{\circ} \mathrm{C}$ was added potassium graphite ( $30 \mathrm{mg}, 0.220 \mathrm{mmol}$ ). The reaction was filtered over Celite, and the volatiles were removed under reduced pressure. The residue was then washed with pentanes to yield $3.4-\mathrm{K}$ as a dark pink solid ( $117 \mathrm{mg}, 0.110 \mathrm{mmol}, 50 \%$ yield). ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): 47.54 $(1 \mathrm{H}, \mathrm{s}), 42.12(4 \mathrm{H}, \mathrm{s}), 15.32(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=6.0 \mathrm{~Hz}), 13.35(4 \mathrm{H}, \mathrm{s}), 11.73(3 \mathrm{H}, \mathrm{s}), 10.23(2 \mathrm{H}, \mathrm{t}, J=7.5$ $\mathrm{Hz}), 9.32(1 \mathrm{H}, 2, J=6 \mathrm{~Hz}), 8.70(1 \mathrm{H}, \mathrm{t}, 7.5 \mathrm{~Hz}),-8.77(54 \mathrm{H}, \mathrm{s})$. $\mathrm{IR}(\mathrm{KBr}$ pellet): $3054(\mathrm{~m}), 2951$ (s), 2893 (m), 2274 (w), 2083 (w), 1915 (w), 1588 (m), 1489 (m), 1442 (m), 1249 (s), 1182 (m), 1115 (m), 1033 (m), 939 (s), 837 (s), 755 (m), 700 (m), 665 (m), 602 (m), 485 (m). Compound 3.4-K was chemically unstable toward desolvation; elemental analysis was attempted for 3.4-K but was unobtainable due to its instability, based on two attempts.
3.5.14 Synthesis of $\mathrm{K}\left[\mathrm{U}\left[=\mathrm{NC}(2-\text { naph })_{3}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ (3.5-K).

To a solution of compound 3.5 ( $573 \mathrm{mg}, 0.509 \mathrm{mmol}$ ) in toluene cooled to $-21^{\circ} \mathrm{C}$ was added potassium graphite $(62 \mathrm{mg}, 0.458 \mathrm{mmol})$. The reaction mixture was filtered over Celite, the solution was reduced to a small volume, and precipitated with pentane to yield $\mathbf{3 . 5 - K}$ as a dark pink solid (264 mg, $0.227 \mathrm{mmol}, 49 \%$ yield). ${ }^{1} \mathrm{H}$ NMR (benzene- $\mathrm{d}_{6}$ ): $49.29(3 \mathrm{H}, \mathrm{s}), 40.75(3 \mathrm{H}, \mathrm{s})$, $13.63(3 \mathrm{H}, \mathrm{s}, J=6 \mathrm{~Hz}), 10.14(3 \mathrm{H}, \mathrm{s}), 9.49(4 \mathrm{H}, \mathrm{t}, J=7.5 \mathrm{~Hz}), 9.09(4 \mathrm{H}, \mathrm{d}, J=6 \mathrm{~Hz}), 8.44(4 \mathrm{H}, \mathrm{t}$, $J=6 \mathrm{~Hz}),-8.85(54 \mathrm{H}, \mathrm{s}) . \mathrm{IR}(\mathrm{KBr}$ pellet): $3056(\mathrm{~m}), 2953(\mathrm{~s}), 2896(\mathrm{~m}), 2484(\mathrm{w}), 2290(\mathrm{w}), 2091$ (m), 1920 (w), 1598 (m), 1502 (m), 1434 (m), 1350 (m), 1251 (s), 1178 (m), 1115 (m), 1051 (m), 937 (s), 831 (s), 765 (m), 662 (m), 608 (m), 476 (m). Compound 3.5-K was chemically unstable toward desolvation; elemental analysis was attempted for $3.5-\mathrm{K}$ but was unobtainable due to its instability, based on two attempts.

### 3.5.15 Synthesis of $K\left[U\left[=N C(2-n a p h) \mathrm{Me}_{2}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right](3.6-\mathrm{K})$.

To a solution of compound $3.6(64 \mathrm{mg}, 0.070 \mathrm{mmol})$ in THF was added potassium graphite ( $21 \mathrm{mg}, 0.153 \mathrm{mmol}$ ). The reaction mixture was filtered over Celite, the solution was reduced to a small volume, layered with pentane, and crystallized at $-21{ }^{\circ} \mathrm{C}$ to yield X-ray quality pink-orange crystals of 3.6-K. ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $58.26(1 \mathrm{H}), 53.24(1 \mathrm{H}), 46.17(6 \mathrm{H}), 23.74$ $(1 \mathrm{H}), 20.26(1 \mathrm{H}, \mathrm{d}, J=7.9 \mathrm{~Hz}), 15.84(1 \mathrm{H}, \mathrm{d}, J=8.22), 13.53(1 \mathrm{H}, \mathrm{t}, J=7.64 \mathrm{~Hz}), 12.36(1 \mathrm{H}, \mathrm{t}, J$ $=7.76),-7.92(54 \mathrm{H})$.

### 3.5.16 Synthesis of $K\left[U[=N(2-n a p h)]\left[N\left(\text { SiMe }_{3}\right)_{2}\right]_{3}\right]$ (THF) (3.7-K).

To a solution of compound 3.7 ( $145 \mathrm{mg}, 0.169 \mathrm{mmol}$ ) in THF cooled to $-21^{\circ} \mathrm{C}$ was added potassium graphite ( $46 \mathrm{mg}, 0.337 \mathrm{mmol}$ ). The reaction mixture was filtered over Celite and the volatiles were removed under reduced pressure. The residue was then extracted with pentanes, filtered over Celtie and crystallized at $-21^{\circ} \mathrm{C}$ to yield $3.7-\mathrm{K}$ as pale pink crystals. Yield: 70 mg , $0.78 \mathrm{mmol}, 46 \% .{ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $32.40(1 \mathrm{H}), 26.49(1 \mathrm{H}), 22.91(1 \mathrm{H}), 13.98(1 \mathrm{H}, \mathrm{d}, \mathrm{J}=6.0$ $\mathrm{Hz}), 12.09(1 \mathrm{H}, \mathrm{d}, J=6.0 \mathrm{~Hz}), 11.73(1 \mathrm{H}, \mathrm{t}, J=6.0 \mathrm{~Hz}), 10.16(1 \mathrm{H}, \mathrm{t}, J=6.0 \mathrm{~Hz}) . \mathrm{IR}(\mathrm{KBr}$ pellet): 3044 (vw), 2951 (s), 2898 (m), 2275 (vw), 2102 (vw), 1912 (vw), 1610 (m), 1579 (m), 1547 (m), 1486 (m), 1459 (m), 1427 (m), 1363 (m), 1341 (m), 1283 (m), 1251 (s), 1184 (m), 1119 (w), 1053
(w), 942 (s), 848 (s), 768 (m), 669 (m), 662 (m), 603 (m). Compound 3.7-K was chemically unstable toward desolvation; elemental analysis was attempted for 3.7-K but was unobtainable due to its instability, based on four attempts.

### 3.6 Crystallographic Analysis.

X-Ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Ka radiation ( $\lambda=0.71073 \AA$ ) at a temperature of $143(1) \mathrm{K}$. In all cases, rotation frames were integrated using SAINT, ${ }^{40}$ producing a listing of unaveraged $F^{2}$ and $\sigma\left(F^{2}\right)$ values which were then passed to the SHELXTL ${ }^{41}$ program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS ${ }^{42}$ or SADABS. ${ }^{43}$ The structures were solved by direct methods (SHELXS-97). ${ }^{44}$ Refinement was by full-matrix least squares based on $\mathrm{F}^{2}$ using SHELXL-97. ${ }^{44}$ All reflections were used during refinements. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Of note, X-ray diffraction data for 3.5 was collected on two occasions, each in the same rhombohedral cell. However, in both data sets significant electron density was located but not assigned. In the first structure, the density was positioned directly over the $\mathrm{U}=\mathrm{N}$ bond but did not interact with any of the naphthyl groups. In the second structure, despite an identical unit cell, the density was positioned next to a naphthyl group on the imido ligand, again with no interaction. The peaks that have been identified as chlorine atoms might be partial uranium atoms. A chlorine atom has about $18 \%$ of the electron density of a uranium atom so the other atoms in the disordered molecule would appear as peaks of 1-2 e/ $/ \AA^{3}$, which is comparable to the noise in this structure. The crystals were of rather poor quality, leading to a final difference map with noise peaks on the order of $3-4 \mathrm{e} / \mathrm{A}^{3}$. However, the bond metrics are very similar to compound $\mathbf{3 . 4}$, so the bond lengths and angles are evidently unaffected by this unassigned electron density.


Figure 3.6.1 Thermal ellipsoid plots of 3.5 including anomalous q-peak.

### 3.7 Spectroscopic Analysis.

${ }^{1} \mathrm{H}$ NMR spectra were obtained on a Bruker DMX-300 Fourier transform NMR spectrometer at 300 MHz . Chemical shifts were recorded in units of parts per million referenced to residual solvent peaks ( ${ }^{1} \mathrm{H}$ ). The UV-Visible absorption spectra were obtained from 2000-290 nm using a Perkin Elmer 950 UV-Vis/NIR Spectrophotometer, and all samples were prepared under an $\mathrm{N}_{2}$ environment. 1 mm pathlength screw cap quartz cells were used with a blank measured before each run.


Figure 3.7.1. ${ }^{1} \mathrm{H}$ NMR of 3.1 in chloroform $-d_{3}$.


Figure 3.7.2. ${ }^{13} \mathrm{C}$ NMR of 3.1 in chloroform $-d_{3}$.


Figure 3.7.3. ${ }^{1} \mathrm{H}$ NMR of 3.2 in chloroform- $d_{3}$.


Figure 3.7.5. ${ }^{1} \mathrm{H}$ NMR of 3.3 in chloroform $-d_{3}$.


Figure 3.7.6. ${ }^{1} \mathrm{H}$ NMR of 3.4 in benzene- $d_{6}$.


Figure 3.7.7. ${ }^{1} \mathrm{H}$ NMR of 3.5 in benzene- $d_{6}$.

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Figure 3.7.8. ${ }^{1} \mathrm{H}$ NMR of 3.6 in benzene- $d_{6}$.


Figure 3.7.9. ${ }^{1} \mathrm{H}$ NMR of 3.7 in benzene- $d_{6}$.


Figure 3.7.10. Crude ${ }^{1} \mathrm{H}$ NMR of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}+($ naph $) \mathrm{N}_{3}$ showing both compound 3.7 and the inserted azide product 3.8.


Figure 3.7.11. ${ }^{1} \mathrm{H}$ NMR of $3.4-\mathrm{K}$ benzene- $d_{6}$.


Figure 3.7.12. ${ }^{1} \mathrm{H}$ NMR of $3.5-\mathrm{K}$ benzene $-d_{6}$.


Figure 3.7.13. ${ }^{1} \mathrm{H}$ NMR of $3.6-\mathrm{K}$ benzene- $d_{6}$.


Figure 3.7.14. ${ }^{1} \mathrm{H}$ NMR of $3.7-\mathrm{K}$ benzene- $d_{6}$.


Figure 3.7.15. Electronic absorption spectrum of 3.4 (red trace), $\mathbf{3 . 5}$ (blue trace), and $\mathbf{3 . 6}$ (green trace) in toluene.


Figure 3.7.16. Electronic absorption spectrum of 3.4-K (red trace), 3.5-K (blue trace), and 3.6-K (green trace) in toluene (small amount of uranium(V) impurity unobservable by ${ }^{1} \mathrm{H}$ NMR of sample marked with *).


Figure 3.7.17. NIR of compound 3.4 in toluene.


Figure 3.7.18. NIR of compound 3.5 in toluene.


Figure 3.7.19. NIR of compound 3.4-K in toluene.


Figure 3.7.20. NIR of compound $3.5-\mathrm{K}$ in toluene.

### 3.8 Electrochemical Analysis.

Voltammetry experiments (CV, DPV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation, and the data were processed using CHI software v9.24. All experiments were performed in an $\mathrm{N}_{2}$ atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The quasi-reference electrode was prepared by dipping a length of silver wire in concentrated hydrochloric acid. The working electrode surfaces were polished prior to each set of experiments. Potentials were reported versus ferrocene, which was added as an internal standard for calibration at the end of each run. Solutions employed during these studies were $\sim 3 \mathrm{mM}$ in analyte and 100 mM in $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ in 2 mL of dichloromethane. All data were collected in a positive-feedback IR compensation mode.
a)

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b)


c)

d)

e)


Figure 3.8.1. a) Full scan cyclic voltammetry of compound 3.4 in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with 0.1 M [ $\left.{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$; [analyte] = ca. 1 mM ; $\mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$. b) Left: Isolated uranium $(\mathrm{V} / \mathrm{VI})$ redox couple at varying scan rates. Right: Current versus $v^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(V/VI) couple. c) Left: Isolated uranium(IV/V) redox couple at varying scan rates. Right: Current versus $v^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(IV/V) couple. d) Left: Isolated naph ${ }^{0} /$ naph $^{-1}$ redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated naph $/$ naph $^{-1}$ couple. e) Differential pulse voltammetry.
a)


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b)

c)


d)


e)


Figure 3.8.2. a) Full scan cyclic voltammetry of compound 3.5 in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$; [analyte] = ca. $1 \mathrm{mM} ; \mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$. b) Left: Isolated uranium(V/VI) redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(V/VI) couple. c) Left: Isolated uranium(IV/V) redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(IV/V) couple. d) Left: Isolated naph $/$ naph $^{-1}$ redox couple at varying scan rates. Right: Current versus $v^{1 / 2}$ plot from the scan rate dependence of the isolated naph $/$ naph $^{-1}$ couple. e) Differential pulse voltammetry.
a)

b)

c)

d)


Figure 3.8.3. a) Full scan cyclic voltammetry of compound 3.6 in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[P F_{6}\right]$; [analyte] = ca. 1 mM ; v = $0.25 \mathrm{~V} / \mathrm{sec} . \mathrm{b}$ ) Left: Isolated uranium(IV/V) redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(IV/V)

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couple. c) Left: Isolated naph ${ }^{0} /$ naph $^{-1}$ redox couple at varying scan rates. Right: Current versus $v^{1 / 2}$ plot from the scan rate dependence of the isolated naph ${ }^{0} /$ naph $^{-1}$ couple. d) Differential pulse voltammetry.
a)

b)


c)


Figure 3.8.4. a) Full scan cyclic voltammetry of compound 3.2 in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ with 0.1 M [ $\left.{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$; [analyte] = ca. 1 mM ; v = $0.25 \mathrm{~V} /$ sec. b) Isolated naph $^{0} /$ naph $^{-1}$ redox couple at varying scan rates. c) Differential pulse voltammetry.

### 3.9 Computational Details.

All calculations were performed with Gaussian 09 Revision D.01, ${ }^{45}$ with the B3LYP hybrid DFT method. An effective core potential incorporating quasi-relativistic effects were applied to uranium, with a 60 electron core and the corresponding segmented natural orbital basis set. ${ }^{46,47}$ The $6-31 \mathrm{G}^{*}$ basis set was used for all small molecules. ${ }^{48}$ Geometry optimizations were carried out in $C_{1}$ symmetry for all uranium complexes and all small molecules, as higher symmetry solutions were either higher in energy or were not successfully converged. Default settings were used for the integration grid, SCF, and geometry convergence criteria. All frequency calculations found no imaginary frequencies, confirming that the optimized structures are minima.

Table 3.9.1. Correlation of $\mathrm{U}(\mathrm{V} / \mathrm{VI}) \mathrm{E}_{1 / 2}$ values with Mulliken charges on uranium $(\mathrm{V})$ center.

| $U^{\mathrm{V}}[=\mathrm{NR}]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ Derivative | $\mathrm{E}_{1 / 2}(\mathrm{~V})$ of <br> $\mathrm{U}(\mathrm{VI} / \mathrm{V})$ couple | Mulliken charge of $\mathrm{U}(\mathrm{V})$ <br> center |
| :--- | :--- | :--- |
| $\mathbf{1 , R}=\mathrm{CPh}_{3}$ | 0.38 | +1.148 |
| $\mathbf{2 , R}=\mathrm{C}(2$-naph $) \mathrm{Ph}_{2}$ | -0.17 | +1.097 |
| 3, $\mathrm{R}=\mathrm{C}(2 \text {-naph })_{3}$ | 0.29 | +1.169 |
| $\mathbf{4}, \mathrm{R}=$ 2-naph | 0.12 | +1.126 |

Table 3.9.2. Sum of electronic and thermal free energies for computed compounds in Hartrees.

| U[=NR][N(SiMe $\left.3_{2}\right]_{3}$ Derivative | Neutral, Gas Phase | Monoanion, GasPhase |
| :--- | :---: | :---: |
| $R=\mathrm{C}(2$-naph $) \mathrm{Ph}_{2}$ | -4037.563578 | -4037.651095 |
| $R=\mathrm{C}(2 \text {-naph })_{3}$ | -4344.760171 | -4344.844895 |
| $R=C(2$-naph $) \mathrm{Me}_{2}$ | -3654.210134 | -3654.299071 |

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| $R=2$-naph | -3536.226122 | -3536.474362 |
| :--- | :--- | :--- |


| $\mathrm{U}\left[=\mathrm{NC}(2-n a p h) \mathrm{Ph}_{2}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ Dianion |  |  |  |
| :--- | :--- | :--- | :--- |
| Gas Phase |  | $\mathrm{CH}_{2} \mathrm{Cl}_{2} \mathrm{CPCM}$ |  |
| No counterions | With K counterions | No Counterions | With K counterions |
| -4037.586969 | -5237.405111 | -4037.742086 | -5237.467823 |
|  |  |  | -5237.683502 (with <br> Grimme's dispersion) |

Table 3.9.3. Geometry optimized coordinates of compound 3.4 in the gas phase.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -0.8697 | -0.14315 | 0.013259 |
| Si | -2.54713 | 2.824063 | 0.724844 |
| Si | -3.94689 | 1.225933 | -1.41854 |
| Si | -0.6711 | -1.24225 | -3.27845 |
| Si | -1.54124 | -3.45209 | -1.41569 |
| Si | 0.110237 | -2.23877 | 2.617191 |
| Si | -2.60235 | -1.01195 | 3.117491 |
| N | -2.59601 | 1.34378 | -0.26001 |
| N | -1.09115 | -1.73898 | -1.6238 |
| N | -1.20403 | -1.19496 | 2.024864 |
| N | 0.877772 | 0.741313 | -0.05568 |
| C | -0.98405 | 2.841903 | 1.802545 |
| H | -0.69313 | 1.876431 | 2.233551 |
| H | -1.1793 | 3.500293 | 2.659645 |
| H | -0.10615 | 3.238613 | 1.289585 |
| C | -2.5064 | 4.397482 | -0.3422 |
| H | -1.7363 | 4.351376 | -1.12031 |
| H | -2.2874 | 5.266445 | 0.292044 |
| H | -3.46456 | 4.590684 | -0.83798 |
| C | -3.98586 | 3.045605 | 1.948988 |
| H | -4.94167 | 3.262591 | 1.46618 |
| H | -3.7466 | 3.898797 | 2.598094 |
| H | -4.12901 | 2.175544 | 2.597077 |
| C | -3.52853 | 2.045918 | -3.07973 |
| H | -3.31219 | 3.112408 | -2.94789 |

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| H | -4.3887 | 1.967009 | -3.75759 |
| :---: | :---: | :---: | :---: |
| H | -2.66895 | 1.597705 | -3.58461 |
| C | -4.45985 | -0.57499 | -1.70229 |
| H | -3.62767 | -1.22536 | -1.97682 |
| H | -5.20469 | -0.61841 | -2.50778 |
| H | -4.92785 | -0.98444 | -0.79992 |
| C | -5.55659 | 2.068299 | -0.85232 |
| H | -5.93689 | 1.663404 | 0.091394 |
| H | -6.31357 | 1.866933 | -1.62228 |
| H | -5.48137 | 3.155907 | -0.7523 |
| C | -2.0945 | -1.29572 | -4.53777 |
| H | -2.46993 | -2.30199 | -4.73672 |
| H | -1.71628 | -0.8941 | -5.48772 |
| H | -2.94455 | -0.67477 | -4.23917 |
| C | 0.729435 | -2.29796 | -4.01183 |
| H | 1.595116 | -2.35893 | -3.34334 |
| H | 1.067994 | -1.85703 | -4.95839 |
| H | 0.405848 | -3.32268 | -4.22694 |
| C | -0.08013 | 0.563439 | -3.29442 |
| H | -0.62229 | 1.244914 | -2.62754 |
| H | -0.24123 | 0.954132 | -4.30799 |
| H | 0.982519 | 0.679615 | -3.07376 |
| C | -0.02171 | -4.54421 | -1.09637 |
| H | 0.693959 | -4.47322 | -1.92358 |
| H | -0.32973 | -5.59511 | -1.01706 |
| H | 0.511438 | -4.28659 | -0.17759 |
| C | -2.79666 | -3.67299 | -0.01496 |
| H | -2.48038 | -3.21882 | 0.925721 |
| H | -2.9572 | -4.74449 | 0.162939 |
| H | -3.76271 | -3.23794 | -0.2954 |
| C | -2.40321 | -4.24113 | -2.91893 |
| H | -3.33863 | -3.73733 | -3.18527 |
| H | -2.65814 | -5.27205 | -2.63822 |
| H | -1.77877 | -4.29826 | -3.81664 |
| C | 1.575085 | -2.20148 | 1.411515 |
| H | 1.311986 | -2.20776 | 0.347035 |
| H | 2.163292 | -3.1143 | 1.575614 |
| H | 2.246952 | -1.35588 | 1.570984 |
| C | 0.767564 | -1.67676 | 4.310777 |
| H | 1.033311 | -0.61393 | 4.321542 |
| H | 1.671506 | -2.24719 | 4.5614 |
| H | 0.043617 | -1.84445 | 5.116352 |


| C | -0.32453 | -4.08116 | 2.799176 |
| :---: | :---: | :---: | :---: |
| H | -1.04733 | -4.28683 | 3.59204 |
| H | 0.599357 | -4.61921 | 3.050964 |
| H | -0.71153 | -4.51676 | 1.872985 |
| C | -2.97394 | -2.5356 | 4.194398 |
| H | -3.19699 | -3.42821 | 3.600283 |
| H | -3.87161 | -2.30426 | 4.783454 |
| H | -2.17959 | -2.7878 | 4.904295 |
| C | -2.3581 | 0.41231 | 4.348492 |
| H | -1.47809 | 0.242022 | 4.979243 |
| H | -3.22969 | 0.480728 | 5.012798 |
| H | -2.2337 | 1.386019 | 3.867568 |
| C | -4.20988 | -0.74587 | 2.152128 |
| H | -4.15967 | 0.085359 | 1.446714 |
| H | -5.02447 | -0.54136 | 2.85943 |
| H | -4.47818 | -1.65096 | 1.595328 |
| C | 2.196728 | 1.405152 | -0.1091 |
| C | 3.301446 | 0.330982 | -0.30628 |
| C | 4.463939 | 0.30149 | 0.437558 |
| H | 4.631764 | 1.027516 | 1.225562 |
| C | 5.480929 | -0.66784 | 0.204558 |
| C | 6.674246 | -0.70266 | 0.974661 |
| H | 6.80861 | 0.032401 | 1.764834 |
| C | 7.645343 | -1.64895 | 0.729017 |
| H | 8.553593 | -1.66464 | 1.32548 |
| C | 7.467092 | -2.60549 | -0.3003 |
| H | 8.239925 | -3.34685 | -0.4849 |
| C | 6.320778 | -2.59695 | -1.06502 |
| H | 6.18005 | -3.32966 | -1.85641 |
| C | 5.303307 | -1.63396 | -0.8351 |
| C | 4.105727 | -1.57971 | -1.59906 |
| H | 3.959827 | -2.30205 | -2.39942 |
| C | 3.142866 | -0.63458 | -1.34133 |
| H | 2.238169 | -0.61622 | -1.9356 |
| C | 2.228845 | 2.405747 | -1.29958 |
| C | 3.331083 | 2.516296 | -2.15741 |
| H | 4.186328 | 1.863013 | -2.02911 |
| C | 3.351886 | 3.466966 | -3.18385 |
| H | 4.218273 | 3.52626 | -3.8376 |
| C | 2.275002 | 4.331963 | -3.36705 |
| H | 2.290836 | 5.070506 | -4.16407 |
| C | 1.175764 | 4.241142 | -2.50906 |
| H | 0.330606 | 4.914072 | -2.63124 |

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| C | 1.157333 | 3.28997 | -1.49105 |
| :--- | :--- | :--- | :--- |
| H | 0.298896 | 3.229862 | -0.83341 |
| C | 2.456875 | 2.175945 | 1.215824 |
|  |  | 3.442194 | 1.238763 |
| C | 3.056902 | 3.938983 | 0.309936 |
| H | 3.337954 | 4.083386 | 2.449744 |
| H | 3.798695 | 5.067843 | 2.436808 |
| C | 3.032345 | 3.468708 | 3.662462 |
|  |  |  |  |
| H | 3.250376 | 3.967193 | 4.603183 |
| C | 2.44421 | 2.201412 | 3.653342 |
| H | 2.203893 | 1.703813 | 4.589669 |
| C | 2.162527 | 1.567837 | 2.444452 |

Table 3.9.4. Geometry optimized coordinates of compound $3.4-\mathrm{K}$ in the gas phase.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -0.91131 | -0.19915 | 0.024478 |
| Si | -2.64837 | 2.949541 | 0.614425 |
| Si | -3.96819 | 1.207308 | -1.42229 |
| Si | -0.60621 | -1.48739 | -3.35226 |
| Si | -1.4619 | -3.55504 | -1.3679 |
| Si | 0.241792 | -2.20631 | 2.803472 |
| Si | -2.4576 | -0.99061 | 3.252906 |
| N | -2.66635 | 1.440134 | -0.2735 |
| N | -1.03844 | -1.88905 | -1.70491 |
| N | -1.08221 | -1.23403 | 2.197151 |
| N | 0.841669 | 0.738597 | -0.08512 |
| C H H | $\begin{aligned} & -1.07883 \\ & -0.82943 \end{aligned}$ | $\begin{aligned} & 3.169047 \\ & 2.295586 \end{aligned}$ | $\begin{aligned} & 1.653584 \\ & 2.265589 \end{aligned}$ |
| H | -1.23292 | 4.009674 | 2.344569 |
| H | -0.19464 | 3.395037 | 1.053148 |
| C | -2.73144 | 4.492114 | -0.51279 |
| H | -1.89788 | 4.512038 | -1.22555 |
| H | -2.66713 | 5.405546 | 0.094229 |
| H | -3.66132 | 4.547793 | -1.09153 |
| C | -4.07356 | 3.154162 | 1.872333 |
| H | -5.05823 | 3.251773 | 1.405415 |
| H | -3.89903 | 4.061683 | 2.466991 |
| H | -4.12074 | 2.311036 | 2.570745 |
| C | -3.58042 | 1.926693 | -3.14524 |

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| H | 0.16354 | -1.69982 | 5.293963 |
| :---: | :---: | :---: | :---: |
| C | -0.1697 | -4.05718 | 3.045068 |
| H | -0.91173 | -4.23855 | 3.828282 |
| H | 0.746888 | -4.59399 | 3.326324 |
| H | -0.54506 | -4.51194 | 2.121545 |
| C | -2.87115 | -2.44953 | 4.418642 |
| H | -3.09433 | -3.36868 | 3.864774 |
| H | -3.7706 | -2.18473 | 4.991803 |
| H | -2.07999 | -2.6769 | 5.141975 |
| C | $-2.24418$ | 0.502724 | 4.418317 |
| H | -1.35092 | 0.390259 | 5.044661 |
| H | -3.11043 | 0.599386 | 5.087355 |
| H | -2.14247 | 1.445714 | 3.87153 |
| C | -4.06755 | -0.74332 | 2.275796 |
| H | -3.99015 | 0.048144 | 1.525341 |
| H | -4.88468 | -0.48085 | 2.961839 |
| H | -4.34989 | -1.6695 | 1.760752 |
| C | 2.118287 | 1.436831 | -0.1617 |
| C | 3.275551 | 0.407783 | -0.3324 |
| C | 4.455542 | 0.452037 | 0.383998 |
| H | 4.613083 | 1.221406 | 1.132932 |
| C | 5.500711 | -0.49352 | 0.176813 |
| C | 6.71166 | -0.45285 | 0.918818 |
| H | 6.834643 | 0.3227 | 1.671967 |
| C | 7.712732 | -1.37439 | 0.696167 |
| H | 8.633237 | -1.32953 | 1.273505 |
| C | 7.547045 | -2.38433 | -0.28263 |
| H | 8.340997 | -3.10827 | -0.45044 |
| C | 6.382879 | -2.45035 | -1.01841 |
| H | 6.249119 | -3.22623 | -1.76969 |
| C | 5.335759 | -1.51434 | -0.81211 |
| C | 4.118788 | -1.53957 | -1.54702 |
| H | 3.977269 | -2.30969 | -2.30296 |
| C | 3.128288 | -0.61817 | -1.31043 |
| H | 2.199341 | -0.66811 | -1.8636 |
| C | 2.143909 | 2.410053 | -1.38044 |
| C | 3.302339 | 2.648668 | -2.13418 |
| H | 4.2164 | 2.112462 | -1.90117 |
| C | 3.305925 | 3.572107 | -3.1851 |
| H | 4.218614 | 3.728725 | -3.75634 |
| C | 2.150201 | 4.285123 | -3.5 |

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| H | 2.149774 | 5.002496 | -4.31757 |
| :--- | :---: | :---: | :---: |
| C | 0.989949 | 4.059779 | -2.75462 |
| H | 0.07668 | 4.602317 | -2.98899 |
| C | 0.98922 | 3.131922 | -1.71405 |
| H | 0.07871 | 2.941605 | -1.15854 |
| C | 2.375956 | 2.263244 | 1.136652 |
| C | 2.981295 | 3.52789 | 1.131885 |
| H | 3.255694 | 3.992853 | 0.191267 |
|  | 3.23837 | 4.212571 | 2.324906 |
| H | 3.699975 |  |  |
|  |  | 5.197144 | 2.286455 |
| C | 2.904938 | 3.642574 | 3.551998 |
| H | 3.102967 | 4.174114 | 4.480055 |
| H | 2.307101 | 2.379468 | 3.572054 |
| C | 2.035857 | 1.918345 | 4.5192 |
| H | 2.045149 | 1.70562 | 2.3806 |

Table 3.9.5. Geometry optimized coordinates of compound $\left[\mathrm{U}\left(=\mathrm{NCnaphPh}_{2}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]^{2}$ in the gas phase.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | 0.92271 | -0.22662 | -0.02584 |
| Si | 2.902886 | 2.928104 | -0.4757 |
| Si | 4.106891 | 1.02364 | 1.482553 |
| Si | 0.50962 | -1.60673 | 3.450938 |
| Si | 1.145976 | -3.67082 | 1.385456 |
| Si | -0.32479 | -2.06346 | -3.08248 |
| Si | 2.45335 | -1.02776 | -3.3527 |
| N | 2.867039 | 1.41129 | 0.346835 |
| N | 0.892554 | -2.02329 | 1.823353 |
| N | 1.031181 | -1.23847 | -2.4008 |
| N | -0.855 | 0.819641 | 0.087153 |
| C | 1.370684 | 3.253796 | -1.54613 |
| H | 1.172831 | 2.434601 | -2.24635 |
| H | 1.527158 | 4.165357 | -2.14209 |
| H | 0.457947 | 3.384309 | -0.96007 |
| C | 3.031424 | 4.448333 | 0.69206 |
| H | 2.185383 | 4.47515 | 1.390643 |
| H | 3.019095 | 5.386848 | 0.119353 |
| H | 3.951642 | 4.438171 | 1.290865 |
| C | 4.358951 | 3.141536 | -1.71079 |

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| H | 5.341516 | 3.141968 | -1.22655 |
| :---: | :---: | :---: | :---: |
| H | 4.254139 | 4.092154 | -2.25403 |
| H | 4.359034 | 2.335841 | -2.45528 |
| C | 3.78539 | 1.691558 | 3.24899 |
| H | 3.662833 | 2.7823 | 3.242641 |
| H | 4.620855 | 1.451913 | 3.923176 |
| H | 2.875742 | 1.264623 | 3.684714 |
| C | 4.390182 | -0.85039 | 1.654034 |
| H | 3.463941 | -1.38986 | 1.878823 |
| H | 5.110084 | -1.05736 | 2.459655 |
| H | 4.797942 | -1.26426 | 0.723497 |
| C | 5.862899 | 1.6979 | 1.075225 |
| H | 6.218179 | 1.3405 | 0.101102 |
| H | 6.571336 | 1.342981 | 1.837894 |
| H | 5.913016 | 2.793987 | 1.066557 |
| C | 1.946756 | -1.8473 | 4.702837 |
| H | 2.263252 | -2.89249 | 4.793706 |
| H | 1.641583 | -1.50279 | 5.70193 |
| H | 2.825685 | -1.26188 | 4.406649 |
| C | -0.95027 | -2.60541 | 4.201829 |
| H | -1.85763 | -2.48397 | 3.596977 |
| H | -1.18075 | -2.25986 | 5.219883 |
| H | -0.73562 | -3.6806 | 4.258622 |
| C | 0.02179 | 0.215726 | 3.667657 |
| H | 0.742653 | 0.901499 | 3.208754 |
| H | -0.02427 | 0.458787 | 4.739512 |
| H | -0.95078 | 0.453122 | 3.229233 |
| C | -0.46303 | -4.61493 | 0.955704 |
| H | -1.15947 | -4.61504 | 1.804036 |
| H | -0.25879 | -5.66247 | 0.689606 |
| H | -0.98495 | -4.153 | 0.109744 |
| C | 2.302236 | -3.85259 | -0.1157 |
| H | 1.974258 | -3.25335 | -0.97261 |
| H | 2.353905 | -4.90259 | -0.43917 |
| H | 3.31899 | -3.53037 | 0.142797 |
| C | 1.979107 | -4.77201 | 2.72528 |
| H | 2.964459 | -4.3817 | 3.008821 |
| H | 2.12531 | -5.78702 | 2.328007 |
| H | 1.382002 | -4.86143 | 3.641406 |
| C | -1.89369 | -1.98923 | -2.01888 |
| H | -1.71803 | -2.29348 | -0.98133 |
| H | -2.65034 | -2.66838 | -2.43907 |
| H | -2.32723 | -0.9869 | -1.97684 |

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| H | -2.05024 | 4.982142 | 4.448733 |
| :---: | :---: | :---: | :---: |
| C | -0.91918 | 4.054863 | 2.851852 |
| H | 0.010829 | 4.561867 | 3.103129 |
| C | -0.94478 | 3.157379 | 1.785753 |
| H | -0.04312 | 2.933564 | 1.226609 |
| C | -2.36155 | 2.411499 | -1.09041 |
| C | -3.09932 | 3.605241 | -1.07066 |
| H | -3.49349 | 3.978102 | -0.13032 |
| C | -3.33523 | 4.334552 | -2.24183 |
| H | -3.90269 | 5.263162 | -2.19049 |
| C | -2.84453 | 3.879858 | -3.46559 |
| H | -3.02411 | 4.446183 | -4.37817 |
| C | -2.10811 | 2.691856 | -3.50008 |
| H | -1.70801 | 2.324774 | -4.4435 |
| C | -1.86581 | 1.976657 | -2.32773 |
| H | -1.26034 | 1.0768 | -2.33653 |
| C | -3.10747 | -0.56189 | 1.241524 |
| H | -2.15335 | -0.6422 | 1.747734 |
| C | -3.24808 | 3.620719 | 3.272649 |

Table 3.9.6. Geometry optimized coordinates of compound $\left[\mathrm{U}\left(=\mathrm{NCnaphPh}_{2}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]^{2-}$ in a dichloromethane CPCM solvent field.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -0.90085 | -0.25812 | 0.039853 |
| Si | -3.06927 | 2.910533 | 0.551761 |
| Si | -4.15349 | 0.980538 | -1.43225 |
| Si | -0.5077 | -1.68546 | -3.54485 |
| Si | -0.96595 | -3.71853 | -1.4366 |
| Si | 0.449801 | -2.13198 | 3.125058 |
| Si | -2.34669 | -1.1815 | 3.430993 |
| N | -2.94241 | 1.402417 | -0.27736 |
| N | -0.7906 | -2.0563 | -1.88187 |
| N | -0.93327 | -1.34745 | 2.454126 |
| N | 0.842362 | 0.883032 | -0.0637 |
| C | -1.57065 | 3.352546 | 1.639481 |
| H | -1.31453 | 2.551128 | 2.342419 |
| H | -1.80339 | 4.25182 | 2.227779 |
| H | -0.66771 | 3.55299 | 1.054954 |
| C | -3.26037 | 4.424587 | -0.61261 |

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| H | -2.41508 | 4.483725 | -1.31156 |
| :---: | :---: | :---: | :---: |
| H | -3.28565 | 5.364644 | -0.04358 |
| H | -4.17698 | 4.379392 | -1.21435 |
| C | -4.53973 | 3.030273 | 1.78085 |
| H | -5.51641 | 2.980314 | 1.287652 |
| H | -4.49661 | 3.977485 | 2.337031 |
| H | -4.50426 | 2.216193 | 2.516555 |
| C | -3.78309 | 1.620109 | -3.19842 |
| H | -3.68787 | 2.713654 | -3.21273 |
| H | -4.58167 | 1.345724 | -3.90235 |
| H | -2.84493 | 1.207002 | -3.58604 |
| C | -4.41179 | -0.90074 | -1.60197 |
| H | -3.48176 | -1.42686 | -1.84113 |
| H | -5.1364 | -1.11204 | -2.40154 |
| H | -4.80844 | -1.32656 | -0.67153 |
| C | -5.93214 | 1.621024 | -1.08526 |
| H | -6.32683 | 1.244868 | -0.13301 |
| H | -6.60107 | 1.26372 | -1.88106 |
| H | -6.00622 | 2.715122 | -1.06478 |
| C | -2.01693 | -1.97396 | -4.69293 |
| H | -2.35169 | -3.01663 | -4.70213 |
| H | -1.77025 | -1.69467 | -5.72718 |
| H | -2.87038 | -1.35862 | -4.38164 |
| C | 0.924272 | -2.68892 | -4.33753 |
| H | 1.863418 | -2.52975 | -3.79184 |
| H | 1.09129 | -2.37823 | -5.37859 |
| H | 0.73176 | -3.76888 | -4.34427 |
| C | -0.0349 | 0.124571 | -3.91863 |
| H | -0.70399 | 0.854123 | -3.44993 |
| H | -0.08557 | 0.281125 | -5.00584 |
| H | 0.983379 | 0.370472 | -3.60039 |
| C | 0.697111 | -4.58701 | -1.0532 |
| H | 1.364707 | -4.56708 | -1.92394 |
| H | 0.54499 | -5.63965 | -0.77489 |
| H | 1.228396 | -4.10067 | -0.2263 |
| C | -2.06128 | -3.97116 | 0.102535 |
| H | -1.72691 | -3.37893 | 0.961599 |
| H | -2.05876 | -5.03042 | 0.397718 |
| H | -3.10187 | -3.69086 | -0.10906 |
| C | -1.79182 | -4.87248 | -2.73275 |
| H | -2.81535 | -4.55628 | -2.97024 |
| H | -1.85212 | -5.8889 | -2.31836 |
| H | -1.23962 | -4.93854 | -3.6778 |

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| C | 2.00471 | -2.01864 | 2.039149 |
| :---: | :---: | :---: | :---: |
| H | 1.815531 | -2.37587 | 1.019436 |
| H | 2.801225 | -2.64389 | 2.467123 |
| H | 2.382901 | -0.99666 | 1.944271 |
| C | 1.006676 | -1.44239 | 4.828771 |
| H | 1.243982 | -0.37246 | 4.758375 |
| H | 1.91141 | -1.95713 | 5.181881 |
| H | 0.240036 | -1.55662 | 5.605816 |
| C | 0.251408 | -4.0222 | 3.394686 |
| H | -0.5501 | -4.27751 | 4.096191 |
| H | 1.185158 | -4.44912 | 3.787813 |
| H | 0.032247 | -4.53241 | 2.447925 |
| C | -2.72522 | -2.63882 | 4.621955 |
| H | -2.85672 | -3.5838 | 4.079808 |
| H | -3.66174 | -2.43582 | 5.160457 |
| H | -1.94352 | -2.79732 | 5.374688 |
| C | -2.32164 | 0.355649 | 4.575742 |
| H | -1.46464 | 0.330723 | 5.261128 |
| H | -3.23402 | 0.418465 | 5.18594 |
| H | -2.24716 | 1.28496 | 3.99763 |
| C | -3.94722 | -1.03226 | 2.406655 |
| H | -3.89975 | -0.22065 | 1.67167 |
| H | -4.80445 | -0.84262 | 3.068667 |
| H | -4.15011 | -1.96341 | 1.861107 |
| C | 2.049026 | 1.650866 | -0.19421 |
| C | 3.253341 | 0.676805 | -0.38464 |
| C | 4.406571 | 0.686144 | 0.376221 |
| H | 4.541102 | 1.429581 | 1.155873 |
| C | 5.454606 | -0.26177 | 0.182502 |
| C | 6.632699 | -0.25833 | 0.977214 |
| H | 6.727571 | 0.485289 | 1.766115 |
| C | 7.641838 | -1.1754 | 0.760233 |
| H | 8.536622 | -1.1575 | 1.377659 |
| C | 7.516176 | -2.1433 | -0.26561 |
| H | 8.314484 | -2.86286 | -0.4295 |
| C | 6.382545 | -2.17307 | -1.05356 |
| H | 6.280045 | -2.91701 | -1.84119 |
| C | 5.330192 | -1.24145 | -0.85413 |
| C | 4.141673 | -1.23101 | -1.63966 |
| H | 4.030165 | -1.9713 | -2.43037 |
| C | 3.141676 | -0.31827 | -1.40397 |
| H | 2.222501 | -0.35672 | -1.97733 |

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| C | 2.000372 | 2.613137 | -1.43036 |
| :--- | :---: | :---: | :---: |
| C | 3.104844 | 2.868061 | -2.25819 |
| H | 4.049432 | 2.369785 | -2.06172 |
| C | 3.0196 | 3.756419 | -3.33846 |
| H | 3.892311 | 3.922495 | -3.96699 |
| C | 1.82528 | 4.424399 | -3.60709 |
| H | 0.717582 | 5.115032 | -4.44427 |
| C | -0.22198 | 4.188441 | -2.78467 |
| H | 0.805958 | 3.702088 | -2.97927 |
| H | -0.06102 | 3.082167 | -1.72057 |
| C | 2.326186 | 2.541548 | -1.10438 |
|  |  |  | 1.069077 |
| C | 3.02029 | 3.761247 |  |
| H | 3.378748 | 4.141744 | 0.023038 |
| C | 3.260676 | 4.508894 | 2.182312 |
| H | 3.791929 | 5.4559 | 2.109401 |
| H | 2.821375 | 4.046357 | 3.423555 |
| C | 3.005193 | 4.625638 | 4.325602 |
| H | 2.136833 | 2.828208 | 3.487449 |
| C | 1.785819 | 2.450955 | 4.446229 |
| H | 1.891956 | 2.095073 | 2.325548 |

Table 3.9.7. Geometry optimized coordinates of compound $\mathrm{K}_{2}\left[\mathrm{U}\left(=\mathrm{NCnaphPh}_{2}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ in a dichloromethane CPCM solvent field.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -1.17146 | -0.31315 | -0.06293 |
| Si | -2.71668 | 3.037633 | 0.602431 |
| Si | -3.74071 | 1.662438 | -1.8283 |
| Si | -0.44283 | -1.55165 | -3.47514 |
| Si | -1.78766 | -3.56203 | -1.74253 |
| Si | -0.7136 | -2.52872 | 2.895702 |
| Si | -3.33391 | -1.13854 | 2.843981 |
| N | -2.67555 | 1.641244 | -0.43979 |
| N | -1.15009 | -1.94405 | -1.92063 |
| N | -1.79561 | -1.44596 | 2.065485 |
| N | 0.674658 | 0.440136 | 0.066136 |
| C | -1.32412 | 3.050665 | 1.899445 |
| H | -1.3863 | 2.218648 | 2.609539 |
| H | -1.39818 | 3.978947 | 2.483547 |
| H | -0.32781 | 3.002494 | 1.451531 |

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| C | -2.49488 | 4.702708 | -0.3197 |
| :---: | :---: | :---: | :---: |
| H | -1.52924 | 4.744975 | -0.83858 |
| H | -2.52494 | 5.534409 | 0.398423 |
| H | -3.27408 | 4.889395 | -1.06765 |
| C | -4.31437 | 3.241605 | 1.62919 |
| H | -5.18997 | 3.473128 | 1.014446 |
| H | -4.18743 | 4.064234 | 2.346546 |
| H | -4.54346 | 2.337044 | 2.203627 |
| C | -2.93026 | 2.440736 | -3.37146 |
| H | -2.63029 | 3.478974 | -3.18028 |
| H | -3.63159 | 2.450059 | -4.21712 |
| H | -2.03543 | 1.896254 | -3.69325 |
| C | -4.34122 | -0.07497 | -2.32537 |
| H | -3.5315 | -0.78924 | -2.50803 |
| H | -4.93336 | -0.00158 | -3.24775 |
| H | -4.99282 | -0.49509 | -1.54861 |
| C | -5.38024 | 2.623786 | -1.60972 |
| H | -6.00206 | 2.199177 | -0.8126 |
| H | -5.95017 | 2.545097 | -2.54572 |
| H | -5.24932 | 3.690567 | -1.39789 |
| C | -1.70104 | -1.39011 | -4.90636 |
| H | -2.2547 | -2.3102 | -5.1159 |
| H | -1.16684 | -1.10873 | -5.82459 |
| H | -2.43497 | -0.6014 | -4.70157 |
| C | 0.865978 | -2.81792 | -4.05731 |
| H | 1.706968 | -2.86038 | -3.35406 |
| H | 1.270856 | -2.51746 | -5.03344 |
| H | 0.470892 | -3.83469 | -4.16525 |
| C | 0.46343 | 0.114832 | -3.49735 |
| H | -0.15218 | 0.948504 | -3.1447 |
| H | 0.751222 | 0.337825 | -4.53433 |
| H | 1.369187 | 0.106136 | -2.88639 |
| C | -0.47146 | -4.81024 | -1.14544 |
| H | 0.382028 | -4.85012 | -1.83344 |
| H | -0.89233 | -5.82259 | -1.07609 |
| H | -0.08313 | -4.54788 | -0.1545 |
| C | -3.23106 | -3.64745 | -0.50631 |
| H | -2.97779 | -3.23427 | 0.474639 |
| H | -3.53653 | -4.69323 | -0.36585 |
| H | -4.10245 | -3.09988 | -0.88893 |
| C | -2.53092 | -4.34924 | -3.31803 |
| H | -3.38564 | -3.77526 | -3.69565 |
| H | -2.89951 | -5.35143 | -3.05938 |
| H | -1.81736 | -4.46582 | -4.14068 |

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| C | 1.011612 | -2.63205 | 2.091177 |
| :---: | :---: | :---: | :---: |
| H | 1.007737 | -3.20518 | 1.157102 |
| H | 1.653592 | -3.16589 | 2.807568 |
| H | 1.430774 | -1.64541 | 1.870354 |
| C | -0.35845 | -2.02029 | 4.703652 |
| H | 0.058751 | -1.0067 | 4.761492 |
| H | 0.37007 | -2.70655 | 5.157006 |
| H | -1.25779 | -2.0393 | 5.330257 |
| C | -1.25762 | -4.3583 | 2.957556 |
| H | -2.12029 | -4.53534 | 3.606726 |
| H | -0.42793 | -4.97166 | 3.336281 |
| H | -1.51279 | -4.73267 | 1.959082 |
| C | -4.09241 | -2.62002 | 3.784471 |
| H | -4.24518 | -3.48843 | 3.132969 |
| H | -5.07761 | -2.31865 | 4.166093 |
| H | -3.49834 | -2.94842 | 4.645049 |
| C | -3.25283 | 0.255294 | 4.144693 |
| H | -2.55336 | 0.009766 | 4.952737 |
| H | -4.24038 | 0.415221 | 4.598552 |
| H | -2.93345 | 1.20881 | 3.71133 |
| C | -4.69298 | -0.66346 | 1.60211 |
| H | -4.40187 | 0.160818 | 0.943056 |
| H | -5.59659 | -0.35638 | 2.145735 |
| H | -4.96243 | -1.52134 | 0.97342 |
| C | 1.993619 | 1.045361 | 0.089695 |
| C | 3.134499 | 0.002699 | -0.16334 |
| C | 4.485035 | 0.23632 | 0.233945 |
| H | 4.742912 | 1.114605 | 0.816499 |
| C | 5.562732 | -0.61512 | -0.15859 |
| C | 6.915635 | -0.36779 | 0.202644 |
| H | 7.143968 | 0.52679 | 0.781286 |
| C | 7.95 | -1.2458 | -0.17135 |
| H | 8.975303 | -1.02357 | 0.119021 |
| C | 7.662527 | -2.39158 | -0.91222 |
| H | 8.46099 | -3.0698 | -1.20698 |
| C | 6.334162 | -2.67229 | -1.28651 |
| H | 6.108755 | -3.56779 | -1.86456 |
| C | 5.265691 | -1.81196 | -0.92576 |
| C | 3.895709 | -2.07016 | -1.23197 |
| H | 3.647718 | -2.96846 | -1.79603 |
| C | 2.870982 | -1.1627 | -0.88226 |
| H | 1.848222 | -1.37201 | -1.17247 |
| C | 2.079992 | 2.167062 | -1.00637 |
| C | 3.266803 | 2.486674 | -1.68777 |

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| H | 4.168091 | 1.920775 | -1.47939 |
| :--- | :--- | :--- | :--- |
| C | 3.312734 | 3.513033 | -2.6391 |
| H | 4.248838 | 3.726173 | -3.14951 |
| C | 2.163158 | 4.245309 | -2.94907 |
| H | 2.191395 | 5.028439 | -3.70239 |
| C | 0.967387 | 3.92724 | -2.29567 |
| H | 0.051879 | 4.457117 | -2.54977 |
| C | 0.932865 | 2.911128 | -1.33313 |
| H | -0.00641 | 2.651826 | -0.85869 |
| C | 2.260282 | 1.723935 | 1.478709 |
| C | 3.139998 | 2.809154 | 1.642942 |
| H | 3.675125 | 3.201635 | 0.78231 |
| H | 3.391515 | 3.368287 | 2.902091 |
| C | 4.089857 | 4.197877 | 2.992078 |
| H | 2.769768 | 2.849614 | 4.039818 |
| C | 2.962221 | 3.279517 | 5.019251 |
| H | 1.899958 | 1.765049 | 3.896099 |
| C | 1.403268 | 1.34791 | 4.769322 |
| K | 1.649603 | 1.21884 | 2.63478 |
| K | 0.948698 | 0.399893 | 2.526372 |

Table 3.9.8. Geometry optimized coordinates of compound $\mathrm{K}_{2}\left[\mathrm{U}\left(=\mathrm{NCnaphPh}_{2}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ in the gas phase.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -1.10871 | -0.36498 | -0.05969 |
| Si | -3.01766 | 2.712176 | 0.36565 |
| Si | -3.82872 | 1.118226 | -2.0413 |
| Si | -0.2348 | -1.76982 | -3.32275 |
| Si | -1.13209 | -3.78782 | -1.32867 |
| Si | -0.49751 | -2.08384 | 3.104842 |
| Si | -3.32786 | -1.25857 | 2.735327 |
| N | -2.79441 | 1.312766 | -0.6309 |
| N | -0.82069 | -2.09414 | -1.69319 |
| N | -1.68427 | -1.2921 | 2.091069 |
| N | 0.645091 | 0.628188 | 0.049562 |
| C | -1.7613 | 2.690057 | 1.799231 |
| H | -2.01463 | 1.920112 | 2.534607 |
| H | -1.77033 | 3.644407 | 2.349947 |
| H |  | -0.74443 | 2.450922 |
| C | -2.74088 | 4.375164 | -0.56136 |



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| C | 5.283125 | -1.50553 | -0.76193 |
| :--- | :---: | :---: | :---: |
| C | 3.926609 | -1.85703 | -1.02859 |
| H | 3.715566 | -2.81945 | -1.48862 |
| C | 2.886858 | -0.96373 | -0.79117 |
| H | 1.871315 | -1.2447 | -1.04368 |
| C | 1.92454 | 2.267453 | -1.30533 |
| H | 3.074119 | 2.566324 | -2.05169 |
| C | 4.009011 | 2.064618 | -1.8277 |
| H | 3.040332 | 3.492202 | -3.10028 |
| C | 3.948106 | 3.690189 | -3.66471 |
| H | 1.853217 | 4.144019 | -3.43464 |
| C | 1.82393 | 4.852003 | -4.25841 |
| C | 0.692994 | 3.841952 | -2.71687 |
| H | -0.25534 | 4.293693 | -3.00056 |
| C | 0.732108 | 2.915304 | -1.66979 |
| H | -0.18865 | 2.613607 | -1.17747 |
| C | 2.192234 | 2.216071 | 1.189273 |
| H | 3.038664 | 3.343144 | 1.145159 |
| C | 3.53378 | 3.609772 | 0.21663 |
| C | 3.251887 | 4.145058 | 2.273894 |
| H | 3.918014 | 5.002014 | 2.204735 |
| C | 2.615636 | 3.844921 | 3.483161 |
| K | 2.776396 | 4.46566 | 4.360312 |
| K | 1.784958 | 2.722672 | 3.547748 |

Table 3.9.9. Geometry optimized coordinates of compound $\mathrm{K}_{2}\left[\mathrm{U}\left(=\mathrm{NCnaphPh}_{2}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ in a dichloromethane CPCM solvent field with Grimme's dispersion forces.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -1.16754 | -0.37642 | 0.000822 |
| Si | -2.63584 | 2.879264 | 0.782385 |
| Si | -4.0787 | 1.357796 | -1.34251 |
| Si | -0.94229 | -1.60278 | -3.38231 |
| Si | -1.97925 | -3.62 | -1.4279 |
| Si | 0.073041 | -2.49479 | 2.654743 |
| Si | -2.49811 | -1.09891 | 3.3071 |
| N | -2.76831 | 1.459308 | -0.20266 |

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| N | -1.40346 | -2.00764 | -1.75008 |
| :---: | :---: | :---: | :---: |
| N | -1.19573 | -1.40808 | 2.19953 |
| N | 0.602575 | 0.50804 | -0.14973 |
| C | -0.98772 | 2.939619 | 1.719549 |
| H | -0.8119 | 2.055956 | 2.339316 |
| H | -0.97121 | 3.814856 | 2.384939 |
| H | -0.13532 | 2.983577 | 1.038309 |
| C | -2.69325 | 4.501449 | -0.22643 |
| H | -1.96676 | 4.47568 | -1.04713 |
| H | -2.45927 | 5.363872 | 0.414226 |
| H | -3.67836 | 4.682359 | -0.67213 |
| C | -3.96549 | 3.04294 | 2.136066 |
| H | -4.97333 | 3.169883 | 1.728656 |
| H | -3.74853 | 3.914439 | 2.769358 |
| H | -3.97821 | 2.15883 | 2.782972 |
| C | -3.61335 | 2.103596 | -3.0298 |
| H | -3.293 | 3.147251 | -2.91792 |
| H | -4.4633 | 2.083418 | -3.72497 |
| H | -2.78928 | 1.552992 | -3.49623 |
| C | -4.63462 | -0.43561 | -1.62903 |
| H | -3.81989 | -1.09004 | -1.95276 |
| H | -5.42124 | -0.46646 | -2.39459 |
| H | -5.05059 | -0.85323 | -0.703 |
| C | -5.68111 | 2.240892 | -0.8014 |
| H | -6.0775 | 1.808526 | 0.125209 |
| H | -6.44135 | 2.103996 | -1.58217 |
| H | -5.56177 | 3.318612 | -0.64321 |
| C | -2.40109 | -1.5168 | -4.60705 |
| H | -2.88537 | -2.48175 | -4.78281 |
| H | -2.03745 | -1.14342 | -5.57409 |
| H | -3.16793 | -0.8181 | -4.25201 |
| C | 0.330157 | -2.82074 | -4.10745 |
| H | 1.241833 | -2.83691 | -3.49747 |
| H | 0.615491 | -2.51806 | -5.12382 |
| H | -0.0538 | -3.84663 | -4.16211 |
| C | -0.15294 | 0.114777 | -3.51919 |
| H | -0.79337 | 0.91121 | -3.128 |
| H | 0.0147 | 0.329472 | -4.5841 |
| H | 0.80323 | 0.193596 | -2.99887 |
| C | -0.57452 | -4.85876 | -1.08631 |
| H | 0.197028 | -4.80977 | -1.86407 |
| H | -0.96278 | -5.88597 | -1.06049 |
| H | -0.08976 | -4.66637 | -0.1239 |
| C | -3.14315 | -3.6674 | 0.07449 |

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| H | -2.6922 | -3.22972 | 0.970131 |
| :---: | :---: | :---: | :---: |
| H | -3.40855 | -4.70808 | 0.302997 |
| H | -4.07088 | -3.12106 | -0.13669 |
| C | -3.01098 | -4.39708 | -2.82941 |
| H | -3.87597 | -3.77321 | -3.08308 |
| H | -3.38882 | -5.37125 | -2.49087 |
| H | -2.4377 | -4.56752 | -3.74785 |
| C | 1.416703 | -2.56161 | 1.323102 |
| H | 1.059966 | -2.9592 | 0.36856 |
| H | 2.216396 | -3.23995 | 1.655601 |
| H | 1.82926 | -1.57683 | 1.088235 |
| C | 0.974804 | -1.98427 | 4.258317 |
| H | 1.431499 | -0.99191 | 4.157561 |
| H | 1.774242 | -2.70147 | 4.493048 |
| H | 0.299525 | -1.94917 | 5.122258 |
| C | -0.46032 | -4.30816 | 2.896532 |
| H | -0.99843 | -4.47457 | 3.834977 |
| H | 0.427294 | -4.95556 | 2.901557 |
| H | -1.10817 | -4.64182 | 2.078058 |
| C | -2.91917 | -2.55217 | 4.464892 |
| H | -3.19565 | -3.45126 | 3.901951 |
| H | -3.77611 | -2.27356 | 5.092851 |
| H | -2.09236 | -2.8175 | 5.134207 |
| C | -2.12951 | 0.366358 | 4.464824 |
| H | -1.19281 | 0.196146 | 5.010937 |
| H | -2.93139 | 0.497884 | 5.20362 |
| H | -2.02492 | 1.307485 | 3.915861 |
| C | -4.12501 | -0.74047 | 2.391864 |
| H | -4.0305 | 0.045961 | 1.636644 |
| H | -4.89698 | -0.42677 | 3.107059 |
| H | -4.48 | -1.64772 | 1.887818 |
| C | 1.881317 | 1.157103 | -0.30325 |
| C | 3.002864 | 0.141182 | -0.69117 |
| C | 4.371567 | 0.358564 | -0.3604 |
| H | 4.673543 | 1.262665 | 0.160705 |
| C | 5.398587 | -0.57408 | -0.68528 |
| C | 6.759756 | -0.38967 | -0.30485 |
| H | 7.037513 | 0.53125 | 0.208519 |
| C | 7.742043 | -1.35852 | -0.60241 |
| H | 8.775663 | -1.18374 | -0.30801 |
| C | 7.391783 | -2.52597 | -1.27699 |
| H | 8.149756 | -3.27074 | -1.51334 |
| C | 6.053215 | -2.74497 | -1.66345 |
| H | 5.780467 | -3.65752 | -2.19222 |

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| C | 5.036428 | -1.79603 | -1.38189 |
| :--- | :---: | :---: | :--- |
| C | 3.66592 | -1.9758 | -1.72091 |
| H | 3.371665 | -2.88927 | -2.23677 |
| C | 2.684494 | -1.03044 | -1.37637 |
| H | 1.645363 | -1.23839 | -1.59814 |
| C | 1.793578 | 2.270714 | -1.39798 |
| C | 2.919304 | 2.718557 | -2.11053 |
| H | 3.881483 | 2.249367 | -1.93246 |
| C | 2.825145 | 3.744537 | -3.05658 |
| H | 3.717197 | 4.063374 | -3.59053 |
| C | 1.59123 | 4.342297 | -3.33453 |
| H | 1.512435 | 5.127044 | -4.08257 |
| C | 0.454849 | 3.887707 | -2.65688 |
| H | -0.52212 | 4.307004 | -2.88853 |
| C | 0.559213 | 2.872382 | -1.69861 |
| H | -0.33244 | 2.503769 | -1.20669 |
| C | 2.302321 | 1.819967 | 1.053753 |
| C | 3.135175 | 2.94766 | 1.141722 |
| H | 3.515272 | 3.407926 | 0.234216 |
| C | 3.522502 | 3.478747 | 2.380084 |
| H | 4.17376 | 4.349791 | 2.409558 |
| C | 3.088498 | 2.886149 | 3.567755 |
| C | 3.383102 | 3.296272 | 4.530106 |
| H | 2.265089 | 1.756326 | 3.496349 |
| C | 1.904507 | 1.289048 | 4.409975 |
| H | 1.877278 | 1.238881 | 2.258708 |
| K | 1.202606 | 0.392448 | 2.206857 |
| K | 1.151696 | 5.586736 | 0.259259 |

Table 3.9.10. Geometry optimized coordinates of 3.5 in the gas phase.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -1.34955 | -0.00138 | 0.000033 |
| Si | -3.41425 | 1.833747 | -2.40052 |
| Si | -1.53629 | -0.27451 | -3.46571 |
| Si | -3.40257 | -3.00865 | -0.39258 |
| Si | -1.53156 | -2.85995 | 1.970736 |
| Si | -1.52919 | 3.132704 | 1.494391 |
| Si | -3.40693 | 1.162095 | 2.799527 |
| N | 0.611199 | -0.00199 | -0.00314 |
| N | -2.20927 | 0.56599 | -2.04943 |
| N | -2.20431 | 1.48708 | 1.522675 |
| N | -2.20321 | -2.06365 | 0.529035 |
| C | -2.59461 | 3.515656 | -2.72402 |

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| C | -4.48966 | 1.509808 | -3.93693 |
| :---: | :---: | :---: | :---: |
| C | -4.67802 | 1.996675 | -0.9997 |
| C | -2.76697 | -1.3367 | -4.45259 |
| C | -0.75019 | 0.928239 | -4.71073 |
| C | -0.1769 | -1.48202 | -2.9223 |
| C | -2.57922 | -4.12522 | -1.6889 |
| C | -4.67721 | -1.88753 | -1.23304 |
| C | -4.46677 | -4.18393 | 0.659979 |
| C | -0.18048 | -1.7713 | 2.740914 |
| C | -2.76448 | -3.18025 | 3.382557 |
| C | -0.73524 | -4.53838 | 1.565978 |
| C | -0.17822 | 3.259595 | 0.166502 |
| C | -2.75913 | 4.51843 | 1.067302 |
| C | -0.73594 | 3.613311 | 3.153958 |
| C | -4.47352 | 2.659891 | 3.288304 |
| C | -2.58646 | 0.596298 | 4.415457 |
| C | -4.67595 | -0.12658 | 2.237443 |
| C | 5.068602 | 5.453173 | -2.29771 |
| C | 5.634794 | 5.101735 | -1.0478 |
| C | 5.173089 | 4.000417 | -0.36026 |
| C | 4.125076 | 3.199944 | -0.8888 |
| C | 3.631962 | 2.055743 | -0.19918 |
| C | 2.606704 | 1.284027 | -0.70801 |
| C | 2.090132 | 0.000398 | -0.00301 |
| C | 2.608471 | -0.02989 | 1.460478 |
| C | 3.637086 | -0.85349 | 1.872241 |
| C | $\begin{aligned} & 4.133267 \\ & 5.186137 \end{aligned}$ | $\begin{array}{r} -0.82656 \\ -1.68003 \end{array}$ | $\begin{aligned} & 3.206677 \\ & 3.632795 \end{aligned}$ |
| C | 5.65176 | -1.63274 | 4.928857 |
| C | 5.08442 | -0.72825 | 5.859655 |
| C | 5.102252 | -4.70694 | -3.55644 |
| C | 5.673887 | -3.44872 | -3.867 |
| C | 5.205437 | -2.30348 | -3.26056 |
| C | 4.145463 | -2.36199 | -2.31644 |
| C | 3.646463 | -1.19393 | -1.67286 |
| C | 2.611136 | -1.25036 | -0.76143 |
| C | 2.052934 | -2.52451 | -0.45675 |
| C | 2.514646 | -3.67337 | -1.05178 |
| C | 3.570056 | -3.63364 | -2.00323 |
| C | 4.073092 | -4.79619 | -2.64447 |
| C | 3.562424 | 0.087014 | 4.147674 |
| C | 2.514138 | 0.937153 | 3.701486 |

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| C | 2.054608 | 0.87736 | 2.408238 |
| :---: | :---: | :---: | :---: |
| C | 4.062403 | 0.112719 | 5.4763 |
| C | 4.05149 | 4.695855 | -2.83689 |
| C | 3.555244 | 3.555724 | -2.15163 |
| C | 2.511362 | 2.739881 | -2.66694 |
| C | 2.05432 | 1.648415 | -1.9692 |
| H | -3.36413 | 4.265207 | -2.95111 |
| H | -2.01278 | 3.886892 | -1.87639 |
| H | -1.92151 | 3.464765 | -3.58766 |
| H | -5.22232 | 2.326214 | -3.9932 |
| H | -5.05258 | 0.5728 | -3.87053 |
| H | -3.93564 | 1.509988 | -4.88124 |
| H | -5.31648 | 2.869893 | -1.18736 |
| H | -5.32821 | 1.115024 | -0.96574 |
| H | -4.22046 | 2.118281 | -0.01654 |
| H | -3.29438 | -2.06452 | -3.82838 |
| H | -3.5175 | -0.75249 | -4.99027 |
| H | -2.19563 | -1.90262 | -5.20084 |
| H | -0.04019 | 1.612711 | -4.23347 |
| H | -1.49793 | 1.537772 | -5.23069 |
| H | -0.20344 | 0.360888 | -5.47518 |
| H | -0.38676 | -2.04278 | -2.00356 |
| H | -0.06945 | -2.23807 | -3.71156 |
| H | 0.799992 | -1.01217 | -2.79557 |
| H | -3.34643 | -4.70863 | -2.21484 |
| H | -2.01133 | -3.57356 | -2.44257 |
| H | -1.89298 | -4.83718 | -1.21564 |
| H | -5.32783 | -2.49932 | -1.87176 |
| H | -5.3145 | -1.40209 | -0.48518 |
| H | -4.23027 | -1.10919 | -1.8539 |
| H | -5.18999 | -4.65811 | -0.01716 |
| H | -5.03987 | -3.65938 | 1.431813 |
| H | -3.90286 | -4.98917 | 1.141784 |
| H | -0.3898 | -0.69458 | 2.744168 |
| H | -0.08458 | -2.05552 | 3.797256 |
| H | 0.801363 | -1.90658 | 2.283388 |
| H | -3.30284 | -2.27709 | 3.685394 |
| H | -3.5052 | -3.94968 | 3.152951 |
| H | -2.19316 | -3.52648 | 4.254457 |
| H | -0.02515 | -4.47116 | 0.734429 |
| H | -1.47781 | -5.3013 | 1.305809 |
| H | -0.18662 | -4.90408 | 2.443811 |
| H | -0.38347 | 2.722734 | -0.76771 |

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| H | -0.08878 | 4.316962 | -0.11608 |
| :---: | :---: | :---: | :---: |
| H | 0.805892 | 2.937452 | 0.511571 |
| H | -3.2863 | 4.339065 | 0.12528 |
| H | -3.5094 | 4.694502 | 1.841522 |
| H | -2.18747 | 5.448744 | 0.948002 |
| H | -0.04026 | 2.84893 | 3.517105 |
| H | -1.48278 | 3.77933 | 3.938747 |
| H | -0.1729 | 4.548378 | 3.036492 |
| H | -5.20549 | 2.306741 | 4.027205 |
| H | -5.03719 | 3.071848 | 2.444639 |
| H | -3.9132 | 3.475783 | 3.756355 |
| H | -3.35375 | 0.439168 | 5.184939 |
| H | -2.02542 | -0.33652 | 4.314771 |
| H | -1.8939 | 1.357446 | 4.792929 |
| H | -5.30094 | -0.42059 | 3.090842 |
| H | -5.33895 | 0.299285 | 1.475719 |
| H | -4.22158 | -1.02897 | 1.824726 |
| H | 4.093515 | 1.800747 | 0.748583 |
| H | 1.2554 | 1.045486 | -2.38214 |
| H | 2.074523 | 2.992494 | -3.6308 |
| H | 3.614101 | 4.962474 | -3.79635 |
| H | 5.440972 | 6.324052 | -2.83048 |
| H | 6.436922 | 5.705904 | -0.63252 |
| H | 5.605714 | 3.728572 | 0.599769 |
| H | 4.098879 | -1.54579 | 1.176664 |
| H | 5.619702 | -2.37384 | 2.916291 |
| H | 6.457835 | -2.29077 | 5.242128 |
| H | 5.459882 | -0.70025 | 6.879062 |
| H | 3.624247 | 0.808637 | 6.188116 |
| H | 2.075996 | 1.643706 | 4.403241 |
| H | 1.252737 | 1.533621 | 2.094397 |
| H | 1.245532 | -2.5803 | 0.262416 |
| H | 2.07315 | -4.63456 | -0.79713 |
| H | 4.111617 | -0.24528 | -1.91794 |
| H | 5.64238 | -1.33613 | -3.49724 |
| H | 3.631594 | -5.76055 | -2.40356 |
| H | 5.48 | -5.60316 | -4.04124 |
| H | 6.485476 | -3.39043 | -4.5873 |

Table 3.9.11. Geometry optimized coordinates of $3.5-\mathrm{K}$ in the gas phase.

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| U | 1.422828 | -0.02071 | 0.013646 |
| :---: | :---: | :---: | :---: |
| Si | 3.424034 | -0.76641 | -2.93685 |
| Si | 1.619679 | 1.585046 | -3.20621 |
| Si | 3.336341 | 2.965762 | 0.879242 |
| Si | 1.467957 | 2.053339 | 2.992924 |
| Si | 1.478186 | -3.66669 | 0.240449 |
| Si | 3.255934 | -2.27599 | 2.211172 |
| N | -0.54804 | -0.00747 | -0.01666 |
| N | 2.217659 | 0.28154 | -2.22572 |
| N | 2.149098 | -2.17373 | 0.85779 |
| N | 2.140387 | 1.827257 | 1.402933 |
| C | 2.653823 | -2.22338 | -3.90187 |
| C | 4.608116 | 0.077635 | -4.17619 |
| C | 4.580078 | -1.4821 | -1.60683 |
| C | 2.899695 | 2.928617 | -3.65803 |
| C | 0.895827 | 0.995132 | -4.874 |
| C | 0.231032 | 2.516096 | -2.31365 |
| C | 2.598582 | 4.531581 | 0.07706 |
| C | 4.54636 | 2.174904 | -0.36683 |
| C | 4.491124 | 3.636561 | 2.255702 |
| C | 0.037806 | 0.86335 | 3.376421 |
| C | 2.701276 | 1.738318 | 4.413606 |
| C | 0.756319 | 3.804388 | 3.265702 |
| C | 0.064021 | -3.34444 | -0.98582 |
| C | 2.726365 | -4.73063 | -0.74165 |
| C | 0.740141 | -4.81048 | 1.578921 |
| C | 4.414075 | -3.80976 | 2.235517 |
| C | 2.374067 | -2.28003 | 3.901774 |
| C | 4.49234 | -0.82836 | 2.198897 |
| C | -5.10543 | -4.10241 | -4.20138 |
| C | -5.70102 | -4.17665 | -2.91978 |
| C | -5.22264 | -3.40484 | -1.88683 |
| C | -4.13296 | -2.52018 | -2.0787 |
| C | -3.62971 | -1.71333 | -1.02373 |
| C | -2.56035 | -0.86439 | -1.19705 |
| C | -1.99669 | 0.038979 | -0.05149 |
| C | -2.58751 | -0.49519 | 1.287162 |
| C | -3.70851 | 0.026814 | 1.89823 |
| C | -4.23592 | -0.52328 | 3.100167 |
| C | -5.39131 | 0.014829 | 3.731314 |
| C | -5.88824 | -0.53743 | 4.891135 |
| C | -5.24844 | -1.65662 | 5.480003 |
| C | -5.05347 | 5.772049 | -1.41232 |
| C | -5.64894 | 4.727752 | -2.16008 |

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| C | -5.18289 | 3.438704 | -2.04454 |
| :---: | :---: | :---: | :---: |
| C | -4.09793 | 3.127893 | -1.18658 |
| C | -3.59479 | 1.806364 | -1.0543 |
| C | -2.50658 | 1.504134 | -0.2541 |
| C | -1.91104 | 2.568492 | 0.481028 |
| C | -2.39119 | 3.85593 | 0.405327 |
| IC | -3.49242 | 4.183177 | -0.43506 |
| C | -3.99998 | 5.502711 | -0.56622 |
| C | -3.59111 | -1.65335 | 3.697351 |
| C | -2.4444 | -2.18071 | 3.0503 |
| C | -1.96847 | -1.62501 | 1.890258 |
| C | -4.12597 | -2.19846 | 4.892941 |
| C | -4.04462 | -3.25217 | -4.42251 |
| C | -3.53229 | -2.44002 | -3.37687 |
| C | -2.44631 | -1.53231 | -3.5558 |
| C | -1.98025 | -0.77392 | -2.5031 |
| H | 3.438232 | -2.84336 | -4.35727 |
| H | 2.045241 | -2.87719 | -3.26371 |
| H | 2.008679 | -1.8598 | -4.71285 |
| H | 5.342088 | -0.66537 | -4.51519 |
| H | 5.161067 | 0.90266 | -3.71024 |
| H | 4.11089 | 0.468672 | -5.07475 |
| H | 5.261409 | -2.2231 | -2.04727 |
| H | 5.193277 | -0.68571 | -1.15948 |
| H | 4.021155 | -1.97941 | -0.80806 |
| H | 3.369867 | 3.372551 | -2.77303 |
| H | 3.692784 | 2.540053 | -4.30311 |
| H | 2.392776 | 3.736081 | -4.20398 |
| H | 0.142433 | 0.214894 | -4.71595 |
| H | 1.655431 | 0.590422 | -5.55833 |
| H | 0.40366 | 1.829598 | -5.39086 |
| H | 0.401498 | 2.62047 | -1.23824 |
| H | 0.15392 | 3.526328 | -2.72844 |
| H | -0.74011 | 2.027627 | -2.43492 |
| H | 3.392738 | 5.218442 | -0.24742 |
| H | 1.981185 | 4.298848 | -0.79874 |
| H | 1.969421 | 5.077521 | 0.789955 |
| H | 5.236919 | 2.950269 | -0.72841 |
| H | 5.144518 | 1.397211 | 0.119288 |
| H | 4.04166 | 1.735437 | -1.23365 |
| H | 5.234417 | 4.294106 | 1.782537 |
| H | 5.032609 | 2.831644 | 2.768396 |
| H | 3.980851 | 4.232616 | 3.022782 |
| H | 0.229614 | -0.16643 | 3.067105 |

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| H | -0.12037 | 0.849639 | 4.462786 |
| :---: | :---: | :---: | :---: |
| H | -0.90739 | 1.151188 | 2.916182 |
| H | 3.135272 | 0.733837 | 4.337639 |
| H | 3.531339 | 2.447688 | 4.459361 |
| H | 2.165487 | 1.788297 | 5.370924 |
| H | -0.0024 | 4.045545 | 2.51004 |
| H | 1.523176 | 4.585503 | 3.227913 |
| H | 0.275613 | 3.866815 | 4.251216 |
| H | 0.259267 | -2.51713 | -1.68404 |
| H | -0.07778 | -4.24742 | -1.59088 |
| H | -0.88797 | -3.12919 | -0.49074 |
| H | 3.186882 | -4.16633 | -1.56379 |
| H | 3.540854 | -5.11296 | -0.11682 |
| H | 2.21078 | -5.59544 | -1.18445 |
| H | -0.02273 | -4.28267 | 2.16595 |
| H | 1.484978 | -5.19001 | 2.286948 |
| H | 0.256517 | -5.67922 | 1.113438 |
| H | 5.088824 | -3.719 | 3.095447 |
| H | 5.045825 | -3.8743 | 1.337614 |
| H | 3.890578 | -4.77 | 2.327718 |
| H | 3.089109 | -2.38743 | 4.728456 |
| H | 1.809521 | -1.35984 | 4.073247 |
| H | 1.662696 | -3.11219 | 3.96425 |
| H | 5.049809 | -0.83061 | 3.143996 |
| H | 5.220007 | -0.94959 | 1.386026 |
| H | 4.018244 | 0.154197 | 2.10625 |
| H | -4.11897 | -1.78607 | -0.05791 |
| H | -1.14103 | -0.10578 | -2.64324 |
| H | -1.97808 | -1.46034 | -4.53748 |
| H | -3.57844 | -3.19405 | -5.4051 |
| H | -5.48864 | -4.71818 | -5.01036 |
| H | -6.54026 | -4.84618 | -2.75581 |
| H | -5.67794 | -3.46218 | -0.90279 |
| H | -4.22438 | 0.880456 | 1.470845 |
| H | -5.87342 | 0.880849 | 3.282641 |
| H | -6.77045 | -0.11152 | 5.362209 |
| H | -5.64746 | -2.08258 | 6.397017 |
| H | -3.63128 | -3.05658 | 5.341793 |
| H | -1.93774 | -3.03535 | 3.493479 |
| H | -1.078 | -2.03218 | 1.427593 |
| H | -1.05369 | 2.347669 | 1.099651 |
| H | -1.91811 | 4.64936 | 0.981079 |
| H | -4.09521 | 1.020569 | -1.60691 |
| H | -5.63748 | 2.637813 | -2.62147 |

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| H | -3.53219 | 6.301912 | 0.006394 |
| :--- | :--- | :--- | :--- |
| H | -5.42651 | 6.787961 | -1.51009 |
| H | -6.47678 | 4.950859 | -2.82749 |

Table 3.9.12. Geometry optimized coordinates of 3.6 in the gas phase.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | 0.65016 | -0.00178 | 0.074532 |
| N | -0.78081 | 0.077728 | 1.406605 |
| Si | 2.355405 | 2.050455 | 2.235963 |
| Si | 0.79878 | -3.38945 | 0.541165 |
| Si | 4.210377 | 0.023174 | 0.968607 |
| Si | 1.146295 | 2.619525 | -2.45342 |
| Si | -1.5952 | 1.388377 | -2.06184 |
| Si | 1.08754 | -2.69027 | -2.39002 |
| N | 0.924967 | -2.13896 | -0.71003 |
| C | -3.22189 | -0.1448 | 1.829012 |
| C | -1.53298 | -0.82131 | 3.583885 |
| C | -1.8173 | 1.59104 | 3.056528 |
| c | -1.83316 | 0.175937 | 2.436306 |
| C | -4.14075 | 0.839327 | 1.516669 |
| C | -3.60205 | -1.49723 | 1.587895 |
| C | 0.957214 | 3.17736 | 1.612556 |
| N | 2.579357 | 0.71611 | 1.087753 |
| N | 0.131664 | 1.413893 | -1.63481 |
| C | -1.99854 | 1.666901 | -3.89829 |
| C | 2.695903 | -3.63243 | -2.76873 |
| C | 1.309793 | 2.396372 | -4.33583 |
| C | 0.496486 | 4.388231 | -2.19198 |
| c | 1.131778 | -1.24238 | -3.60672 |
| C | 1.980295 | 1.417127 | 3.984946 |
| C | 1.30488 | -2.64276 | 2.215944 |
| C | 5.56827 | 1.223331 | 0.385219 |
| C | 1.952387 | -4.88726 | 0.344 |
| C | -0.34491 | -3.83334 | -2.89639 |
| C | -6.3493 | 1.563032 | 0.631155 |
| C | -7.92606 | -0.10306 | -0.15317 |
| C | -5.4135 | 0.542867 | 0.955812 |
| C | -2.29355 | -0.33559 | -1.68267 |
| C | -0.95142 | -4.11395 | 0.647715 |
| C | -2.56317 | 2.712048 | -1.11132 |
| C | 3.830932 | 3.231053 | 2.442481 |
| C | -4.8246 | -1.82488 | 1.050072 |
| C | 4.275842 | -1.3706 | -0.30997 |
| C | -7.04204 | -1.11421 | 0.152672 |

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| C | -7.57578 | 1.248687 | 0.088481 |
| :---: | :---: | :---: | :---: |
| C | 2.936914 | 2.554969 | -1.84341 |
| C | 4.807031 | -0.6704 | 2.635743 |
| C | -5.76935 | -0.82089 | 0.711014 |
| H | -8.28156 | 2.038122 | -0.15577 |
| H | -8.89708 | -0.33821 | -0.58066 |
| H | -7.30736 | -2.15311 | -0.02975 |
| H | -6.07956 | 2.599867 | 0.819044 |
| H | -5.08269 | -2.86844 | 0.883697 |
| H | -2.91812 | -2.29658 | 1.843161 |
| H | -3.91501 | 1.884313 | 1.695981 |
| H | -0.8549 | 1.772079 | 3.5398 |
| H | -1.96276 | 2.37195 | 2.306368 |
| H | -2.60515 | 1.685444 | 3.812433 |
| H | -0.5959 | -0.55258 | 4.080039 |
| H | -2.33611 | -0.79247 | 4.329325 |
| H | -1.43452 | -1.84732 | 3.223679 |
| H | 0.919137 | -1.64196 | 2.441123 |
| H | 0.94441 | -3.29543 | 3.021879 |
| H | 2.396504 | -2.60126 | 2.290189 |
| H | 3.006806 | -4.60782 | 0.244254 |
| H | 1.858819 | -5.50296 | 1.24905 |
| H | 1.687593 | -5.52398 | -0.50682 |
| H | -1.71825 | -3.34108 | 0.549008 |
| H | -1.12255 | -4.84403 | -0.15149 |
| H | -1.10535 | -4.63204 | 1.6035 |
| H | -0.31261 | -4.01068 | -3.97937 |
| H | -0.28571 | -4.81311 | -2.40771 |
| H | -1.32439 | -3.40414 | -2.65757 |
| H | 3.58116 | -3.00865 | -2.60535 |
| H | 2.825408 | -4.5501 | -2.19 |
| H | 2.684702 | -3.91375 | -3.83053 |
| H | 1.978366 | -0.57468 | -3.41339 |
| H | 1.271474 | -1.65389 | -4.61545 |
| H | 0.226668 | -0.63207 | -3.61535 |
| H | 1.982634 | 3.181845 | -4.70661 |
| H | 1.754727 | 1.432615 | -4.60437 |
| H | 0.368115 | 2.491149 | -4.88226 |
| H | 3.055497 | 2.775859 | -0.78107 |
| H | 3.393844 | 1.575436 | -2.02955 |
| H | 3.519605 | 3.292709 | -2.41096 |
| H | -0.42816 | 4.568599 | -2.75323 |
| H | 0.292914 | 4.611699 | -1.13911 |
| H | 1.238406 | 5.113125 | -2.5515 |
| H | -3.38967 | -0.28027 | -1.69443 |

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| H | -1.98747 | -1.05643 | -2.44828 |
| :---: | :---: | :---: | :---: |
| H | -2.03538 | -0.74829 | -0.70055 |
| H | -1.80926 | 2.69265 | -4.23301 |
| H | -1.45997 | 0.986566 | -4.56648 |
| H | -3.07231 | 1.47706 | -4.03155 |
| H | 1.732065 | 2.24786 | 4.658378 |
| H | 1.146125 | 0.709851 | 3.99872 |
| H | 2.851318 | 0.901341 | 4.406073 |
| H | 4.941675 | 0.120696 | 3.383047 |
| H | 4.115031 | -1.4068 | 3.058902 |
| H | 5.780549 | -1.16147 | 2.506797 |
| H | 3.504197 | 4.057841 | 3.087895 |
| H | 4.6949 | 2.765781 | 2.92874 |
| H | 4.167717 | 3.667147 | 1.496014 |
| H | 1.333075 | 3.822174 | 0.810916 |
| H | 0.069427 | 2.661195 | 1.232346 |
| H | 0.61443 | 3.82703 | 2.428321 |
| H | 5.302741 | -1.75768 | -0.3462 |
| H | 3.60715 | -2.20614 | -0.09658 |
| H | 4.036265 | -1.00773 | -1.31719 |
| H | 5.848321 | 1.974804 | 1.128051 |
| H | 6.466943 | 0.629579 | 0.16924 |
| H | 5.295309 | 1.747304 | -0.53634 |
| H | -2.29194 | 3.719891 | -1.44498 |
| H | -3.64255 | 2.586708 | -1.26348 |
| H | -2.36776 | 2.652267 | -0.03679 |

Table 3.9.13. Geometry optimized coordinates of $3.6-\mathrm{K}$ in the gas phase.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -0.70364 | -0.00418 | -0.04312 |
| N | 0.777084 | 0.076699 | -1.35108 |
| Si | -2.75885 | 1.003917 | -2.78676 |
| Si | -0.02614 | -3.51056 | 0.385653 |
| Si | -4.07273 | -1.12599 | -1.13437 |
| Si | -2.08905 | 2.268024 | 2.355211 |
| Si | 0.539526 | 3.217969 | 1.29436 |
| Si | 0.359025 | -1.93419 | 2.918111 |
| N | -0.07697 | -1.98848 | 1.232241 |
| C | 3.244684 | -0.02919 | -1.58049 |
| C | 1.787058 | -1.25515 | -3.17176 |
| C | 1.793019 | 1.250435 | -3.24955 |
| C | 1.873364 | 0.030765 | -2.30101 |
| C | 4.389441 | 0.568673 | -2.073 |
| C | 3.358593 | -0.79022 | -0.38045 |

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| C | -1.71656 | 2.557886 | -2.47239 |
| :---: | :---: | :---: | :---: |
| N | -2.7422 | -0.03465 | -1.38645 |
| N | -0.69773 | 1.977576 | 1.349727 |
| C | 0.811431 | 4.126091 | 2.958551 |
| C | -1.16417 | -2.08946 | 4.057056 |
| C | -1.76983 | 2.215147 | 4.237426 |
| C | -2.96953 | 3.924166 | 2.000818 |
| C | 1.261976 | -0.32669 | 3.370692 |
| C | -2.10285 | 0.150952 | -4.36094 |
| C | -0.79651 | -3.36531 | -1.35028 |
| C | -5.77048 | -0.30678 | -0.80366 |
| C | -1.01027 | -4.90843 | 1.244836 |
| C | 1.563884 | -3.30002 | 3.507626 |
| C | 6.825183 | 1.06468 | -1.92791 |
| C | 8.128626 | 0.152514 | -0.10004 |
| C | 5.649678 | 0.444455 | -1.42404 |
| C | 2.245705 | 2.536644 | 0.846961 |
| C | 1.721798 | -4.22458 | 0.101674 |
| C | 0.160462 | 4.607925 | 0.044288 |
| C | -4.47378 | 1.687422 | -3.29125 |
| C | 4.560942 | -0.94348 | 0.268371 |
| C | -3.8157 | -2.2335 | 0.403968 |
| C | 7.006042 | -0.45978 | 0.414975 |
| C | 8.036225 | 0.923369 | -1.28487 |
| C | -3.40342 | 0.927742 | 2.069504 |
| C | -4.3983 | -2.28083 | -2.62274 |
| C | 5.745397 | -0.33342 | -0.22618 |
| H | 8.925589 | 1.404891 | -1.68495 |
| H | 9.087726 | 0.047065 | 0.401627 |
| H | 7.070228 | -1.05106 | 1.326425 |
| H | 6.751661 | 1.658003 | -2.83737 |
| H | 4.616198 | -1.53349 | 1.181433 |
| H | 2.457809 | -1.23566 | 0.027502 |
| H | 4.355804 | 1.160904 | -2.98273 |
| H | 0.804953 | 1.26906 | -3.71662 |
| H | 1.926531 | 2.185733 | -2.69557 |
| H | 2.540409 | 1.210296 | -4.05239 |
| H | 0.835509 | -1.27498 | -3.71449 |
| H | 2.607362 | -1.2977 | -3.90063 |
| H | 1.840524 | -2.14944 | -2.54404 |
| H | -0.50949 | -2.45147 | -1.88358 |
| H | -0.4532 | -4.20924 | -1.96451 |
| H | -1.88886 | -3.40869 | -1.31897 |

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| H | -2.05646 | -4.62009 | 1.401002 |
| :---: | :---: | :---: | :---: |
| H | -1.00542 | -5.81209 | 0.619356 |
| H | -0.59408 | -5.18584 | 2.220727 |
| H | 2.364909 | -3.53044 | -0.45075 |
| H | 2.233506 | -4.47288 | 1.037673 |
| H | 1.649504 | -5.14862 | -0.48884 |
| H | 1.7427 | -3.16863 | 4.583824 |
| H | 1.188695 | -4.31895 | 3.361533 |
| H | 2.535788 | -3.22767 | 3.004746 |
| H | -1.87176 | -1.26669 | 3.899657 |
| H | -1.70455 | -3.02503 | 3.865302 |
| H | -0.87709 | -2.07931 | 5.11749 |
| H | 0.700374 | 0.569695 | 3.091147 |
| H | 1.44896 | -0.28698 | 4.452722 |
| H | 2.233691 | -0.27841 | 2.862723 |
| H | -2.72813 | 2.262867 | 4.773532 |
| H | -1.27583 | 1.280672 | 4.529035 |
| H | -1.14851 | 3.041774 | 4.595746 |
| H | -3.75195 | 0.915484 | 1.032986 |
| H | -3.05788 | -0.08205 | 2.324085 |
| H | -4.27182 | 1.130582 | 2.710692 |
| H | -2.3411 | 4.792336 | 2.232692 |
| H | -3.25451 | 3.996751 | 0.943796 |
| H | -3.88589 | 4.011731 | 2.60057 |
| H | 2.967096 | 3.361513 | 0.766507 |
| H | 2.618933 | 1.841738 | 1.607616 |
| H | 2.233546 | 2.000924 | -0.10508 |
| H | -0.0562 | 4.708779 | 3.290388 |
| H | 1.077403 | 3.432555 | 3.765061 |
| H | 1.6481 | 4.828405 | 2.839992 |
| H | -2.06718 | 0.847714 | -5.20991 |
| H | -1.0926 | -0.24148 | -4.20427 |
| H | -2.74185 | -0.69278 | -4.64962 |
| H | -4.7227 | -1.71484 | -3.50526 |
| H | -3.50478 | -2.84718 | -2.90847 |
| H | -5.19332 | -3.00174 | -2.38662 |
| H | -4.33694 | 2.415936 | -4.10261 |
| H | -5.15495 | 0.912701 | -3.6627 |
| H | -4.97409 | 2.204839 | -2.46415 |
| H | -2.17047 | 3.184289 | -1.6954 |
| H | -0.6955 | 2.317299 | -2.15716 |
| H | -1.64085 | 3.161183 | -3.38771 |
| H | -4.41435 | -1.85871 | 1.242695 |
| H | -4.15171 | -3.25766 | 0.193953 |

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| H | -2.7808 | -2.30243 | 0.754492 |
| :--- | :---: | :---: | :---: |
| H | -6.17729 | 0.217203 | -1.67401 |
| H | -6.49142 | -1.08782 | -0.52201 |
| H | -5.72635 | 0.40865 | 0.025799 |
| H | -0.79965 | 5.096036 | 0.251007 |
| H | 0.94205 | 5.379469 | 0.085033 |

Table 3.9.14. Geometry optimized coordinates of 3.7 in the gas phase.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -0.53954 | -0.02093 | 0.05379 |
| N | 1.333144 | -0.29909 | -0.43649 |
| C | 2.684568 | -0.4111 | -0.69444 |
| C | 3.63198 | 0.246972 | 0.089883 |
| C | 5.020344 | 0.136899 | -0.16877 |
| C | 5.468345 | -0.67117 | -1.26557 |
| C | 4.490272 | -1.33494 | -2.0574 |
| C | 3.149768 | -1.21353 | -1.789 |
| N | -0.99029 | -2.03658 | 1.006457 |
| Si | 0.348723 | -2.8579 | 1.847178 |
| C | 1.428569 | -1.59253 | 2.759493 |
| C | 1.424439 | -3.8569 | 0.649886 |
| C | -0.20964 | -4.05746 | 3.21409 |
| Si | -2.50457 | -2.93679 | 0.810086 |
| C | -3.71426 | -1.99757 | -0.30902 |
| C | -2.23514 | -4.63817 | 0.009109 |
| C | -3.45582 | -3.18498 | 2.435559 |
| N | -0.44522 | 1.843949 | 1.34847 |
| Si | 0.36004 | 3.287477 | 0.69235 |
| C | 1.109693 | 2.938704 | -1.01519 |
| C | -0.81542 | 4.759239 | 0.437994 |
| C | 1.7746 | 3.882854 | 1.809442 |
| Si | -1.07747 | 1.890678 | 3.003904 |
| C | 0.283978 | 1.79283 | 4.321981 |
| C | -2.09708 | 3.444215 | 3.398631 |
| C | -2.25994 | 0.42804 | 3.256526 |
| N | -1.65953 | 0.377185 | -1.87592 |
| Si | -1.00757 | -0.42116 | -3.32496 |
| C | -0.50128 | -2.19901 | -2.88201 |
| C | 0.483161 | 0.511805 | -4.03047 |
| C | -2.23771 | -0.60564 | -4.76026 |
| Si | -3.01457 | 1.509932 | -2.014707 |
| C | -3.58725 | 2.056254 | -0.28651 |

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| C | -2.52509 | 3.050061 | -3.00999 |
| :---: | :---: | :---: | :---: |
| C | -4.58339 | 0.797069 | -2.81528 |
| H | 3.295509 | 0.860114 | 0.921597 |
| H | 4.822817 | -1.94894 | -2.89161 |
| H | 2.415623 | -1.72349 | -2.40363 |
| H | 2.332643 | -2.09554 | 3.127352 |
| H | 1.764836 | -0.75439 | 2.140055 |
| H | 0.900414 | -1.19165 | 3.631967 |
| H | 2.219133 | -4.37856 | 1.199064 |
| H | 0.838494 | -4.61496 | 0.117396 |
| H | 1.905128 | -3.21611 | -0.09641 |
| H | -0.78119 | -3.55355 | 4.001685 |
| H | -0.80618 | -4.90165 | 2.852142 |
| H | 0.691143 | -4.47679 | 3.682136 |
| H | -4.05157 | -1.05114 | 0.131062 |
| H | -3.31502 | -1.78186 | -1.30316 |
| H | -4.60956 | -2.62098 | -0.43505 |
| H | -3.20341 | -5.12925 | -0.15373 |
| H | -1.73902 | -4.54908 | -0.96434 |
| H | -1.62949 | -5.30944 | 0.627921 |
| H | -3.63167 | -2.23105 | 2.946103 |
| H | -4.43769 | -3.62348 | 2.212286 |
| H | -2.95099 | -3.85208 | 3.139482 |
| H | 1.405744 | 3.905933 | -1.44429 |
| H | 2.004508 | 2.311577 | -0.96863 |
| H | 0.413666 | 2.483251 | -1.72897 |
| H | -0.25899 | 5.57592 | -0.04081 |
| H | -1.65457 | 4.507705 | -0.22013 |
| H | -1.23186 | 5.149801 | 1.370992 |
| H | 1.41193 | 4.323284 | 2.74516 |
| H | 2.461076 | 3.068663 | 2.068597 |
| H $H$ | $\begin{aligned} & 2.356083 \\ & -0.16633 \end{aligned}$ | $\begin{aligned} & 4.655102 \\ & 1.653165 \end{aligned}$ | $\begin{aligned} & 1.289294 \\ & 5.313686 \end{aligned}$ |
| H | 0.973296 | 0.960656 | 4.148225 |
| H | 0.879748 | 2.711284 | 4.359767 |
| H | -1.48145 | 4.346735 | 3.480538 |
| H | -2.87935 | 3.635798 | 2.655825 |
| H | -2.59067 | 3.301328 | 4.369142 |
| H | -2.61113 | 0.434265 | 4.296698 |
| H | -3.15012 | 0.512668 | 2.619434 |
| H | -1.80504 | -0.55008 | 3.072464 |
| H | -1.38837 | -2.82622 | -2.7339 |

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| H | 0.073153 | -2.63334 | -3.71132 |
| :--- | :---: | :---: | :---: |
| H | 0.119993 | -2.28452 | -1.98333 |
| H | 1.30507 | 0.583433 | -3.3113 |
| H | 0.863323 | 0.003315 | -4.92623 |
| H | 0.207174 | 1.531812 | -4.32461 |
| H | -2.55447 | 0.352887 | -5.18626 |
| H | -1.73397 | -1.1632 | -5.5613 |
| H | -3.13552 | -1.16799 | -4.48359 |
|  | -4.09765 | 1.243349 | 0.245827 |
| H |  |  |  |
|  | -2.78906 | 2.437233 | 0.35554 |
| H | -4.32311 |  | 2.862195 |
| H | -1.6839 | 3.586705 | -0.40852 |
| H | -2.2336 | 2.789338 | -4.55736 |
| H | -3.36849 | 3.749366 | -3.07997 |
| H | -5.41519 | 1.484548 | -2.61096 |
| H | -4.50821 | 0.689542 | -3.90051 |
| H | -4.85551 | -0.17766 | -2.39576 |
| C | 5.993104 | 0.804729 | 0.62678 |
| C | 5.655704 | 1.418419 | 1.458893 |
| H | 7.336926 | 0.679527 | 0.352974 |
| C | 6.859464 | -0.77928 | -1.52081 |
| H | 7.191762 | -1.39395 | -2.35447 |

Table 3.9.15. Geometry optimized coordinates of $3.7-\mathrm{K}$ in the gas phase.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -0.56666 | 0.032773 | -0.07431 |
| N | 1.345425 | 0.30487 | 0.451943 |
| C | 2.683523 | 0.384353 | 0.702829 |
| C | 3.652724 | -0.22007 | -0.11419 |
| C | 5.037738 | -0.13581 | 0.159011 |
| C | 5.493544 | 0.590498 | 1.312 |
| C | 4.510812 | 1.201878 | 2.140148 |
| N | 3.172725 | 1.105225 | 1.854085 |
| Si | -0.99823 | 2.232197 | -0.92383 |
| C | 0.360978 | 3.145638 | -1.54531 |
| C | 1.512231 | 2.047035 | -2.58102 |
| C | 1.380068 | 3.98248 | -0.17744 |

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| Si | -2.54676 | 2.997682 | -0.73282 |
| :---: | :---: | :---: | :---: |
| C | -3.77915 | 1.835179 | 0.134023 |
| C | -2.4908 | 4.580655 | 0.332219 |
| $\stackrel{\text { C }}{\text { N }}$ | $\begin{aligned} & -3.41889 \\ & -0.43784 \end{aligned}$ | $\begin{aligned} & 3.465186 \\ & -1.86295 \end{aligned}$ | $\begin{gathered} -2.366 \\ -1.52231 \end{gathered}$ |
| Si | 0.394454 | -3.3055 | -0.99371 |
| C | 1.175599 | -3.08844 | 0.721017 |
| C | -0.75418 | -4.82297 | -0.82021 |
| C | 1.798651 | -3.84426 | -2.16793 |
| Si | -1.04449 | -1.7301 | -3.14741 |
| C | 0.301345 | -1.36225 | -4.44459 |
| C | -1.97186 | -3.27098 | -3.78748 |
| C | -2.30644 | -0.30834 | -3.25361 |
| N | -1.6948 | -0.53108 | 1.949237 |
| Si | -1.00946 | 0.124636 | 3.421022 |
| C | -0.58857 | 1.966188 | 3.193559 |
| C | 0.55567 | -0.79702 | 3.976438 |
| C | -2.17315 | 0.090482 | 4.938099 |
| Si | -3.01647 | -1.66429 | 1.990453 |
| C | -3.57746 | -2.1362 | 0.232616 |
| C | -2.56305 | -3.28839 | 2.882818 |
| C | -4.61692 | -1.02725 | 2.815583 |
| H | 3.322393 | -0.77281 | -0.99056 |
| H | 4.840578 | 1.755191 | 3.018745 |
| H | 2.437965 | 1.574226 | 2.501705 |
| H | 2.406197 | 2.609548 | -2.8826 |
| H | 1.854764 | 1.166136 | -2.02772 |
| H | 1.008816 | 1.711093 | -3.4963 |
| H | 2.197251 | 4.581067 | -0.6027 |
| H | 0.754556 | 4.651683 | 0.42662 |
| H | 1.82212 | 3.237453 | 0.491646 |
| H | -0.64629 | 4.18336 | -3.63353 |
| H | -0.75176 | 5.328341 | -2.28549 |
| H | 0.796247 | 5.052382 | -3.09102 |
| H | -4.05871 | 0.985328 | -0.50185 |
| H | -3.39959 | 1.435469 | 1.080383 |
| H | -4.70387 | 2.387059 | 0.351419 |
| H | -3.49621 | 5.008455 | 0.447853 |
| H | -2.10162 | 4.363204 | 1.334513 |
| H | -1.85147 | 5.356959 | -0.10521 |
| H | -3.49021 | 2.598136 | -3.03428 |
| H | -4.44253 | 3.80752 | -2.15911 |


| H | -2.90712 | 4.263697 | -2.91257 |
| :---: | :---: | :---: | :---: |
| H | 1.554114 | -4.06341 | 1.059624 |
| H | 2.012727 | -2.38406 | 0.713214 |
| H | 0.459829 | -2.74203 | 1.47613 |
| H | -0.17837 | -5.6857 | -0.45738 |
| H | -1.55387 | -4.63483 | -0.0937 |
| H | -1.2285 | -5.11528 | -1.76316 |
| H | 1.424868 | -4.17226 | -3.1462 |
| H | 2.508497 | -3.0264 | -2.34018 |
| H | 2.358147 | -4.68358 | -1.7331 |
| H | -0.14332 | -1.20949 | -5.43774 |
| H | 0.864969 | -0.45844 | -4.18748 |
| H | 1.022431 | -2.18372 | -4.52584 |
| H | -1.31302 | -4.13953 | -3.90523 |
| H | -2.78859 | -3.56119 | -3.11597 |
| H | -2.40923 | -3.05644 | -4.77223 |
| H | -2.60332 | -0.15673 | -4.30036 |
| H | -3.21803 | -0.53576 | -2.6858 |
| H | -1.91227 | 0.649435 | -2.89133 |
| H | -1.50168 | 2.557856 | 3.049203 |
| H | -0.07603 | 2.357934 | 4.083195 |
| H | 0.065138 | 2.144889 | 2.332494 |
| H | 1.323527 | -0.77052 | 3.196973 |
| H | 0.978504 | -0.35007 | 4.886661 |
| H | 0.33671 | -1.85033 | 4.194307 |
| H | -2.48035 | -0.92311 | 5.222337 |
| H | -1.63931 | 0.521122 | 5.796498 |
| H | -3.08066 | 0.684999 | 4.782528 |
| H | -4.11018 | -1.30955 | -0.25443 |
| H | -2.75634 | -2.44329 | -0.42272 |
| H | -4.28225 | -2.9765 | 0.298531 |
| H | -1.7239 | -3.79277 | 2.38884 |
| H | -2.26711 | -3.10877 | 3.924248 |
| H | -3.41133 | -3.98644 | 2.896692 |
| H | -5.43434 | -1.73327 | 2.612947 |
| H | -4.5333 | -0.92181 | 3.90148 |
| H | -4.91384 | -0.05446 | 2.405484 |
| C | 6.018795 | -0.75229 | -0.67166 |
| H | 5.682707 | -1.30564 | -1.54645 |
| C | 7.363027 | -0.65764 | -0.3836 |
| C | 6.882672 | 0.669424 | 1.579855 |
| H | 7.211659 | 1.223813 | 2.457817 |
| C | 7.806495 | 0.060793 | 0.75437 |


| H | 8.091673 | -1.13789 | -1.03366 |
| :--- | :--- | :--- | :--- |
| H | 8.869579 | 0.129616 | 0.973166 |

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## Chapter 4: <br> Coordination Chemistry of Uranium(III) and (IV) in a Chelating PN Ligand Framework

### 4.1 Introduction.

While the chemistry of uranium nitrogen multiple bonds has recently been marked by significant advances, a fundamental gap in knowledge of that group remains in comparison with uranium-oxo bonds. ${ }^{1-3}$ Recent advances in uranium nitrogen multiple bonds include isolation of the first examples of a terminal, molecular uranium-nitride ${ }^{4-6}$ and uranium tris-imido moieties. ${ }^{7,8}$ These results have demonstrated that there are clear differences between uranium nitrogen and oxygen multiple bonds. ${ }^{1,9,10}$ For example, while cis uranyl complexes have remained elusive, cis bis(imido) complexes are common. ${ }^{11-13}$ To bridge this gap in understanding, the reactivity of uranium-nitrogen multiple bonds, the relative donating ability of imido and nitride ligands, and the uranium 6d and $5 f$ valence orbital involvement in bonding must be further investigated.

In the context of these recent accomplishments in the chemistry of uranium nitrogen multiple bonds, the sinlge example of a uranium complex with a terminal parent imido $\mathrm{U}=\mathrm{NH}$ moiety, $\left[U^{\text {IV }}\left(\operatorname{Tren}^{\text {TIPS }}\right)(=\mathrm{NH})\right]\left[\mathrm{K}(15-\text { crown-5 })_{2}\right] \quad\left(\operatorname{Tren}^{\text {TIPS }}=\mathrm{N}-\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NSiPr}_{3}^{i}\right)_{3}\right)$, has been reported by Liddle and coworkers. ${ }^{14}$ Interestingly, even in the d-block, where M-L multiple bonding is more prevalent, there are only 24 crystallographically characterized parent imido complexes reported to date. ${ }^{15-35}$ The small number of parent imido complexes is surprising because complexes of this type have been proposed as intermediates in dinitrogen reduction. ${ }^{23,36,37}$ Indeed, uranium parent imido complexes are relevant in this context because of the high activity of uranium toward ammonia production reported in Haber's original patent in 1909. ${ }^{38}$

### 4.2 Previous Uranium Complexes in Phosphine Amide Ligand Frameworks.

Portions of this chapter are adapted from work submitted to Angewandte Chemie, International Edition.

The Mindiola group has developed a monoanionic bidentate $\mathrm{PN}^{-}\left(\mathrm{PN}^{-}=(N-(2-\right.$ (diisopropylphosphino)-4-methylphenyl)-2,4,6-trimethylanilide) ligand for use with first row transition metals. ${ }^{39}$ This ligand has proven robust in supporting titanium-ligand multiple bonds and has afforded the first crystallographically characterized titanium nitride and methylidene complexes. ${ }^{40-42}$ Previously, Kiplinger and co-workers published a series of uranium complexes in a $\mathrm{PNP}^{-}\left(\mathrm{PNP}^{-}=\right.$bis[2-(diisopropyl-phosphino)-4-methylphenyl]amido) pincer framework. ${ }^{43,44}$ These complexes were noted to have similar steric and electronic profiles to uranium pentamethylcyclopentadienide $\left(\mathrm{C}_{5} \mathrm{Me}_{5}{ }^{-}\right)$complexes, but differences in their reactivity. For example, reaction of $(P N P)_{2} U^{I I I} I$ with potassium graphite and pyridine- $N$-oxide showed clean conversion to $(P N P)_{2} U^{\mathrm{VI}} \mathrm{O}_{2}$, while the analogous reaction with $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{U}^{\mathrm{III}} \mathrm{I}(\mathrm{THF})$ showed decomposition to uranium oxides coupled with formation of the $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2}$ dimer. ${ }^{43}$ However, it was noted that one phosphine arm of the $\mathrm{PNP}^{-}$pincer ligand did not coordinate to the uranium center (Scheme 4.2.1). We hypothesized that the $\mathrm{PN}^{-}$ligand framework would be well-matched to the uranium coordination sphere, and avoid the potential issue of dangling phosphine arms. Additionally, this softer ligand was expected to be less donating than Tren ${ }^{\text {TIPS }}$, allowing it to stabilize low- and mid-valent uranium oxidation states.


Scheme 4.2.1. Previously reported uranium PNP complex, $(P N P)_{2} U^{1 /} \mathrm{Cl}_{2}$, with two dangling phosphines. ${ }^{44}$

Examples of other phosphine amide ligand frameworks for actinides are limited to a few examples. Thorium(IV) and uranium(IV) and (V) complexes were synthesized with the ligand $\mathrm{N}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{PR}_{2}\right)_{2}\left(\mathrm{R}={ }^{\mathrm{i}} \mathrm{Pr}, \mathrm{Et}\right) .{ }^{45,46}$ Salt metathesis reactions of $\mathrm{LiN}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{PR}_{2}\right)_{2}$ with thorium and uranium tetrachloride starting materials gave tetravalent products with some phosphine arms coordinated to the metal centers. ${ }^{46}$ When stoichiometric amounts of dry oxygen were present during reactions of $\mathrm{UCl}_{4}$ with $\mathrm{LiN}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{P}^{i} \mathrm{Pr}_{2}\right)_{2}$, oxidation to the +5 oxidation state was observed, giving $\mathrm{U}^{\mathrm{V}} \mathrm{Cl}_{2}\left[\mathrm{~N}\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{P}^{\mathrm{P}} \mathrm{Pr}_{2}\right)_{2}\right]_{3}$ in $36 \%$ isolated yield. ${ }^{45}$ Other examples of phosphine amide ligands for uranium have been designed for the purposes of developing heterobimetallic frameworks with transition metals. In this context, the Bart and Thomas groups have used $N^{\prime} P_{2}\left(R^{\prime}={ }^{\prime} \operatorname{Pr}\right.$, Mes, $\mathrm{R}=\mathrm{Ph},{ }^{i} \mathrm{Pr}$ ) ligand frameworks, which support short Co-U dative interactions. ${ }^{47}$ In these compounds, the hard anionic amide ligands are coordinated to uranium, while the softer phosphines support the cobalt ion. However, in uranium starting materials with these ligands, both phosphine and amide donors are coordinated to the uranium center. The Arnold group has used the tripodal ligand, $\left.\mathrm{N}\left[0-\left(\mathrm{NCH}_{2} \mathrm{P}^{\prime} \mathrm{Pr}_{2}\right) \mathrm{C}_{6} \mathrm{H}_{4}\right)_{3}\right]$, also for the purpose of supporting short U-Co interactions. ${ }^{48}$

Herein, we report the synthesis of uranium halide complexes coordinated by a $\mathrm{PN}^{-}$ligand in the +3 and +4 oxidation states. We pursued oxidation and salt metathesis reactions with these new uranium starting materials. In all cases, uranium(IV) products were obtained, including a rare example of a uranium parent imido complex ( $U=N H$ ), which we propose was formed from a transient uranium(IV) nitride intermediate.

### 4.3 Results and Discussion.

### 4.3.1 Synthesis.

First, we isolated the potassium salt of the ligand for salt metathesis reactions with uranium starting materials. This was accomplished by deprotonating HPN with 1.5 equivalents of potassium benzyl in a mixture of diethyl ether and hexanes. After workup, the clean product, KPN, was afforded in $95 \%$ yield. We then reacted $\mathrm{UI}_{3}(\mathrm{THF})_{4}$ with two equivalents of KPN in THF solution to yield 4.1 (Scheme 4.3.1). The salt metathesis reaction was completed in 2 hours, and
the product was isolated in a crystalline yield of $48 \%$. The ${ }^{1} \mathrm{H}$ NMR of 4.1 showed that the compound was $\mathrm{C}_{2}$ symmetric in solution, and was significantly paramagnetically shifted, with peaks ranging from 54.13 to -33.29 ppm . The peaks associated with the isopropyl groups were not observed in the ${ }^{1} \mathrm{H}$ NMR at room temperature, due to fast rotation along the $\mathrm{P}-\mathrm{C}$ bond. At 200 K all peaks associated with the $\mathrm{PN}^{-}$ligand could be identified and assigned.


Scheme 4.3.1 Synthesis of compounds 4.1, 4.2-IF, 4.2-CI, 4.2-I, and 4.2-N ${ }_{3}$.
An X-ray crystal structure of 4.1 allowed comparison with $(\mathrm{PNP})_{2} \mathrm{U}^{\text {III }}$ I reported by Kiplinger and coworkers (Figure 4.3.1). ${ }^{44}$ The structure of compound 4.1 revealed a $C_{2}$ symmetric complex with amide ligands positioned trans to one another. Upon comparison with the unsymmetrical PNP complex, $(P N P)_{2} U^{I I I}$, all uranium-ligand bond lengths for 4.1 were found to be shorter than those in $(P N P)_{2} U^{I I I I}$. For example, the $U-N$ bond lengths in 4.1 were $2.337(4) \AA$, while in $(P N P)_{2} U^{I I I I}$ the average U-N bond length was 2.408(5) Å. Compared to the starting material, the U-I bond length was significantly shorter for 4.1 at $3.0633(4) \AA$, compared to $3.130(2) \AA$ for $U^{\prime \prime \prime} I_{3}(\mathrm{THF})_{4} .{ }^{49}$


Figure 4.3.1 Thermal ellipsoid plot of 4.1 at $50 \%$ probability. Bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right)$ : $\mathrm{U}(1)-\mathrm{N}(1) 2.337(4), \mathrm{U}(1)-\mathrm{P}(1) 3.0542(12), \mathrm{U}(1)-\mathrm{I}(1) 3.0633(4), \mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(1) 126.2(2), \mathrm{P}(1)-$ $\mathrm{U}(1)-\mathrm{P}(1) 169.21(5), \mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(1)$ 126.2(2), $\mathrm{N}(1)-\mathrm{U}(1)-\mathrm{P}(1)$ 109.69(11).

We were interested in synthesizing a uranium oxo complex in the PN ligand framework. We first reacted 4.1 with sodium nitrite, with the expectation that we could eliminate sodium iodide and NO gas to yield $(\mathrm{PN})_{2} \mathrm{U}^{\text {IV }}(=\mathrm{O})$, as had been shown previously in other ligand frameworks. ${ }^{50,51}$ However, reactions with sodium nitrite resulted in a mixture of diamagnetic products. Reasoning that a terminal uranium(IV) oxo may be too reactive to isolate, ${ }^{52}$ we then tried reacting 4.1 with $N$-methylmorpholine $N$-oxide (NMNO) with the goal of synthesizing $(\mathrm{PN})_{2} \mathrm{U}^{\mathrm{V}}(=\mathrm{O}) \mathrm{I}$, the uranium $(\mathrm{V})$ oxo product. However, upon reacting 4.1 with NMNO in a solution of diethyl ether, a disproportionation reaction occurred which resulted in $(\mathrm{PN})_{2} \mathrm{U}^{\mathrm{IV}} \mathrm{I}_{2}(4.2-\mathrm{I})$ as the only paramagnetic product (Scheme 4.3.1). We attempted to react 4.2-I with sodium nitrite, however, this reaction resulted in decomposition of 4.2-I to unidentified diamagnetic compounds. The ${ }^{1} \mathrm{H}$ NMR of 4.2-I showed broad peaks, with the aryl protons ranging from 50.68 to 29.45 ppm . One methyl peak was shifted downfield to 21.45 ppm , but other methyl and isopropyl groups were shifted upfield, ranging from -4.59 to -12.75 ppm .

Since our attempt to use a two-electron oxidant resulted in the formation of a uranium(IV) product, we attempted to use single-electron oxidants such as trityl hexafluorophosphate and trityl
chloride (Scheme 4.3.1). Upon reacting 4.1 with trityl hexafluorophosphate in a solution of diethyl ether there was an immediate color change from dark blue to pale orange, giving a mixture of $(P N)_{2} \mathrm{U}^{\mathrm{IV}} \mathrm{IF}(4.2-\mathrm{IF})$ and unidentified paramagnetic products. The ${ }^{1} \mathrm{H}$ NMR of 4.2 -IF was similar to 4.2-I, with aryl peaks shifted downfield between 29.86 and 12.27 ppm . One methyl group was also shifted downfield to 9.66 ppm , but the remaining methyl and isopropyl peaks were shifted upfield between -5.23 and -19.96 ppm .

In contrast, when trityl chloride was added to 4.1 in a solution of diethyl ether, the mixed halide complex, $(\mathrm{PN})_{2} \mathrm{U}^{\mathrm{IV} I C I}$, was not observed (Scheme 4.3.1). Instead, the only substantial paramagnetic product observed was $(\mathrm{PN})_{2} \mathrm{U}^{\mathrm{IV}} \mathrm{Cl}_{2}(4.2-\mathrm{Cl})$. This compound was also able to be synthesized by a salt metathesis reaction with $\mathrm{UCl}_{4}$ and two equivalents of KPN in a THF solution to yield 4.2-CI in 62\% yield. Similar to the other uranium(IV) halide complexes, 4.2-I and 4.2-IF, the aryl protons were shifted downfield between 36.02 and 10.76 ppm , and one methyl group was shifted to 15.50 ppm in the ${ }^{1} \mathrm{H}$ NMR. The isopropyl and the remaining three methyl groups were shifted upfield between -0.84 and -12.55 ppm .

The propensity of reactions with 4.1 to disproportionate to uranium(IV) products was also observed when we tried to access uranium(III) products through salt metathesis reactions of 4.1. When 4.1 was reacted with one equivalent of sodium azide for 1.5 h , the only paramagnetically shifted product observed corresponded to $(\mathrm{PN})_{2} \mathrm{U}^{\mathrm{IV}}\left(\mathrm{N}_{3}\right)_{2}\left(4.2-\mathrm{N}_{3}\right)$ in a mixture with free HPN (Scheme 4.3.1). This reaction was presumably accompanied by the deposition of uranium metal. This type of reaction has been observed previously for uranium(III) compounds. For example, reaction of $\mathrm{U}^{1 I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with MeLi results in $\mathrm{MeU}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} .{ }^{53}$ The more rational reaction of 4.2-CI with 2 equivalents of sodium azide also resulted in clean conversion to $\mathbf{4 . 2 - \mathbf { N } _ { 3 }}$ in $94 \%$ yield. The ${ }^{1} \mathrm{H}$ NMR of $4.2-\mathrm{N}_{3}$ had well defined peaks in comparison with 4.2-I. The $C_{2}$ symmetric NMR featured aryl peaks shifted downfield between 16.04 and 11.03 ppm , while the methyl and isopropyl peaks were shifted upfield between 4.74 and -28.70 ppm .

### 4.3.2 Structural Characterization of Uranium(IV) Halides and Pseudohalides.

X-Ray crystallography allowed structural comparison within this series of compounds (Table 4.3.1, Figures 4.3.2-4.3.5). Compounds $4.2-\mathrm{I}$ and $4.2-\mathrm{IF}$ were crystallized from concentrated solutions of THF layered with pentane at $-21^{\circ} \mathrm{C}$. Compounds $4.2-\mathrm{Cl}$ and $4.2-\mathrm{N}_{3}$ were crystallized from concentrated solutions of toluene, also at $-21^{\circ} \mathrm{C}$. Although 4.1 crystallized in a geometry with trans amides, the uranium(IV) halide and pseudohalide complexes crystallized with cis amides. For comparison, the $\mathrm{N}_{\text {amide }}-\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond angle for 4.1 was $126.2(2)^{\circ}$, while for the uranium(IV) complexes it ranged from $134.6(3)^{\circ}$ for $4.2-\mathrm{I}$ to $141.51(11)^{\circ}$ for $4.2-\mathrm{N}_{3}$. Additionally, the $\mathrm{N}_{\text {amide }}-\mathrm{U}-\mathrm{P}$ bond angle for 4.1 was $109.69(11)^{\circ}$, and for the uranium(IV) complexes it ranged from $151.02(8)^{\circ}$ for $4.2-\mathrm{N}_{3}$ to $160.53(17)^{\circ}$ for 4.2 I . It is notable that this orientation of ligands likely has a shallow potential energy landscape, and the orientation of the amide ligands in 4.1 in the crystal structure we obtained may not be identical to the compound in solution. However, 4.1 showed different behavior in the solution ${ }^{1} \mathrm{H}$ NMR spectrum compared with the 4.2-X complexes, which may indicate that the phosphine arms of the PN ligand for this compound were in a different environment in solution as well. At room temperature ( 300 K ), 4.1 was characterized by $C_{2 v}$ symmetry (free rotation of the mesityl moieties) and the absence of signals for the isopropyl groups. At $200 \mathrm{~K}, C_{2}$ symmetry was observed. Notably, isopropyl groups were desymmetrized, resulting in four sets of $\mathrm{CH}_{3}$ resonances and two sets of CH resonances. Moreover, limitation of the mesityl free rotation and decoalescence of the resulting signals was observed between 260-270 K.

Table 4.3.1 Experimental bond lengths ( $\AA$ ) and angles (deg) for 4.1 and uranium(IV) trans halide and pseudohalide complexes.

| Compound | Avg. U- $\mathrm{N}_{\text {amide }}$ | Avg. U-P | $\mathrm{N}_{\text {amide }}-\mathrm{U}-\mathrm{N}_{\text {amide }}$ | $\mathrm{N}_{\text {amide }}-\mathrm{U}-\mathrm{P}$ | $\mathrm{X}-\mathrm{U}-\mathrm{X}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| 4.1 | $2.377(4)$ | $3.0542(12)$ | $126.2(2)$ | $109.69(11)$ | -- |
| 4.2-CI | $2.2764(17)$ | $3.1496(6)$ | $138.77(9)$ | $156.29(5)$ | $166.58(3)$ |
| 4.2-I | $2.254(7)$ | $3.098(2)$ | $134.6(3)$ | $160.53(17)$ | $158.121(18)$ |
| 4.2-IF | $2.277(5)$ | $3.0867(17)$ | $137.07(19)$ | $158.19(14)$ | $164.89(14)$ |
| 4.2- $\mathbf{N}_{3}$ | $2.283(3)$ | $3.0721(10)$ | $141.51(11)$ | $151.02(8)$ | $170.6(8)$ |



Figure 4.3.2 Thermal ellipsoid plot of 4.2-I at $50 \%$ probability. Bond lengths ( A ) and angles ( ${ }^{\circ}$ ): $\mathrm{U}(1)-\mathrm{l}(1) 3.0181(6), \mathrm{U}(1)-\mathrm{l}(2) 3.0030(6), \mathrm{U}(1)-\mathrm{N}(1) 2.244(7), \mathrm{U}(1)-\mathrm{N}(2) 2.263(7) \quad \mathrm{U}(1)-\mathrm{P}(1)$ $3.097(2), \mathrm{U}(1)-\mathrm{P}(2) 3.098(2), \mathrm{I}(1)-\mathrm{U}(1)-\mathrm{I}(2) 158.121(18), \mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(2) 134.6(3), \mathrm{N}(1)-\mathrm{U}(1)-$ $\mathrm{P}(2)$ 160.53(17).


Figure 4.3.3 Thermal ellipsoid plot of 4.2-IF at $50 \%$ probability. Hydrogen atoms and iodide disorder are omitted for clarity. Bond lengths ( $\AA$ ) and angles $\left({ }^{\circ}\right): \mathrm{U}(1)-\mathrm{N}(1) 2.278(5), \mathrm{U}(1)-\mathrm{N}(2)$ $2.275(5), \mathrm{U}(1)-\mathrm{P}(1) 3.0998(18), \mathrm{U}(1)-\mathrm{P}(2) 3.0736(16), \mathrm{U}(1)-\mathrm{I}(1) 2.9825(6), \mathrm{U}(1)-\mathrm{F}(1) 2.073(6)$, $\mathrm{F}(1)-\mathrm{U}(1)-\mathrm{l}(1) 164.89(14), \mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(2) 137.07(19), \mathrm{N}(1)-\mathrm{U}(1)-\mathrm{P}(2) 158.19(14)$.


Figure 4.3.4 Thermal ellipsoid plot of $4.2-\mathrm{Cl}$ at $50 \%$ probability. Hydrogen atoms omitted for clarity. Bond lengths ( $\AA$ ) and angles ( ${ }^{\circ}$ ): $\mathrm{U}(1)-\mathrm{N}(1) 2.2764(17), \mathrm{U}(1)-\mathrm{P}(1) 3.1496(6), \mathrm{U}(1)-\mathrm{Cl}(1)$ 2.6203(5), $\mathrm{Cl}(1)-\mathrm{U}(1)-\mathrm{Cl}(1) 166.58(3), \mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(2) 138.77(9), \mathrm{N}(1)-\mathrm{U}(1)-\mathrm{P}(1) 156.29(5)$.


Figure 4.3.5 Thermal ellipsoid plot of $4.2-\mathrm{N}_{3}$ at $50 \%$ probability. Hydrogen atoms and azide disorder are omitted for clarity. Bond lengths ( $\AA$ ) and angles $\left({ }^{\circ}\right): \mathrm{U}(1)-\mathrm{N}(1) 2.285(3), \mathrm{U}(1)-\mathrm{N}(2)$ $2.281(3), \mathrm{U}(1)-\mathrm{P}(1) 3.0544(10), \mathrm{U}(1)-\mathrm{P}(2) 3.0897(9), \mathrm{U}(1)-\mathrm{N}(3) 2.20(4), \mathrm{U}(1)-\mathrm{N}(6) 2.273(3)$, $\mathrm{N}(3)-\mathrm{U}(1)-\mathrm{N}(6) 170.6(8) \mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(2)$ 141.51(11), $\mathrm{N}(1)-\mathrm{U}(1)-\mathrm{P}(2) 151.02$ (8).

The $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond lengths were longest for 4.1 due to the larger size of the uranium(III) ion. The average $U-N_{\text {amide }}$ bond length for 4.1 was $2.377(4)$ and ranged from 2.254(7) to 2.283(3) for compounds 4.2-I and $4.2-\mathbf{N}_{3}$, respectively. However, U-P bond lengths did not change as much between complexes with +3 and +4 oxidation states. Compounds 4.1 and $4.2-\mathrm{N}_{3}$ had similar average U-P bond lengths of $3.0542(12)$ and $3.0721(10) \AA$, respectively. While some uranium(IV) complexes, such as 4.2-CI, had a significantly longer U-P bond length of 3.1496(6) $\AA$, despite the smaller size of the uranium(IV) ion. Last, among the 4.2-X complexes there was significant variation for the $\mathrm{X}-\mathrm{U}-\mathrm{X}$ bond angles. The $\mathrm{N}_{\text {azide }}-\mathrm{U}-\mathrm{N}_{\text {azide }}$ bond angle for 4.2- $\mathrm{N}_{3}$ was near linear at $170.6(8)^{\circ}$, while the I-U-I bond angle of 4.2-I was considerably bent, with an angle of $158.121(18)^{\circ}$.

For comparison with previously reported complexes, the structure of $(\mathrm{PNP})_{2} \mathrm{U}^{\mathrm{IV}} \mathrm{Cl}_{2}$ was significantly different from 4.2-CI, with cis-chlorides and a $\mathrm{CI}-\mathrm{U}-\mathrm{Cl}$ bond angle of $101.37(4)^{\circ}$. In contrast, compound $4.2-\mathrm{Cl}$ had trans chloride ligands, with a $\mathrm{Cl}-\mathrm{U}-\mathrm{Cl}$ bond angle of $166.58(3)^{\circ}$. The amide bond lengths in $(P N P)_{2} \mathrm{U}^{\mathrm{IV}} \mathrm{Cl}_{2}$ and $4.2-\mathrm{Cl}$ were similar, with distances of 2.285(3) and 2.2764(4) $\AA$, respectively. However, the $U-P$ bonds were significantly longer in 4.2-Cl at $3.1496(6) \AA$, while the coordinated phosphines in $(P N P)_{2} \mathrm{U}^{\mathrm{IV}} \mathrm{Cl}_{2}$ had an average bond length of $3.000(1) \AA .^{44}$ Of the three uranium(IV) halide complexes in the PN ligand framework, 4.2-CI had the largest $\mathrm{N}-\mathrm{U}-\mathrm{N}$ angle and longest $\mathrm{U}-\mathrm{N}$ bond lengths, of 138.77(9) degrees and 2.337(4) $\AA$, respectively.

We obtained X-ray quality of crystals of $\mathbf{4 . 2}-\mathbf{N}_{3}$ from a concentrated solution of toluene at $-21^{\circ} \mathrm{C}$. The axial geometry was more linear in 4.2- $\mathbf{N}_{3}$ than the uranium(IV) halide complexes, with a $N(3)-U(1)-N(6)$ bond angle of $170.6(8)^{\circ}$. The average $U-N_{\text {amide }}$ bond lengths in 4.2- $\mathrm{N}_{3}$ were slightly longer than those in $4.2-\mathbf{C l}$, with bond lengths of $2.283(3)$ and $2.2763(17) \AA$, respectively. The average $\mathrm{U}-\mathrm{N}_{\text {azide }}$ bond lengths in $4.2-\mathrm{N}_{3}$ were shorter than those reported for $\left\{\left[\mathrm{Na}(\mathrm{THF})_{4}\right]\left[\mathrm{U}^{\mathrm{IV}}\left(\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(\mathrm{~N}_{3}\right)_{2}\right]\right\}_{x}$, with bond lengths of $2.24(4)$ and $2.337(6) \AA$, respectively. ${ }^{54}$

Surprisingly, the $\mathrm{U}-\mathrm{N}_{\text {azide }}$ bonds in 4.2- $\mathrm{N}_{3}$ were of similar lengths to those in the uranium $(\mathrm{V})$ azide, $U^{\vee}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(\mathrm{~N}_{3}\right)_{2}$, which has $\mathrm{U}-\mathrm{N}_{\text {azide }}$ bond lengths of $2.226(3) \AA$. . $^{54}$

### 4.3.3 Synthesis of a Parent Imido Uranium(IV) Complex.

Compound $4.2-\mathrm{N}_{3}$ was reacted with potassium graphite in a THF solution (Scheme 4.3.2). The reaction mixture changed from pale orange to dark green, and gas evolution was observed. Within several seconds the solution became dark red, and following filtration the resulting ${ }^{1} \mathrm{H}$ NMR spectrum was highly desymmetrized and ranged from 52.64 ppm to -39.04 ppm . The red uranium(IV) metallacycle parent imido complex, $\left[K(T H F)_{3}\right]\left[(P N) U^{I V}(=N H)\left[{ }^{\prime} \mathrm{Pr}_{2} \mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{3} \mathrm{Me}\right) \mathrm{N}\left(\mathrm{C}_{6} \mathrm{H}_{2} \mathrm{Me}_{2} \mathrm{CH}_{2}\right]\right]\right.$ (4.3), was crystallized from a minimal hexanes solution in $15 \%$ yield. We propose that upon addition of potassium graphite, nitrogen gas was released, and one equivalent of potassium azide was eliminated, generating the uranium $(\mathrm{IV})$ nitride complex, $\mathrm{K}\left[(\mathrm{PN})_{2} \mathrm{U}^{\mathrm{IV}}(\equiv \mathrm{N})\right]$ (4.3-I) (Scheme 4.3.2). This strongly basic nitride then deprotonated a methyl group from a PN ligand mesityl substituent, forming a $\mathrm{U}-\mathrm{C}$ bond and a $\mathrm{U}=\mathrm{NH}$ functional group. Previously, Liddle and co-workers used deprotonation of a uranium amide $\left(\mathrm{U}-\mathrm{NH}_{2}\right)$ complex to provide the single other reported example of a uranium parent imido (U=NH) complex. ${ }^{14}$ The Mazzanti group has shown that addition of a reducing compound, $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$, to the uranium azide complex, $\mathrm{Cs}_{3}\left[\mathrm{U}\left(\mathrm{N}_{3}\right)_{7}\right]$, results in the release of nitrogen gas and formation of a tetranuclear azido/nitrido uranium(IV) cluster. ${ }^{55}$


Scheme 4.3.2 Synthesis of complex 4.3 with proposed uranium(IV) nitride intermediate.
The reactivity of the proposed uranium(IV) nitride intermediate was contrasted by the reactivity of previously reported uranium(VI) nitride complexes. The first isolated uranium(VI) nitride complex, (Tren $\left.{ }^{\mathrm{TIPS}}\right) \mathrm{U}^{V 1}(\equiv \mathrm{~N})$, reported by Liddle and coworkers, inserted into a nearby $\mathrm{C}-\mathrm{H}$ bond of the Tren ${ }^{\text {TIPS }}$ ligand framework upon photolysis (Scheme 4.3.3a). ${ }^{6}$ Kiplinger and coworker's putative uranium(VI) nitride species, $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{U}^{\mathrm{VI}}(\equiv \mathrm{N})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]$, which was formed under photolytic conditions, also intramolecularly inserted into a nearby $\mathrm{C}-\mathrm{H}$ bond of a $\mathrm{C}_{5} \mathrm{Me}_{5}$ ancillary ligand (Scheme 4.3.3a). ${ }^{56}$ However, our system instead adds the $\mathrm{C}-\mathrm{H}$ bond across the $\mathrm{U} \equiv \mathrm{N}$ moiety. This step of the reaction mechanism, from 4.3-I to 4.3 , had a $\Delta \mathrm{G}$ of $-0.89 \mathrm{kcal} / \mathrm{mol}$. This small negative value was contrasted by a small positive $\Delta G$ value of $11.2 \mathrm{kcal} / \mathrm{mol}$ for the calculated reaction of the Kiplinger putative nitride complex, $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{U}^{\mathrm{VI}}(\equiv \mathrm{N})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]$, to the analogous cyclometalated parent imido complex, $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)\left(\mathrm{C}_{5} \mathrm{Me}_{4} \mathrm{CH}_{2}\right) \mathrm{U}^{\mathrm{V1}}(=\mathrm{NH})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]^{56}$
a)


b)


Scheme 4.3.3 Previously reported insertion reactions of uranium(VI) nitride complexes into nearby C-H bonds. ${ }^{6,56}$

Compound 4.3 crystallized as a dimer (Figure 4.3.6) or a monomer (Figure 4.3.7) depending on the amount of THF from the reaction mixture present in the crystallization from hexanes. The crystal structure of 4.3 revealed a six-coordinate complex. The newly formed $\mathrm{U}(1)-$ C(42) bond was $2.577(5)$ and $2.594(3) \AA$ for the dimer and monomer, respectively. These bond lengths are long compared to reported uranium(IV)-carbon bonds, but comparable to other uranium metallacycle complexes, such as $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{U}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right) \mathrm{SiMe}_{2} \mathrm{CH}_{2}\right]$, which had a U-C distance of $2.52(2) \AA .{ }^{57}$ The average $U-N_{\text {amide }}$ bond length was 2.418(3) and 2.431(2) $\AA$, for the dimer and monomer, respectively, which was also significantly longer than those found in 4.2-CI and 4.2- $\mathrm{N}_{3}$, which were $2.2763(17)$ and $2.283(3) \AA$, respectively. The $U=N$ bond, however, was short at $2.003(4)$ and $1.999(2) \AA$, for the dimer and monomer, respectively, both of which were shorter than the other known uranium parent imido compound, which had a $\mathrm{U}=\mathrm{N}$ bond length of 2.034(3) $\AA$. $^{14}$


Figure 4.3.6 Thermal ellipsoid plot of 4.3 as a dimer at $50 \%$ probability. Hydrogen atoms are omitted for clarity. Bond lengths $(\AA)$ and angles $\left({ }^{\circ}\right): ~ U(1)-N(1) 2.421(3), U(1)-N(2) 2.414(3), U(1)-$ $N(3) 2.003(3), U(1)-P(1) 3.0018(10), U(1)-P(2) 3.0462(11), U(1)-C(42) 2.577(5)$.


Figure 4.3.7 Thermal ellipsoid plot of 4.3 as a monomer at $50 \%$ probability. Hydrogen atoms except for the imido nitrogen are omitted for clarity. Bond lengths (A) and angles ( ${ }^{\circ}$ ): $\mathrm{U}(1)-\mathrm{N}(1)$ $2.452(2), \mathrm{U}(1)-\mathrm{N}(2) 2.409(2), \mathrm{U}(1)-\mathrm{N}(3) 1.999(2), \mathrm{U}(1)-\mathrm{P}(1) 3.0108(7), \mathrm{U}(1)-\mathrm{P}(2) 3.0847(7)$, $\mathrm{U}(1)-\mathrm{C}(42)$ 2.594(3).

Efforts were made to perform in situ reactions with the putative transient uranium(IV) nitride. For example, methyl triflate was added to the green solution formed upon addition of potassium graphite. We expected the nucleophilic nitride to react preferentially with the electrophile to form the uranium(IV) imido complex, $(\mathrm{PN})_{2} \mathrm{U}^{\mathrm{IV}}(=\mathrm{NMe})$ and eliminate potassium triflate. However, this resulted in decomposition of the compound to HPN and multiple unidentified paramagnetic species. Additionally, $\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{3}$ was added to $4.2-\mathrm{N}_{3}$ before addition of $\mathrm{KC}_{8}$, with the expectation that the uranium(IV) nitridoborate complex, $\mathrm{K}\left[(\mathrm{PN})_{2} \mathrm{U}^{1 \mathrm{~V}}\left(\equiv \mathrm{~N}-\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{3}\right]\right.$, could be trapped in analogy to the uranium(VI) nitridoborate complex isolated by Cummins. ${ }^{58}$ While HPN was present in large amounts in the crude NMR, there did appear to be a $C_{2}$ symmetric paramagnetic species present. However, we were unable to crystallize this compound as it decomposed over the course of two days. We also considered routes to the parent imide and nitride species that would avoid deprotonation of the PN ligand, such as deprotonation of the amide compound, $(\mathrm{PN})_{2} \mathrm{U}^{I \prime \prime}\left(\mathrm{NH}_{2}\right)$. Toward this end we attempted salt metathesis reactions with both 4.1 and $4.2-\mathrm{Cl}$ and lithium and sodium amide. However, in all cases, decomposition to HPN was observed.

### 4.3.4 Electronic Characterization of PN Complexes.

Electrochemical analysis allowed us to compare the redox properties of these new compounds with the previously reported low and mid-valent uranium PNP complexes, (PNP) $)_{2} U^{\prime \prime \prime}$ I and $(\mathrm{PNP})_{2} \mathrm{U}^{\mathrm{IV}} \mathrm{Cl}_{2}$. The measurements were performed in THF with $\left[{ }^{n} \mathrm{Pr}_{4} \mathrm{~N}\right]\left[\mathrm{BAr}{ }^{\mathrm{F}}\right]$ supporting electrolyte and referenced to $\mathrm{Fc}^{+/ 0}$. With an open circuit potential at -1.75 V , we observed a reversible anodic wave for 4.1 at $\mathrm{E}_{1 / 2}=-1.22 \mathrm{~V}$ in the cyclic voltammogram, which we assigned as the $U^{I I I I V}$ couple. This was slightly shifted compared to $(\mathrm{PNP})_{2} \mathrm{U}^{\mathrm{III} I}$, which had a $U^{I I I I V}$ couple at $-1.47 \mathrm{~V}^{44}$ This 250 mV shift can be attributed to the additional phosphine arms that are coordinated in the case of $(\mathrm{PNP})_{2} \mathrm{U}^{\text {III }}$. Compound 4.1 also featured an irreversible reduction wave
with an $\mathrm{E}_{\mathrm{pc}}$ of -1.76 V . Upon oxidation of 4.1, the preference for cisoid-( $\mathrm{N}, \mathrm{N}$ ) increased, resulting in reduction waves for both conformations. The transoid- $(\mathrm{N}, \mathrm{N})$ compound had $\mathrm{E}_{\mathrm{pc}}$ of -1.25 V , and the cisoid- $(\mathrm{N}, \mathrm{N})$ compound had an $\mathrm{E}_{\mathrm{pc}}$ of -1.76 V , which was observed only on the second sweep of the cyclic voltammogram. This was further supported by the transoid configuration of amide nitrogen atoms in both uranium(IV) complexes that we isolated (4.2-X). A similar effect was observed by Kiplinger and coworkers for $U^{I I I}(P N P)_{2}$, in which upon oxidation, the $\mathrm{PNP}^{-}$ coordination mode changed from $\kappa^{3}-(\mathrm{P}, \mathrm{N}, \mathrm{P})$ to $\kappa^{2}-(\mathrm{P}, \mathrm{N})$, resulting in a second metal-based feature at -1.9 V . Complex 4.2-CI and the analogous PNP complex, $(\mathrm{PNP})_{2} \mathrm{U}^{1 \mathrm{C}} \mathrm{Cl}_{2}$, had more similar electrochemical behavior due to the two dangling phosphine arms in $(\mathrm{PNP})_{2} \mathrm{U}^{\mathrm{IV}} \mathrm{Cl}_{2}$. The $\mathrm{U}^{\mathrm{IIIIV} / \mathrm{V}}$ couple for $4.2-\mathrm{Cl}$ was at -2.09 V , while the PNP complex was at -2.19 V . Both compounds also exhibited ligand oxidation processes between -0.1 and 0.67 V . ${ }^{44}$


Figure 4.3.8 Cyclic voltammogram of 4.2-CI (top) and 4.1 (bottom) in THF, at a scan rate of 250 $\mathrm{mV} / \mathrm{s}$ with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Pr}_{4} \mathrm{~N}\right]\left[B A r^{\mathrm{F}}\right]$ electrolyte.

Table 4.3.2 Reduction potentials of 4.1 and $4.2-\mathrm{Cl}$, compared to the previously reported PNP complexes.

|  | $E_{1 / 2}(\mathrm{~V})$ |
| :--- | :--- |
|  | $\mathrm{U}(\mathrm{IV} / \mathrm{II})$ |
| 4.1 | -1.22 |
| $(\mathrm{PNP})_{2} \mathrm{U}^{\prime \prime \prime} \mathrm{I}$ | -1.12 |
| $4.2-\mathrm{Cl}$ | -2.09 |
| $(\mathrm{PNP})_{2} \mathrm{U}^{I V} \mathrm{Cl}_{2}$ | -2.19 |

To understand the electronic structure of 4.3 and compare it to the previously reported uranium parent imido, $\left[\left(\operatorname{Tren}^{\text {TIPS }}\right) \mathrm{U}^{\mathrm{IV}}(=\mathrm{NH})\right]\left[\mathrm{K}(15-\mathrm{c}-5)_{2}\right](4.4),{ }^{14}$ we performed density functional theory (DFT) and natural bond orbital (NBO) calculations using the NBO 6.0 package. The calculated bond lengths for both compounds compared well with the experimental bond lengths (Table 4.3.3). In most cases the calculated bond lengths were slightly longer than the bond lengths from the crystal structure. The exception to this in the inner-coordination sphere of 4.3 was the U-C bond, which was calculated to be slightly shorter than was found experimentally. For compound 4.4, the $\mathrm{U}=\mathrm{NH}$ and $\mathrm{U}-\mathrm{N}_{\text {dative }}$ bonds were calculated to be shorter than found experimentally.

Table 4.3.3 Experimental and calculated bond lengths for 4.3 (top) and 4.4 (bottom) in angstroms.

| Bond | Bond Length ( $\AA$ exp |  |
| :--- | :---: | :---: |
|  | exptl | calcd |
| $\mathrm{U}=\mathrm{N}$ | $1.999(2)$ | 2.005 |
| (avg.) $\mathrm{U}-\mathrm{N}_{\text {amide }}$ | $2.431(2)$ | 2.471 |
| (avg.) $\mathrm{U}-\mathrm{P}$ | $3.0478(7)$ | 3.143 |
| $\mathrm{U}-\mathrm{C}$ | $2.594(3)$ | 2.576 |


| Bond | Bond Length ( $\AA$ ) |  |
| :--- | :---: | :---: |
|  | exptl | calcd |
| $\mathrm{U}=\mathrm{N}$ | $2.034(3)$ | 1.982 |
| (avg.) $\mathrm{U}-\mathrm{N}_{\text {amide }}$ | $2.370(3)$ | 2.423 |
| $\mathrm{U}-\mathrm{N}_{\text {dative }}$ | $2.749(3)$ | 2.741 |

NBO analysis showed that 4.3 and 4.4 had similar Mayer bond orders of 4.3 and 4.4 had similar Mayer bond orders of 1.62 and 1.92, respectively. The polarizations of the $U=N$ bond were similar, with natural charges of 1.36 and 1.88 localized on the uranium center and -1.28 and 1.26 localized on the imido nitrogen, for 4.3 and 4.4 , respectively. Analysis with NBO 6.0 revealed one $\sigma$-bonding interaction and two $\pi$-bonding interactions in the $U=N$ bond for both complexes. In the $\sigma$ interaction, which had modest contributions from uranium of 13.3 and $13.9 \%$ for $\mathbf{4 . 3}$ and $\mathbf{4 . 4}$, respectively, compound 4.3 had a larger contribution from the 6 d orbitals than the 5 f orbitals (5f/6d 7:72\%) compared to 4.4, which had approximately equal 5f/6d contributions to the bonding. The $\pi$ interactions showed increased uranium contribution of 21.7 and $21.1 \%$ for 4.3 and 4.4 , respectively, and approximately equal $5 \mathrm{f} / 6 \mathrm{~d}$ contribution to the bond. (Table 4.3.4).

Table 4.3.4 Selected NBO data for the $\mathrm{U}=\mathrm{N}$ linkage in 4.3 compared with the previously reported values for 4.4. ${ }^{14}$

| Compound | $B l^{\text {b }}$ | Spin densitiy and charge |  |  | $\begin{gathered} \text { NBO }(\sigma \\ \text { component) } \end{gathered}$ |  |  | $\begin{gathered} \text { NBO ( }(\pi \\ \text { components) } \end{gathered}$ |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $m_{U}{ }^{\text {c }}$ | $q_{u}{ }^{\text {d }}$ | $q_{N}{ }^{e}$ | \%N | \%U | $\underset{5 f: 6 d}{U}$ | \%N | \%U | $\begin{gathered} U \\ 5 f: 6 d \end{gathered}$ |
| 4.3 | 1.62 | 2.15 | 1.36 | -1.28 | 86.7 | 13.3 | 7:72 | 78.3 | 21.7 | 51:48 |
| $4.4{ }^{14}$ | 1.92 | 2.16 | 1.88 | -1.26 | 86.1 | 13.9 | 48:49 | 78.8 | 21.2 | 56:42 |

${ }^{b}$ Mayer bond indices. ${ }^{c}$ Spin density on uranium. ${ }^{d}$ Natural charge on uranium. ${ }^{e}$ Natural charge on imido nitrogen. ${ }^{f} \mathrm{NBO}$ analysis for sigma bonds, the remaining contributions were $7 \mathrm{~s} / 7 \mathrm{p}$. ${ }^{g} \mathrm{NBO}$ analysis for pi bonds, these values are averages of the two pi interactions found by NBO.

The valence Kohn-Sham orbitals of 4.3 were rendered for comparison with those found in
4.4. The HOMO of 4.3 shows a sigma interaction between the $p_{z}$ orbital on the imido nitrogen and the $5 f_{z}{ }^{3}$ orbital on the uranium atom (Figure 4.3.9). The HOMO and $\mathrm{HOMO}-1$ of 4.4 , however, are completely f-orbital based, with no bonding interactions with ligands. The sigma-bonding interaction of 4.4 is at much lower energy, and the primary interaction is found in the HOMO-19 molecular orbital. No similar interaction is observed for 4.3 in these lower energy molecular orbitals. However, the pi-bonding interactions for 4.3 and 4.4 are at similar relative energy levels and are primarily found in the $\mathrm{HOMO}-5$ and $\mathrm{HOMO}-6$ molecular orbitals.


Figure 4.3.9 Kohn-Sham depictions of HOMO (left) and $\mathrm{HOMO}-5$ (right) molecular orbitals. Hydrogen atoms were omitted for clarity.

### 4.4 Summary.

In conclusion, we have synthesized complexes 4.1 and $4.2-\mathrm{CI}$, new uranium halide starting materials in the +3 and +4 oxidation states, coordinated by a chelating PN ligand. The electronic structures of 4.1 and $4.2-\mathbf{C l}$ were compared to previously reported uranium PNP analogues. It was found that 4.1 stabilized the +3 oxidation state by 250 mV compared to the PNP $^{-}$analogue. However, 4.2-Cl was virtually identical to its PNP analogue because the PNP analogue contains two decoordinated phosphine arms, giving similar coordination environments for the two compounds. The reactivity of 4.1 was investigated, and it was found disproportionation reactions to yield uranium(IV) products, 4.2-N $\mathbf{N}_{3}$ and 4.2-I, were observed instead of the desired uranium(III) and (V) products. Both 4.1 and $4.2-\mathrm{Cl}$ reacted with sodium azide to give the uranium(IV) diazide complex, 4.2- $\mathbf{N}_{3}$, which was reacted with potassium graphite to yield a rare example of a parent imido complex, 4.3 Complex 4.3 had the shortest $U=N H$ bond length at 1.999(2) $\AA$ and the $\mathrm{U}=\mathrm{N}$ bond was examined by DFT and NBO analyses, revealing three uranium imido bonding interactions. There was slightly more uranium contribution to bonding, which had more 6d contribution, compared with previously reported 4.4.

### 4.5 Experimental.

### 4.5.1 Methods.

All reactions and manipulations were performed under an inert atmosphere $\left(\mathrm{N}_{2}\right)$ using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at $150^{\circ} \mathrm{C}$ prior to use. Unless otherwise noted, reactions were conducted in 20 mL scintillation vials in approximately $5-10 \mathrm{~mL}$ of solvent. ${ }^{1} \mathrm{H}$ NMR were obtained on a Bruker DMX300 Fourier transform NMR spectrometer at 300 MHz . Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks. Elemental analyses were performed at the University of Pennsylvania. The infrared spectra were obtained from 400-4000 $\mathrm{cm}^{-1}$ using a Perkin Elmer 1600 series infrared spectrometer.

### 4.5.2 Materials.

Tetrahydrofuran, $\mathrm{Et}_{2} \mathrm{O}, \mathrm{CH}_{2} \mathrm{Cl}_{2}$, hexanes, pentane, and toluene were purchased from Fisher Scientific. These solvents were sparged for 20 min with dry argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina, respectively (for hexanes and pentane), or two columns of neutral alumina (for THF, $\mathrm{Et}_{2} \mathrm{O}$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ). All solvents were stored over $3 \AA$ molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and stored over potassium mirror overnight prior to use. Starting materials: $\mathrm{HPN}^{39}, \mathrm{Ul}_{3}(\mathrm{THF})_{4}{ }^{59}$ and $\mathrm{UCl}_{4}{ }^{60}$ were prepared according to the reported procedures. $\mathrm{NaN}_{3}$ was dried under vacuum at room temperature overnight. Subsequently it was stirred in THF, toluene, and pentane in series for 24 hours each.

### 4.5.3 Potassium $N$-(2-(Diisopropylphosphino)-4-methylphenyl)-2,4,6-trimethylaniline (KPN).

Potassium benzyl ( $3.58 \mathrm{~g}, 27.5 \mathrm{mmol}, 1.5$ equiv) was added in a solid portion to N -(2-(diisopropylphosphino)-4-methylphenyl)-2,4,6-trimethylaniline ( $6.00 \mathrm{~g}, 18.3 \mathrm{mmol}, 1$ equiv) in a solution of diethyl ether and hexanes in a 1:1 mixture. The reaction mixture was stirred at room temperature for 1 h and filtered through a medium-porosity frit. Volatiles were removed under reduced pressure from the filtrate to give an oily residue. This residue was dissolved in hexanes,
and volatiles were subsequently removed to yield KPN as a yellow solid. Yield: $95 \%$ ( $6.26 \mathrm{~g}, 17.1$ $\mathrm{mmol}) .{ }^{1} \mathrm{H}$ NMR ( $360 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta 6.97$ (s, 2H, Ar-H), 6.90 (m, 1H, Ar-H), 6.75 (dd, $J=8.43$, $2.12 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}-H$ ), 5.93 (dd, $J=8.37,5.82 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{Ar}-H$ ), $2.33\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ar}-\mathrm{CH}_{3}\right), 2.27(\mathrm{~s}, 3 \mathrm{H}, \mathrm{Ar}-$ $\mathrm{CH}_{3}$ ), $2.14\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Ar}-\mathrm{CH}_{3}\right), 2.07\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{PCH}\left(\mathrm{CH}_{3}\right)_{2}\right), 1.10\left(\mathrm{~m}, 12 \mathrm{H}, \mathrm{PCH}\left(\mathrm{CH}_{3}\right)_{2}\right) \cdot{ }^{31} \mathrm{P}\left\{{ }^{1} \mathrm{H}\right\}(146$ MHz, $\mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta-5.68$ (s). IR (KBr) : 2953 (s), 2727 (m), 2548 (w), 2406 (w), 2256 (w), $2140(\mathrm{w})$, 2052 (w), 1893 (w), 1757 (w), 1590 (s), 1463 (s), 1344 (s), 1273 (m), 1209 (m), 1146 (m), 1030 (m), 927 (w), 865 (m), 813 (m), 733 (w), 687 (w), 653 (w), 607 (w), 541 (w), 498 (m). Anal. found (calcd) for $\mathrm{C}_{22} \mathrm{H}_{31} \mathrm{KNP:} \mathrm{C}$,69.97 (69.62); H, 8.16 (8.23); N, 3.51 (3.69).

### 4.5.4 (PN) ${ }_{2} \mathrm{U}^{\mathrm{II} I} \mathrm{I}$ (4.1).

A solution of KPN ( $8.50 \mathrm{~g}, 22.05 \mathrm{mmol}$, 2 equiv) in THF ( 30 mL ) was added dropwise to a suspension of $\mathrm{Ul}_{3}(\mathrm{THF})_{4}(10.00 \mathrm{~g}, 11.02 \mathrm{mmol}, 1$ equiv) in THF $(40 \mathrm{~mL})$. The reaction mixture was stirred for 3 h , filtered over Celite, and the volatiles were removed under reduced pressure. The residue was extracted with hexanes, filtered over Celite, and crystallized at $-21^{\circ} \mathrm{C}$ to yield $(\mathrm{PN})_{2} \mathrm{UI}$ as a black, crystalline solid. Yield: $48 \%(5.39 \mathrm{~g}, 5.30 \mathrm{mmol}) .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta$ $54.13(2 \mathrm{H}) 31.81(2 \mathrm{H}), 21.94(2 \mathrm{H}), 14.03(6 \mathrm{H}),-4.26(4 \mathrm{H}),-4.65(6 \mathrm{H}),-33.29(12 \mathrm{H})$. The peaks associated with the isopropyl groups are not observed in the NMR, potentially due to fast rotation along the P-C bond. IR (KBr) : 2956 (w), 2919 (w), 2867 (w), 1597 (m), 1558(w), 1540 (w), 1467(s), 1391 (m), 1305 (m), 1274 (s), 1249 (s), 1215 (m), 1188 (m), 1153 (w), 1134 (w), 1027 (m), 926 (m), 891 (s), 856 (s), 813 (s), 729 (w), 709 (m), 691 (m), 654 (w), 617 (w), 584 (w), 563 (m), $543(\mathrm{~m}), 490(\mathrm{~m}), 465(\mathrm{w}), 435(\mathrm{~m})$. Anal. found (calcd) for $\mathrm{C}_{44} \mathrm{H}_{62} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{U}: \mathrm{C}, 49.93$ (50.53); H, 5.35 (5.98); N, 2.81 (2.68).

### 4.5.5 ( PN$)_{2} \mathrm{U}^{1 \mathrm{~V}} \mathrm{Cl}_{2}(4.2-\mathrm{Cl})$.

From 4.1 and $\left[\mathrm{Ph}_{3} \mathrm{C}\right][\mathrm{Cl}]$. To a solution of $4.1(50 \mathrm{mg}, 0.05 \mathrm{mmol})$ in diethyl ether was added trityl chloride ( $14 \mathrm{mg}, 0.05 \mathrm{mmol}$ ). The reaction mixture immediately changed color from dark blue to pale orange. The reaction mixture was evaporated under reduced pressure, extracted with toluene, and crystallized at $-21^{\circ} \mathrm{C}$ to yield pale orange crystals of $(\mathrm{PN})_{2} \mathrm{UCl}_{2}$.

From $\mathrm{UCl}_{4}$ and $K P N$. A solution of $\mathrm{KPN}(4.00 \mathrm{~g}, 10.94 \mathrm{mmol}, 2.2$ equiv) in a solution of THF ( 20 mL ) was added dropwise to a solution of uranium tetrachloride ( $1.88 \mathrm{~g}, 4.98 \mathrm{mmol}, 1$ equiv) in THF ( 30 mL ). The reaction mixture was stirred at room temperature for 2 h , filtered through a medium-porosity frit, and the volatiles were removed under reduced pressure. Pentane was added to the residue; and the volatiles were removed under reduced pressure. A subsequent portion of pentane was added, and the solid was collected on a medium-porosity frit. This solid was recrystallized from fluorobenzene at $-21^{\circ} \mathrm{C}$ to yield $(\mathrm{PN})_{2} \mathrm{UCl}_{2}$ as an orange solid. Yield: $62 \%$ (2.96 g, 3.08 mmol). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta 36.02$ (s, 2H), 28.77 (s, 2H), 28.57 (s, 2H), $15.50(\mathrm{~s}, 6 \mathrm{H}), 10.76(\mathrm{~s}, 4 \mathrm{H}),-0.84(\mathrm{~s}, 12 \mathrm{H}),-6.18(\mathrm{~s}, 6 \mathrm{H}),-7.66(\mathrm{~s}, 12 \mathrm{H}),-9.33(\mathrm{~s}, 4 \mathrm{H}),-12.55$ (s, 12H). IR (KBr) : 2963 (s), 2919 (s), 2868 (s), 2733 (w), 1946 (w), 1884 (w), 18750 (w), 1714 (w), 1597 (m), 1490 (s), 1466 (s), 1389 (m), 1274 (m), 1240 (s), 1213 (m), 1187 (m), 1060 (m), $1025(\mathrm{~m}), 928(\mathrm{w}), 890(\mathrm{~m}), 857(\mathrm{~m}), 830(\mathrm{~m}), 810(\mathrm{~m}), 754(\mathrm{~m}), 714(\mathrm{~m}), 685(\mathrm{~m}), 651(\mathrm{w}), 609$ (w), 543 (w), 517 (w), 493 (w), 436 (w). Anal. found (calcd) for $\mathrm{C}_{44} \mathrm{H}_{62} \mathrm{Cl}_{2} \mathrm{~N}_{2} \mathrm{P}_{2} \mathrm{U}$ : C, 53.71 (53.39); H, 6.01 (6.31); N, 2.53 (2.83).

### 4.5.6 (PN) $\mathbf{2} \mathrm{U}^{\text {IV }}$ IF (4.2-IF).

To a solution of 4.1 ( $50 \mathrm{mg}, 0.05 \mathrm{mmol}$ ) in diethyl ether was added trityl hexafluorophosphate ( $19 \mathrm{mg}, 0.05 \mathrm{mmol}$ ). The reaction mixture immediately changed color from dark blue to pale orange. Volatiles were removed under reduced pressure, and the crude material was extracted with toluene, filtered over Celite, and crystallized at $-21^{\circ} \mathrm{C}$ to produce X -ray quality crystals of $(\mathrm{PN})_{2}$ UIF as pale orange crystals. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta 29.86(2 \mathrm{H}), 15.29(2 \mathrm{H})$, $13.63(2 \mathrm{H}), 12.29(4 \mathrm{H}), 9.68(6 \mathrm{H}),-5.21(12 \mathrm{H}),-6.93(12 \mathrm{H}),-19.93(6 \mathrm{H})$.

### 4.5.7 (PN $)_{2} \mathrm{U}^{\mathrm{IV}} \mathrm{I}_{2}(4.2-\mathrm{I})$.

A solution of $4.1(100 \mathrm{mg}, 0.10 \mathrm{mmol})$, dissolved in diethyl ether, was cooled to $-21^{\circ} \mathrm{C}$. $N$-Methylmorpholine $N$-oxide ( $11 \mathrm{mg}, 0.10 \mathrm{mmol}$ ) was added, and the volatiles were immediately removed from the reaction mixture under reduced pressure. The residue was washed with hexanes to remove the starting material, and was then filtered over Celite. The insoluble material was extracted with THF, layered with hexanes, and crystallized at $-21^{\circ} \mathrm{C}$ to yield $(\mathrm{PN})_{2} \mathrm{Ul}_{2}$ as red
crystals. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta 50.68(2 \mathrm{H}), 41.18(2 \mathrm{H}), 37.12(2 \mathrm{H}), 29.45(4 \mathrm{H}), 21.45(6 \mathrm{H})$, $-4.59(12 \mathrm{H}),-8.35(12 \mathrm{H}),-12.75(6 \mathrm{H})$.

### 4.5.8 $(\mathrm{PN})_{2} \mathrm{U}^{\mathrm{IV}}\left(\mathrm{N}_{3}\right)_{2}\left(4.2-\mathrm{N}_{3}\right)$.

From (PN) $\mathbf{2}_{2}$ UI (4.1). To a suspension of sodium azide ( $3 \mathrm{mg}, 0.05 \mathrm{mmol}, 1$ equiv) dissolved in THF was added 4.1 ( $50 \mathrm{mg}, 0.05 \mathrm{mmol}, 1$ equiv) dissolved in THF. The reaction stirred for 1.5 h and then was filtered over Celite and volatiles were removed under reduced pressure. The residue was extracted with hexanes, filtered over Celite, and crystallized at $-21^{\circ} \mathrm{C}$ to yield $(\mathrm{PN})_{2} \mathrm{U}\left(\mathrm{N}_{3}\right)_{2}$ as pale orange crystals.

From $\left(\mathrm{PN}_{2}\right)_{2} \mathrm{UCl}_{2}(4.2-\mathrm{Cl})$. To a solution of $4.2-\mathrm{Cl}(1.50 \mathrm{~g}, 1.56 \mathrm{mmol}, 1$ equiv) in THF (5 mL ) was added sodium azide ( $0.22 \mathrm{~g}, 3.44 \mathrm{mmol}, 2.2$ equiv) as a solid portion. The reaction mixture was stirred for 1 h at room temperature, and the volatiles were removed under reduced pressure. The residue was extracted with pentane, filtered, reduced to a small volume, and crystallized at $-21^{\circ} \mathrm{C}$ to yield $(\mathrm{PN})_{2} \mathrm{U}\left(\mathrm{N}_{3}\right)_{2}$ as a red/orange solid. Yield: $94 \%(1.43 \mathrm{~g}, 1.47 \mathrm{mmol})$. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ): $\delta 16.03$ (s, 2H), 15.87 (s, 2H), 11.06 (m, 4H), 4.73 (s, 12H), 0.25 (s, $12 \mathrm{H}),-4.77(\mathrm{~s}, 4 \mathrm{H}),-7.53(\mathrm{~s}, 6 \mathrm{H}),-9.16(\mathrm{~s}, 4 \mathrm{H}),-12.14(\mathrm{~s}, 12 \mathrm{H}),-16.91(\mathrm{~s}, 2 \mathrm{H}),-28.69(\mathrm{~s}, 2 \mathrm{H})$. IR (KBr) : 2966 (m), 2920 (m), 2869 (m), 2724 (w), 2665 (w), 2538 (w), 2363 (w), 2077 (s), 1761 (w), 1597 (m), 1542 (w), 1464 (s), 1360 (s), 1251 (s), 1154 (m), 1100 (w), 1061 (w), 1027 (m), 929 (w), 888 (m), 863 (m), 818 (m), 752 (m), 711 (w), 684 (w), 649 (w), $602(\mathrm{w}), 543$ (w), 493 (w), 433 (w). Anal. found (calcd) for $\mathrm{C}_{44} \mathrm{H}_{62} \mathrm{~N}_{8} \mathrm{P}_{2} \mathrm{U} \cdot \mathrm{C}_{12} \mathrm{H}_{10} \mathrm{~F}_{2}$ : C, 56.06 (56.28); H, 5.69 (6.07); N, 9.39 (9.38).

### 4.5.9 $\left[\mathrm{K}(\mathrm{THF})_{3}\right]\left[(\mathrm{PN}) \mathrm{U}^{\mathrm{IV}}(=\mathrm{NH}){ }^{\prime} \mathrm{Pr}_{2} \mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{3} \mathrm{Me}\right) \mathrm{N}\left(\mathrm{C}_{6} \mathrm{H}_{2} \mathrm{Me}_{2} \mathrm{CH}_{2}\right]\right]$ (4.3).

To a solution of $4.2-\mathrm{N}_{3}(100 \mathrm{mg}, 0.10 \mathrm{mmol}, 1$ equiv) in THF was added potassium graphite ( $55 \mathrm{mg}, 0.41 \mathrm{mmol}, 4$ equiv) as a solid portion. The reaction mixture, which immediately turned green and subsequently to red over the course of seconds, was then filtered, and the volatiles were removed under reduced pressure. The residue was dissolved in minimal THF and layered with pentane. The layered solution was crystallized at $-21{ }^{\circ} \mathrm{C}$ to yield $\left[K(T H F)_{3}\right]\left[(P N) U^{I V}(=N H)\left[{ }^{\prime} \mathrm{Pr}_{2} \mathrm{P}\left(\mathrm{C}_{6} \mathrm{H}_{3} \mathrm{Me}\right) \mathrm{N}\left(\mathrm{C}_{6} \mathrm{H}_{2} \mathrm{Me}_{2} \mathrm{CH}_{2}\right]\right]\right.$ as red crystals. Yield: $15 \%,(18 \mathrm{mg}, 0.02$
$\mathrm{mmol}) .{ }^{1} \mathrm{H}\left(300 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}\right): \delta 52.64(3 \mathrm{H}), 41.26(1 \mathrm{H}), 40.38(3 \mathrm{H}), 22.09(1 \mathrm{H}), 18.79(1 \mathrm{H}), 18.44$ (1H), $13.79(3 \mathrm{H}), 12.69(1 \mathrm{H}), 9.11(3 \mathrm{H}), 2.20(12 \mathrm{H}, \mathrm{THF}), 1.14$ (12H, THF), $-1.75(3 \mathrm{H}),-3.83$ $(1 \mathrm{H}),-4.74(1 \mathrm{H}),-5.61(3 \mathrm{H}),-7.41(1 \mathrm{H}),-7.56(1 \mathrm{H}),-9.26(1 \mathrm{H}),-2.76(3 \mathrm{H}),-9.74(3 \mathrm{H}),-12.34$ $(1 \mathrm{H}),-14.40(3 \mathrm{H}),-16.93(3 \mathrm{H}),-19.53(1 \mathrm{H}),-29.47(3 \mathrm{H}),-32.00(3 \mathrm{H}),-32.93(1 \mathrm{H}),-39.03(1 \mathrm{H})$. Twelve protons are obscured by THF and benzene solvent peaks. IR (KBr): 3355 (w), 2950 (s), 2919 (s), 2864 (s), 1600 (m), 1496 (s), 1464 (s), 1391 (m), 1270 (s), 1213 (w), 1192 (w), 1153 (w), 1032 (w), 881 (m), 856 (m), 812 (m), 748 (w), 730 (w), 699 (w), $660(\mathrm{w}), 611$ (w), 545 (w), 497 (m). Elemental analysis was not obtained for this compound, as it was unstable to desolvation.

### 4.6 Crystallographic Analysis.

X-Ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Ka radiation ( $\lambda=0.71073 \AA$ ) at a temperature of 143(1) K. In all cases, rotation frames were integrated using SAINT, ${ }^{61}$ producing a listing of unaveraged $\mathrm{F}^{2}$ and $\sigma\left(F^{2}\right)$ values, which were then passed to the SHELXTL ${ }^{62}$ program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS ${ }^{63}$ or SADABS. ${ }^{64}$ The structures were solved by direct methods (SHELXS-97). ${ }^{65}$ Refinement was by full-matrix least squares based on $\mathrm{F}^{2}$ using SHELXL-97. ${ }^{65}$ All reflections were used during refinements. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model.

### 4.7 Spectroscopic Analysis.

${ }^{1} \mathrm{H}$ NMR spectra were obtained on a Bruker DMX-300 Fourier transform NMR spectrometer at 300 MHz . Chemical shifts were recorded in units of parts per million referenced to residual solvent peaks ( ${ }^{1} \mathrm{H}$ ). The UV-Visible absorption spectra were obtained from 2000-290 nm using a Perkin Elmer 950 UV-Vis/NIR Spectrophotometer, and all samples were prepared under an $\mathrm{N}_{2}$ environment. 1 mm pathlength screw cap quartz cells were used with a blank measured before each run.


Figure 4.7.1. ${ }^{1} \mathrm{H}$ NMR of 4.1 in benzene $-d_{6}$.




Figure 4.7.2. ${ }^{1} \mathrm{H}$ NMR of $4.2-\mathrm{Cl}$ in benzene- $d_{6}$.


Figure 4.7.2. Crude ${ }^{1} \mathrm{H}$ NMR of 4.2-IF in benzene- $d_{6}$.


Figure 4.7.4. ${ }^{1} \mathrm{H}$ NMR of $4.2-\mathrm{I}$ in benzene- $d_{6}$.


Figure 4.7.5. ${ }^{1} \mathrm{H}$ NMR of $4.2-\mathrm{N}_{3}$ in benzene- $d_{6}$.


Figure 4.7.6. ${ }^{1} \mathrm{H}$ NMR of 4.3 in benzene- $d_{6}$.


Figure 4.7.7. ${ }^{1} \mathrm{H}$ NMR of reaction of $4.2-\mathrm{N}_{3}$ with potassium graphite in the presence of $\mathrm{B}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{3}$ in benzene- $d_{6}$.


Figure 4.7.8. ${ }^{1} \mathrm{H}$ NMR of 4.1 in toluene- $d_{8}$ at 200 K .

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Figure 4.7.9. $\mathrm{VT}^{-1} \mathrm{H}$ NMR of 4.1 in toluene- $d_{8}$.


Figure 4.7.10. Decoalescence of $\mathrm{H}_{\mathrm{a}}$ (left) and $\mathrm{H}_{\mathrm{h}}$ (right) in VT- ${ }^{-1} \mathrm{H}$ NMR of 4.1 in Tol- $d_{8}$.


Figure 4.7.11. Electronic absorption spectrum of $4.2-\mathrm{Cl}$ (red trace) and $4.2-\mathrm{N}_{3}$ (blue trace) in toluene in the UV region.


Figure 4.7.12. Electronic absorption spectrum of $4.2-\mathrm{Cl}$ (red trace) and $4.2-\mathrm{N}_{3}$ (blue trace) in toluene in the near-IR region.

### 4.8 Electrochemical Analysis

Voltammetry experiments (CV, DPV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v9.24. All experiments were performed in an $\mathrm{N}_{2}$ atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The quasi-reference electrode was prepared by dipping a length of silver wire in concentrated hydrochloric acid. The working electrode surfaces were polished prior to each set of experiments. Potentials were reported versus ferrocene, which was added as an internal standard for calibration at the end of each run. Solutions employed during these studies were $\sim 3 \mathrm{mM}$ in analyte and 100 mM in $\left[{ }^{n} B^{n} u_{4} N\right]\left[B A r^{F}\right]$ in 2 mL of THF. All data were collected in a positive-feedback IR compensation mode.
a)

b)

c)


Figure 4.8.1. a) Full scan cyclic voltammetry of HPN in THF with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{BAr}{ }^{\mathrm{F}}\right]$; [analyte] = ca. 1 mM ; v $=0.25 \mathrm{~V} / \mathrm{sec}$. b) Left: Isolated $\mathrm{PN}^{0 /+}$ redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated $\mathrm{PN}^{0 /+}$ couple. d) Differential pulse voltammetry.
a)

b)


c)


Figure 4.8.2. a) Full scan cyclic voltammetry of compound 4.1 in THF with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{BA} r^{\mathrm{F}}\right]$; [analyte] = ca. $1 \mathrm{mM} ; \mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$. b) Left: Isolated uranium(III/V) redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(III/IV) couple. c) Differential pulse voltammetry.
a)

b)


c)


Figure 4.8.3. a) Full scan cyclic voltammetry of compound $4.2-\mathrm{Cl}$ in THF with 0.1 M [ $\left.{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[B A r^{{ }^{F}}\right] ;$ [analyte] = ca. $1 \mathrm{mM} ; \mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$. b) Left: Isolated uranium(III/IV) redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(III/IV) couple. c)Differential pulse voltammetry.

### 4.9 Computational Details.

All calculations were performed with Gaussian 09 Revision D.01, ${ }^{66}$ with the B3LYP hybrid DFT method. An effective core potential incorporating quasi-relativistic effects were applied to uranium, with a 60 electron core and the corresponding segmented natural orbital basis set. ${ }^{67,68}$ The $6-31 \mathrm{G}^{*}$ basis set was used for all small molecules. ${ }^{69}$ Geometry optimizations were carried out in $C_{1}$ symmetry for all uranium complexes and all small molecules, as higher symmetry solutions were either higher in energy or were not successfully converged. Default settings were used for the integration grid, SCF, and geometry convergence criteria. The frequency calculations found one small negative frequency of -4.34 for 4.3-I. Natural Bond Order (NBO) analyses were carried out using the NBO 6.0 package. ${ }^{70}$

Table 4.9.1. Geometry optimized coordinates of compound 4.3.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | 0.683888 | 0.060208 | 0.040182 |
| K | -2.76664 | -1.50089 | -0.75039 |
| P | 1.840054 | -2.72321 | 0.745297 |
| P | -0.04662 | 2.938257 | -1.12952 |
| N | 3.106159 | -0.26623 | -0.43551 |
| N | -0.08388 | 1.797991 | 1.590983 |
| H | -0.2441 | -0.64893 | -1.5901 |
| C | -0.32195 | -0.91274 | -2.57571 |
| H | 3.90495 | -1.39178 | -0.56049 |
| C | 5.212035 | -1.35702 | -1.12754 |
| H | 5.618056 | -0.4062 | -1.455 |
| C | 5.980689 | -2.50114 | -1.28178 |
| C | 6.969739 | -2.40842 | -1.72942 |
| C | 5.521811 | -3.76602 | -0.8839 |
| C | 4.258349 | -3.8089 | -0.29203 |
| H | 3.880827 | -4.7752 | 0.034732 |
| H | 3.457372 | -2.67105 | -0.10728 |
| C | 6.351249 | -5.01219 | -1.08984 |
| H | 5.891385 | -5.88016 | -0.60378 |
| C | 7.363127 | -4.90252 | -0.67775 |


| H | 3.352738 | -2.27253 | 4.199698 |
| :---: | :---: | :---: | :---: |
| H | 2.704252 | -1.07457 | 3.074927 |
| H | 4.12833 | -2.03458 | 2.622812 |
| C | 2.860082 | -4.54727 | 2.800646 |
| H | 3.843326 | -4.64674 | 2.329529 |
| H | 2.223045 | -5.36141 | 2.438081 |
| H | 2.997115 | -4.69679 | 3.87995 |
| C | 1.036597 | -4.29906 | 0.083739 |
| H | 1.728519 | -5.13092 | 0.265538 |
| C | 0.810828 | -4.19085 | -1.43226 |
| H | 0.303796 | -5.09337 | -1.80264 |
| H | 1.758857 | -4.08991 | -1.96946 |
| H | 0.200243 | -3.31212 | -1.67315 |
| C | -0.27709 | -4.60717 | 0.818756 |
| H | -1.01011 | -3.80655 | 0.671128 |
| H | -0.13426 | -4.72875 | 1.898142 |
| H | -0.71657 | -5.53776 | 0.435143 |
| C | 3.666291 | 0.94598 | -0.93742 |
| C | 4.304607 | 1.849461 | -0.05324 |
| C | 4.871567 | 3.024862 | -0.55752 |
| H | 5.372421 | 3.702698 | 0.132051 |
| C | 4.825656 | 3.347259 | -1.91722 |
| C | 4.193683 | 2.445444 | -2.77969 |
| H | 4.162905 | 2.663925 | -3.84651 |
| C | 3.618709 | 1.254161 | -2.32167 |
| C | 4.423023 | 1.523331 | 1.41731 |
| H | 5.026107 | 2.276568 | 1.935401 |
| H | 4.888689 | 0.543557 | 1.569254 |
| H | 3.444422 | 1.482975 | 1.911307 |
| C | 5.423136 | 4.635688 | -2.43557 |
| H | 6.264556 | 4.965043 | -1.81571 |
| H | 4.686203 | 5.451098 | -2.43863 |
| H | 5.785 | 4.525256 | -3.4641 |
| C | 3.024081 | 0.279135 | -3.31137 |
| H | 2.926382 | 0.740329 | -4.30032 |
| H | 2.040172 | -0.07847 | -2.98948 |
| H | 3.661017 | -0.60899 | -3.41418 |
| C | -1.03841 | 2.779855 | 1.457375 |
| C | -1.92145 | 3.169012 | 2.50334 |
| H | -1.83754 | 2.674092 | 3.466211 |
| C | -2.88359 | 4.155315 | 2.318445 |
| H | -3.52662 | 4.422462 | 3.157 |
| C | -3.04637 | 4.817647 | 1.091475 |
| C | -2.18968 | 4.432428 | 0.051988 |
| H | -2.30071 | 4.924021 | -0.91278 |
| C | -1.20631 | 3.446841 | 0.200523 |
| C | -4.0616 | 5.924516 | 0.915456 |
| H | -5.01148 | 5.691899 | 1.413682 |
| H | -4.27921 | 6.103567 | -0.144 |
| H | -3.70985 | 6.877558 | 1.336144 |
| C | 1.17166 | 4.393777 | -1.23024 |
| H | 1.971636 | 4.027044 | -1.88519 |
| C | 1.779994 | 4.651244 | 0.157595 |


| H | 2.593427 | 5.383203 | 0.078021 |
| :---: | :---: | :---: | :---: |
| H | 2.192794 | 3.739744 | 0.595782 |
| H | 1.02792 | 5.051624 | 0.845988 |
| C | 0.61343 | 5.700735 | -1.81273 |
| H | -0.20866 | 6.089869 | -1.20149 |
| H | 0.254155 | 5.59078 | -2.8414 |
| H | 1.402024 | 6.465037 | -1.82315 |
| C | -1.03598 | 3.09027 | -2.72702 |
| H | -1.40791 | 4.118856 | -2.81384 |
| C | -2.24139 | 2.137674 | -2.72038 |
| H | -2.79485 | 2.224595 | -3.66653 |
| H | -2.92904 | 2.367457 | -1.89998 |
| H | -1.89867 | 1.102925 | -2.60149 |
| C | -0.12628 | 2.795928 | -3.93191 |
| H | 0.262302 | 1.772613 | -3.88142 |
| H | 0.730554 | 3.47591 | -3.98731 |
| H | -0.69117 | 2.89832 | -4.86826 |
| C | 0.059586 | 1.111705 | 2.828644 |
| C | -0.44487 | -0.22061 | 2.886305 |
| C | -0.22755 | -0.96403 | 4.065558 |
| H | -0.62813 | -1.97566 | 4.123714 |
| C | 0.44557 | -0.43331 | 5.164768 |
| C | 0.920879 | 0.885009 | 5.084634 |
| H | 1.447031 | 1.314011 | 5.936077 |
| C | 0.745841 | 1.663761 | 3.937965 |
| C | -1.12142 | -0.75978 | 1.684936 |
| H | -1.96937 | -0.10965 | 1.41094 |
| H | -1.48168 | -1.78421 | 1.846317 |
| C | 0.671437 | -1.2542 | 6.414741 |
| H | 0.439336 | -0.68154 | 7.321132 |
| H | 1.718091 | -1.57722 | 6.500909 |
| H | 0.049396 | -2.15608 | 6.419229 |
| C | 1.276404 | 3.07614 | 3.887745 |
| H | 1.888083 | 3.296441 | 4.768935 |
| H | 0.463537 | 3.812424 | 3.847044 |
| H | 1.886044 | 3.240158 | 2.992547 |
| 0 | -4.90166 | 0.201335 | -0.13398 |
| C | -4.93804 | 0.838674 | 1.170792 |
| H | -3.95688 | 1.279227 | 1.378403 |
| H | -5.14348 | 0.067003 | 1.920438 |
| C | -6.02489 | 1.912855 | 1.088179 |
| H | -5.81991 | 2.751662 | 1.758632 |
| H | -7.00724 | 1.496331 | 1.342798 |
| C | -5.97269 | 2.303654 | -0.39665 |
| H | -6.893 | 2.773777 | -0.75678 |
| H | -5.13881 | 2.992589 | -0.57141 |
| C | -5.70331 | 0.954891 | -1.06629 |
| H | -6.63828 | 0.408188 | -1.25894 |
| H | -5.15022 | 1.039389 | -2.00768 |
| O | -3.5421 | -2.5619 | -3.18787 |
| C | -3.69696 | -1.75681 | -4.37218 |
| H | -3.44845 | -0.72304 | -4.11277 |
| H | -4.7441 | -1.79354 | -4.70824 |

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| C | -2.76023 | -2.37571 | -5.4081 |
| :---: | :---: | :---: | :---: |
| H | -1.73299 | -2.02993 | -5.24439 |
| H | -3.04551 | -2.1324 | -6.43592 |
| C | -2.88717 | -3.87234 | -5.07989 |
| H | -3.78573 | -4.289 | -5.54964 |
| H | -2.02835 | -4.46147 | -5.41391 |
| C | -3.02936 | -3.86747 | -3.55008 |
| H | -3.7222 | -4.63301 | -3.18326 |
| H | -2.0633 | -4.00534 | -3.04991 |
| O | -4.21861 | -3.54492 | 0.42148 |
| C | -4.43785 | -3.60747 | 1.845224 |
| H | -3.78461 | -2.86035 | 2.305312 |
| H | -4.14544 | -4.59857 | 2.215985 |
| C | -5.94701 | -3.33469 | 2.07598 |
| H | -6.43377 | -4.21401 | 2.510457 |
| H | -6.11493 | -2.49606 | 2.757946 |
| C | -6.48808 | -3.0517 | 0.656856 |
| H | -7.51628 | -3.3984 | 0.513763 |
| H | -6.44186 | -1.98089 | 0.432176 |
| C | -5.47648 | -3.79006 | -0.21942 |
| H | -5.68328 | -4.87227 | -0.24854 |
| H | -5.40072 | -3.41723 | -1.24477 |

Sum of electronic and thermal Free Energies $=-4334.211668$ Hartrees
Table 4.9.2. Geometry optimized coordinates of compound 4.3-I.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | 0.823754 | 0.240885 | 0.069721 |
| K | -2.87046 | -1.26837 | -1.28329 |
| P | 2.685297 | -2.18349 | 0.631776 |
| P | -0.69397 | 2.893225 | 0.096792 |
| N | 3.153709 | 0.45483 | -0.77316 |
| N | -0.58079 | 0.62487 | 2.163869 |
| N | -0.31625 | -0.56637 | -1.13781 |
| C | 4.190227 | -0.43142 | -0.95837 |
| H | 5.36019 | -0.1086 | -1.70441 |
| C | 5.449564 | 0.887728 | -2.12659 |
| H | 6.372599 | -1.03074 | -1.91964 |
| C | 7.239936 | -0.72858 | -2.50594 |
| C | 6.306726 | -2.33902 | -1.41327 |
| H | 5.175999 | -2.66064 | -0.66012 |
| C | 5.101037 | -3.66854 | -0.25833 |
| C | 4.13589 | -1.75176 | -0.40606 |
| H | 7.404581 | -3.34418 | -1.67468 |
| H | 7.198727 | -4.29595 | -1.17198 |
| H | 8.380548 | -2.98903 | -1.31669 |
| C | 7.519683 | -3.55914 | -2.74616 |

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| H | 2.471703 | -2.64415 | 2.980713 |
| :---: | :---: | :---: | :---: |
| C | 4.007012 | -1.15215 | 2.88152 |
| H | 4.314401 | -1.26099 | 3.929275 |
| H | 3.307086 | -0.31196 | 2.829044 |
| H | 4.893896 | -0.89361 | 2.292134 |
| C | 4.339015 | -3.63321 | 2.56774 |
| H | 5.267948 | -3.47654 | 2.00999 |
| H | 3.908635 | -4.59033 | 2.254058 |
| H | 4.604743 | -3.72642 | 3.629398 |
| C | 2.190442 | -3.90598 | 0.043011 |
| H | 3.073245 | -4.55575 | 0.102308 |
| C | 1.73124 | -3.84302 | -1.42275 |
| H | 1.417042 | -4.84079 | -1.7595 |
| H | 2.537802 | -3.50263 | -2.07991 |
| H | 0.88806 | -3.15086 | -1.53748 |
| C | 1.089021 | -4.49661 | 0.936481 |
| H | 0.186113 | -3.87702 | 0.901704 |
| H | 1.395035 | -4.58285 | 1.984462 |
| H | 0.819165 | -5.50152 | 0.584662 |
| C | 3.270934 | 1.764022 | -1.30877 |
| C | 3.797397 | 2.814728 | -0.51561 |
| C | 3.831269 | 4.116775 | -1.02689 |
| H | 4.246532 | 4.912046 | -0.40945 |
| C | 3.366976 | 4.421366 | -2.31071 |
| C | 2.871354 | 3.371755 | -3.09117 |
| H | 2.52983 | 3.580054 | -4.10437 |
| C | 2.814694 | 2.054882 | -2.62074 |
| C | 4.373082 | 2.520237 | 0.850078 |
| H | 4.716934 | 3.438709 | 1.337059 |
| H | 5.22284 | 1.830798 | 0.778714 |
| H | 3.643324 | 2.037661 | 1.510804 |
| C | 3.393952 | 5.83853 | -2.83736 |
| H | 4.140806 | 6.445885 | -2.31438 |
| H | 2.423161 | 6.337949 | -2.71031 |
| H | 3.628826 | 5.86431 | -3.9078 |
| C | 2.323421 | 0.945498 | -3.5232 |
| H | 2.021908 | 1.346702 | -4.4976 |
| H | 1.471118 | 0.407871 | -3.08918 |
| H | 3.110074 | 0.1999 | -3.69177 |
| C | -1.63757 | 1.47928 | 2.35221 |
| C | -2.55051 | 1.348736 | 3.445486 |
| H | -2.3837 | 0.553575 | 4.165412 |
| C | -3.6312 | 2.200011 | 3.619218 |
| H | -4.2821 | 2.049518 | 4.480559 |
| C | -3.90504 | 3.246745 | 2.722697 |
| C | -3.01657 | 3.395728 | 1.654189 |

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| H | -3.20135 | 4.208271 | 0.954871 |
| :---: | :---: | :---: | :---: |
| C | -1.89836 | 2.570077 | 1.449552 |
| C | -5.06668 | 4.191362 | 2.933771 |
| H | -6.01623 | 3.658246 | 3.079841 |
| H | -5.19536 | 4.859877 | 2.074822 |
| H | -4.92521 | 4.8266 | 3.819549 |
| C | 0.167653 | 4.5176 | 0.577654 |
| H | 0.906865 | 4.659036 | -0.22223 |
| C | 0.939525 | 4.322717 | 1.890765 |
| H | 1.519764 | 5.224086 | 2.126393 |
| H | 1.6378 | 3.482884 | 1.828609 |
| H | 0.256151 | 4.132888 | 2.725669 |
| C | -0.71299 | 5.772616 | 0.658916 |
| H | -1.4586 | 5.684261 | 1.456044 |
| H | -1.23829 | 5.984441 | -0.27846 |
| H | -0.08976 | 6.64749 | 0.887349 |
| C | -1.76182 | 3.413947 | -1.37428 |
| H | -2.41914 | 4.231302 | -1.05196 |
| C | -2.63971 | 2.244613 | -1.84165 |
| H | -3.26578 | 2.558296 | -2.68936 |
| H | -3.29996 | 1.896942 | -1.03901 |
| H | -2.00932 | 1.405602 | -2.15962 |
| C | -0.88443 | 3.924252 | -2.52892 |
| H | -0.17476 | 3.156661 | -2.85703 |
| H | -0.30502 | 4.811328 | -2.25352 |
| H | -1.51237 | 4.193517 | -3.38882 |
| C | -0.30737 | -0.33104 | 3.180755 |
| C | -0.85232 | -1.63642 | 3.128081 |
| C | -0.50685 | -2.57577 | 4.108703 |
| H | -0.9386 | -3.57414 | 4.052195 |
| C | 0.360494 | -2.26852 | 5.159002 |
| C | 0.877591 | -0.9685 | 5.212706 |
| H | 1.54387 | -0.69503 | 6.029825 |
| C | 0.561085 | -0.00241 | 4.254578 |
| C | -1.83248 | -2.01572 | 2.041579 |
| H | -2.6962 | -1.33858 | 2.040867 |
| H | -2.19908 | -3.03812 | 2.189025 |
| C | 0.731179 | -3.29781 | 6.202654 |
| H | 0.603459 | -2.90534 | 7.21911 |
| H | 1.780531 | -3.6088 | 6.110799 |
| H | 0.113602 | -4.19781 | 6.112162 |
| C | 1.12206 | 1.393413 | 4.379131 |
| H | 1.771292 | 1.4774 | 5.256897 |
| H | 0.3221 | 2.137044 | 4.472144 |
| H | 1.705107 | 1.677633 | 3.495673 |
| 0 | -5.25701 | -0.21759 | -0.36885 |

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| C | -5.49743 | -0.17776 | 1.061243 |
| :---: | :---: | :---: | :---: |
| H | -4.61653 | 0.254172 | 1.548173 |
| H | -5.63516 | -1.20441 | 1.420471 |
| C | -6.73828 | 0.699454 | 1.26745 |
| H | -6.69187 | 1.255946 | 2.207301 |
| H | -7.65066 | 0.091082 | 1.272613 |
| C | -6.70573 | 1.605166 | 0.026448 |
| H | -7.67925 | 2.03849 | -0.22268 |
| H | -5.98667 | 2.418728 | 0.173033 |
| C | -6.19694 | 0.63844 | -1.0421 |
| H | -7.01747 | 0.032311 | -1.45589 |
| H | -5.67476 | 1.130166 | -1.8691 |
| 0 | -2.73158 | -1.52408 | -4.02672 |
| C | -3.43354 | -1.12065 | -5.20407 |
| H | -4.43781 | -0.8058 | -4.90511 |
| H | -3.52376 | -1.97026 | -5.90108 |
| C | -2.57182 | -0.0051 | -5.80285 |
| H | -2.8007 | 0.945185 | -5.30886 |
| H | -2.73884 | 0.12365 | -6.87689 |
| C | -1.13108 | -0.46338 | -5.46173 |
| H | -0.62591 | -0.88197 | -6.33786 |
| H | -0.52249 | 0.367534 | -5.0958 |
| C | -1.32329 | -1.54329 | -4.36911 |
| H | -1.06701 | -2.54305 | -4.74883 |
| H | -0.76621 | -1.34479 | -3.44704 |
| 0 | -3.70341 | -3.8901 | -1.28339 |
| C | -4.43829 | -4.69772 | -0.34273 |
| H | -5.2674 | -4.08851 | 0.034625 |
| H | -3.78938 | -4.9584 | 0.502864 |
| C | -4.9218 | -5.94904 | -1.10984 |
| H | -4.31747 | -6.82156 | -0.83838 |
| H | -5.96698 | -6.1897 | -0.89497 |
| C | -4.68239 | -5.57346 | -2.58447 |
| H | -4.50843 | -6.44336 | -3.22509 |
| H | -5.53481 | -5.01339 | -2.98672 |
| C | -3.46356 | -4.66034 | -2.47288 |
| H | -2.53813 | -5.24698 | -2.36322 |
| H | -3.33907 | -3.95198 | -3.29553 |
| H | -1.36814 | -1.95485 | 1.049038 |

Sum of electronic and thermal Free Energies $=-4334.213081$ Hartrees
Table 4.9.3. Geometry optimized coordinates of compound 4.4.

| Atomic Number | X | Y | Z |
| :---: | :---: | :---: | :---: |
| C | 6.633512 | 0.018662 | 0.448778 |


| C | 4.743748 | -1.09906 | -2.53121 |
| :---: | :---: | :---: | :---: |
| C | 4.345624 | 3.171096 | -0.23311 |
| C | 4.224102 | 1.931919 | -1.14146 |
| C | 5.246319 | 0.122478 | 1.113389 |
| C | 3.237016 | 2.221115 | -2.28699 |
| C | 5.08683 | -1.00719 | 2.149376 |
| C | 3.681953 | -1.12199 | -1.41402 |
| C | 3.658346 | -2.51484 | -0.75549 |
| C | 2.183973 | 1.051239 | 1.999487 |
| C | 0.346577 | 4.375906 | -0.80855 |
| C | 1.402759 | 0.193698 | 3.008022 |
| C | 0.349625 | -3.8933 | -2.25294 |
| C | 0.556535 | -5.35712 | -0.21531 |
| C | -0.87647 | 3.677383 | -1.43478 |
| C | -1.42386 | 4.550513 | -2.58278 |
| C | -0.17973 | -2.42079 | 2.016006 |
| C | -1.61127 | 4.915953 | 2.105437 |
| C | -0.42933 | -4.6091 | -1.13325 |
| C | -0.54023 | -1.31357 | 3.017971 |
| C | -0.87508 | 1.122974 | 3.018422 |
| C | -2.69475 | 4.487339 | 1.097443 |
| C | -3.28543 | 5.73571 | 0.411771 |
| C | -2.02147 | 1.364461 | 2.024607 |
| C | -3.58109 | 1.637583 | -2.23578 |
| C | -2.77802 | -2.58008 | -1.42477 |
| C | -3.26481 | -3.48612 | -2.5737 |
| C | -2.54773 | -4.57648 | 1.090864 |
| C | -3.80544 | 2.67111 | -1.11645 |
| C | -3.36612 | -5.68437 | 0.398484 |
| C | -3.4282 | -3.86507 | 2.136267 |
| C | -3.98843 | -1.88418 | -0.77273 |
| C | -4.93736 | 2.19167 | -0.18735 |
| H | 7.436779 | 0.037873 | 1.202156 |
| H | 6.742476 | -0.92106 | -0.10733 |
| H | 6.824015 | 0.838548 | -0.25318 |
| H | 5.214028 | 1.758405 | -1.59508 |
| H | 4.753377 | -0.15296 | -3.08233 |
| H | 5.755553 | -1.25739 | -2.1359 |
| H | 4.603505 | 4.0699 | -0.81435 |
| H | 5.11539 | 3.050867 | 0.539733 |
| H | 4.557837 | -1.90088 | -3.26168 |
| H | 3.518239 | 3.136692 | -2.83158 |
| H | 5.884727 | -0.96392 | 2.907607 |
| H | 5.143961 | -1.99556 | 1.679589 |
| H | 3.191213 | 1.403173 | -3.01387 |
| H | 5.246494 | 1.067947 | 1.679906 |


| H | 3.396265 | 3.379608 | 0.275948 |
| :---: | :---: | :---: | :---: |
| H | 2.218825 | 2.358925 | -1.91016 |
| H | 4.128048 | -0.95644 | 2.674892 |
| H | 2.700111 | -0.97094 | -1.89202 |
| H | 4.635202 | -2.7702 | -0.32409 |
| H | 3.417952 | -3.29616 | -1.49027 |
| H | 3.175971 | 1.22525 | 2.448148 |
| H | 2.913628 | -2.57723 | 0.045681 |
| H | 1.139707 | 4.524732 | -1.55443 |
| H | 1.876814 | -0.79146 | 3.048167 |
| H | 1.715274 | 2.052493 | 1.963038 |
| H | 0.777326 | 3.797866 | 0.016466 |
| H | 0.083985 | 5.368278 | -0.4187 |
| H | 1.450436 | 0.630229 | 4.02359 |
| H | 1.01604 | -4.59324 | -2.78148 |
| H | 0.968242 | -3.08368 | -1.85271 |
| H | 0.921113 | -2.51508 | 1.986206 |
| H | -0.63673 | 4.752942 | -3.32453 |
| H | 0.051419 | -0.0417 | -3.14237 |
| H | 1.217966 | -4.65395 | 0.305841 |
| H | 1.201628 | -6.0379 | -0.79188 |
| H | -0.78264 | 5.434227 | 1.610391 |
| H | -0.31225 | -3.43885 | -2.99776 |
| H | -0.51829 | 2.736809 | -1.88621 |
| H | -1.18274 | 4.063123 | 2.641032 |
| H | -1.77666 | 5.525215 | -2.22063 |
| H | -2.02208 | 5.608407 | 2.85721 |
| H | -0.53154 | -3.36806 | 2.457746 |
| H | -0.18722 | -1.5641 | 4.036408 |
| H | -0.26024 | 2.027486 | 3.0478 |
| H | 0.046819 | -5.95988 | 0.546707 |
| H | -2.25694 | 4.07846 | -3.11387 |
| H | -1.07451 | -5.36534 | -1.61029 |
| H | -2.52508 | 6.268881 | -0.17273 |
| H | -1.26185 | 0.948055 | 4.040377 |
| H | -2.86137 | 1.982052 | -2.98587 |
| H | -2.15265 | -1.79208 | -1.8767 |
| H | -1.63066 | -1.23581 | 3.054395 |
| H | -2.43889 | -3.95611 | -3.11758 |
| H | -3.6761 | 6.449284 | 1.154087 |
| H | -3.18696 | 0.698281 | -1.83448 |
| H | -1.74915 | -5.08692 | 1.653317 |
| H | -3.51237 | 4.042576 | 1.687831 |
| H | -2.66192 | 0.464087 | 2.007825 |
| H | -2.65401 | 2.151459 | 2.468676 |
| H | -2.76974 | -6.26151 | -0.31745 |



Sum of electronic and thermal Free Energies $=-2921.775804$ Hartrees

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## Chapter 5:

## Reduction of Carbonyl Groups by Uranium(III) and Formation of a Stable Amide Radical Anion

### 5.1 Introduction.

The reduction of carbonyl $\pi$-bonds has been accomplished by alkali metals, ${ }^{1-3}$ transition metals, ${ }^{4,5}$ and f-block complexes. ${ }^{6-9}$ The ketyl radical intermediates proposed in such chemistry, however, are often too reactive to isolate or observe. In uranium chemistry, the reductive homocoupling of carbonyl functional groups to form pinacols ${ }^{7,10-12}$ and heterocoupling of carbonyl functional groups ${ }^{10,13}$ are similarly proposed to proceed through radical ketyl intermediates. Recently, two charge-separated uranium ketyl compounds were isolated and studied. ${ }^{14,15}$ The Meyer group isolated the first uranium ketyl radical complex, $\left[\left(\left({ }^{t-\mathrm{Bu}} \mathrm{ArO}\right)_{3} \operatorname{tacn}\right) \mathrm{U}^{\mathrm{IV}}\left(\mathrm{OC} \cdot \cdot^{4,4^{-t-B u}} \mathrm{Ph}_{2}\right)\right]$, which was accomplished using a sterically hindered ketone and supporting ligand to prevent homocoupling or abstraction of $\mathrm{H} \cdot$ from solvent. These decomposition pathways were observed when the tert-butyl groups on the ketone were omitted. ${ }^{14}$ Additionally, the Bart group isolated the first uranium(III) ketyl radical complex, $\mathrm{Tp}^{*}{ }_{2} \mathrm{U}^{\text {III }}\left(\mathrm{OC} \cdot \mathrm{Ph}_{2}\right)$. This compound was shown to act as a uranium(II) synthon by accomplishing two-electron chemistry with mesityl azide and TEMPO to afford the uranium(IV) imido and oxo complexes, respectively. ${ }^{15}$

Previously, $\left[\mathrm{Sm}^{11}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{2}(\mathrm{THF})_{2}\right]$ has been demonstrated to reduce fluorenone and couple it to its pinacolate. ${ }^{16}$ Conversely, $\mathrm{Ce}^{\mathrm{II}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ has been reacted with benzophenone and fluorenone without evidence of reduction. ${ }^{17}$ However, we reasoned that $\mathrm{U}^{111}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, which is able to reduce organic and inorganic azides, ${ }^{18-20}$ molecular oxygen, ${ }^{21}$ arenes, ${ }^{22}$ and other small molecules ${ }^{23}$ would also be reactive toward carbonyl
functional groups. Additionally, while the chemistry of ketone and aldehyde functional groups have been probed with low-valent uranium complexes, ${ }^{7,10,14,15,24}$ other carbonyl functional groups have not. The Procter and Flowers groups have recently used divalent samarium in the reduction of organic lactones, esters, and amides, and they implicated ketyl-type radicals in the mechanism (Scheme 5.5.1). ${ }^{25-28}$ However, these highly-reactive intermediates have not been isolated.


## $\mathbf{R}=\mathrm{H}, 1^{\circ}, 2^{\circ}, 3^{\circ}$ alkyl, aryl, heterocyclic R', R" = H, alkyl, aryl, benzylic, alicyclic

Scheme 5.1.1 Reduction of amides reported by Procter and coworkers, showing proposed amide radical anion intermediate. ${ }^{25}$

We hypothesized that due to the varying reduction potentials of ketone, amide, and ester functional groups, we could access different electronic structures and reactivities upon reduction of those substrates with uranium(III). Reaction of $U^{I I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with benzophenone results in the ketyl radical complex, $\mathrm{U}^{\mathrm{lV}}\left[\mathrm{OC} \cdot \mathrm{Ph}_{2}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(5.1-1)$, which dimerizes upon crystallization to form a weaklybonded dinuclear complex $\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} \mathrm{U}^{\mathrm{IV}}-\left(\mathrm{OCPhPh}-\mathrm{CPh}_{2} \mathrm{O}\right)-\mathrm{U}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (5.1-2). Additionally, we report the formation of the first stable charge-separated amide radical, $U^{\mathrm{IV}}\left[\mathrm{OC} \cdot(\mathrm{Ph})\left(\mathrm{NMe}_{2}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (5.2), from the reduction of $\mathrm{N}, \mathrm{N}$-dimethylbenzamide. Reactivity of the uranium(IV) ketyl radical shows the redox-active ligand participates in two-electron chemistry to afford a uranium(V) product. Interestingly, reaction of $U^{\prime \prime \prime}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with methyl benzoate results in methoxy group transfer to the uranium cation to yield $\mathrm{U}^{\mathrm{IV}}(\mathrm{OMe})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (5.3), presumably through decomposition of a transient $\mathrm{U}^{\mathrm{IV}}[\mathrm{OC} \cdot(\mathrm{Ph})(\mathrm{OMe})]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(5.3-\mathrm{I})$ intermediate.

### 5.2 Results and Discussion.

### 5.2.1 Reactivity of Uranium(III) with Carbonyl Substrates.

We first reacted $U^{\text {III }}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with benzophenone to test whether uranium(III) in the silylamide framework would reduce ketones in the same manner as the $\left({ }^{\mathrm{Ad}} \mathrm{ArO}\right)_{3} \operatorname{tacn}{ }^{14}$ and $T p^{* 15}$ complexes had. When benzophenone was added to a solution of $U^{\text {III }}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ in diethyl ether the solution immediately turned a bright fuchsia, presumably from the reduction of benzophenone, resulting in clean conversion to 5.1-1 (Scheme 5.2.1). The solution was reduced to a minimal volume, which produced 5.1-2 as colorless crystals suitable for X -ray diffraction upon chilling at $-21^{\circ} \mathrm{C}$ (Figure 5.2.1).


solid $\|$ solution

(5.1-2)

(5.3)
$\mathbf{N}^{*}=\mathbf{N}\left(\mathrm{SiMe}_{3}\right)_{2}$

Scheme 5.2.1 Reactivity of $\mathrm{U}^{\text {II }}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with carbonyl functional groups.

The structure of 5.1-2 revealed a uranium(IV) dinuclear complex resulting from the coupling of two uranium(IV) benzophenone radicals. This reactivity has been observed previously in cases where the steric constraints of the complex were too great to allow pinacol coupling. ${ }^{11,14,29,30}$ The bond metrics in the bridging aryl group of $5.1-2$ were essentially identical to those in the previously reported uranium complex, $\left[\left({ }^{\mathrm{Ad}} \mathrm{ArO}\right)_{3}\right.$ tacn $) \mathrm{U}^{\mathrm{IV}}(\mathrm{OCPhPh}-$ $\left.\mathrm{CPh}_{2} \mathrm{O}\right) \mathrm{U}^{\mathrm{IV}}\left(\left(\left(^{\mathrm{Ad}} \mathrm{ArO}\right)_{3} \mathrm{tacn}\right)\right]^{14}$ The one notable difference was the newly formed carbon-carbon bond, $C(37)-C(38)$, which had a bond length of $1.610(11) \AA$ in compound 5.1 -2, significantly longer than 1.560(9) in the reported compound. The Werner group has reported similar dinuclear compounds, $\left[(\text { DippForm })_{2}(\mathrm{THF}) \mathrm{Ln}{ }^{\text {II' }}\left(\mathrm{OCPhPh}-\mathrm{CPh}_{2} \mathrm{O}\right) \mathrm{Ln}^{\text {III }}(\text { (DippForm })_{2}\right]$ (DippForm $=\mathrm{N}, \mathrm{N}$-bis(2,6diisopropylphenyl)formamidinate; $\mathrm{Ln}=\mathrm{Sm}, \mathrm{Yb}$ ), which were reported as purple in solution and colorless as crystals. ${ }^{30}$ In the Sm and Yb compounds, the $\mathrm{C}-\mathrm{C}$ bond formed by ketyl radical coupling was also long for a carbon-carbon single bond at $1.601(6)$ and $1.595(4) \AA$ for the Sm and Yb complexes, respectively. The single other reported crystal structure of this type was published by Thomas and co-workers in their studies of $\mathrm{Co} / \mathrm{Zr}$ heterobimetallic catalytic hydrosilylation, $\left[\mathrm{N}_{2} \mathrm{Co}\left(\mathrm{MesNP}^{\prime} \mathrm{Pr}_{2}\right)_{3} \mathrm{Zr}\left(\mathrm{OCPhPh}-\mathrm{CPh}_{2} \mathrm{O}\right) \mathrm{Zr}\left(\mathrm{MesNP}^{\prime} \mathrm{Pr}_{2}\right)_{3} \mathrm{CoN}_{2}\right]$, which had the shortest coupled $\mathrm{C}-\mathrm{C}$ bond length at $1.496(5) ~ \AA . .^{31}$ Compared with the reported $\mathrm{U}^{\mathrm{IV}}\left(\mathrm{OCPh}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, which had a U-O bond length of 2.098(3) $\AA$, compound 5.1-2 had similar U-O bond lengths, averaging 2.102(5) $\AA . .^{32}$ Additionally, the average $U-N_{\text {amide }}$ bonds were comparable, with bond lengths of $2.281(4)$ and 2.284(6) $\AA$ for $U^{\mathrm{lV}}\left(\mathrm{OCPh}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ and 5.1-2, respectively.


Figure 5.2.1 Thermal ellipsoid plot of 5.1-2 at $50 \%$ probability. All hydrogen atoms and amide methyl groups omitted for clarity. Bond lengths ( $\AA$ ) and angles (deg): U(1)-O(1) 2.094(5), U(1)$\mathrm{N}(1) 2.287(6), \mathrm{U}(1)-\mathrm{N}(2) 2.269(6), \mathrm{U}(1)-\mathrm{N}(3)$ 2.297(6), $\mathrm{C}(37)-\mathrm{C}(38) 1.610(11), \mathrm{C}(38)-\mathrm{C}(39)$ $1.488(11), \mathrm{C}(38)-\mathrm{C}(43) 1.500(10), \mathrm{C}(39)-\mathrm{C}(40) 1.346(10), \mathrm{C}(43)-\mathrm{C}(42) 1.327(10), \mathrm{C}(42)-\mathrm{C}(41)$ 1.441 (11), C(40)-C(41) 1.446(10), C(41)-C(44) 1.365(10).

When the colorless crystals of $\mathbf{5 . 1 - 2}$ were dissolved in organic solvents, the initially observed bright fuchsia color returned, and 5.1-2 was converted back to 5.1-1 (Figure 5.2.2). The ${ }^{1} \mathrm{H}$ NMR of $\mathbf{5 . 1 - 1}$, recorded in benzene- $d_{6}$, was consistent with a $\mathrm{C}_{3}$ symmetric species and contained a broad peak centered at -5.73 ppm , corresponding to the bis(trimethylsilylamide) ligands. The protons associated with the benzophenone ligand were paramagnetically shifted with peaks at $92.78,-222.19$, and -235.22 ppm for the meta, ortho, and para protons, respectively. Although temperature dependence has been observed in related $f$-element mediated radical couplings, ${ }^{16,33,34}$ we did not observe the presence of 1.2 in solution either by variable temperature UV-Vis or ${ }^{1} \mathrm{H}$ NMR
spectroscopy. Alternation between the radical and pinacolate forms of fluorenone upon solvation and crystallization were previously documented. ${ }^{16}$


Figure 5.2.2 Pictures of 5.1 as colorless crystals in its solid state (5.1-2) (left), which gives a fuchsia solution (5.1-1) (right) upon addition of toluene.

Having established that uranium(III) in the tris bis(trimethylsilyl)amide ligand framework reduced benzophenone, we reacted $U^{I I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with an organic amide. Amide radical anions are much less common than ketone radical anions and have only been implicated as transient species in pulse radiolysis and electrolysis studies. ${ }^{35-38}$ No examples of amide radical anions have been isolated and fully characterized. Although the isolation of amide radical anions is unprecedented, the Procter group has also studied these compounds extensively as intermediates in their studies of low-valent, lanthanidemediated amide reduction. ${ }^{39-41}$ Using radical clock experiments and isotopic labeling, the evidence for the formation of these radical anions as intermediates was provided. ${ }^{39}$

Upon reacting $U^{1 I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with $\mathrm{N}, \mathrm{N}$-dimethylbenzamide, the purple solution darkened, and a stable amide ketyl radical, $\mathrm{U}^{\mathrm{IV}}\left[\mathrm{OC} \cdot(\mathrm{Ph})\left(\mathrm{NMe}_{2}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (5.2) (Scheme 5.2.1), was formed. The reduction potential of $N, N$-dimethylbenzamide reported in DMF was -2.53 V versus $\operatorname{SCE}$, which was significantly shifted compared with the reduction potential of benzophenone in DMF of -1.72 V versus SCE. Nonetheless, $\mathrm{U}^{111}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ reduced $N, N$-dimethylbenzamide, and 5.2 was isolated as dark purple crystals by crystallization from pentane at $-21^{\circ} \mathrm{C}$.

The crystal structure of 5.2 revealed $N, N$-dimethylbenzamide coordinated to a uranium cation (Figure 5.2.3). In comparison to the reported crystal structure of $N, N$ dimethylbenzamide, which has a C-O bond length of $1.242(1) \AA$, the $C(19)-O(1)$ bond length was longer at $1.262(3) \AA$, which was still in the range of a $C=O$ double bond. ${ }^{42}$ In comparison to the slight elongation of the $\mathrm{C}-\mathrm{O}$ bond, the $\mathrm{C}-\mathrm{N}$ bond was shorter than that of the free amide. The $\mathrm{C}(19)-\mathrm{N}(4)$ bond in 5.2 was $1.323(4) \AA$ in comparison to a $\mathrm{C}-\mathrm{N}$ bond length of $1.351(1) \AA$ for free $N, N$-dimethylbenzamide. Also, the $\mathrm{C}-\mathrm{C}-\mathrm{N}$ bond angle in $N, N$-dimethylbenzamide is $118.8(1)^{\circ}$, but was larger in 5.2 , with a $\mathrm{C}(22)-\mathrm{C}(19)-\mathrm{N}(4)$ bond angle of $120.1(3)^{\circ}$, presumably due to some delocalization of the radical across the three atoms. ${ }^{42}$ The average $U-N_{\text {amide }}$ bond length was $2.364(2) \AA$, which was long for a $\mathrm{U}(\mathrm{IV})-\mathrm{N}_{\text {amide }}$ bond and was much closer to that of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ at $2.320(4) \AA .^{43}$ The long $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond lengths may imply that the simple adduct, $\mathrm{U}^{\mathrm{III}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left[\mathrm{O}=\mathrm{C}\left(\mathrm{NMe}_{2}\right)(\mathrm{Ph})\right]$, contributed to the electronic structure.


Figure 5.2.3 Thermal ellipsoid plot of 5.2 at $50 \%$ probability. All hydrogen atoms and amide methyl groups omitted for clarity. Bond lengths (A) and angles (deg): U(1)-O(1)2.376(2), U(1)$\mathrm{N}(1) \quad 2.364(2), \quad \mathrm{U}(1)-\mathrm{N}(2) \quad 2.366(2), \quad \mathrm{U}(1)-\mathrm{N}(3)$ 2.363(2), $\mathrm{O}(1)-\mathrm{C}(19) \quad 1.262(3), \mathrm{N}(4)-\mathrm{C}(19)$ 1.323(4), C(22)-C(19)-N(4) 120.1(3), C(19)-O(1)-U(1) 166.5(2).

The ${ }^{1} \mathrm{H}$ NMR of 5.2 showed one peak centered at -6.53 ppm corresponding to the silyl amide ligands. The $N, N$-dimethylbenzamide was NMR silent, presumably due to delocalization of the radical across the ligand (Figure S2). When closed-shell neutral donors, such as hexamethylphophoramide (HMPA), are coordinated to $U^{I I I}\left[\mathrm{NCH}_{2} \mathrm{CH}_{2} \mathrm{~N}\left(\mathrm{SiMe}_{2}\right)\left({ }^{t} \mathrm{Bu}\right)\right]_{3}$ minimal affect is observed on the ${ }^{1} \mathrm{H}$ shift of HMPA, which is observed as a singlet at $1.75 \mathrm{ppm} .{ }^{44}$ To provide evidence that the NMR silence of $\mathrm{N}, \mathrm{N}$ dimethylbenzamide was not due to fluxional coordination in solution, we reacted an $f^{0}$ analog, $\mathrm{La}^{\text {III }}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, with $N, N$-dimethylbenzamide to form $\mathrm{La}^{\mathrm{III}}\left[\mathrm{O}=\mathrm{CPh}\left(\mathrm{NMe}_{2}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (5.2-La). In the case of 5.2-La, the amide was coordinated and observable by ${ }^{1} \mathrm{H}$ NMR. The methyl peaks in the amide coordinated to $\mathrm{La}^{\text {III }}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ were shifted to 2.91 and 2.18 ppm when compared to 2.74 and 2.32 ppm in the free amide.

Next, we attempted reduction of an ester functional group by $U^{I I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$. Methyl benzoate was chosen because it had a reduction potential of -2.29 V versus SCE, close to that of $N, N$-dimethylbenzamide at -2.53 V versus $\mathrm{SCE}^{35}$ Reaction of $\mathrm{U}^{111}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with methyl benzoate gave immediate formation of $U^{\text {IV }}(\mathrm{OMe})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(5.3)$ accompanied by formation of benzaldehyde (Scheme 5.2.1). Previously, the installation of methoxy ligands to uranium ions has been accomplished by salt metathesis with sodium methoxide, ${ }^{45-47}$ reaction of uranium(III) iodide with methanol, ${ }^{48}$ and irradiation of uranyl in the presence of methanol. ${ }^{49}$ Compound 5.3 was isolated from the crude reaction mixture as a light brown powder in $41 \%$ yield.

X-Ray quality crystals of 5.3 were obtained from a concentrated solution of 5.3 in $\left(\mathrm{SiMe}_{3}\right)_{2} \mathrm{O}$ at $-21^{\circ} \mathrm{C}$ (Figure 5.2.4). Compared with compounds 5.1-2 and 5.2, compound 5.3 had the shortest $\mathrm{U}-\mathrm{O}$ and $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond lengths at $2.039(16)$ and $2.258(15) \AA$, respectively. The $\mathrm{U}_{-}$ O-Me was linear, with an angle of $180.0(1)^{\circ}$. Additionally, the O-C bond length was indistinguishable from that in compound 5.1-2, with a distance of $1.40(3) \AA$, both of which were significantly longer than the $\mathrm{C}-\mathrm{O}$ bond length of $\mathbf{5 . 2}$.


Figure 5.2.4 Thermal ellipsoid plots of 5.3 at $50 \%$ probability. All hydrogen atoms, amide methyl groups, and disorder of omitted for clarity. Bond lengths ( $\AA$ ) and angles (deg): $\mathrm{U}(1)-\mathrm{O}(1)$ 2.039(16), $\mathrm{U}(1)-\mathrm{N}(1)$ 2.258(15), $\mathrm{O}(1)-\mathrm{C}(7)$ 1.40(3), $\mathrm{O}(1)-\mathrm{U}(1)-\mathrm{N}(1)$ 97.3(3), U(1)-O(2)-C(7) 180.0(1).

The crude ${ }^{1} \mathrm{H}$ NMR from this reaction mixture showed compound 5.3 appearing as a broad peak at -3.38 ppm corresponding to the silyl amide protons and a sharp peak at -25.93 ppm corresponding to the methoxy group protons. In the diamagnetic region of the crude ${ }^{1} \mathrm{H}$ NMR the aldehyde proton of benzaldehyde was clearly detected at 9.64 ppm , consistent with the value reported in the literature. ${ }^{50}$ Based on the two products in the crude ${ }^{1} \mathrm{H}$ NMR, as well as the reactivity observed with benzophenone and $N, N$-dimethylbenzamide, we propose that $U^{\text {III }}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ first reduces the ester by a one electron transfer to generate an ester ketyl radical (Scheme 5.2.1). Due to the oxophilic nature of uranium, this ketyl radical was not stable and was followed by methoxy group transfer to uranium to give the uranium(IV) product. While reduction of esters has not been reported with low valent uranium complexes, samarium(II) was recently shown to reduce esters using the $\mathrm{Sml}_{2}-\mathrm{H}_{2} \mathrm{O}$-amine system. ${ }^{28,39}$ The reduced carbonyl radical generated at this step was very reactive and abstracted $\mathrm{H} \cdot$ to form benzaldehyde.

### 5.2.2 EPR Spectroscopy.

To confirm the presence of ligand radical character in compounds 5.1-1 and 5.2, X-band EPR spectra were collected at 80 K (Figure 5.2 .5 ). The spectrum of $5.1 \mathbf{- 1}$ was recorded in a

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pentane glass and showed an axial signal (Figure 5.2 .5 , top). This signal was modeled with a $g_{\perp}$ value of 2.009 and $\mathrm{g}_{\|}$value of 2.034 . The spectrum of 5.2 was recorded as a powder and, similarly, showed an axial signal that could be simulated using EasySpin with a $g_{\perp}$ value of 2.010 and $\mathrm{g}_{\|}$value of 2.048 (Figure 5.2.5, bottom). ${ }^{51}$ At room temperature, 5.1-1 and 5.2 gave isotropic signals, with g values of 2.030 and 2.029 , respectively (Figure 5.2.6).

Field (mT)

| 320 | 325 | 330 | 335 | 340 | 345 |
| :--- | :--- | :--- | :--- | :--- | :--- |



Figure 5.2.5 Experimental (black) and simulated (red) EPR spectra of 5.1-1 (top) in a pentane glass and 5.2 (bottom) as a powder sample at 80 K . The spectrum of 5.1-1 was simulated with $g_{\perp}=2.009$ and $g_{\|}=2.034$ and 5.2 was simulated with $g_{\perp}=2.010$ and $g_{\|}=2.048$.


Figure 5.2.6 X-band EPR spectra of 5.1-1 (top) in a pentane solution and 5.2 (bottom) as a powder recorded at room temperature collected at 5 G with 50 mW power. Compound $5.1-1 \mathrm{~g}$ iso $=$ 2.030 and compound $5.2 \mathrm{~g}_{\text {iso }}=2.029$.

Recently, the Bart and Meyer groups have published examples of EPR spectra of uranium(IV) ligand radical complexes. ${ }^{52,53}$ The spectra of $5.1-1$ and 5.2 compare well with $\left[\left(\left(^{\text {Ad,tBu }} \mathrm{ArO}\right)_{3}\right.\right.$ tacn $) \mathrm{U}^{\mathrm{IV}}($ bipy $\left.)\right]$, which showed an axial signal at 80 K with a $\mathrm{g}_{\perp}$ value of 2.002 and $\mathrm{g}_{\|}$ value of $2.035 .{ }^{52}$ This compound also showed an isotropic signal at room temperature with ag value of 2.02. Meyer and coworkers reported that the trivalent uranium complex, $\left[\left(\left({ }^{\text {Ad,tBu }} \mathrm{ArO}\right)_{3}\right.\right.$ tacn $\left.) \mathrm{U}^{\text {III }}\right]$, exhibited a broad isotropic signal below 14 K , and the tetravalent uranium complex, $[K(2.2 .2-\mathrm{crypt})]\left[\left[\left(\left(^{\mathrm{Ad}, \mathrm{Bu}} \mathrm{ArO}\right)_{3}\right.\right.\right.$ tacn $) \mathrm{U}^{\mathrm{IV}}$ (bipy) $)$, with a diamagnetic bipy ${ }^{2-}$ ligand was EPR silent at all temperatures. These results suggested that the EPR signal observed for 5.1-1 and 5.2 at 80 K and room temperature are ligand radical based, and the anisotropy of the signal at low temperature implies minor delocalization of the electron on the uranium center. ${ }^{52,53}$

### 5.2.3 Electronic Absorption Spectroscopy.

The electronic absorption spectrum of $5.1-1$ showed a $\pi-\pi^{*}$ transition centered at 543 nm with an extinction coefficient of $3239 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$ (Figure 5.2.7, purple trace). This transition occurred at a similar wavelength to the reported ketyl radical complex, [( $\left(^{t}\right.$ $\left.\left.\left.{ }^{\mathrm{Bu}} \mathrm{ArO}\right)_{3} \operatorname{tacn}\right) \mathrm{U}^{\mathrm{lV}}\left(\mathrm{OC}^{. t \mathrm{Bu}} \mathrm{Ph}_{2}\right)\right]$, which exhibits a $\pi-\pi^{*}$ transition at 562 nm . Both of these
compounds were blue shifted with respect to sodium benzophenone, which exhibited a $\pi-$ $\pi^{*}$ transition centered at $618 \mathrm{~nm},{ }^{14}$ and as reported for transition metal ${ }^{5}$ and lanthanide ${ }^{16}$ ketyl complexes. Overall, these observations were consistent with the uranium(IV) ketyl radical, 5.1-1, being present in solution. In the near-infrared region of 5.1-1, absorptions of weak intensity were observed between 1000 and 1800 nm (Figure 5.2.8, purple trace). These f-f transitions were likely partially obscured by a trailing visible band, as has been reported for U (III) and $\mathrm{U}(\mathrm{IV})$ ligand radical complexes. ${ }^{15,53}$


Figure 5.2.7 Electronic absorption spectra of 5.1-1 (purple), 5.2 (black), 5.3 (blue), and $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(\mathrm{red})$ in toluene plotted as extinction coefficient $(\varepsilon)$ versus wavelength $(\mathrm{nm})$ in the UV/vis region.


Figure 5.2.8 Electronic absorption spectra of $5.1-1$ (purple), 5.2 (black), 5.3 (blue), and $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (red) in toluene plotted as extinction coefficient ( $\varepsilon$ ) versus wavelength ( nm ) in the near-IR region.

The electronic absorption spectrum of 5.2 was recorded using a toluene solution (Figure 5.2.7, black trace). Compound 5.2 also exhibited a $\pi-\pi^{*}$ transition centered at 538 nm with a molar extinction coefficient of $1267 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$. This transition was blue shifted in comparison with the $\pi-\pi^{*}$ transitions of $5 \cdot 1-1$. Additionally, the molar extinction coefficient was lower in comparison. Conversely to the uranium ketyl complexes, $\mathrm{Tp}^{*}{ }_{2} \mathrm{U}^{\prime \prime \prime}\left(\mathrm{OC} \cdot \mathrm{Ph}_{2}\right),{ }^{15}$ which had a molar absorptivity of $863 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$, the molar absorptivity of 5.2 was larger. In the near-infrared region, 5.2 was similar to $5.1-1$ and exhibited weak f-f transitions obscured by a broad visible band (Figure 5.2.8, black trace).

The electronic absorption spectrum of 5.3 (Figure 5.2.7, blue trace) featured a broad peak centered at 448 nm with a molar extinction coefficient of $640 \mathrm{M}^{-1} \mathrm{~cm}^{-1}$. The near-infrared region of the spectrum exhibited two weak but sharp peaks at 1165 and 1089 nm followed by two broader peaks centered at 1756 and 1517 nm corresponding to $\mathrm{f}-\mathrm{f}$ transitions. This was similar to previously reported uranium(IV) complexes (Figure 5.2.8). ${ }^{53,54}$ For comparison with this series of uranium(IV) compounds, the absorption spectrum of $\mathrm{U}^{\text {II }}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ was recorded (Figure
5.2.7, red trace). In the UV region, $U^{I I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ exhibits two broad 5f-6d transitions at 476 and 555 nm . Notably, the near infrared region of $U^{I I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ contained similar poorly defined f-f transitions to compounds $\mathbf{1 . 1}$ and 2 (Figure 5.2.8, red trace). ${ }^{55}$

### 5.2.4 Magnetism.

To investigate further the electronic structure of 5.2 , variable-temperature magnetic susceptibility data for $5.1-2,5.2$, and $\mathrm{U}^{\mathrm{II}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ were collected at a field of 2 Tesla. The data showed a value of 0.35 for XT at 2 K , which was consistent with a ligandbased radical doublet and a uranium(IV) center with a singlet ground state (Figure 5.2.9). ${ }^{14,56-59}$ The variable temperature magnetic susceptibility of $U^{I I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ was similar with a XT value of 0.34 at 2 K and saturating at a XT value of 0.90 at 300 K . The field dependent data for 5.2 at 2 K showed saturation at $1.00 \mu_{\mathrm{B}}$ at high field $(7 \mathrm{~T})$, which confirmed assignment of a U(IV) singlet, with one unpaired ligand-based radical on the benzamide ligand (Figure 5.2.10). The field dependence of $U^{I I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ showed similar field dependent data at 2 K , although it saturated at $0.84 \mu_{\mathrm{B}}$ at 7 T . However, the field dependent data for 5.2 matched well with an idealized Brillouin function with a $g$ value of 2, which indicated an organic radical was present. In contrast to 5.2 and $U^{\prime \prime \prime}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, compound 5.1-2 appeared as a uranium(IV) compound with no ligand radical character, with a $\mathrm{X}^{\top}$ value of 0.06 at 2 K , and a $\mathrm{X}^{\top}$ value of 1.09 at 300 K . Additionally, the field dependent data showed negligible magnetization at 2 K , which was consistent with the singlet ground state for uranium(IV). This data was consistent with previously reported uranium(IV) magnetism ${ }^{60,61}$ and confirmed that in the solid state the long bond between $C(37)$ and $C(38)$ was indeed spin-paired.

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Figure 5.2.9 Variable temperature magnetic susceptibility data per ion for 5.1-2 (purple diamonds), 5.2 (black circles), and $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (red triangles). The data was collected at $\mathrm{H}=2$ Tesla.


Figure 5.2.10 Field-dependent magnetic data for 5.1-2 (purple diamonds), 5.2 (black circles), and $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (red triangles). Field dependent data were collected at 2 K and the data for 5.2 was plotted with an idealized Brillouin function with a g value of 2 (blue line).

### 5.2.5 Electrochemistry.

Electrochemical analysis of 5.2 in comparison with 5.2-La and $\mathrm{N}, \mathrm{N}$-dimethylbenzamide helped to elucidate the electronic structure of 5.2 (Figure 5.2.11). The electrochemistry of $\mathrm{N}, \mathrm{N}$ dimethylbenzamide has previously been reported in DMF, which shows a reversible one-electron reduction at -2.53 V versus SCE. ${ }^{35}$ The oxidation wave, amide ${ }^{0 / 4}$, has also been recorded in acetonitrile at +2.04 V versus SCE. ${ }^{62}$ In THF the reduction of $\mathrm{N}, \mathrm{N}$-dimethylbenzamide did not occur in the electrochemical window, and there was a small irreversible oxidation feature at 0.91 $V$ versus $\mathrm{Fc}^{+/ 0}$ (Figure 5.2.11, purple trace).


Figure 5.2.11 Cyclic voltammogram of 5.2 (red trace), 5.2-La (blue trace), and $N, N-$ dimethylbenzamide (purple trace) in THF at a scan rate of $250 \mathrm{mV} / \mathrm{s}$ with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Pr}_{4} \mathrm{~N}\right]\left[\mathrm{BAr}^{\mathrm{F}}{ }_{6}\right.$ ] electrolyte. Arrows indicate the OCP and direction scanned.

The cyclic voltammogram of 5.2-La in THF showed that the $\mathrm{N}, \mathrm{N}$-dimethylbenzamide ${ }^{0 /-}$ feature had been shifted to -2.43 V versus $\mathrm{Fc}^{+/ 0}$. This Lewis-acid-promoted potential shift (LAPPS) has been observed previously by our group. In the case of $p$-benzoquinone the potential was shifted by 1.6 V versus $\mathrm{Fc}^{+/ 0}$ upon coordination to $\left[\mathrm{Li}_{3}(\mathrm{THF})_{4}\right]\left[(\mathrm{BINOLate})_{3} \mathrm{Ce}(\mathrm{THF})\right] .{ }^{63}$ This concept has also been observed in the chemistry of $\mathrm{SmI}_{2}$, which is able to reduce substrates with reduction potentials close to -3 V versus SCE despite having a reduction potential of -0.89 V versus SCE in THF. ${ }^{64,65}$ In the cyclic voltammogram of 5.2 , the reversible $N, N$ -
dimethylbenzamide ${ }^{0 /-}$ feature has been shifted a further 910 mV to -1.52 V versus ferrocene (Figure 5.2.11 red trace). In the cyclic voltammogram of 5.2 the open circuit potential occurred at a more negative potential when compared to the $\mathrm{N}, \mathrm{N}$-dimethylbenzamide ${ }^{0 /-}$ couple, while in 5.2La the open circuit potential occurred at a less negative potential compared to $\mathrm{N}, \mathrm{N}$ dimethylbenzamide ${ }^{0 /-}$ couple. The relative positions of the open circuit potential allowed the assignment of the $N, N$-dimethylbenzamide ligand in 5.2 as the radical anion. Additionally, an irreversible reduction was observed for compound 5.2 with an $\mathrm{E}_{\mathrm{pc}}$ of -2.57 V versus ferrocene. An $E_{1 / 2}$ of -2.44 V versus ferrocene was determined from differential pulse voltammetry.

### 5.2.6 Chemical Reactivity.

Following electrochemical analysis, we were interested in chemical reduction and oxidation reactions of 5.2. We first reacted 5.2 with 1.1 equiv of potassium graphite, which yielded $\left[\mathrm{U}(\mu-\mathrm{O})\left[\mathrm{O}=\mathrm{C}\left(\mathrm{NMe}_{2}\right)(\mathrm{Ph})\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{2}\right]_{2}$ (5.4) in a $24 \%$ yield (Scheme 5.2.2). Presumably, this product was formed from 4 equiv of 5.2 and accompanied by loss of 2 equiv of $\mathrm{K}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ and 2 equiv of dimethylbenzylamine, which was detected in the crude ${ }^{1} \mathrm{H}$ NMR spectrum. The structure of this compound was determined by X-ray crystallography (Figure 5.2.12). This structure featured a $[\mathrm{U}(\mu-\mathrm{O})]_{2}$ core with average $\mathrm{U}-\mathrm{O}$ bond lengths of $2.1138(3)$, that were substantially longer than terminal uranium(IV) oxo bond lengths. ${ }^{66}$ Uranium(V) compounds exhibiting dioxo-bridged diuranium diamond-core motifs are established. ${ }^{67-69}$

(2)
(6)

(5)

$$
\mathbf{N}^{*}=\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}
$$

Scheme 5.2.2 Chemical reduction and oxidation reactions of compound 5.2.


Figure 5.2.12 Thermal ellipsoid plots of 5.4 at $50 \%$ probability. Hydrogen atoms omitted for clarity. Bond lengths ( $\AA$ ) and angles (deg): $\mathrm{U}(1)-\mathrm{O}(1)$ 2.3911(11), $\mathrm{U}(1)-\mathrm{O}(2) 2.1067(10), \mathrm{U}(1)-\mathrm{O}(2){ }^{\prime}$ $2.1209(10), \mathrm{U}(1)-\mathrm{N}(1) 2.3649(12), \mathrm{U}(1)-\mathrm{N}(2)$ 2.3273(12).

To avoid the formation of this product we added 2 equiv of 15 -crown- 5 to 5.2 prior to the addition of potassium graphite. This reaction gave $\left[(15-c r o w n-5)_{2} \mathrm{~K}\right]\left[\mathrm{UO}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right](5.5)$ in $41 \%$ isolated yield, accompanied by dimethylbenzylamine, which was observed in the ${ }^{1} \mathrm{H}$ NMR of the hexanes extract of the crude reaction mixture (Scheme 5.2.2). This reactivity coupled with the electrochemistry and other physical data further supported the radical anion electronic structure of 5.2 which became fully reduced to dimethylbenzylamine when 1.1 equiv of $\mathrm{KC}_{8}$ was added.

Previously, the Hayton group synthesized $\left[\mathrm{Cp}^{*}{ }_{2} \mathrm{Co}\right]\left[\mathrm{UO}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$, and comparison of the $\left[\mathrm{U}^{\mathrm{IV}} \mathrm{O}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]^{-}$anion revealed crystallographically indistinguishable anion structures (Figure 5.2.13). ${ }^{66}$ Both structures featured U-O bond distances of $1.88 \AA$ and average $\mathrm{U}-\mathrm{N}$ bond distances of 2.37 Å. Additionally, the ${ }^{1} \mathrm{H}$ NMR of compound 5.4 revealed a broad resonance at 2.13 ppm , which was identical to the previously reported compound. Generally, terminal uranium(IV) mono-oxo compounds are rare because of their highly polarized bonding and require stabilization by interactions with bases or alkali metals. ${ }^{70,71}$ With the exception of the previously reported compound, $\left[\mathrm{Cp}^{*}{ }_{2} \mathrm{Co}\right]\left[\mathrm{UO}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$, ${ }^{66}$ and an example from the Bart group, $T p^{*} U^{\text {IV }} \mathrm{O},{ }^{15,70}$ there are no other crystallographically characterized base-free terminal mono-oxo uranium(IV) complexes reported. Synthesis of $\left[\mathrm{Cp}^{*}{ }_{2} \mathrm{Co}\right]\left[\mathrm{UO}^{I V}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ was reportedly accomplished by reduction of $\mathrm{U}^{\vee} \mathrm{O}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with decamethylcobaltocene. ${ }^{66}$ Synthesis of Tp* $U^{\text {IV }} O$ was accomplished by O -atom transfer from pyridine- $N$-oxide and TEMPO to $T p^{*}{ }_{2} U^{\prime \prime \prime}\left(2,2^{\prime}-\right.$ bpy) and $\mathrm{Tp}^{*} 2 \mathrm{U}^{\text {III }}\left(\mathrm{OC} \cdot \mathrm{Ph}_{2}\right)$, respectively. ${ }^{15,70}$ The Hayton group has synthesized a capped uranium(IV) oxo complex, $[\mathrm{K}(18-c r o w n-6)]\left[U^{1 V} \mathrm{O}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right.$, by reductive deprotection of a trityl alkoxide complex, $\mathrm{U}^{\mathrm{IV}}\left(\mathrm{OCPh}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}{ }^{32}$ This is a similar strategy to ours, though differentiated by our use of organic amides as oxo transfer reagents.


Figure 5 .2.13. Thermal ellipsoid plot of 5.5 at $50 \%$ probability. Hydrogen atoms omitted for clarity. Bond lengths ( $\AA$ ) and angles (deg): $\mathrm{U}(1)-\mathrm{O}(1) 1.878(3), \mathrm{U}(1)-\mathrm{N}(1) 2.361(4), \mathrm{U}(1)-\mathrm{N}(2) 2.369(4)$, 2.396(8).

Next, we pursued oxidation reactions of 5.2. Compound 5.2 was dissolved in diethyl ether, and trityl triflate was added, resulting in an immediate color change to pale green/brown. After workup, $\mathrm{U}^{\mathrm{IV}}\left[\mathrm{O}=\mathrm{C}\left(\mathrm{NMe}_{2}\right)(\mathrm{Ph})\right](\mathrm{OTf})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(5.6)$ was crystallized from THF layered with pentane at $-21^{\circ} \mathrm{C}$ in a yield of $29 \%$ (Scheme 5.2.2). The crystal structure of 5.6 revealed innersphere $N, N$-dimethylbenzamide and triflate ligands (Figure 5.2.14). The U-O bond of the triflate ligand was shorter than the $\mathrm{U}-\mathrm{O}$ bond of the $\mathrm{N}, \mathrm{N}$-dimethylbenzamide ligand with bond lengths of 2.3409 (15) and $2.4509(14) \AA$, respectively. The average $U-N_{\text {amide }}$ bond length was $2.2616(16) \AA$. Compared with $U^{\text {IV }}(\mathrm{OTf})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, a compound previously reported by Ephritikhine and coworkers, the U-O and U-Namide bond lengths of 5.6 were longer, likely due to the added steric demand of the $\mathrm{N}, \mathrm{N}$-dimethylbenzamide ligand present in the inner coordination sphere. ${ }^{72}$


Figure 5.2.14 Thermal ellipsoid plot of 5.6 at $50 \%$ probability. Hydrogen atoms omitted for clarity. Bond lengths ( $\AA$ ) and angles (deg): $\mathrm{U}(1)-\mathrm{O}(1) 2.3409(15), \mathrm{U}(1)-\mathrm{O}(2) 2.4509(14), \mathrm{U}(1)-\mathrm{N}(1)$ $2.2542(17), \mathrm{U}(1)-\mathrm{N}(2) 2.2580(16), \mathrm{U}(1)-\mathrm{N}(3) 2.2727(16)$.

We were also interested in whether the redox-active $\mathrm{N}, \mathrm{N}$-dimethylbenzamide ligand could facilitate two-electron chemistry with the uranium cation. We reacted 5.2 with trimethylsilyl azide in a solution of $\mathrm{C}_{6} \mathrm{D}_{6}$ to yield the known compound, $\mathrm{U}^{\mathrm{V}}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ through twoelectron chemistry (Scheme 5.2.3). The identity of this product was confirmed by ${ }^{1} \mathrm{H}$ NMR, which matched well with previously reported characterization. ${ }^{19}$

(5.2)

(2.1)

$$
\mathbf{N}^{*}=\mathbf{N}\left(\mathrm{SiMe}_{3}\right)_{2}
$$

Scheme 5.2.3 Reactivity of 5.2 with trimethylsilyl azide.

With compound 5.3 in hand, we used a previously established method established by our group to generate compounds of the general formula $\mathrm{U}^{\mathrm{VI}} \mathrm{O}(\mathrm{R})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ from uranium(IV) starting materials by the addition of $N$-methylmorpholine $N$-oxide. ${ }^{73}$ Our group has previously proposed an inverse trans influence (ITI) ligand series based on a combination of computational and experimental data. While a number of the compounds within the series have been synthesized, ${ }^{73,74}$ some have only been evaluated computationally. In an effort to complete our proposed series with experimental data, we were interested in synthesizing $\mathrm{U}^{\mathrm{VII}} \mathrm{O}(\mathrm{OMe})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (5.7). Accordingly, 5.3 was oxidized to yield 5.7 as a dark red powder and crystallized from pentane in $18 \%$ yield (Scheme 5.2.4). The ${ }^{1} \mathrm{H}$ NMR of 5.7 revealed a peak at 4.83 ppm corresponding to the methoxy group. Two peaks at 0.59 ppm and 0.33 ppm were assigned to the three bis(trimethylsilyl)amide ligands, which were split due to hindered rotation of the silyl amide. ${ }^{73,75}$


Scheme 5.2.4 Oxidation of 5.3 with $N$-methylmorpholine $N$-oxide.
The crystal structure of 5.7 was obtained and revealed a five-coordinate structure (Figure 5.2.15). The equatorial $U-N_{\text {amide }}$ bond distances were $2.235(2) \AA$, slightly longer than our group's previously reported $\mathrm{U}^{\mathrm{VI}} \mathrm{O}(\mathrm{Me})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, which had average $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond lengths of $2.221(2) \AA .{ }^{73}$ Uranyl in the tris(bistrimethylsilyl)amide framework, e.g., $\left[\mathrm{Cp}^{*}{ }_{2} \mathrm{Co}\right]\left[\mathrm{UO}_{2}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right.$ has significantly longer average $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond lengths at
2.319(6) A. ${ }^{76}$ The $\mathrm{O}-\mathrm{U}-\mathrm{O}$ bond angle in compound 6 was 180.000(3), in $\left[\mathrm{Cp}^{*}{ }_{2} \mathrm{Co}\right]\left[\mathrm{UO}_{2}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right.$ the bond angle was slightly distorted from linearity at 178.8(3).


Figure 5.2.15 Thermal ellipsoid plot of 5.7 at $50 \%$ probability. All hydrogen atoms other than the methoxy ligand omitted for clarity. Bond lengths ( A ) and angles (deg): $\mathrm{U}(1)-\mathrm{O}(1) 1.801(8), \mathrm{U}(1)-$ $\mathrm{O}(2) 1.991(8), \mathrm{U}(1)-\mathrm{N}(1)^{\prime} 2.235(2), \mathrm{O}(2)-\mathrm{C}(7) 1.437(10), \mathrm{O}(1)-\mathrm{U}(1)-\mathrm{O}(2) 180.000(3), \mathrm{U}(1)-\mathrm{O}(2)-$ $\mathrm{C}(7)$ 180.000(1), O(1)-U(1)-N(1)' 89.64(7).

Electrochemical data of 5.7 was collected to compare with the calculated $\mathrm{U}(\mathrm{V} / \mathrm{VI})$ reduction potential reported by our group (Figure 5.2.16). The $\mathrm{E}_{1 / 2}$ as determined by the DPV experiment was -0.89 V versus ferrocene. The reduction potential of this compound was previously calculated with a value of -0.82 V , which matches the experimental data well. $^{73}$


Figure 5.2.16 Cyclic voltammogram of 5.7 in fluorobenzene at a scan rate of $250 \mathrm{mV} / \mathrm{s}$ with 0.1 M [ $\left.{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ electrolyte.

### 5.2.7 Computational Studies.

To understand the electronic structures of the ketyl radical complexes better, we performed DFT calculations on 5.1-1, 5.2, and $U^{\mathrm{IV}}[\mathrm{OC} \cdot(\mathrm{Ph})(\mathrm{OMe})]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(5.3-1)$, the putative radical intermediate, resulting in the formation of 5.3. Additionally, we performed a DFT calculation on 5.6, a simple uranium(IV) complex with a neutral $\mathrm{N}, \mathrm{N}$ dimethylbenzamide ligand, for comparison with 5.2. In performing these gas phase calculations, we used a 60 -electron core incorporating quasi-relativistic effects for uranium and $6-21 \mathrm{G}^{*}$ basis sets for all other atoms.

The experimental and computed bond lengths compared well for compounds 5.2 and 5.6 (Table 5.2.1). In the series of compounds it can be seen that the average $U-N_{\text {amide }}$ bond lengths are long for compounds 5.1-1, 5.2, and 5.3-I at 2.291, 2.369, and 2.328 Å, respectively. In comparison, compound 5.3 had average computed $U-N_{\text {amdie }}$ bond lengths of $2.287 \AA$. These long $U-N_{\text {amide }}$ bond lengths can be attributed to the difference in electronic structure of uranium(IV) $\mathrm{L}^{--}$complexes, which had some delocalization of the radical onto the uranium center, as seen in the experimental EPR spectra, ${ }^{52}$ when
compared with 5.6, a uranium(IV)L ${ }^{0}$ complex. Additionally, the longest computed $\mathrm{U}-\mathrm{O}$ bond length was for 5.6 , at $2.459 \AA$ A , closely followed by 5.2 at 2.419 Å. Compounds 5.3-I and 5.1-1 had shorter U-O bond lengths of 2.318 and 2.150 Å, respectively. Surprisingly, the $\mathrm{C}-\mathrm{O}$ bond lengths did not follow the same trend. Compounds 5.2 and 5.3-I had the shortest C-O bond lengths of 1.259 and 2.265 Å, respectively. Compound 5.6 has a similar C-O bond length of 1.268 Å, although it was expected to have the shortest C-O bond length since the carbonyl functional group was not reduced for this compound. Compound 5.1-1 had the longest C-O bond length of 1.342 Å.

Table 5.2.1. Experimental and calculated bond lengths for compounds 5.1-1, 5.2, 5.3-I, and 5.6 in $\AA$.

| Cmpd | Avg. U- $\mathrm{Namide}^{\text {[ }}$ [ ${ }^{\text {] }}$ |  | U-O [Å] |  | C-O [Å] |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | ExptI | Calcd | ExptI | Calcd | ExptI | Calcd |
| 5.1-1 | -- | 2.291 | -- | 2.150 | -- | 1.342 |
| 5.2 | 2.364(2) | 2.369 | 2.376(2) | 2.419 | 1.262(3) | 1.259 |
| 5.3-1 | -- | 2.328 | -- | 2.318 | -- | 1.265 |
| 5.6 | 2.2616(16) | 2.287 | 2.3409(15) | 2.459 | 1.275(2) | 1.268 |

While the trends in bond lengths for these compounds were affected by different steric and electronic factors, the localization of spin density on the compounds gave a clearer picture of the relative electronic structures of the compounds (Figure 5.2.17, Table 5.2.2). Compound 5.6, which we expected to be a simple uranium(IV)L ${ }^{0}$ complex, indeed showed no spin density on the ligand, and a spin density of 2.134 on the uranium center. Compound 5.2, in comparison, did show a spin density of 0.024 based on the ligand. Compounds 5.3-I and 5.1-1 showed increased spin density based on the carbonyl ligand, of 0.151 and 0.873 , respectively. These amounts of spin density localized on the ligands trended well with their reported reduction potentials. ${ }^{35,77}$ However, even for 5.3-I and 5.2, which showed only modest spin density localized on the ligands, evidence of this delocalization of spin was observed in their reactivity or spectroscopy.


Figure 5.2.17 Spin density plots of compounds 5.1-1 (top left), 5.2 (top right), 5.3-I (lower left), and 5.6 (lower right).

Table 5.2.2. Spin density localized on uranium and carbonyl ligands and the reported ligand reduction potentials versus SCE recorded in DMF.

| Cmpd | Uranium Spin <br> Density | Ligand Spin <br> Density | Ligand Reduction <br> Potential (vs. SCE) |
| :---: | :---: | :---: | :---: |
| $\mathbf{1 . 1}$ | 2.225 | 0.873 | $-1.72^{77}$ |
| $\mathbf{2}$ | 3.045 | 0.024 | $-2.53^{35}$ |
| $\mathbf{3 - 1}$ | 2.923 | 0.151 | $-2.29^{35}$ |
| $\mathbf{6}$ | 2.132 | 0.000 | $-2.53^{35}$ |

### 5.3 Summary.

We have described reactivity of $U^{I I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with ketone, amide, and ester functional groups. Reduction of benzophenone led to formation of a rare example of a uranium ketyl radical complex, 5.1-1. Notably, reactivity with $N, N$-dimethylbenzamide resulted in the formation of a stable ketyl radical, 5.2, which was the first example of an isolated amide radical anion. This compound was shown to act as a $U$ (III) synthon with trimethylsilyl azide to yield $\mathrm{U}^{\vee}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$. Additionally, reactivity with methyl benzoate resulted in formation of a transient ketyl radical, which transferred a methoxy group to $U^{\text {III }}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ to yield $\mathrm{U}^{\mathrm{IV}}(\mathrm{OMe})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}, 5.3$, which was unprecedented in the reactivity of uranium compounds. The electronic structures of the ketyl radical complexes have been contrasted using spectroscopic and computational methods. Overall, we have expanded the reduction chemistry of uranium(III) and demonstrated that the $\mathrm{U}(\mathrm{III} / \mathrm{IV})$ couple can be exploited to trap reactive intermediates implicated in $\mathrm{Ln}(\mathrm{II} / \mathrm{III})$ chemistry.

### 5.4 Experimental.

### 5.4.1 Methods.

All reactions and manipulations were performed under an inert atmosphere $\left(\mathrm{N}_{2}\right)$ using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a
molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at $150^{\circ} \mathrm{C}$ prior to use. Unless otherwise noted, reactions were conducted in 20 mL scintillation vials in approximately $5-10 \mathrm{~mL}$ of solvent. ${ }^{1} \mathrm{H}$ NMR were obtained on a Bruker DMX300 Fourier transform NMR spectrometer at 300 MHz . Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks. Elemental analyses were performed at Midwest Microlab, Inc., Indianapolis, Indiana and at the University of Pennsylvania in the Earth \& Environmental Science department on a Costech ECS 4010 analyzer. The infrared spectra were obtained from $400-4000 \mathrm{~cm}^{-1}$ using a Perkin Elmer 1600 series infrared spectrometer. EPR spectra were collected of 5.1-1 as a pentane glass and 5.2 as a powder on a Bruker Elexsys 500 spectrometer at X-band frequency ( 9.4 GHz ), with a temperature set to 80 K with an Oxford Instrument ESR900 helium flow cryostat. EPR data was simulated using the EasySpin software package. ${ }^{51}$ Magnetic data were collected on a Quantum Design Multi-Property Measurement System (MPMS-7) with a reciprocating sample option. Temperature-dependence measurements were performed under applied 1 T DC fields from 2 to 300 K , and fielddependence measurements were performed at 2 K with varying applied magnetic field strengths ranging from 0 to 7 T . Corrections for the intrinsic diamagnetism of the samples were made using Pascal's constants. ${ }^{78}$ Each magnetism sample was prepared in the glovebox and placed in a heat-sealed compartment of a plastic drinking straw. The plastic drinking straws were evacuated overnight prior to use. These straws were then sealed at one end (approx. 9.5 cm from the top) by heating a pair of forceps and crimping the sides of the straw until the two sides were fused together. Microcrystalline compound ( 40 mg ) was loaded into the straw, capped with about 50 mg of quartz wool (dried at $250^{\circ} \mathrm{C}$ prior to use), and packed tightly. The other end of the plastic drinking draw was then sealed directly above the quartz wool, forming a small compartment. The sample and wool were massed four times each to the nearest 0.1 mg , and the values used were averages of these mass measurements.

### 5.4.2 Materials.

Tetrahydrofuran, $\mathrm{Et}_{2} \mathrm{O}, \mathrm{CH}_{2} \mathrm{Cl}_{2}$, hexanes, pentane, and toluene were purchased from Fisher Scientific. These solvents were sparged for 20 min with dry argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina, respectively (for hexanes and pentane), or two columns of neutral alumina (for THF, $\mathrm{Et}_{2} \mathrm{O}$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ). All solvents were stored over $3 \AA$ molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and stored over potassium mirror overnight prior to use. Starting materials: $\mathrm{Ul}_{3}(\mathrm{THF})_{4}{ }^{79}$ and $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}{ }^{80}$ were prepared according to the reported procedures. N,N-Dimethylbenzamide and methyl benzoate were distilled under reduced pressure prior to use. Methyl benzoate was stored over $3 \AA$ molecular sieves. Benzophenone was dried at $50^{\circ} \mathrm{C}$ under reduced pressure prior to use.

### 5.4.3 $\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} \mathrm{U}^{\mathrm{IV}}-\left(\mathrm{OCPhPh}-\mathrm{CPh}_{2} \mathrm{O}\right)-\mathbf{U}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ and $\mathrm{U}^{\mathrm{IV}}\left[\mathrm{OC} \cdot \mathrm{Ph}_{2}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(5.1-1$,

 5.1-2).To a solution of $U^{I I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ ( $200 \mathrm{mg}, 0.28 \mathrm{mmol}$, 1.0 equiv) in $\mathrm{Et}_{2} \mathrm{O}$ was added benzophenone ( $51 \mathrm{mg}, 0.28 \mathrm{mmol}, 1.0$ equiv) resulting in an immediate color change to fuchsia. The reaction mixture was concentrated to a small volume under reduced pressure and stored at $21^{\circ} \mathrm{C}$ to give colorless crystals of $5.1-2$. Yield: $144 \mathrm{mg}, 0.08 \mathrm{mmol}, 58 \% .{ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $92.49(4 \mathrm{H}),-5.73(54 \mathrm{H}),-222.19(4 \mathrm{H}),-235.22(2 \mathrm{H}) . \mathrm{IR}(\mathrm{KBr}): 3052(\mathrm{~m}), 2957(\mathrm{~s}), 2897(\mathrm{~m})$, 2485 (w), 2369 (w), 2250 (w), 2211 (w), 2086 (w), 1919 (w), 1657 (m), 1572 (m), 1493 (m), 1442 (m), 1493 (m), 1252 (s), 1187 (m), 1125 (m), 930 (s), 843 (s), 765 (s), 695 (m), 608 (m). Anal. found (calcd) for $\mathrm{C}_{62} \mathrm{H}_{128} \mathrm{~N}_{6} \mathrm{O}_{2} \mathrm{Si}_{12} \mathrm{U}_{2}$ : C, 41.32 (41.31); H, 7.01 (7.16); N, 4.44 (4.66).

### 5.4.4 $\mathrm{U}^{\mathrm{IV}}\left[\mathrm{OC} \cdot(\mathrm{Ph})\left(\mathrm{NMe}_{2}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (5.2).

To a solution of $U^{I I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(323 \mathrm{mg}, 0.45 \mathrm{mmol}, 1\right.$ equiv) in $\mathrm{Et}_{2} \mathrm{O}$ was added $\mathrm{N}, \mathrm{N}$ dimethylbenzamide ( $100 \mathrm{mg}, 0.67 \mathrm{mmol}, 1.5$ equiv). The volatiles were removed under reduced pressure, to yield a dark purple residue. The residue was extracted with hexanes, filtered over Celite, and reduced to a small volume under reduced pressure. Storage at $-21^{\circ} \mathrm{C}$ gave dark purple crystals of 5.2 . Yield: $250 \mathrm{mg}, 0.33 \mathrm{mmol}, 73 \%$. ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $-6.53(54 \mathrm{H})$. IR (KBr): 2954 (s), 2899 (m), 2467 (w), 2038 (w), 1905 (w), 1635 (s), 1514 (m), 1448 (m), 1401 (m),

1252 (s), 1184 (m), 1084 (m), 938 (s), 841 (s), 766 (m), 704 (m), 602 (w). Anal. found (calcd) for $\mathrm{C}_{27} \mathrm{H}_{65} \mathrm{~N}_{4} \mathrm{OSi}_{6} \mathrm{U}: \mathrm{C}, 37.34$ (37.34); H, 7.49 (7.55); N, 6.44 (6.45).

### 5.4.5 $\mathrm{La}^{\text {I"I }}\left[\mathrm{OC}(\mathrm{Ph})\left(\mathrm{NMe}_{2}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ (5.2-La) .

To a solution of $\mathrm{La}^{11 \mathrm{l}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(230 \mathrm{mg}, 0.37 \mathrm{mmol}, 1$ equiv $)$ in $\mathrm{Et}_{2} \mathrm{O}$ was added $\mathrm{N}, \mathrm{N}$ dimethylbenzamide ( $24 \mathrm{mg}, 0.37 \mathrm{mmol}, 1$ equiv). The reaction was stirred for 1 h and subsequently filtered. Volatiles were removed under reduced pressure, and white crystals of 5.2La precipitated from minimal pentane $(2 \mathrm{~mL})$ at $-21^{\circ} \mathrm{C}$. Yield: $170 \mathrm{mg}, 0.22 \mathrm{mmol}, 60 \% .{ }^{1} \mathrm{H}$ NMR (benzene-d6): 7.31 (m, 3H), 7.16 (m, 2H), 2.91 (s, 3H), 2.18 (s, 3H), 0.54 (54 H). IR (KBr): 3067 (w), 2958 (s), 2896 (m), 1596 (s), 1562 (m), 1543 (m), 1479 (m), 1447 (m), 1407 (m), 1256 (s), 1184 (m), 1098 (m), 1074 (m), 981 (s), 938 (s), 843 (s) 767 (m), 716 (m), 697 (w), 667 (w), 645 (w), 595 (m), 562 (w). Anal. found (calcd) for $\mathrm{C}_{27} \mathrm{H}_{64} \mathrm{LaN}_{4} \mathrm{OSi}_{6}$ : C, 42.39 (42.16); H, 8.18 (8.52); N, 7.10 (7.28).

### 5.4.6 $\mathrm{U}^{\mathrm{IV}}(\mathrm{OMe})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} \cdot\left(\mathrm{C}_{7} \mathrm{H}_{6} \mathrm{O}\right)(5.3)$.

To a solution of $\mathrm{U}^{\mathrm{II}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(500 \mathrm{mg}, 0.70 \mathrm{mmol}\right.$, 1 equiv) in $\mathrm{Et}_{2} \mathrm{O}$ was added methyl benzoate ( $95 \mathrm{mg}, 0.70 \mathrm{mmol}, 1$ equiv), causing an immediate color change to light brown. Volatiles were removed under reduced pressure, leaving a brown residue. Impurities were removed by successive crystallization from hexanes to yield 5.3 as a light brown solid in a 1:1 mixture with benzaldehyde. Yield: $214 \mathrm{mg}, 0.29 \mathrm{mmol}, 41 \%$. A crystal suitable for X-ray analysis was grown from a concentrated solution of $\left(\mathrm{Me}_{3} \mathrm{Si}\right)_{2} \mathrm{O}$ at $-21^{\circ} \mathrm{C}$. ${ }^{1} \mathrm{H}$ NMR (benzene $\left.-\mathrm{d}_{6}\right):-3.37(54$ H), -25.89 (3H). IR (KBr): 2955 (s), 2898 (w), 2817 (w), 1708 (m), 1568 (w), 1445 (w), 1405(w), 1295 (w), 1252 (s), 1180 (w), 1113 (w), 1063 (w), 935 (s), 843 (s), 765 (m), 664 (w), 607 (w). Anal. found (cald) for $\mathrm{C}_{26} \mathrm{H}_{63} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{Si}_{6} \mathrm{U}: \mathrm{C}, 36.27$ (36.47); $\mathrm{H}, 6.87$ (7.42); $\mathrm{N}, 4.53$ (4.91).

### 5.4.7 $\left[\mathrm{U}(\mu-\mathrm{O})\left[\mathrm{OC}(\mathrm{Ph})\left(\mathrm{NMe}_{2}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{2}\right]_{2}(5.4)$.

To a solution of $\mathrm{U}\left[\mathrm{OC} \cdot(\mathrm{Ph})\left(\mathrm{NMe}_{2}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(5.2)\left(508 \mathrm{mg}, 0.59 \mathrm{mmol}, 1\right.$ equiv) in $\mathrm{Et}_{2} \mathrm{O}$ was added potassium graphite ( $95 \mathrm{mg}, 0.70 \mathrm{mmol}, 1.2$ equiv). The reaction mixture was filtered over Celite, and the volatiles were removed under reduced pressure. Crystallization from THF layered with pentane at $-21^{\circ} \mathrm{C}$ gave 5.4 as light brown crystals. Yield: $51 \mathrm{mg}, 0.04 \mathrm{mmol}, 24 \% .{ }^{1} \mathrm{H}$

NMR (benzene-d6): $12.93(4 \mathrm{H}), 8.41(4 \mathrm{H}), 7.85(2 \mathrm{H}), 1.14(6 \mathrm{H}), 0.79(6 \mathrm{H}),-2.34(72 \mathrm{H})$. IR (KBr): 2956 (s), 2897 (m), 1628 (m), 1457 (w), 1400 (w), 1252 (s), 1183 (w), 977 (s), 941 (s), 842 (s), $765(\mathrm{~m}), 668(\mathrm{~m}), 600(\mathrm{~m})$. Anal. found (cald) for $\mathrm{C}_{42} \mathrm{H}_{94} \mathrm{~N}_{6} \mathrm{O}_{4} \mathrm{Si}_{8} \mathrm{U}_{2}: \mathrm{C}, 34.64$ (34.84); H, 6.50 (6.54); N, 5.76 (5.80).

### 5.4.8 [(15-crown-5) $\left.)_{2} \mathrm{~K}\right]\left[\mathrm{U}^{\mathrm{IV}} \mathrm{O}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ (5.5).

To a solution of $\mathrm{U}\left[\mathrm{OC} \cdot(\mathrm{Ph})\left(\mathrm{NMe}_{2}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(5.2)\left(140 \mathrm{mg}, 0.18 \mathrm{mmol}, 1\right.$ equiv) in $\mathrm{Et}_{2} \mathrm{O}$ was added 15 -crown-5 ( $81 \mathrm{mg}, 0.367 \mathrm{mmol}, 2$ equiv). Potassium graphite ( $24 \mathrm{mg}, 0.201 \mathrm{mmol}$, 1.1 equiv) was then added, resulting in a color change to light brown. The reaction mixture was filtered over Celite, and the volatiles were removed under reduced pressure. The resulting solid was washed thoroughly with hexanes and recrystallized from THF layered with hexanes at $-21^{\circ} \mathrm{C}$ to yield 5.5 as a light brown solid. Yield: $91 \mathrm{mg}, 0.07 \mathrm{mmol}, 41 \% .{ }^{1} \mathrm{H}$ NMR (pyridine- $d_{5}$ ): 4.28 ( 40 H), -2.13 (54 H). IR (KBr): 3058 (w), 3024 (w), 2949 (s), 2893 (s), 1636(s), 1573 (w), 1508 (m), 1476 (m), 1450 (m), 1397 (s), 1358 (m), 1246 (s), 1122 (s), 1092 (s), 1034 (w), 988 (m), 940 (s), 836 (s), 762 (w), 708 (w), 667 (w), $600(w)$. Anal. found (calcd) for $\mathrm{C}_{38} \mathrm{H}_{94} \mathrm{KN}_{3} \mathrm{O}_{11} \mathrm{Si}_{6} \mathrm{U}: \mathrm{C}, 37.39$ (37.57); H, 7.61 (7.80); N, 3.21 (3.46).

### 5.4.9 $\mathrm{U}^{\mathrm{IV}}\left[\mathrm{OC}(\mathrm{Ph})\left(\mathrm{NMe}_{2}\right)\right](\mathrm{OTf})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(5.6)$.

To a solution of $\mathrm{U}\left[\mathrm{OC} \cdot(\mathrm{Ph})\left(\mathrm{NMe}_{2}\right)\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(\mathbf{2})\left(260 \mathrm{mg}, 0.30 \mathrm{mmol}, 1\right.$ equiv) in $\mathrm{Et}_{2} \mathrm{O}$ was added trityl triflate ( $176 \mathrm{mg}, 0.45 \mathrm{mmol}, 1.5$ equiv). The volatiles were removed under reduced pressure, and the residue was washed with hexanes and crystallized from a small volume of $\mathrm{Et}_{2} \mathrm{O}$ layered with pentane $-21^{\circ} \mathrm{C}$ to yield $\mathbf{6}$ as light green crystals. Yield: $89 \mathrm{mg}, 0.09$ mmol, 29\%. ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $6.82(5 \mathrm{H}), 1.74(6 \mathrm{H}),-1.51(54 \mathrm{H}) .{ }^{19} \mathrm{~F}(339 \mathrm{MHz}):-99.66$. IR (KBr): 3067 (w), 2953 (m), 2899 (m), 1596 (s), 1576 (m), 1502 (m), 1446 (m), 1413 (m), 1323 (m), 1253 (s), 1199 (s), 1102 (w), 1031 (m), 1012 (m), 991 (m), 879 (s), 847 (s), 775 (m), 715 (w), 704 (w), 661 (w), 633 (w), 615 (m), 513 (w). Anal. found (calcd) for $\mathrm{C}_{28} \mathrm{H}_{65} \mathrm{~F}_{3} \mathrm{~N}_{4} \mathrm{O}_{4} \mathrm{SSi}_{6} \mathrm{U}: \mathrm{C}, 33.16$ (33.05); H, 6.07 (6.44); N, 5.09 (5.51).

### 5.4.10 $\mathrm{U}^{\mathrm{VI}} \mathrm{O}(\mathrm{OMe})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(5.7)$.

To a solution of $\mathrm{U}^{\mathrm{IV}}(\mathrm{OMe})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(5.3)\left(250 \mathrm{mg}, 0.34 \mathrm{mmol}\right.$, 1 equiv) in $\mathrm{Et}_{2} \mathrm{O}$ was added $N$-methylmorpholine $N$-oxide ( $40 \mathrm{mg}, 0.34 \mathrm{mmol}, 1$ equiv). The volatiles were removed under reduced pressure, leaving a dark brown residue. The residue was extracted with hexanes and filtered over Celite. Storage at $-21^{\circ} \mathrm{C}$ gave black crystals of 5.7 ( $45 \mathrm{mg}, 0.06 \mathrm{mmol}, 18 \%$ ). ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $4.83(3 \mathrm{H}), 0.59(27 \mathrm{H}), 0.33(27 \mathrm{H})$. IR (KBr): $2953(\mathrm{~m})$, $2897(\mathrm{~m}), 2815(\mathrm{w})$, 1718 (w), 1653 (w), 1448 (w), 1247 (s), 1179 (w), 1116 (w), 1068 (w), 1035 (s), 941 (m), 900 (s), 841 (s), 772 (m), 660 (s), 618 (s), 527 (w) 501 (w), 480 (w).

### 5.5 Crystallographic Analysis.

X-Ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Ka radiation ( $\lambda=0.71073 \AA$ ) at a temperature of 143(1) K. In all cases, rotation frames were integrated using SAINT, ${ }^{81}$ producing a listing of unaveraged $F^{2}$ and $\sigma\left(F^{2}\right)$ values, which were then passed to the SHELXTL ${ }^{82}$ program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS ${ }^{83}$ or SADABS. ${ }^{84}$ The structures were solved by direct methods (SHELXS-97). ${ }^{85}$ Refinement was by full-matrix least squares based on $\mathrm{F}^{2}$ using SHELXL-97. ${ }^{85}$ All reflections were used during refinements. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using a riding model.

### 5.6 Spectroscopic Analysis.

${ }^{1} \mathrm{H}$ NMR spectra were obtained on a Bruker DMX-300 Fourier transform NMR spectrometer at 300 MHz . Chemical shifts were recorded in units of parts per million referenced to residual solvent peaks ( ${ }^{1} \mathrm{H}$ ). The UV-Visible absorption spectra were obtained from 2000-290 nm using a Perkin Elmer 950 UV-Vis/NIR Spectrophotometer, and all samples were prepared under an $\mathrm{N}_{2}$ environment. 1 mm pathlength screw cap quartz cells were used with a blank measured before each run.


Figure 5.6.1. ${ }^{1} \mathrm{H}$ NMR of $5.1-1$ in benzene- $d_{6}$.


Figure 5.6.2. ${ }^{1} \mathrm{H}$ NMR of 5.2 in benzene- $d_{6}$.


Figure 5.6.3. ${ }^{1} \mathrm{H}$ NMR of 5.2-La in benzene- $d_{6}$.


Figure 5.6.4. ${ }^{1} \mathrm{H}$ NMR of $N, N$-dimethylbenzamide in benzene- $d_{6}$.


Figure 5.6.5. ${ }^{1} \mathrm{H}$ NMR of $\mathrm{U}^{\vee}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ formed by reaction of 5.2 with trimethylsilyl azide in benzene- $d_{6}$.


Figure 5.6.6. Crude ${ }^{1} \mathrm{H}$ NMR of 5.3 and benzaldehyde in benzene- $d_{6}$.

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Figure 5.6.7. ${ }^{1} \mathrm{H}$ NMR of 5.4 in benzene $-d_{6}$.


Figure 5.6.8. Crude ${ }^{1} \mathrm{H}$ NMR of reaction mixture to yield 5.4 showing the formation of benzylamine (*) in benzene- $d_{6}$.


Figure 5.6.9. ${ }^{1} \mathrm{H}$ NMR of hexanes extract of crude reaction mixture to yield 5.5 showing the formation of benzylamine (*) in benzene- $d_{6}$.


Figure 5.6.10 ${ }^{1} \mathrm{H}$ NMR and ${ }^{19} \mathrm{~F}$ NMR (insert) of 5.6 in benzene- $d_{6}$.


Figure 5.6.11 ${ }^{1} \mathrm{H}$ NMR of 5.7 in benzene- $d_{6}$.

### 5.7 Electrochemical Analysis.

Voltammetry experiments (CV, DPV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v9.24. All experiments were performed in an $\mathrm{N}_{2}$ atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The quasi-reference electrode was prepared by dipping a length of silver wire in concentrated hydrochloric acid. The working electrode surfaces were polished prior to each set of experiments. Potentials were reported versus ferrocene, which was added as an internal standard for calibration at the end of each run. Solutions employed during these studies were $\sim 3 \mathrm{mM}$ in analyte and 100 mM in $\left[{ }^{n} \mathrm{Pr}_{4} \mathrm{~N}\right]\left[B A r^{\mathrm{F}}\right]$ in 2 mL of THF for 5.2, 5.2-La, and $\mathrm{N}, \mathrm{N}$-dimethylbenzamide and 100 mM in $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[P F_{6}\right]$ in 2 mL of fluorobenzene for 5.7. All data were collected in a positive-feedback IR compensation mode.
a)

b)


c)

d)


Figure 5.7.1. a) Full scan cyclic voltammetry of 5.2 in THF with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Pr}_{4} \mathrm{~N}\right]\left[\mathrm{BAr}{ }^{\mathrm{F}}\right.$ ]; [analyte] = ca. $1 \mathrm{mM} ; \mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$. b) Left: Isolated benzamide ${ }^{0 /-}$ redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated benzamide ${ }^{0 /-}$ couple. C) Isolated benzamide ${ }^{0 /+}$ redox couple at varying scan rates. d) Differential pulse voltammetry.
a)

b)


c)


Figure 5.7.2. a) Full scan cyclic voltammetry of compound 5.2 -La in THF with 0.1 M [ $\left.{ }^{n} \mathrm{Pr}_{4} \mathrm{~N}\right]\left[B A r^{\mathrm{F}}\right] ;$ [analyte] $=\mathrm{ca}$.1 mM ; v=0.25 V/sec. b) Left: Isolated benzamide ${ }^{0 /-}$ redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated benzamide ${ }^{0 /-}$ couple. c) Differential pulse voltammetry.
a)

b)


Figure 5.7.3. a) Full scan cyclic voltammetry of $N, N$-dimethylbenzamide in THF with 0.1 M [ $\left.{ }^{n} \mathrm{Pr}_{4} \mathrm{~N}\right]\left[B A r^{\mathrm{F}}\right] ;$ analyte] $=\mathrm{ca} .1 \mathrm{mM} ; \mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$. b) Differential pulse voltammetry.
a)

b)

c)


Figure 5.7.4. a) Full scan cyclic voltammetry of 5.7 in fluorobenzene with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$; [analyte] $=$ ca. $1 \mathrm{mM} ; \mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$. b) Left: Isolated uranium(VI/V) redox couple at varying scan rates. Right: Current versus $\mathrm{v}^{1 / 2}$ plot from the scan rate dependence of the isolated uranium(VI/V). c) Differential pulse voltammetry.

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### 5.8 Computational Details.

All calculations were performed with Gaussian 09 Revision D.01, ${ }^{86}$ with the B3LYP hybrid DFT method. An effective core potential incorporating quasi-relativistic effects were applied to uranium, with a 60 electron core and the corresponding segmented natural orbital basis set. ${ }^{87,88}$ The $6-31 \mathrm{G}^{*}$ basis set was used for all small molecules. ${ }^{89}$ Geometry optimizations were carried out in $C_{1}$ symmetry for all uranium complexes and all small molecules, as higher symmetry solutions were either higher in energy or were not successfully converged. Default settings were used for the integration grid, SCF, and geometry convergence criteria. All frequency calculations found no imaginary frequencies, confirming that the optimized structures are minima.

Table 5.8.1. Geometry optimized coordinates of compound 5.1-1.

| Atomic Number | X | y | Z |
| :---: | :---: | :---: | :---: |
| U | -0.44932 | -0.07585 | -0.05053 |
| Si | 0.695042 | -1.39154 | -2.98306 |
| Si | -0.21968 | -3.56867 | -1.08663 |
| Si | -2.68226 | -1.05386 | 2.39506 |
| Si | 0.010165 | -0.41785 | 3.573138 |
| Si | -1.74258 | 3.154362 | -0.17841 |
| Si | -3.32434 | 1.248055 | -1.8911 |
| O | 1.550932 | 0.703476 | 0.061139 |
| N | -0.02672 | -1.8395 | -1.42165 |
| N | -1.00086 | -0.56872 | 2.114252 |
| N | -1.96239 | 1.505736 | -0.78869 |
| C | 2.544369 | -1.77185 | -3.14072 |
| H | 3.116731 | -1.37474 | -2.29633 |
| H | 2.9268 | -1.29751 | -4.05482 |
| H | 2.75659 | -2.84246 | -3.21349 |
| C | 0.571764 | 0.49669 | -3.23165 |
| H | -0.40551 | 0.945931 | -3.0249 |
| H | 0.785815 | 0.693958 | -4.29078 |
| H | 1.329836 | 1.03829 | -2.65445 |
| C | -0.17233 | -2.22114 | -4.45618 |
| H | -0.02095 | -3.30671 | -4.4627 |
| H | 0.246878 | -1.83192 | -5.39338 |
| H | -1.2512 | -2.03694 | -4.46999 |
| C | -0.17523 | -3.91072 | 0.77894 |
| H | 0.839443 | -3.77189 | 1.171414 |
| H | -0.45089 | -4.95819 | 0.959238 |
| H | -0.84102 | -3.28418 | 1.376865 |
| C | 1.170361 | -4.65751 | -1.7898 |

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| H | 1.210778 | -4.67243 | -2.8841 |
| :---: | :---: | :---: | :---: |
| H | 0.99581 | -5.69031 | -1.45924 |
| H | 2.155876 | -4.35486 | -1.41867 |
| C | -1.84403 | -4.24696 | -1.80151 |
| H | -2.72727 | -3.7127 | -1.43507 |
| H | -1.96305 | -5.30543 | -1.53469 |
| H | -1.85352 | -4.18094 | -2.8955 |
| C | -0.91897 | 0.395675 | 5.023527 |
| H | -1.2325 | 1.416127 | 4.771283 |
| H | -0.23144 | 0.470438 | 5.876262 |
| H | -1.80384 | -0.14859 | 5.368802 |
| C | 1.536356 | 0.679757 | 3.342781 |
| H | 2.293695 | 0.255302 | 2.679615 |
| H | 2.002283 | 0.793485 | 4.331114 |
| H | 1.290808 | 1.682636 | 2.981449 |
| C | 0.659842 | -2.1049 | 4.155959 |
| H | -0.13937 | -2.8138 | 4.394467 |
| H | 1.271136 | -1.97542 | 5.058724 |
| H | 1.297763 | -2.56992 | 3.394965 |
| C | -3.79158 | 0.402194 | 2.888741 |
| H | -3.47376 | 0.873332 | 3.82435 |
| H | -4.82798 | 0.065273 | 3.021767 |
| H | -3.79199 | 1.172662 | 2.10953 |
| C | -2.89707 | -2.4375 | 3.680514 |
| H | -2.34051 | -3.33903 | 3.399556 |
| H | -3.95986 | -2.70983 | 3.727924 |
| H | -2.58793 | -2.15556 | 4.691582 |
| C | -3.41988 | -1.80359 | 0.808958 |
| H | -3.29597 | -1.21116 | -0.10357 |
| H | -4.50412 | -1.90216 | 0.952336 |
| H | -3.02792 | -2.80716 | 0.617994 |
| C | -0.95774 | 4.311226 | -1.46764 |
| H | -0.14375 | 3.826908 | -2.01854 |
| H | -0.54475 | 5.201596 | -0.97608 |
| H | -1.69056 | 4.651787 | -2.20675 |
| C | -0.61138 | 3.129585 | 1.346306 |
| H | -1.03033 | 2.526434 | 2.160017 |
| H | -0.52694 | 4.15934 | 1.718481 |
| H | 0.41045 | 2.789376 | 1.149084 |
| C | -3.34325 | 3.994165 | 0.407688 |
| H | -4.06086 | 4.169747 | -0.40089 |
| H | -3.0893 | 4.973621 | 0.834453 |
| H | -3.85118 | 3.417918 | 1.189529 |
| C | -3.48198 | 2.602273 | -3.21712 |
| H | -3.76984 | 3.577126 | -2.80863 |
| H | -4.2605 | 2.309946 | -3.9343 |

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| H | -2.55085 | 2.737627 | -3.7799 |
| :--- | :--- | :--- | :--- |
| C | -4.99962 | 1.166252 | -0.99763 |
| H | -5.03636 | 0.374582 | -0.24213 |
| H | -5.79299 | 0.960896 | -1.72863 |
| H | -5.25023 | 2.107556 | -0.49835 |
| C | -3.13141 | -0.3664 | -2.87404 |
| H | -2.42817 | -0.23271 | -3.70271 |
| H | -4.10354 | -0.62803 | -3.3123 |
| H | -2.79211 | -1.23309 | -2.29814 |
| C | 2.879297 | 0.885368 | 0.107213 |
| C | 3.373324 | 2.254386 | 0.012318 |
| H | 4.576426 | 2.667807 | 0.633888 |
| C | 5.148722 | 1.955247 | 1.217992 |
| H | 5.013009 | 3.985928 | 0.544984 |
| C | 5.934714 | 4.276995 | 1.042344 |
| H | 4.268849 | 4.936817 | -0.16079 |
| C | 4.614669 | 5.964407 | -0.22977 |
| H | 3.068864 | 4.551674 | -0.76621 |
| C | 2.475876 | 5.279113 | -1.31459 |
| H | 2.624489 | 3.236716 | -0.67536 |
| C | 1.695231 | 2.948729 | -1.15174 |
| C | 3.723529 | -0.28905 | 0.245138 |
| C | 5.082551 | -0.29554 | -0.16483 |
| C | 3.197099 | -1.50675 | 0.744263 |
| C | 5.863562 | -1.4402 | -0.05268 |
| C | 3.986107 | -2.64603 | 0.860052 |
| H | 5.327906 | -2.62379 | 0.466988 |
| H | 5.510401 | 0.596878 | -0.60766 |
| H | 2.161384 | -1.54694 | 1.062445 |
| H | 6.897314 | -1.41302 | -0.38764 |
| H | 3.552978 | -3.5574 | 1.26467 |
|  | 5.942675 | -3.51484 | 0.555795 |

Sum of electronic and thermal Free Energies $=\mathbf{- 3 6 7 2 . 9 4 0 1 5 4 ~ H a r t r e e s . ~}$
Table 5.8.2. Geometry optimized coordinates of compound 5.2.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | 0.360983 | 0.028024 | -0.0007 |
| Si | 0.074657 | 2.665625 | -2.31641 |
| Si | 1.915028 | 3.355781 | -0.02777 |
| Si | 2.817759 | -1.22005 | 2.185298 |
| Si | 0.236846 | -0.60953 | 3.601901 |
| Si | -0.35096 | -3.10391 | -1.28942 |
| Si | 2.058245 | -1.91222 | -2.65068 |
| O | -1.98789 | 0.593485 | 0.11327 |

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| N | 0.843072 | 2.210603 | -0.81077 |
| :---: | :---: | :---: | :---: |
| N | 1.182509 | -0.59753 | 2.13578 |
| N | 0.775599 | -1.77521 | -1.46118 |
| N | -3.42848 | 2.155824 | 0.92673 |
| C | -1.33791 | 3.935338 | -2.11586 |
| H | -2.1731 | 3.513541 | -1.54272 |
| H | -1.73058 | 4.211843 | -3.10359 |
| H | -1.02037 | 4.857276 | -1.61857 |
| C | -0.79086 | 1.181866 | -3.14643 |
| H | -0.12346 | 0.354248 | -3.40183 |
| H | -1.25011 | 1.534569 | -4.0803 |
| H | -1.60332 | 0.774299 | -2.53126 |
| C | 1.265594 | 3.392468 | -3.6103 |
| H | 1.696891 | 4.347985 | -3.28888 |
| H | 0.733381 | 3.577124 | -4.55284 |
| H | 2.096922 | 2.711933 | -3.82516 |
| C | 1.995436 | 3.043444 | 1.846107 |
| H | 1.046296 | 3.317112 | 2.326731 |
| H | 2.777174 | 3.670213 | 2.295688 |
| H | 2.204751 | 2.003911 | 2.11747 |
| C | 1.367188 | 5.178801 | -0.17083 |
| H | 1.336488 | 5.545476 | -1.20308 |
| H | 2.081428 | 5.809079 | 0.37563 |
| H | 0.378548 | 5.348756 | 0.273344 |
| C | 3.684078 | 3.291462 | -0.72213 |
| H | 4.125945 | 2.291998 | -0.64036 |
| H | 4.34061 | 3.989135 | -0.18548 |
| H | 3.702039 | 3.569576 | -1.78252 |
| C | 0.25615 | -2.28832 | 4.503543 |
| H | -0.12455 | -3.09161 | 3.860433 |
| H | -0.38386 | -2.24704 | 5.394917 |
| H | 1.258257 | -2.58179 | 4.837029 |
| C | -1.60993 | -0.26046 | 3.273519 |
| H | -1.77989 | 0.752499 | 2.893055 |
| H | -2.14633 | -0.34054 | 4.228501 |
| H | -2.06751 | -0.97461 | 2.580146 |
| C | 0.749332 | 0.719104 | 4.864794 |
| H | 1.759273 | 0.557729 | 5.255615 |
| H | 0.060562 | 0.719019 | 5.720359 |
| H | 0.729167 | 1.720992 | 4.418886 |
| C | 2.900076 | -3.0998 | 1.931707 |
| H | 2.364026 | -3.63518 | 2.724304 |
| H | 3.938674 | -3.45599 | 1.934474 |
| H | 2.452323 | -3.38652 | 0.973961 |
| C | 3.780283 | -0.83948 | 3.784082 |
| H | 3.835626 | 0.237039 | 3.984065 |

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| H | 4.809554 | -1.2084 | 3.680379 |
| :---: | :---: | :---: | :---: |
| H | 3.352343 | -1.32272 | 4.66995 |
| C | 3.84345 | -0.39136 | 0.810423 |
| H | 3.38136 | -0.40243 | -0.18526 |
| H | 4.804054 | -0.9109 | 0.698135 |
| H | 4.063174 | 0.651892 | 1.063836 |
| C | -1.67346 | -3.14378 | -2.65944 |
| H | -2.20588 | -2.18679 | -2.72088 |
| H | -2.41685 | -3.92622 | -2.45645 |
| H | -1.24235 | -3.34207 | -3.64634 |
| C | -1.31452 | -2.95513 | 0.349186 |
| H | -0.64908 | -2.94211 | 1.219847 |
| H | -1.96872 | -3.83211 | 0.447974 |
| H | -1.97079 | -2.07722 | 0.399506 |
| C | 0.451477 | -4.82823 | -1.24491 |
| H | 0.967546 | -5.07764 | -2.17901 |
| H | -0.32063 | -5.59249 | -1.08514 |
| H | 1.178636 | -4.91734 | -0.4293 |
| C | 1.48454 | -2.63118 | -4.3204 |
| H | 1.152898 | -3.67337 | -4.24668 |
| H | 2.318954 | -2.60689 | -5.03393 |
| H | 0.662621 | -2.05063 | -4.75672 |
| C | 3.497796 | -3.01305 | -2.06884 |
| H | 3.953821 | -2.6415 | -1.1445 |
| H | 4.282605 | -3.04053 | -2.83675 |
| H | 3.181119 | -4.04567 | -1.88514 |
| C | 2.81552 | -0.22245 | -3.0928 |
| H | 2.165486 | 0.338118 | -3.77311 |
| H | 3.767577 | -0.38669 | -3.61513 |
| H | 3.024773 | 0.429429 | -2.23789 |
| C | -3.16541 | 0.950354 | 0.382233 |
| C | -4.77381 | 2.683517 | 1.154225 |
| H | -5.52249 | 2.061378 | 0.669231 |
| H | -4.82984 | 3.695279 | 0.738821 |
| H | -4.99059 | 2.738468 | 2.228013 |
| C | -2.34602 | 3.059151 | 1.328071 |
| H | -1.39313 | 2.706475 | 0.938306 |
| H | -2.30295 | 3.12591 | 2.421906 |
| H | -2.54289 | 4.05521 | 0.920766 |
| C | -4.28002 | -0.00517 | 0.090705 |
| C | -5.13845 | -0.45474 | 1.105497 |
| H | -5.03213 | -0.07088 | 2.116142 |
| C | -6.1064 | -1.41922 | 0.825648 |
| H | -6.75786 | -1.77352 | 1.619292 |
| C | -6.23256 | -1.93038 | -0.46788 |
| H | -6.99033 | -2.67777 | -0.6852 |

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| C | -5.37731 |  |  |
| :--- | :---: | :---: | :---: |
| H | -5.46607 |  |  |
| C | -4.3943 |  |  |
| H | -3.71739 | -1.48744 | -1.47974 |

Sum of electronic and thermal Free Energies $=-3575.874316$ Hartrees.
Table 5.8.3. Geometry optimized coordinates of compound 5.3-I.

| Atomic Number | X | y | z |
| :---: | :---: | :---: | :---: |
| U | 0.261133 | 0.050119 | 0.033847 |
| Si | -0.6087 | 2.407742 | -2.36271 |
| Si | 1.421435 | 3.48497 | -0.40976 |
| Si | 3.255104 | -0.67542 | 1.80466 |
| Si | 0.829123 | -0.25144 | 3.544844 |
| Si | -0.11311 | -3.22155 | -0.93949 |
| Si | 1.886012 | -1.83393 | -2.71356 |
| O | -2.04294 | 0.124211 | 0.282025 |
| N | 0.447098 | 2.130709 | -0.97918 |
| N | 1.553808 | -0.25064 | 1.943699 |
| N | 0.767947 | -1.7583 | -1.35369 |
| C | -2.12172 | 3.478651 | -1.93234 |
| H | -2.61466 | 3.08894 | -1.03456 |
| H | -2.85093 | 3.457558 | -2.75298 |
| H | -1.866 | 4.525421 | -1.74287 |
| C | -1.36353 | 0.781263 | -3.00968 |
| H | -0.62802 | 0.02858 | -3.3059 |
| H | -1.95991 | 1.024825 | -3.89961 |
| H | -2.04704 | 0.31565 | -2.29015 |
| C | 0.265297 | 3.221915 | -3.84134 |
| H | 0.636456 | 4.225427 | -3.6048 |
| H | -0.43521 | 3.323109 | -4.68079 |
| H | 1.117839 | 2.628262 | -4.18909 |
| C | 1.816984 | 3.315724 | 1.437101 |
| H | 0.900488 | 3.41032 | 2.034044 |
| H | 2.492163 | 4.125166 | 1.744982 |
| H | 2.283519 | 2.365335 | 1.709305 |
| C | 0.56462 | 5.182553 | -0.53853 |
| H | 0.344262 | 5.493979 | -1.56544 |
| H | 1.231699 | 5.940909 | -0.10712 |
| H | -0.37262 | 5.21182 | 0.029763 |
| C | 3.053762 | 3.639236 | -1.37034 |
| H | 3.654151 | 2.724407 | -1.31546 |
| H | 3.66206 | 4.459907 | -0.96775 |
| H | 2.874998 | 3.849995 | -2.43108 |
| C | 1.161645 | -1.86337 | 4.500944 |

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| H | 0.800949 | -2.74131 | 3.950982 |
| :---: | :---: | :---: | :---: |
| H | 0.640666 | -1.84283 | 5.467277 |
| H | 2.226139 | -2.02038 | 4.709765 |
| C | -1.06485 | -0.09543 | 3.440802 |
| H | -1.40163 | 0.844139 | 2.988371 |
| H | -1.45105 | -0.10517 | 4.468987 |
| H | -1.54695 | -0.92763 | 2.91513 |
| C | 1.374864 | 1.193723 | 4.651755 |
| H | 2.438454 | 1.15681 | 4.907258 |
| H | 0.809254 | 1.173757 | 5.59301 |
| H | 1.184948 | 2.159693 | 4.170144 |
| C | 3.522446 | -2.5473 | 1.651822 |
| H | 3.153031 | -3.07908 | 2.536316 |
| H | 4.588596 | -2.7851 | 1.542532 |
| H | 2.999898 | -2.94976 | 0.777871 |
| C | 4.349972 | -0.07777 | 3.241746 |
| H | 4.308266 | 1.010328 | 3.367178 |
| H | 5.392617 | -0.34307 | 3.020913 |
| H | 4.097537 | -0.53657 | 4.204103 |
| C | 3.996609 | 0.168034 | 0.270313 |
| H | 3.423102 | 0.029562 | -0.65319 |
| H | 4.997849 | -0.23648 | 0.072023 |
| H | 4.105991 | 1.245647 | 0.434804 |
| C | -1.56869 | -3.58151 | -2.11295 |
| H | -2.19651 | -2.69576 | -2.2675 |
| H | -2.2053 | -4.37486 | -1.69935 |
| H | -1.22828 | -3.91211 | -3.10001 |
| C | -0.86937 | -3.0538 | 0.802969 |
| H | -0.11475 | -2.84786 | 1.571389 |
| H | -1.33728 | -4.01257 | 1.063191 |
| H | -1.66236 | -2.29975 | 0.874944 |
| C | 0.938597 | -4.8045 | -0.88035 |
| H | 1.367295 | -5.06715 | -1.85395 |
| H | 0.307702 | -5.6463 | -0.56539 |
| H | 1.763809 | -4.72454 | -0.16357 |
| C | 1.176833 | -2.75653 | -4.22136 |
| H | 1.018541 | -3.8249 | -4.03448 |
| H | 1.880819 | -2.67585 | -5.0602 |
| H | 0.221466 | -2.33128 | -4.55116 |
| C | 3.521714 | -2.70178 | -2.28096 |
| H | 4.064788 | -2.18462 | -1.48318 |
| H | 4.174142 | -2.72342 | -3.16418 |
| H | 3.371267 | -3.73717 | -1.95765 |
| C | 2.345356 | -0.10985 | -3.37218 |
| H | 1.553642 | 0.293949 | -4.01204 |
| H | 3.248115 | -0.20091 | -3.99077 |

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| H | 2.552332 | 0.640962 | -2.60298 |
| :--- | :---: | :---: | :---: |
| C | -3.14735 | 0.569413 | 0.709969 |
| C | -4.38339 | -0.19166 | 0.572216 |
| C | -5.46685 | -0.05423 | 1.469777 |
| H | -5.39893 | 0.632727 | 2.305502 |
| C | -6.60655 | -0.83804 | 1.323559 |
| H | -7.42433 | -0.72937 | 2.030535 |
| C | -6.69796 | -1.76974 | 0.284675 |
| H | -7.59245 | -2.37546 | 0.172097 |
| C | -5.62527 | -1.92627 | -0.60065 |
| H | -5.6837 | -2.65427 | -1.40479 |
| C | -4.47796 | -1.15637 | -0.45676 |
| O | -3.64496 | -1.28308 | -1.13861 |
| C | -3.08024 | 1.754801 | 1.351275 |
| H | -4.15932 | 2.705316 | 1.343353 |
| H | -3.70523 | 3.676726 | 1.138675 |
| H | -4.89446 | 2.469428 | 0.57127 |

Sum of electronic and thermal Free Energies $=-3556.459094$ Hartrees.
Table 5.8.4. Geometry optimized coordinates of compound 5.6.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -0.51792 | -0.04677 | 0.020572 |
| S | 2.683764 | -2.00305 | -0.25446 |
| Si | -1.32786 | 3.302081 | -0.35784 |
| Si | -3.72329 | 1.644625 | -0.94328 |
| Si | -1.40997 | -1.84983 | -2.9321 |
| Si | -1.63383 | -3.38771 | -0.35831 |
| Si | -2.18677 | 0.113152 | 3.117302 |
| Si | 0.789302 | 0.250378 | 3.378078 |
| F | 4.524637 | -3.57133 | 0.750166 |
| F | 2.575698 | -3.80707 | 1.687713 |
| F | 3.800524 | -2.06508 | 2.142853 |
| O | 1.251083 | 1.000848 | -1.32816 |
| O | 1.44973 | -1.38034 | 0.392926 |
| O | 2.366567 | -3.03006 | -1.25169 |
| O | 3.691356 | -0.99133 | -0.61886 |
| N | -2.00807 | 1.659671 | -0.44883 |
| N | 2.910417 | 0.87228 | -2.8854 |
| N | -1.31335 | -1.82042 | -1.15494 |
| N | -0.61632 | 0.114968 | 2.287476 |
| C | -2.49332 | 4.669958 | 0.273267 |
| H | -3.3707 | 4.849793 | -0.35507 |
| H | -1.91306 | 5.602698 | 0.293521 |

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| H | -2.84018 | 4.483528 | 1.295454 |
| :---: | :---: | :---: | :---: |
| C | -4.38285 | -0.08243 | -1.3985 |
| H | -4.67978 | -0.10249 | -2.45392 |
| H | -5.27782 | -0.30692 | -0.80586 |
| H | -3.66967 | -0.89276 | -1.24371 |
| C | -4.92121 | 2.267836 | 0.39691 |
| H | -4.87042 | 1.661676 | 1.306549 |
| H | -5.94212 | 2.175115 | 0.001263 |
| H | -4.77575 | 3.312072 | 0.683491 |
| C | -4.05649 | 2.72341 | -2.47986 |
| H | -3.90456 | 3.794359 | -2.31126 |
| H | -5.10696 | 2.58806 | -2.77027 |
| H | -3.43953 | 2.429896 | -3.33684 |
| C | 0.10645 | 3.383108 | 0.879886 |
| H | -0.25466 | 3.189658 | 1.895084 |
| H | 0.521259 | 4.399532 | 0.859276 |
| H | 0.942204 | 2.709114 | 0.679871 |
| C | 2.372632 | 1.389554 | -1.77473 |
| C | 4.26201 | 1.186712 | -3.35405 |
| H | 4.623422 | 2.112607 | -2.91432 |
| H | 4.240654 | 1.290596 | -4.44324 |
| H | 4.9395 | 0.368128 | -3.08578 |
| C | 2.296447 | -0.26265 | -3.57028 |
| H | 1.247937 | -0.32939 | -3.30633 |
| H | 2.80116 | -1.18915 | -3.28018 |
| H | 2.388381 | -0.11634 | -4.65052 |
| C | 3.128445 | 2.500924 | -1.09357 |
| C | 2.855343 | 3.834779 | -1.4244 |
| H | 2.098373 | 4.066125 | -2.16635 |
| C | 3.558299 | 4.865786 | -0.79962 |
| H | 3.34171 | 5.8982 | -1.05975 |
| C | 4.536229 | 4.571088 | 0.152678 |
| H | 5.081832 | 5.375032 | 0.639011 |
| C | 4.815851 | 3.241227 | 0.472841 |
| H | 5.580103 | 3.005991 | 1.208163 |
| C | 4.120308 | 2.2032 | -0.14967 |
| H | 4.341413 | 1.167814 | 0.084428 |
| C | -2.97849 | -2.66684 | -3.63047 |
| H | -3.00182 | -3.74641 | -3.44577 |
| H | -2.97495 | -2.52908 | -4.72063 |
| H | -3.90698 | -2.23678 | -3.24466 |
| C | -1.43311 | -0.07003 | -3.61112 |
| H | -2.42988 | 0.365652 | -3.50216 |
| H | -1.20468 | -0.10198 | -4.68483 |
| H | -0.72791 | 0.630523 | -3.15175 |
| C | 0.027638 | -2.78968 | -3.753 |

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Sum of electronic and thermal Free Energies $=-4537.318416$ Hartrees.

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## Chapter 6: <br> Use of ${ }^{13} \mathrm{C}$ NMR as an Indicator of Temperature Independent Paramagnetism in Uranium(VI) Complexes

### 6.1 Introduction.

Interest in organometallic uranium complexes developed in the 1950s for applications in isotope separations processes. Actinide organometallic complexes were expected to be volatile, in analogy with transition metal organometallic complexes. ${ }^{1,2}$ Since that time, a number of uranium(IV) alkyl complexes have been synthesized, supported by substituted cyclopentadienyl, ${ }^{3-}$ ${ }^{6}$ amide, ${ }^{7-10}$ alkoxide, ${ }^{11}$ phosphine, ${ }^{12,13}$ and homoleptic ligand frameworks. ${ }^{14-17}$ However, uranium alkyl complexes in the $+3,{ }^{18,19}+5,{ }^{20}$ and $+6^{10,20,21}$ oxidation states remain relatively scarce. Among the known organometallic uranium complexes are a number of uranium(IV) acetylide complexes. ${ }^{22-32}$ However, as in the chemistry of uranium alkyls, there are few examples of uranium acetylides in the other available oxidation states of uranium. ${ }^{10,25,33}$

Work from our group recently reported the first example of a uranium(VI) acetylide complex, $\mathrm{U}^{\mathrm{V} 1}(=\mathrm{O})(\mathrm{CCPh})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(6.2-\mathrm{H})$, stabilized through the inverse trans influence by the trans position of the phenyl(acetylide) ligand with respect to an oxo ligand. ${ }^{10}$ The axial U-C bond in this compound was short (2.337(14) Å) when compared with equatorial U-C bonds, as in the uranyl-alkyl complex reported by Hayton and coworkers, $\left[\mathrm{Li}(\mathrm{DME})_{1.5]_{2}}\left[\mathrm{U}^{\mathrm{VI}} \mathrm{O}_{2}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{4}\right]\right.$ (2.489(6) Å) (Figure 6.1.1). ${ }^{34}$ For equatorial U-C interactions with more dative bonding, as in
 longer bonds of $2.7935(17) \AA$ were observed. ${ }^{35}$ When comparing between this series of compounds, the ${ }^{13} \mathrm{C}$ NMR spectra reveal a large range of chemical shifts for the $\mathrm{U}-\mathrm{C}$ carbon atom, from 7 ppm for the long U-C bond $(2.7935(17) \mathrm{A})^{35}$ to 395 ppm for short $\mathrm{U}-\mathrm{C}$ bonds (Figure
6.1.1). ${ }^{10}$ The homoleptic alkyl compound, $U^{V 1}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{6}$, reported by Hayton and coworkers, has shown the most downfield shifted resonance, at 434 ppm , but has not been crystallized, so the $\mathrm{U}-\mathrm{C}$ bond lengths cannot be compared (Figure 6.1.1). ${ }^{20,34}$

Paramagnetic shifts of the $U(V I)-C$ carbon atom are observed, despite the $f^{0}$ electronic configuration of the uranium $(\mathrm{VI})$ ion. The origin of this chemical shift is the interaction with a weakly paramagnetic uranium $(\mathrm{VI})$ ion, due to temperature independent paramagnetism (TIP), which results from symmetry-allowed mixing of paramagnetic excited states with a diamagnetic ground state. ${ }^{36-38}$ This mixing results in a relativistic spin-orbit effect on the NMR shifts of atoms within a short radius of the uranium center. ${ }^{39-41}$






Figure 6.1.1 Selected previously reported uranium(VI) organometallic complexes, the U-C bond lengths ( $\AA$ ) and ${ }^{13} \mathrm{C}$ chemical shift of the $\mathrm{U}-\mathrm{C}$ carbon. ${ }^{10,20,34,35} \mathrm{~N}^{*}=\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}$

Previously, important information about bonding and electronic structure has been obtained from correlating experimental and computed ${ }^{77} \mathrm{Se}$ and ${ }^{125} \mathrm{Te}$ NMR shifts of high valent actinide complexes bearing actinide-chalcogen multiple bonds. ${ }^{41}$ Also, ${ }^{13} \mathrm{C}$ NMR has been used to examine the covalency of U-C bonds in two isolated uranium(VI) complexes, $\left[\mathrm{Li}(\mathrm{DME})_{1.5]_{2}}\left[\mathrm{U}^{\mathrm{VI}} \mathrm{O}_{2}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{4}\right]\right.$ and $\mathrm{U}^{\mathrm{V1}}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{6} .{ }^{34}$ It was found that $\mathrm{U}^{\mathrm{VI}}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{6}$ had increased uranium contribution to the $\mathrm{U}-\mathrm{C}$ bond compared with $\left[\mathrm{Li}(\mathrm{DME})_{1.5}\right]_{2}\left[\mathrm{U}^{\mathrm{VI}} \mathrm{O}_{2}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{4}\right]$, with contributions of 28.9 and $21.9 \%$ respectively. This was reflected in the chemical shift of the

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uranium-bound carbon, which was shifted downfield to 434 ppm for $\mathrm{U}^{\mathrm{VI}}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{6}$, compared with 243 for $\left[\mathrm{Li}(\mathrm{DME})_{1.5]_{2}}\left[\mathrm{U}^{\mathrm{VI}} \mathrm{O}_{2}\left(\mathrm{CH}_{2} \mathrm{SiMe}_{3}\right)_{4}\right]\right.$ (Figure 6.1.1) ${ }^{20,34}$

This data indicated that increased U-C covalency can be observed in the extent of the downfield chemical shift in ${ }^{13} \mathrm{C}$ NMR. However, few examples of uranium(VI) organometallic complexes have been isolated and prevent this observation from being substantiated. Herein, we present the synthesis and characterization of a series of uranium(VI) phenyl(acetylide) complexes with varying substitution in the para position, $\mathrm{U}^{\mathrm{Vl}}(=\mathrm{O})(\mathrm{CCPh}-\mathrm{R})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(\mathrm{R}=\mathrm{NMe}_{2}, \mathrm{OMe}, \mathrm{Me}\right.$, $\mathrm{Ph}, \mathrm{H}, \mathrm{Cl})(6.2-\mathrm{R})$. These complexes exhibited extreme downfield shifts of uranium-bound acetylide carbon, U-C=C-Ar, ranging from 409.7 to 392.1 ppm, correlating well with computed U-C bond lengths and Mayer bond orders, which vary slightly due to the identity of the para substituent.

### 6.2 Results and Discussion.

### 6.2.1 Synthesis of Uranium(VI) Complexes.

Previously, compound 6.2-H had been synthesized and reported by our group (Figure 6.2.1). ${ }^{10}$ The synthesis of $6.2-\mathrm{H}$ was accomplished by reaction of $\mathrm{U}^{111}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with CuCCPh in a solution of diethyl ether. This reaction generated the uranium(IV) phenyl(acetylide) complex, $U^{\text {IV }}(\mathrm{CCPh})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(6.1-\mathrm{H})$, which was filtered before reaction with N -methylmorpholine N oxide, an oxygen-atom transfer reagent, to yield 6.2-H in 59\% crystalline yield. In the work done previously by our group, the intermediate complex, 6.1-H, had not been crystallized. However, we crystallized 6.1-H from a concentrated solution of hexanes (Scheme 6.2.1). Compared with 6.2-H, 6.1-H had an identical U-C末C bond angle, with angles of 177.2(7) and 177.6(2) degrees, respectively. The average $\mathrm{U}-\mathrm{N}$ bond length for $6.1-\mathrm{H}$ was slightly longer than those of $6.2-\mathrm{H}$, with bond lengths of $2.2398(18)$ and $2.207(6) \AA$, respectively, due to the larger radius of the $\mathrm{U}(\mathrm{IV})$ ion. The U-C bond length of $6.1-\mathrm{H}$, however, was not statistically different from that of $6.2-\mathrm{H}$, with bond lengths of $2.367(2)$ and 2.337 (14) $\AA$, respectively.


Scheme 6.2.1 Synthesis of uranium(VI) oxo phenyl(acetylide) complexes (6.2-R).


Figure 6.2.1 Thermal ellipsoid plot of 6.1-H at $50 \%$ probability. All hydrogen atoms and amide methyl groups omitted for clarity. Bond lengths ( $\AA$ ) and angles (deg): $\mathrm{U}(1)-\mathrm{C}(19)$ 2.367(2), U(1)$\mathrm{N}(1) 2.2445(18), \mathrm{U}(1)-\mathrm{N}(2) 2.2311(18), \mathrm{U}(1)-\mathrm{N}(3) 2.2439(19), \mathrm{C}(19)-\mathrm{C}(20) 1.218(3), \mathrm{U}(1)-$ C(19)-C(20) 177.6(2).

To generate our library of uranium(VI) phenyl(acetylide) complexes with varying substituents in the para position, we employed a similar synthetic strategy to that used in the synthesis of $6.2-\mathrm{H}$. We synthesized copper(I) phenyl(acetylides) by a literature procedure in which Cul is reacted with para substituted terminal phenyl(alkynes) in an ammonia/ethanol mixed solvent system. ${ }^{42}$ The resulting yellow powders were isolated and washed with copious ammonia, water, and ethanol before drying at $60^{\circ} \mathrm{C}$ under reduced pressure for 24 h . The resulting
powders were reacted with $U^{\text {III }}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ in a solution of diethyl ether for 2 h to generate the uranium(IV) phenyl(acetylide) complexes, $\mathrm{U}^{\mathrm{IV}}(\mathrm{CCPh}-\mathrm{R})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(\mathrm{R}=\mathrm{NMe}_{2}, \mathrm{OMe}, \mathrm{Me}, \mathrm{Ph}, \mathrm{Cl}\right)$ (6.1-R). In contrast to the synthesis of $6.1-\mathbf{H}$, filtration of the diethyl ether solution was not sufficient for removal of the copper $(0)$ side product and coper $(\mathrm{I})$ starting material from the reaction mixtures with -OMe, -Me, and -Ph para phenyl(acetylide) substituents. In these cases, volatiles were removed, and complexes $6.1-\mathrm{R}(\mathrm{R}=\mathrm{OMe}, \mathrm{Me}, \mathrm{Ph})$ were extracted with hexanes and filtered over Celite. Subsequently, the 6.1-R ( $\mathrm{R}=\mathrm{NMe}_{2}, \mathrm{OMe}, \mathrm{Me}, \mathrm{Ph}, \mathrm{Cl}$ ) compounds were reacted with $N$-methylmorpholine $N$-oxide in diethyl ether to generate $\mathbf{6 . 2 - R}\left(\mathrm{R}=\mathrm{NMe}_{2}, \mathrm{OMe}, \mathrm{Me}\right.$, $\mathrm{Ph}, \mathrm{Cl})$ complexes in low to moderate crystalline yields of $3-28 \%$. The low yields were due mainly to isolation of the products, which were very soluble in organic solvents.

In most cases we did not structurally characterize the uranium(IV) 6.1-R complexes, since we were more interested in their uranium $(\mathrm{VI})$ counterparts. However, for 6.1-Ph a crystal structure was obtained (Figure 6.2.2). Compound 6.1-Ph had statistically indistinguishable average $U-N, U-C$, and $C \equiv C$ bond lengths from 6.1-H. However, the $U-C \equiv C$ bond angle was significantly more bent in 6.1-Ph with an angle of 167.8(6) degrees compared with 177.6(2) for 6.1-H.


Figure 6.2.2 Thermal ellipsoid plot of 6.1-Ph at $50 \%$ probability. All hydrogen atoms and amide methyl groups omitted for clarity. Bond lengths ( $\AA$ ) and angles (deg): U(1)-C(19) 2.372(7), U(1)$\mathrm{N}(1) 2.218(5), \mathrm{U}(1)-\mathrm{N}(2) 2.237(6), \mathrm{U}(1)-\mathrm{N}(3) 2.236(5), \mathrm{C}(19)-\mathrm{C}(20) 1.219(10), \mathrm{U}(1)-\mathrm{C}(19)-$ C(20) 167.8(6).

Compounds 6.2-R ( $\mathrm{R}=\mathrm{NMe}_{2}$, $\mathrm{OM}, \mathrm{Me}, \mathrm{Ph}, \mathrm{H}, \mathrm{Cl}$ ) were characterized by ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectroscopy. The ${ }^{1} \mathrm{H}$ NMR spectra appeared within the standard diamagnetic window, with two sets of aryl peaks, ranging from 7.34 and 6.19 for $\mathbf{6 . 2} \mathbf{N M e}_{2}$ to 7.15 and 6.88 for $\mathbf{6 . 2 - C I}$. The $\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}$ ligands appeared as two peaks in the ${ }^{1} \mathrm{H}$ NMR spectra for $6.2-\mathrm{R}$ complexes due to hindered rotation along the $\mathrm{U}-\mathrm{N}$ bond. These peaks ranged from 0.77 and 0.72 ppm for $\mathbf{6 . 2 - \mathbf { N M e } _ { 2 }}$ to 0.68 and 0.65 ppm for $6.2-\mathrm{Cl}$. These chemical shifts agreed well with those in the reported ${ }^{1} \mathrm{H}$ spectrum for $6.2-\mathrm{H}$, which had two aryl peaks at 7.44 and 6.95 ppm . However, in $6.2-\mathrm{H}$ the bis(trimethylsilyl)amide ligands were coincident at $0.70 \mathrm{ppm} .^{10}$

However, the ${ }^{13} \mathrm{C}$ NMR spectra for $6.2-\mathrm{R}\left(\mathrm{R}=\mathrm{NMe}_{2}\right.$, $\left.\mathrm{OMe}, \mathrm{Me}, \mathrm{Ph}, \mathrm{H}, \mathrm{Cl}\right)$ complexes showed isotropic shifts for atoms in close contact with the uranium center. The acetylide carbons

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not directly bound to the uranium center, $U-C \equiv C-A r$, were slightly shifted, when compared with the chemical shifts in the free alkynes, and appeared between 103.34-103.90 ppm for 6.2-R compounds. In the ${ }^{13} \mathrm{C}$ NMR of the free alkynes the secondary carbon, $\mathrm{H}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ar}$, ranged from 83-85 ppm for all compounds, showing isotropic shifts of approximately 19 ppm in the $\mathbf{6 . 2 - R}$ complexes. The acetylide carbons directly bound to the uranium centers, however, were dramatically shifted from their chemical shifts in the free alkynes. The $\mathrm{H}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ar}$ carbon resonances in the alkynes ranged from $79-76 \mathrm{ppm}$ for the -Cl and $-\mathrm{NMe}_{2}$ substituted alkynes, respectively. In 6.2-R complexes, isotropic shifts of approximately 325 ppm were observed, with chemical shifts for the $U-C \equiv C-A r$ carbon atom ranging from 409.7 to 392.1 ppm for $\mathbf{6 . 2 - \mathbf { N M e } _ { 2 }}$ and 6.2-CI, respectively (Figure 6.2.3).


Figure 6.2.3 Excerpt of ${ }^{13} \mathrm{C}$ NMR spectra of $6.2-\mathrm{R}\left(\mathrm{R}=\mathrm{NMe}_{2}, \mathrm{OMe}, \mathrm{Me}, \mathrm{Ph}, \mathrm{H}, \mathrm{Cl}\right)$ complexes in benzene- $d_{6}$ showing the chemical shifts (ppm) of the acetylide carbon, $\mathrm{U}-\mathrm{C}$.

In the ${ }^{13} \mathrm{C}$ NMR spectra of the free alkynes, the chemical shift of the primary carbon, $\mathrm{H}_{-}$ $C \equiv C-A r$, correlated with the Hammett parameters with an $R^{2}$ value of 0.900 (Figure 6.2.4, top). The chemical shifts of the uranium-bound carbon, $\mathrm{U}-\mathrm{C}=\mathrm{C}-\mathrm{Ar}$, in $6.2-\mathrm{R}$ complexes also trended well with the Hammett parameters $\left(\sigma_{p}\right)$ for the substituents, with an $R^{2}$ value of 0.996 (Figure 6.2.4, bottom). ${ }^{43}$ Although the ${ }^{13} \mathrm{C}$ NMR shifts correlated with the Hammett parameters for both the free alkynes and 6.2-R complexes, the trends were in opposing directions. For the simple organic alkynes, the conventional trend in which electron donating groups shield and electron withdrawing groups deshield nearby groups was observed. However, in the uranium complexes the substituents with increased electronic donation shifted the acetylide carbon, $\mathrm{U}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ar}$,
downfield. We hypothesized that this was because with more donating para substituents the U-C bond length was shortened, thus shifting the acetylide carbon resonance downfield as it had an increased interaction with the weakly paramagnetic uranium(VI) center (vide infra).


Figure 6.2.4 Correlation of the chemical shifts of the free alkynes, $\mathrm{HCCPh}-\mathrm{R}\left(\mathrm{R}=\mathrm{NMe}_{2}\right.$, OMe , $\mathrm{Me}, \mathrm{H}, \mathrm{Ph}, \mathrm{Cl}$ ) with the Hammett Parameter ( $\sigma_{\mathrm{p}}$ ) showing an $\mathrm{R}^{2}$ value of 0.901 (top). Correlation of the chemical shifts of $\mathrm{U}-\mathrm{C}$ acetylide carbon for $6.2-\mathrm{R}\left(\mathrm{R}=\mathrm{NMe}_{2}, \mathrm{OMe}, \mathrm{Me}, \mathrm{H}, \mathrm{Ph}, \mathrm{Cl}\right)$ complexes with the Hammett Parameter ( $\sigma_{p}$ ) showing an $R^{2}$ value of 0.996 (bottom).

We then structurally characterized the series of uranium(VI) oxo acetylide complexes, 6.2-R $\left(\mathrm{R}=\mathrm{NMe}_{2}, \mathrm{OMe}, \mathrm{Me}, \mathrm{Ph}, \mathrm{Cl}\right)$, and compared these substituted derivatives to $6.2-\mathrm{H}$, which was reported previously (Figures 6.2.5-6.2.9, Table 6.2.1). ${ }^{10}$ The $U-O$ and $U-N$ bond lengths for 6.2-H were $1.811(10)$ and $2.201(6) ~ \AA$, respectively, and were crystallographically indistinguishable across the $\mathbf{6 . 2 - R}$ series of compounds. The $\mathrm{O}-\mathrm{U}-\mathrm{C}$ bond angle did vary slightly within the series, but with no clear trend. Electron-donating and electron-withdrawing substituents both had near linear $\mathrm{O}-\mathrm{U}-\mathrm{C}$ angles of 178.91 (14) and $179.20(9)$ degrees, for $\mathbf{6 . 2 - N M e} \mathbf{2}_{2}$ and 6.2CI, respectively. However, 6.2-H had a slightly bent $\mathrm{O}-\mathrm{U}-\mathrm{C}$ bond angle of 177.2(7) degrees. Also, the U-C-C bond angle was noticeably more bent for $6.2-\mathrm{NMe}_{2}$ at $173.4(4)$ degrees, while for 6.2-H the U-C-C bond angle was $176.9(14)$ degrees and not statistically different from the rest of the compounds in the series.


Figure 6.2.5 Thermal ellipsoid plot of 6.2-NMe ${ }_{2}$ at $50 \%$ probability. All hydrogen atoms and amide methyl groups omitted for clarity. Bond lengths ( $\AA$ ) and angles (deg): $\mathrm{U}(1)-\mathrm{O}(1) 1.819(3), \mathrm{U}(1)-$ $\mathrm{C}(19) 2.279(4), \mathrm{U}(1)-\mathrm{N}(1)$ 2.194(3), $\mathrm{U}(1)-\mathrm{N}(2)$ 2.209(3), U(1)-N(3)2.223(3), C(19)-C(20) 1.227(6), $\mathrm{O}(1)-\mathrm{U}(1)-\mathrm{C}(19)$ 178.91(14), U(1)-C(19)-C(20) 173.4(4).


Figure 6.2.6 Thermal ellipsoid plot of 6.2-OMe at $50 \%$ probability. All hydrogen atoms and amide methyl groups omitted for clarity. Bond lengths ( $\AA \AA$ ) and angles (deg): $\mathrm{U}(1)-\mathrm{O}(1) 1.8121$ (15), $\mathrm{U}(1)-$ $\mathrm{C}(19)$ 2.316(2), $\mathrm{U}(1)-\mathrm{N}(1) 2.2079(17), \mathrm{U}(1)-\mathrm{N}(2) 2.2124(18), \mathrm{U}(1)-\mathrm{N}(3) 2.2012(17), \mathrm{C}(19)-\mathrm{C}(20)$ 1.209(3), O(1)-U(1)-C(19) 179.89(8), U(1)-C(19)-C(20) 176.18(19).


Figure 6.2.7 Thermal ellipsoid plot of 6.2-Me at $50 \%$ probability. All hydrogen atoms and amide methyl groups omitted for clarity. Bond lengths ( $\AA$ ) and angles (deg): U(1)-O(1) 1.811(7), U(1)$\mathrm{C}(19) 2.313(11), \mathrm{U}(1)-\mathrm{N}(1) 2.210(9), \mathrm{U}(1)-\mathrm{N}(2)$ 2.203(8), $\mathrm{U}(1)-\mathrm{N}(3) 2.211(8), \mathrm{C}(19)-\mathrm{C}(20)$ 1.208(14), O(1)-U(1)-C(19) 179.3(4), U(1)-C(19)-C(20) 176.0(9).


Figure 6.2.8 Thermal ellipsoid plots of 6.2-Ph at $50 \%$ probability. All hydrogen atoms, amide methyl groups, and disorder of omitted for clarity. Bond lengths ( $\AA$ ) and angles (deg): $\mathrm{U}(1)-\mathrm{O}(1)$ $1.8013(16), \mathrm{U}(1)-\mathrm{C}(19)$ 2.303(2), $\mathrm{U}(1)-\mathrm{N}(1) \quad 2.2010(17), \mathrm{U}(1)-\mathrm{N}(2) 2.2128(18), \mathrm{U}(1)-\mathrm{N}(3)$ $2.1985(18), \mathrm{C}(19)-\mathrm{C}(20) 1.217(3), \mathrm{O}(1)-\mathrm{U}(1)-\mathrm{C}(19) 179.73(8), \mathrm{U}(1)-\mathrm{C}(19)-\mathrm{C}(20) 176.7(2)$.


Figure 6.2.9 Thermal ellipsoid plots of $6.2-\mathrm{Cl}$ at $50 \%$ probability. All hydrogen atoms, amide methyl groups, and disorder of omitted for clarity. Bond lengths ( $\AA$ ) and angles (deg): $\mathrm{U}(1)-\mathrm{O}(1)$ $1.7989(18), \mathrm{U}(1)-\mathrm{C}(19) 2.315(3), \mathrm{U}(1)-\mathrm{N}(1) 2.195(2), \mathrm{U}(1)-\mathrm{N}(2) 2.208(2), \mathrm{U}(1)-\mathrm{N}(3) 2.200(2)$, $\mathrm{C}(19)-\mathrm{C}(20) 1.217(4), \mathrm{O}(1)-\mathrm{U}(1)-\mathrm{C}(19) 179.20(9), \mathrm{U}(1)-\mathrm{C}(19)-\mathrm{C}(20) 175.3(2)$.

Table 6.2.1 Experimental bond lengths ( $\AA$ ) and angles (deg) for 6.2-R complexes. The data for 6.2-H was reported previously. ${ }^{10}$

| Compound | Bond Lengths (Å) |  |  |  |  | Bond Angles (deg) |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | U-O | Avg. U-N | U-C | CEC | O-U-C | U-C-C |  |
| 6.2-NMe | $1.819(3)$ | $2.209(3)$ | $2.279(4)$ | $1.227(6)$ | $178.91(14)$ | $173.4(4)$ |  |
| 6.2-OMe | $1.8121(15)$ | $2.2072(17)$ | $2.316(2)$ | $1.209(3)$ | $179.89(8)$ | $176.18(19)$ |  |
| 6.2-Me | $1.811(7)$ | $2.208(8)$ | $2.313(11)$ | $1.208(14)$ | $179.3(4)$ | $176.0(9)$ |  |
| 6.2-Ph | $1.8013(16)$ | $2.2041(18)$ | $2.303(2)$ | $1.217(3)$ | $179.73(8)$ | $176.7(2)$ |  |
| 6.2-H | $1.811(10)$ | $2.201(6)$ | $2.337(14)$ | $1.209(1)$ | $177.2(7)$ | $176.9(14)$ |  |
| 6.2-Cl | $1.7989(18)$ | $2.201(2)$ | $2.315(3)$ | $1.217(4)$ | $179.20(9)$ | $175.3(2)$ |  |

The $\mathrm{U}(1)-\mathrm{C}(19)$ bond lengths were of special interest to us because we had hypothesized that the downfield shift of the acetylide carbons, $\mathrm{U}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ar}$, in complexes with electron-donating substituents was due to shortened U-C bonds for these complexes. Although the X -ray data was not of sufficient quality to distinguish between the majority of the $\mathrm{U}-\mathrm{C}$ bond lengths, a statistical difference was observed for the U-C bond length of $6.2-\mathrm{NMe}_{2}$, which was short (2.279(4) $\AA$ ) in comparison with the U-C bond lengths of $6.2-\mathrm{OMe}, 6.2-\mathrm{Ph}, 6.2-\mathrm{H}$, and $6.2-$ CI, which were $2.316(2), 2.303(2), 2.337(14)$, and $2.315(3) \AA$, respectively. Presumably, the downfield shift of the acetylide carbon of $6.2-\mathrm{NMe}_{2}$ to 410 ppm was the result of this short U-C bond length. However, when the experimental U-C bond lengths were correlated with the ${ }^{13} \mathrm{C}$ NMR resonance of the acetylide ligand, a poor $R^{2}$ value of 0.595 was obtained, due to the large standard deviations on the experimental $\mathrm{U}-\mathrm{C}$ bond lengths (Figure 6.2.10).


Figure 6.2.10 Experimental U-C bond lengths ( $\AA$ ) for $6.2-\mathrm{R}$ complexes plotted versus the ${ }^{13} \mathrm{C}$ resonance of the acetylide carbon, $\mathrm{U}-\mathrm{C}(\mathrm{ppm})$. Three standard deviations from the bond lengths are shown as error bars. This data is fit with a linear correlation with an $R^{2}$ value of 0.595 .

To ascertain that the difference we observed in the U-C bond length of 6.2-NMe $\mathbf{N}_{2}$ compared with the other 6.2-R complexes was not the result of crystal packing forces we carried out DFT calculations on the series of 6.2-R complexes. Hybrid DFT with the B3LYP functional using a 60 electron effective core potential applied to uranium, ${ }^{44}$ and the $6-31 \mathrm{G}^{*}$ basis set for all other atoms. The computed bond lengths agreed well with the experimental bond lengths and showed trends that were too subtle to observe in the experimental bond lengths (Table 6.2.2).

Table 6.2.2 Experimental and calculated bond lengths for 6.2-R complexes ( $\AA$ ).

| Compound | U-O |  | U-N (avg.) |  | U-C |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
|  | exp | calcd. | exp. | calcd. | exp. | calcd. |
| 6.2-NMe | $1.819(3)$ | 1.794 | $2.209(3)$ | 2.242 | $2.279(4)$ | 2.307 |
| 6.2-OMe | $1.8121(15)$ | 1.794 | $2.2072(17)$ | 2.238 | $2.316(2)$ | 2.319 |
| 6.2-Me | $1.811(7)$ | 1.795 | $2.208(8)$ | 2.235 | $2.313(11)$ | 2.329 |
| 6.2-Ph | $1.8013(16)$ | 1.795 | $2.2041(18)$ | 2.235 | $2.303(2)$ | 2.330 |
| 6.2-H | $1.811(10)$ | 1.795 | $2.201(6)$ | 2.235 | $2.337(14)$ | 2.332 |
| 6.2-CI | $1.7989(18)$ | 1.795 | $2.201(2)$ | 2.233 | $2.315(3)$ | 2.342 |

By examining the computed bond lengths, we found that $6.2-\mathrm{NMe}_{2}$ had the shortest $\mathrm{U}-\mathrm{C}$ bond length of the $6.2-\mathrm{R}$ series. When examining the entire series of computed U-C bond lengths, a trend was observed in which the U-C bond shortened as donating ability of the para substituent increased. At the most extreme ends of the series $6.2-\mathrm{NMe}_{2}$ had a computed U-C bond length of $2.307 \AA$, while $6.2-\mathbf{C l}$ had a computed bond length of $2.342 \AA$. When the calculated U-C bond lengths were plotted against the experimental ${ }^{13} \mathrm{C}$ NMR acetylide resonances, they showed moderately good agreement with an $R^{2}$ value of 0.942 (Figure 6.2.11). The correlation between calculated U-C bond lengths and experimental ${ }^{13} \mathrm{C}$ NMR resonances and the good correlation between experimental ${ }^{13} \mathrm{C}$ NMR resonances and Hammett parameters of the para substituent (Figure 6.2.4, bottom) supported our hypothesis that with increased electron donation from the substituted phenyl(acetylide) ligand, the $\mathrm{U}-\mathrm{C}$ bond shortened, which in turn shifted the ${ }^{13} \mathrm{C}$ NMR resonance of the acetylide carbon downfield due to its increased interaction with the weakly paramagnetic uranium(VI) ion.


Figure 6.2.11 Calculated $U-C$ bond lengths ( $\AA$ ) plotted versus the experimental ${ }^{13} \mathrm{C}$ NMR resonances of the acetylide carbon (ppm) showing an $R^{2}$ value of 0.942 .

Concurrent with the shortened U-C bonds for compounds with electron-donating substituents, the computed bond lengths showed that $\mathrm{U}-\mathrm{N}$ (avg.) bonds lengthened slightly (Table 6.2.2). While this trend was subtle and U-N bond lengths only varied from 2.242 to 2.233 $\AA$ for $6.2-\mathrm{NMe}_{2}$ and $6.2-\mathrm{CI}$, respectively, there was good correlation with the experimental ${ }^{13} \mathrm{C}$ NMR shifts of the acetylide carbon, $\mathrm{U}-\mathrm{C} \equiv \mathrm{C}-\mathrm{Ar}$, with an $\mathrm{R}^{2}$ value of 0.957 (Figure 6.2.12). It has been established previously that equatorial ligand destabilization occurs in high-valent uranium complexes with strong axial donors through the inverse trans influence. ${ }^{\mathbf{1 0 , 4 5 - 4 7}}$ For example, our group previously investigated compounds of the general structure, $\mathrm{U}^{\mathrm{VI}}(=\mathrm{O}) \mathrm{R}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, and observed that the calculated $U-N$ bond length varied from 2.211 to $2.292 \AA$ for $R=C N$ and $N e_{2}$ complexes, respectively. ${ }^{10}$


Figure 6.2.12. Calculated U-N (avg.) bond lengths ( $\AA$ ) plotted versus the experimental ${ }^{13} \mathrm{C}$ NMR chemical shifts of the acetylide carbon (ppm) showing an $R^{2}$ value of 0.957 .

We also performed NBO 6.0 calculations on the $6.2-\mathbf{R}$ series of compounds and investigated the calculated Mayer bond orders as an additional way of examining the differences in electronic structure (Table 6.2.3). We compared Mayer bond orders for the uranium-acetylide bonding for the compound with the shortest $\mathrm{U}-\mathrm{C}$ bond, $6.2-\mathrm{NMe}_{2}$ with those of the parent compound, 6.2-H (Figure 6.2.13, left). The U-C bond order was higher, at 1.02, for $6.2-\mathrm{NMe}_{2}$, compared with 0.97 for $6.2-\mathrm{H}$. The bond order for the $\mathrm{C} \equiv \mathrm{C}$ bond was also decreased for $6.2-$ $\mathbf{N M e}_{2}$ compared with $6.2-\mathrm{H}$, which had bond orders of 2.27 and 2.33 , respectively. The aryl ring of $6.2-\mathrm{NMe}_{2}$ showed evidence of partial dearomatization, and had four $\mathrm{C}-\mathrm{C}$ bonds of low bond order, averaging 1.35, and two C-C bonds of higher bond order, averaging 1.48 (Table 6.2.3). In contrast, for $6.2-\mathrm{H}$ most of the $\mathrm{C}-\mathrm{C}$ bonds of the aryl ring had identical bond orders, averaging 1.42 with a small standard deviation of 0.03 (compared with 0.07 for $6.2-\mathrm{NMe}_{2}$ ). The bonding of 6.2-NMe ${ }_{2}$ was rationalized as having minor contribution from a uranium-allene electronic structure (Figure 6.2.13, right).

Table 6.2.3 Mayer bond orders for 6.2-R complexes.

| $\mathbf{R}$ | U=O | U-C | C三C | Ar C-C <br> (avg.) | Ar C-C <br> (std dev.) |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{NMe}_{2}$ | 1.94 | 1.02 | 2.27 | 1.39 | 0.07 |
| OMe | 1.94 | 0.99 | 2.30 | 1.40 | 0.05 |
| Me | 1.94 | 0.98 | 2.32 | 1.41 | 0.02 |
| Ph | 1.94 | 0.97 | 2.32 | 1.40 | 0.02 |
| H | 1.94 | 0.97 | 2.33 | 1.42 | 0.03 |
| Cl | 1.94 | 0.95 | 2.34 | 1.41 | 0.02 |



Figure 6.2.13 Calculated Mayer bond orders for 6.2- $\mathrm{NMe}_{2}$ (green) compared with those of $\mathbf{6 . 2 - H}$ (black) shown below (left). Neutral uranium-acetylide (major contribution) and charge separated uranium-allene (minor contributor) resonance structures contributing to $6.2-\mathrm{NMe}_{2}$.

### 6.2.2 Electronic Structure of Uranium(VI) Oxo Acetylide Complexes.

Compounds 6.2-R ( $\left.\mathrm{R}=\mathrm{NMe}_{2}, \mathrm{OMe}, \mathrm{Me}, \mathrm{Ph}, \mathrm{H}, \mathrm{Cl}\right)$ were characterized by solution electrochemistry (Figure 6.2.14). These compounds were not stable for extended time in
electrochemical conditions. However, cyclic voltammograms were able to be collected in THF with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ supporting electrolyte. Uranium $(\mathrm{V} / \mathrm{VI})$ couples ranged from -0.47 to -0.61 for compounds 6.2-CI and 6.2-NMe 2 , respectively (Table 6.2.4).


Figure 6.2.14 Cyclic voltammograms of 6.2-R complexes in THF with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ supporting electrolyte at a scan rate of $250 \mathrm{mV} / \mathrm{s}$.

Table 6.2.4 $\mathrm{E}_{1 / 2}$ values $(\mathrm{V})$ vs. $\mathrm{Fc}^{+/ 0}$ for uranium $(\mathrm{V} / \mathrm{VI})$ and amine ${ }^{+/ 0}$ couples for 6.2-R complexes.

|  | $\mathbf{E}_{1 / 2}(\mathbf{V}) \mathbf{v s} . \mathrm{Fc}^{+/ 0}$ |  |
| :--- | :---: | :---: |
|  | $\mathbf{U}(\mathbf{V} / \mathbf{V I})$ | Amine $^{+/ 0}$ |
| $\mathrm{NMe}_{2}$ | -0.61 | +0.52 |
| OMe | -0.56 | -- |
| Me | -0.56 | -- |
| Ph | -0.50 | -- |
| H | -0.49 | -- |
| Cl | -0.47 | -- |

The 140 mV range of $\mathrm{E}_{1 / 2}$ values for the compounds showed some correlation with the Hammett parameters for the para substituents, with an $R^{2}$ value of 0.885 (Figure 6.2.15). The stabilization of the +6 oxidation state for $\mathbf{6 . 2}-\mathrm{NMe}_{2}$ further indicated that the electron-donating
substituent, $-\mathrm{NMe}_{2}$, was able to increase the electron density at the uranium center by electronic donation through the acetylide ligand.


Figure 6.2.15 Correlation between the $\mathrm{E}_{1 / 2}$ of the uranium $(\mathrm{V} / \mathrm{VI})$ couple and the Hammett parameter, showing a linear relationship with an $R^{2}$ value of 0.885 .

Previously, other structurally related series of high-valent uranium complexes have been synthesized and characterized electrochemically. For example, Kiplinger and Graves developed a series of uranium $(\mathrm{V})$-imido halide complexes of the general formula, $\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)_{2} \mathrm{U}^{\vee}(=\mathrm{NAr}) \mathrm{X}(\mathrm{Ar}=$ 2,6- ${ }^{\prime} \mathrm{Pr}_{2}-\mathrm{C}_{6} \mathrm{H}_{3}$ ), where $\mathrm{X}=\mathrm{F}, \mathrm{Cl}, \mathrm{Br}, \mathrm{I}, \mathrm{OTf}$, SPh, CCPh, NPh, OPh , Me, and $\mathrm{NCPh}_{2}$. Within this series of compounds, the halide compounds exhibited $E_{1 / 2}$ values for the $U(V / V I)$ couple ranging from -0.14 to +0.11 V versus $\mathrm{Fc}^{+/ 0}$, for F and I ligands, respectively. ${ }^{48,49}$ In this series the halide ligands were directly bound to the uranium center, and shifted the $\mathrm{U}(\mathrm{V} / \mathrm{VI})$ couple by 250 mV , so it is noteworthy that in our complexes a distal aryl substituent changed the $\mathrm{U}(\mathrm{V} / \mathrm{VI})$ couple by 140 mV .

We then collected magnetic susceptibility data for compounds $\mathbf{6 . 2 - \mathbf { N M e } _ { 2 }}$ and $\mathbf{6 . 2 - C l}$ to measure the Van Vleck temperature independent paramagnetism (TIP) of the complexes (Figure 6.2.16). We collected field dependent magnetic data at 2 K (Figure 6.2.16, bottom), which
revealed that $6.2-\mathrm{Cl}$ contained no paramagnetic impurities, and saturated at $0.001 \mu_{\mathrm{B}}$ at 7 Tesla. Compound 6.2-NMe 2 had only a slight paramagnetic impurity, which caused it to saturate at 0.024 $\mu_{\mathrm{B}}$ at 7 Tesla. In the temperature dependent data, both compounds showed a linear relationship between XT and temperature, with small positive slopes, indicative of temperature independent paramagnetism. ${ }^{50}$ The slight paramagnetic impurity that contaminated 6.2-NMe ${ }_{2}$ accounted for a slight deviation from linearity below 150 K (Figure 6.2.16, top). This resulted in a linear fit for 6.2$\mathbf{N M e}_{2}$ with an $R^{2}$ value of 0.943 . Compound $\mathbf{6 . 2 - C l}$, however, showed a strong linear relationship between XT and temperature, with an $R^{2}$ value of 0.998 . Both complexes showed similar values for $\mathrm{X}_{\text {TIP }}$ of 0.0005 and 0.0006 XT for $6.2-\mathrm{NMe}_{2}$ and $\mathbf{6 . 2 - \mathrm { CI }}$, respectively.



Figure 6.2.16 Variable-temperature magnetic susceptibility (XT) data for 6.2-NMe ${ }_{2}$ (blue) and 6.2$\mathbf{C l}$ (purple) collected at 1 Tesla (top). Variable field data collected for $6.2-\mathrm{NMe}_{2}$ (blue) and $6.2-\mathrm{Cl}$ (purple) at 2 K (bottom).

### 6.3 Summary.

We have synthesized a series of uranium(VI) oxo acetylide complexes of the general formula, $\mathrm{U}^{\mathrm{VI}}(=\mathrm{O})(\mathrm{CCPh}-\mathrm{R})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(\mathrm{R}=\mathrm{NMe}_{2}, \mathrm{OMe}, \mathrm{Me}, \mathrm{Ph}, \mathrm{H}, \mathrm{Cl}\right)$. Correlation of structural data with the Hammett parameters of the para substituent showed that electron donating groups slightly shortened the U-C bond. This resulted in a correlation between the paramagnetically shifted ${ }^{13} \mathrm{C}$ NMR resonance of the acetylide ligand in which the compounds with strong donors in the para position had increased interaction between the uranium center and acetylide carbon, which increased the isotropic shifts of those carbons. This isotropic shift was due to the Van Vleck temperature independent paramagnetism of the uranium(VI) center, which we measured using SQUID magnetometry. Electrochemical data confirmed that the para substituent on the phenyl(acetylide) ligand affected the electron density at the uranium center, showing a range of

140 mV for the $\mathrm{U}(\mathrm{V} / \mathrm{VI})$ couple, which correlated well with the Hammett parameters of the substituents.

### 6.4 Experimental.

### 6.4.1 Methods.

All reactions and manipulations were performed under an inert atmosphere ( $\mathrm{N}_{2}$ ) using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at $150{ }^{\circ} \mathrm{C}$ prior to use. Unless otherwise noted, reactions were conducted in 20 mL scintillation vials in approximately $5-10 \mathrm{~mL}$ of solvent. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR were obtained on a Bruker DRX-500 Fourier transform NMR spectrometer at 500 MHz . Chemical shifts were recorded in units of parts per million downfield from residual proteo solvent peaks. Elemental analyses were performed at Complete Analysis Laboratories, Inc. (Parsippany, NJ) and at the University of Pennsylvania in the Earth \& Environmental Science department on a Costech ECS 4010 analyzer. The infrared spectra were obtained from $400-4000 \mathrm{~cm}^{-1}$ using a Perkin Elmer 1600 series infrared spectrometer.

### 6.4.2 Materials.

Tetrahydrofuran, $\mathrm{Et}_{2} \mathrm{O}, \mathrm{CH}_{2} \mathrm{Cl}_{2}$, hexanes, pentane, and toluene were purchased from Fisher Scientific. These solvents were sparged for 20 min with dry argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina, respectively (for hexanes and pentane), or two columns of neutral alumina (for $\mathrm{THF}, \mathrm{Et}_{2} \mathrm{O}$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ). All solvents were stored over $3 \AA$ molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and stored over potassium mirror overnight prior to use. Starting materials: $\mathrm{Ul}_{3}(\mathrm{THF})_{4},{ }^{51} \mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3},{ }^{52}$ and $\mathbf{6 . 2 - H}{ }^{10}$ were prepared according to the reported procedures. Substituted copper(I) acetylide compounds were prepared according to the literature procedure to prepare copper(I) phenyl acetylide. ${ }^{42}$ Substituted alkynes were purchased from Fisher and used without further purification and the prepared
copper $(\mathrm{I})$ acetylides were washed with excess ammonia, water, and ethanol and dried at $60^{\circ} \mathrm{C}$ under reduced pressure for 24 h before use.

### 6.4.3 $\mathrm{U}^{\mathrm{VI}} \mathrm{O}\left(\mathrm{CCPh}-\mathrm{NMe}_{2}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(6.2-\mathrm{NMe}_{2}\right)$.

To a stirred solution of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(200 \mathrm{mg}, 0.28 \mathrm{mmol}, 1.0$ eqiv $)$ in $\mathrm{Et}_{2} \mathrm{O}$ was added [(4-(dimethylamino)phenyl)ethynyl]copper ( $115 \mathrm{mg}, 0.56 \mathrm{mmol}, 2.0$ equiv). The mixture was stirred for 2 h and filtered over Celite. N -Methylmorpholine N -oxide ( $33 \mathrm{mg}, 0.28 \mathrm{mmol}, 1.0$ equiv) was added, resulting in an immediate color change to dark red. After being stirred for 1 h , the volatiles were removed under reduced pressure. The resulting black residue was extracted with hexanes, filtered over Celite, and stored at $-21^{\circ} \mathrm{C}$ to give black crystals. Yield $68 \mathrm{mg}, 0.08 \mathrm{mmol}$, $28 \%$. ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $7.34(2 \mathrm{H}), 6.19(2 \mathrm{H}), 2.43(6 \mathrm{H}), 0.77(27 \mathrm{H}), 0.72(27 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (benzene- $d_{6}$ ): 410.28 ( $\mathrm{U}-\mathrm{C}=\mathrm{C}-\mathrm{R}$ ), 151.58 (Ar), 133.52 (Ar), 113.45 (Ar), 103.96 (U-C $=C-R$ ), 39.45 ( $\mathrm{NMe}_{2}$ ), 7.49 ( $\mathrm{SiMe}_{3}$ ). IR (KBr): 2961 (s), 2899 (w), 2799 (w), 2023 (m, CミC), 1607 (m), 1520 (m), 1457 (w), 1358 (w), 1258 (s), 1186 (m), 1117 (w), 1104 (w), 936 (s), 879 (m), 850 (s), 683 (w), 655 (w), 612 (w). Elemental analysis found (calculated) for $\mathrm{C}_{28} \mathrm{H}_{64} \mathrm{~N}_{4} \mathrm{OSi}_{6} \mathrm{U}$ : C 38.12 (38.24), H 7.32 (7.34), N 6.17 (6.37).

### 6.4.4 $\mathrm{U}^{\mathrm{VI}} \mathrm{O}(\mathrm{CCPh}-\mathrm{OMe})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(6.2-\mathrm{OMe})$.

To a stirred solution of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(500 \mathrm{mg}, 0.70 \mathrm{mmol}, 1.0\right.$ eqiv) in $\mathrm{Et}_{2} \mathrm{O}$ was added [4-methoxyphenyl)ethynyl]copper ( $270 \mathrm{mg}, 1.39 \mathrm{mmol}, 2.0$ equiv). The mixture was stirred for 2 h , and volatiles were removed under reduced pressure. The residue was extracted with hexanes, filtered over Celite, and volatiles were removed under reduced pressure. The residue was redissolved in $\mathrm{Et}_{2} \mathrm{O}$ and N -Methylmorpholine N -oxide ( $81 \mathrm{mg}, 0.70 \mathrm{mmol}, 1.0$ equiv) was added resulting in an immediate color change to dark red. After being stirred for 1 h volatiles were removed under reduced pressure. The resulting black residue was extracted with hexanes, filtered over Celite, and stored at $-21^{\circ} \mathrm{C}$ to give black crystals. Yield: $35 \mathrm{mg}, 0.04 \mathrm{mmol}, 6 \% .{ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $7.33(2 \mathrm{H}), 6.53(2 \mathrm{H}), 3.14(3 \mathrm{H}), 0.72(27 \mathrm{H}), 0.70(27 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (benzene$d_{6}$ ): 399.68 ( $\mathrm{U}-\mathrm{C} \equiv \mathrm{C}-\mathrm{R}$ ), 161.32 (Ar), 133.11 (Ar), 115.11 (Ar), 103.37 (U-C $=C-R$ ), 54.76 ( OMe ), $6.97\left(\mathrm{SiMe}_{3}\right)$. IR (KBr): 2957 (s), 2902 (m), 2056 (m, C C C), 1603 (m), 1505 (m), 1463 (m), 1442
(m), 1295 (w), 1261 (s), 1181 (m), 1169 (w), 1108 (m), 1092 (w), 1030 (w), 935 (s), 883 (s), 842 (s), 774 (m), 656 (w), 615 (w). Elemental analysis found (calculated) for $\mathrm{C}_{27} \mathrm{H}_{61} \mathrm{~N}_{3} \mathrm{O}_{2} \mathrm{Si}_{6} \mathrm{U}$ : C, 37.75 (37.43); H, 6.63 (7.10); N, 4.91 (4.85).

### 6.4.5 $\mathrm{U}^{\mathrm{VI}} \mathrm{O}(\mathrm{CCPh}-\mathrm{Me})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(6.2-\mathrm{Me})$.

To a stirred solution of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(500 \mathrm{mg}, 0.70 \mathrm{mmol}, 1.0\right.$ eqiv) in $\mathrm{Et}_{2} \mathrm{O}$ was added ( $p$-tolylethynyl)copper ( $249 \mathrm{mg}, 1.39 \mathrm{mmol}, 2.0$ equiv). The mixture was stirred for 2 h and volatiles were removed under reduced pressure. The residue was extracted with hexanes, filtered over Celite, and volatiles were removed under reduced pressure. The residue was redissolved in $\mathrm{Et}_{2} \mathrm{O}$ and $N$-Methylmorpholine $N$-oxide ( $81 \mathrm{mg}, 0.70 \mathrm{mmol}, 1.0$ equiv) was added resulting in an immediate color change to dark red. After being stirred for 1 h volatiles were removed under reduced pressure. The resulting black residue was extracted with hexanes, filtered over Celite, and crytallized at $-21^{\circ} \mathrm{C}$ to yield black crystals. Yield: $55 \mathrm{mg}, 0.06 \mathrm{mmol}, 9 \%{ }^{1} \mathrm{H}$ NMR (benzene$\left.d_{6}\right): 7.37(2 \mathrm{H}), 6.79(2 \mathrm{H}), 1.95(3 \mathrm{H}), 0.71(27 \mathrm{H}), 0.70(27 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (benzene- $\left.d_{6}\right): .397 .50(\mathrm{U}-$ $C \equiv C-R), 140.05$ (Ar), 131.38 (Ar), 129.95 (Ar), 116.68 (Ar), 103.57 (U-C=C-R ), 21.32 (Me), 6.97 $\left(\mathrm{SiMe}_{3}\right) .(\mathrm{IR}(\mathrm{KBr}): 2952$ (m), 2897 (w), 2059 (m, C $=C$ ), 1504 (m), 1248 (s), 1178 (w), 1039 (w), 873 (s), 844 (s), 773 (m), 681 (w), 653 (s), 620 (s). Elemental analysis found (calculated) for $\mathrm{C}_{27} \mathrm{H}_{61} \mathrm{~N}_{3} \mathrm{OSi}_{6} \mathrm{U}: \mathrm{C}, 37.81$ (38.14); H, 6.82 (7.23); N, 5.02 (4.94).

### 6.4.6 $\mathrm{U}^{\mathrm{VI}} \mathrm{O}(\mathrm{CCPh}-\mathrm{Ph})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(6.2-\mathrm{Ph})$.

To a stirred solution of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(750 \mathrm{mg}, 1.04 \mathrm{mmol}, 1.0\right.$ eqiv) in $\mathrm{Et}_{2} \mathrm{O}$ was added [(1,1'-biphenyl)-4-ethynyl]copper ( $502 \mathrm{mg}, 2.08 \mathrm{mmol}, 2.0$ equiv). The mixture was stirred for 2 h , and volatiles were removed under reduced pressure. The residue was extracted with hexanes, filtered over Celite, and volatiles were removed under reduced pressure. The residue was redissolved in $\mathrm{Et}_{2} \mathrm{O}$ and N -Methylmorpholine N -oxide (122, $1.04 \mathrm{mmol}, 1.0$ equiv) was added resulting in an immediate color change to dark red. After being stirred for 1 h volatiles were removed under reduced pressure. The resulting black residue was extracted with hexanes, filtered over Celite, and stored at $-21^{\circ} \mathrm{C}$ to yield black crystals. Yield: $30 \mathrm{mg}, 0.03 \mathrm{mmol}, 3 \% .{ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $7.46(2 \mathrm{H}), 7.29(2 \mathrm{H}), 7.25(2 \mathrm{H}), 7.14(2 \mathrm{H}), 7.08(1 \mathrm{H}), 0.71(27 \mathrm{H}), 0.68(27 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR (benzene- $d_{6}$ ): 396.65 ( $\mathrm{U}-\mathrm{C} \equiv \mathrm{C}-\mathrm{R}$ ), 143.19 (Ar), 140.91 (Ar), 132.40 (Ar), 128.91 (Ar), 127.91 (Ar), 119.18 (Ar), 104.46 (U-C $\equiv C-R$ ), 7.56 ( $\mathrm{SiMe}_{3}$ ). IR ( KBr ): 2957 (s), 2897 (m), 2797 (m), 2698 ( w ), 2058 (m, C C C), 1600 ( w ), 1484 (m), 1455 (m), 1404 (w), 1288 (w), 1249 (s), 1183 (m), 1145 (w), 1103 (m), 1064 (w), 957 (s), 939 (s), 841 (s), 762 (m), 686 (w), 654 (w), 612 (w). Elemental analysis found (calculated) for $\mathrm{C}_{32} \mathrm{H}_{63} \mathrm{~N}_{3} \mathrm{OSi}_{6} \mathrm{U}: \mathrm{C} 42.85$ (42.12), H 6.44 (6.96), N 4.45 (4.61). We attempted elemental analysis on two occasions. However, the experimental carbon value differed from the calculated by $0.73 \%$.

### 6.4.7 $\mathrm{U}^{\mathrm{VI}} \mathrm{O}(\mathrm{CCPh}-\mathrm{Cl})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(6.1-\mathrm{Cl})$.

To a stirred solution of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(200 \mathrm{mg}, 0.28 \mathrm{mmol}, 1.0\right.$ eqiv) in $\mathrm{Et}_{2} \mathrm{O}$ was added [(4-chlorophenyl)ethynyl]copper ( $110 \mathrm{mg}, 0.56 \mathrm{mmol}, 2.0$ equiv). The mixture was stirred for 2 h and filtered over Celite. $N$-Methylmorpholine $N$-oxide ( $33 \mathrm{mg}, 0.28 \mathrm{mmol}, 1.0$ equiv) was added, resulting in an immediate color change to dark red. After being stirred for 1 h , the volatiles were removed under reduced pressure. The resulting black residue was extracted with hexanes, filtered over Celite, and stored at $-21^{\circ} \mathrm{C}$ to give black crystals. Yield $45 \mathrm{mg}, 0.05 \mathrm{mmol}, 18 \% .{ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $7.15(2 \mathrm{H}), 6.88(2 \mathrm{H}), 0.68(27 \mathrm{H}), 0.65(27 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (benzene- $\left.d_{6}\right): 392.47$ (U-C $=C-R$ ), 136.31 (Ar), 132.83 (Ar), 130.16 (Ar), 119.17 (Ar), 104.14 (U-C $\equiv C-R$ ), 7.56 ( $\mathrm{SiMe}_{3}$ ). IR (KBr): 2965 (s), 2900 (m), 2798 (m), 2698 (w), 2065 (m, C $\equiv C$ ), 1590 (w), 1486 (m), 1457 (m), 1256 (s), 1184 (m), 1146 (w), 1094 (w), 939 (s), 844 (s), 678 (w), 620 (w). Elemental analysis found (calculated) for $\mathrm{C}_{26} \mathrm{H}_{58} \mathrm{CIN}_{3} \mathrm{OSi}_{6} \mathrm{U}: \mathrm{C} 35.74$ (35.86), H 6.58 (6.71), N 4.79 (4.83).

### 6.5 Crystallographic Analysis.

X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Ka radiation ( $\lambda=0.71073 \AA$ ) at a temperature of 143(1) K. In all cases, rotation frames were integrated using SAINT, ${ }^{53}$ producing a listing of unaveraged $F^{2}$ and $\sigma\left(F^{2}\right)$ values which were then passed to the SHELXTL ${ }^{54}$ program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS ${ }^{55}$ or SADABS. ${ }^{56}$ The structures were solved by direct methods (SHELXS-97). ${ }^{57}$ Refinement was by full-matrix least squares based on $\mathrm{F}^{2}$ using SHELXL-97. ${ }^{57}$ All
reflections were used during refinements. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

### 6.6 Spectroscopic Analysis.

${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra were obtained on a Bruker 500-BioDRX Fourier transform NMR spectrometer at 500 and 126 MHz respectively. Chemical shifts were recorded in units of parts per million referenced to residual solvent peaks.


Figure 6.6.1. ${ }^{1} \mathrm{H}$ NMR of $6.2-\mathrm{NMe}_{2}$ in benzene- $\mathrm{d}_{6}$.
$\infty$
$\underset{\sim}{\infty}$
$\underset{\sim}{+}$
$\vdots$

|  |  |
| :---: | :---: |
|  |  |
|  |  |

$\stackrel{\infty}{\stackrel{\infty}{\infty}} \stackrel{+}{\infty}$

$\begin{array}{llllllllll}450 & 400 & 350 & 300 & 250 & 200 & 150 & 100 & 50 & 0\end{array}$
Figure 6.6.2. ${ }^{13} \mathrm{C}$ NMR of $6.2-\mathrm{NMe}_{2}$ in benzene- $d_{6}$.
$\overbrace{\sim}^{0}$



Figure 6.6.3. ${ }^{1} \mathrm{H}$ NMR of $6.2-\mathrm{OMe}$ in benzene $-d_{6}$.
$\left.\begin{array}{llllllllll}\hline & 400 & 300 & 350 & 300 & 250 & 200 & 150 & 100 & 50\end{array}\right) 0$

Figure 6.6.4. ${ }^{13} \mathrm{C}$ NMR of $6.2-\mathrm{OMe}$ in benzene- $\mathrm{d}_{6}$.


Figure 6.6.5. ${ }^{1} \mathrm{H}$ NMR of $6.2-\mathrm{Me}$ in benzene- $d_{6}$.
$\stackrel{+}{\underset{\sim}{\mathbf{~}}}$



| 400 | 350 | 300 | 250 | 200 | 150 | 100 | 50 | 0 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

Figure 6.6.6. ${ }^{13} \mathrm{C}$ NMR of $6.2-\mathrm{Me}$ in benzene- $d_{6}$.




Figure 6.6.7. ${ }^{1} \mathrm{H}$ NMR of 6.2-Ph in benzene- $d_{6}$.

| 10 |
| :--- |
| 0 |
| 0 |



| 6 |
| :--- |
|  |
|  |



|  |  | 1 | 1 | 1 | 1 |  |  |  |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| 400 | 350 | 300 | 250 | 200 | 150 | 100 | 50 | 0 |

Figure 6.6.8. ${ }^{13} \mathrm{C}$ NMR of 6.2-Ph in benzene- $d_{6}$.


Figure 6.6.9. ${ }^{1} \mathrm{H}$ NMR of $6.2-\mathrm{CI}$ in benzene $-d_{6}$.

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| 400 | 350 | 300 | 250 | 200 | 150 | 100 | 50 | 0 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

Figure 6.6.10. ${ }^{13} \mathrm{C}$ NMR of $6.2-\mathrm{Cl}$ in benzene- $d_{6}$.


Figure 6.6.11. ${ }^{13} \mathrm{C}$ NMR of $\mathrm{HCCPh}-\mathrm{NM}_{2}$ in benzene- $d_{6}$.


Figure 6.6.12. ${ }^{13} \mathrm{C}$ NMR of $\mathrm{HCCPh}-\mathrm{OMe}$ in benzene- $d_{6}$.


Figure 6.6.13. ${ }^{13} \mathrm{C}$ NMR of HCCPh-Me in benzene- $d_{6}$.


Figure 6.6.14. ${ }^{13} \mathrm{C}$ NMR of HCCPh-Ph in benzene- $d_{6}$.



Figure 6.6.15. ${ }^{13} \mathrm{C}$ NMR of HCCPh in benzene- $d_{6}$.


Figure 6.6.16. ${ }^{13} \mathrm{C}$ NMR of $\mathrm{HCCPh}-\mathrm{Cl}$ in benzene- $d_{6}$.

### 6.7 Electrochemical Analysis.

Voltammetry experiments (CV, DPV) were performed using a CH Instruments 620D Electrochemical Analyzer/Workstation and the data were processed using CHI software v9.24. All experiments were performed in an $\mathrm{N}_{2}$ atmosphere drybox using electrochemical cells that consisted of a 4 mL vial, glassy carbon working electrode, a platinum wire counter electrode, and a silver wire plated with AgCl as a quasi-reference electrode. The quasi-reference electrode was prepared by dipping a length of silver wire in concentrated hydrochloric acid. The working electrode surfaces were polished prior to each set of experiments. Potentials were reported versus ferrocene, which was added as an internal standard for calibration at the end of each run. Solutions employed during these studies were $\sim 3 \mathrm{mM}$ in analyte and 100 mM in $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$ in 2 mL of THF. All data were collected in a positive-feedback IR compensation mode.


Figure 6.7.1. a) Full scan cyclic voltammetry of compound $6.2-\mathrm{NMe}_{2}$ in THF with 0.1 M $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[P F_{6}\right] ;$ [analyte] $=$ ca. $1 \mathrm{mM} ; \mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$.


Figure 6.7.2. a) Full scan cyclic voltammetry of compound 6.2-OMe in THF with 0.1 M [ $\left.{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[P F_{6}\right]$; [analyte] = ca. 1 mM ; v = $0.25 \mathrm{~V} / \mathrm{sec}$.

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Figure 6.7.3. a) Full scan cyclic voltammetry of compound $6.2-\mathrm{Me}$ in THF with 0.1 M $\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[P F_{6}\right] ;$ analyte] = ca. $1 \mathrm{mM} ; \mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$.


Figure 6.7.4. Full scan cyclic voltammetry of $6.2-\mathrm{Ph}$ in THF with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}^{2}\left[\mathrm{PF}_{6}\right]\right.$; [analyte] = ca. 1 mM ; v = $0.25 \mathrm{~V} / \mathrm{sec}$. b) Differential pulse voltammetry.


Figure 6.7.5. Full scan cyclic voltammetry of 6.2-H in THF with $0.1 \mathrm{M}\left[{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}\right]\left[\mathrm{PF}_{6}\right]$; $[$ analyte $]=$ ca. 1 mM ; v $=0.25 \mathrm{~V} / \mathrm{sec}$.


Figure 6.7.6. Full scan cyclic voltammetry of 6.2-CI in THF with $0.1 \mathrm{M}{ }^{n} \mathrm{Bu}_{4} \mathrm{~N}^{2}\left[\mathrm{PF}_{6}\right]$; [analyte] = ca. 1 mM ; $\mathrm{v}=0.25 \mathrm{~V} / \mathrm{sec}$.

### 6.8 Computational Details

All calculations were performed with Gaussian 09 Revision D.01, ${ }^{58}$ with the B3LYP hybrid DFT method. An effective core potential incorporating quasi-relativistic effects were applied to uranium, with a 60 electron core and the corresponding segmented natural orbital basis set. ${ }^{59,60}$ The $6-31 \mathrm{G}^{*}$ basis set was used for all small molecules. ${ }^{61}$ Geometry optimizations were carried
out in $C_{1}$ symmetry for all uranium complexes and all small molecules, as higher symmetry solutions were either higher in energy or were not successfully converged. Default settings were used for the integration grid, SCF, and geometry convergence criteria. Small negative frequencies were found for 6.2-OMe and 6.2-Ph of -32.70 and $-1.83 \mathrm{~cm}^{-1}$.

Table 6.8.1. Geometry optimized coordinates of compound 6.2-NMe ${ }_{2}$.

| Atomic Number | X | y | z |
| :---: | :---: | :---: | :---: |
| U | 1.160942 | -0.02112 | -0.00932 |
| O | 2.951286 | -0.13575 | -0.04147 |
| N | 1.087057 | -1.13154 | 1.936259 |
| N | 1.289968 | 2.215168 | -0.01392 |
| N | 1.030095 | -1.16216 | -1.93763 |
| Si | 2.570108 | 3.026919 | 0.933483 |
| Si | -0.00291 | -0.6695 | 3.272954 |
| Si | 2.198877 | -2.50209 | 2.219238 |
| Si | 0.220796 | 3.247077 | -1.00069 |
| Si | 2.223826 | -0.86572 | -3.23146 |
| Si | -0.1986 | -2.42169 | -2.22322 |
| C | -0.7892 | -3.21905 | -0.60183 |
| C | 3.16157 | 0.768953 | -2.99956 |
| C | -0.46232 | 1.172467 | 3.22341 |
| C | 2.965523 | -3.17295 | 0.617094 |
| C | -1.59694 | -1.6944 | 3.270972 |
| C | -0.48191 | 2.329304 | -2.50657 |
| C | 4.025441 | 3.572044 | -0.15154 |
| C | 3.663041 | -2.03005 | 3.326278 |
| C | -1.22506 | 3.918708 | 0.024951 |
| C | 3.317961 | 1.905141 | 2.269781 |
| C | 1.880956 | 4.533325 | 1.868111 |
| C | 0.800424 | -0.87349 | 4.98713 |
| C | 1.278229 | -3.9783 | 2.988087 |
| C | 1.125046 | 4.733465 | -1.77224 |
| C | 1.378737 | -0.72411 | -4.92959 |
| C | 3.555282 | -2.21318 | -3.30934 |
| C | 0.470328 | -3.90552 | -3.212 |
| C | -1.70131 | -1.74754 | -3.1602 |
| H | -0.02127 | -3.87378 | -0.17505 |
| H | -1.6563 | -3.85138 | -0.83838 |
| H | 2.529205 | -2.51166 | 0.169657 |
| H | 3.64351 | 1.618927 | -2.72473 |
|  | -0.85679 | 1.017748 | -3.95476 |
|  |  | 0.678944 | -2.23958 |
|  | 1.513779 | 2.263875 |  |

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| H | 0.386397 | 1.810125 | 3.494765 |
| :---: | :---: | :---: | :---: |
| H | -1.24524 | 1.338213 | 3.97642 |
| H | 2.253315 | -3.31065 | -0.2022 |
| H | 3.396803 | -4.15779 | 0.842814 |
| H | 3.769285 | -2.52747 | 0.252928 |
| H | -2.18852 | -1.51243 | 2.368548 |
| H | -2.21673 | -1.42435 | 4.136176 |
| H | -1.39191 | -2.7686 | 3.331445 |
| H | -1.04846 | 1.429649 | -2.25665 |
| H | 0.299564 | 2.056923 | -3.22454 |
| H | -1.16547 | 3.018855 | -3.0213 |
| H | 4.407478 | 2.724874 | -0.73237 |
| H | 4.843777 | 3.933535 | 0.485117 |
| H | 3.770506 | 4.372824 | -0.85222 |
| H | 4.184001 | -1.15345 | 2.924589 |
| H | 4.382492 | -2.85912 | 3.354336 |
| H | 3.372975 | -1.80653 | 4.357014 |
| H | -1.79737 | 3.098182 | 0.469473 |
| H | -1.90401 | 4.503669 | -0.60956 |
| H | -0.88547 | 4.568891 | 0.838188 |
| H | 2.583556 | 1.330485 | 2.842087 |
| H | 3.856971 | 2.544785 | 2.981757 |
| H | 4.03317 | 1.196702 | 1.843209 |
| H | 1.490191 | 5.320578 | 1.215555 |
| H | 2.683724 | 4.977263 | 2.47147 |
| H | 1.077765 | 4.239875 | 2.554656 |
| H | 1.062522 | -1.90377 | 5.24688 |
| H | 0.082139 | -0.52113 | 5.739748 |
| H | 1.703718 | -0.26093 | 5.088934 |
| H | 0.81978 | -3.75964 | 3.957386 |
| H | 1.984299 | -4.80564 | 3.138236 |
| H | 0.487082 | -4.33865 | 2.319781 |
| H | 1.531114 | 5.445924 | -1.04762 |
| H | 0.406572 | 5.279367 | -2.39852 |
| H | 1.945722 | 4.41234 | -2.42396 |
| H | 0.843294 | -1.62791 | -5.23715 |
| H | 2.141607 | -0.52044 | -5.69261 |
| H | 0.664783 | 0.10807 | -4.94895 |
| H | 4.022325 | -2.35288 | -2.32779 |
| H | 4.342928 | -1.91008 | -4.01172 |
| H | 3.170409 | -3.18233 | -3.64005 |
| H | 0.784827 | -3.66781 | -4.23302 |
| H | -0.33227 | -4.65192 | -3.28459 |
| H | 1.314329 | -4.38429 | -2.7023 |
| H | -2.21549 | -0.97011 | -2.58693 |
| H | -2.41946 | -2.5558 | -3.35155 |

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Sum of electronic and thermal Free Energies $=-3613.329168$ Hartrees.
Table 6.8.2. Geometry optimized coordinates of compound 6.2-OMe.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -0.99534 | -0.06943 | 0.003879 |
| 0 | -2.76921 | -0.33945 | 0.026308 |
| N | -0.81236 | -1.19551 | -1.92076 |
| N | -1.30572 | 2.146523 | -0.0211 |
| N | -0.77988 | -1.15538 | 1.951085 |
| Si | -2.6445 | 2.844974 | -0.98139 |
| Si | 0.230692 | -0.65269 | -3.26596 |
| Si | -1.80758 | -2.65812 | -2.18884 |
| Si | -0.32276 | 3.273439 | 0.954777 |
| Si | -2.00694 | -0.93435 | 3.231774 |
| Si | 0.545525 | -2.3049 | 2.27909 |
| C | 1.223663 | -3.08301 | 0.682981 |
| C | -3.06948 | 0.616704 | 2.968338 |
| C | 0.530188 | 1.221673 | -3.23208 |
| C | -2.51243 | -3.37526 | -0.57843 |
| C | 1.908926 | -1.5334 | -3.25317 |
| C | 0.449605 | 2.432241 | 2.470541 |
| C | -4.1411 | 3.284894 | 0.094464 |

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| C | -3.30785 | -2.30724 | -3.29143 |
| :---: | :---: | :---: | :---: |
| C | 1.066268 | 4.049975 | -0.07514 |
| C | -3.29501 | 1.651856 | -2.30691 |
| C | -2.07561 | 4.388477 | -1.93513 |
| C | -0.55292 | -0.94545 | -4.97542 |
| C | -0.76653 | -4.05778 | -2.94643 |
| C | -1.34769 | 4.690729 | 1.70453 |
| C | -1.19195 | -0.69968 | 4.9343 |
| C | -3.2279 | -2.38156 | 3.316582 |
| C | -0.01456 | -3.81745 | 3.290264 |
| C | 1.970511 | -1.48594 | 3.220237 |
| H | 0.508193 | -3.78516 | 0.24084 |
| H | 2.118014 | -3.66215 | 0.952824 |
| H | 1.517267 | -2.36562 | -0.08647 |
| H | -2.50538 | 1.513038 | 2.69295 |
| H | -3.58172 | 0.833938 | 3.91538 |
| H | -3.83141 | 0.455649 | 2.201054 |
| H | 0.960363 | 1.590857 | -2.29862 |
| H | -0.38525 | 1.787135 | -3.43711 |
| H | 1.241642 | 1.454996 | -4.0363 |
| H | -1.79591 | -3.43083 | 0.246658 |
| H | -2.84466 | -4.40081 | -0.78949 |
| H | -3.37741 | -2.80585 | -0.22762 |
| H | 2.473577 | -1.29878 | -2.34572 |
| H | 2.508904 | -1.20762 | -4.11305 |
| H | 1.802366 | -2.62181 | -3.31544 |
| H | 1.101048 | 1.589339 | 2.230409 |
| H | -0.30772 | 2.09045 | 3.184358 |
| H | 1.06124 | 3.185596 | 2.986327 |
| H | -4.46576 | 2.414829 | 0.676 |
| H | -4.97905 | 3.586227 | -0.54788 |
| H | -3.94676 | 4.103143 | 0.794145 |
| H | -3.89316 | -1.47518 | -2.88379 |
| H | -3.96072 | -3.18959 | -3.31988 |
| H | -3.04052 | -2.05772 | -4.32224 |
| H | 1.698556 | 3.277096 | -0.52377 |
| H | 1.700265 | 4.682453 | 0.560235 |
| H | 0.677023 | 4.676585 | -0.88442 |
| H | -2.51409 | 1.152521 | -2.88852 |
| H | -3.90053 | 2.2367 | -3.01246 |
| H | -3.9347 | 0.878076 | -1.8744 |
| H | -1.74961 | 5.215419 | -1.2964 |
| H | -2.91105 | 4.757053 | -2.54482 |
| H | -1.25199 | 4.149539 | -2.61846 |
| H | -0.73833 | -1.99694 | -5.21477 |
| H | 0.139238 | -0.55608 | -5.73413 |

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| H | -1.49833 | -0.40274 | -5.089 |
| :--- | :---: | :---: | :---: |
| H | -0.33813 | -3.81501 | -3.92378 |
| H | -1.39763 | -4.94666 | -3.07676 |
| H | 0.059635 | -4.33552 | -2.28084 |
| H | -1.83066 | 5.338946 | 0.967022 |
| H | -0.67272 | 5.320119 | 2.29988 |
| H | -2.1236 | 4.315274 | 2.381669 |
| H | -0.58996 | -1.55256 | 5.263047 |
| H | -1.97747 | -0.54508 | 5.685751 |
| H | -0.54717 | 0.187238 | 4.946879 |
| H | -3.67381 | -2.5673 | 2.332948 |
| H | -4.04274 | -2.13207 | 4.008912 |
| H | -2.77234 | -3.3143 | 3.661971 |
| H | -0.36184 | -3.58431 | 4.3016 |
| H | 0.844898 | -4.49411 | 3.390132 |
| H | -0.8093 | -4.37485 | 2.781291 |
| H | 2.415747 | -0.66963 | 2.643273 |
| H | 2.758699 | -2.22183 | 3.427279 |
| C | 1.638302 | -1.07726 | 4.180546 |
| C | 1.297995 | 0.275586 | -0.02697 |
| C | 2.527088 | 0.384093 | -0.02858 |
| C | 3.947889 | 0.475025 | -0.02734 |
| H | 4.604309 | 1.727185 | -0.00557 |
| H | 4.737505 | -0.69026 | -0.04638 |
| C | 4.013094 | 2.637174 | 0.010308 |
| C | 4.24984 | -1.65986 | -0.06141 |
| H | 5.986627 | 1.802098 | -0.00378 |
| H | 6.128359 | -0.62108 | -0.04486 |
| O | 6.497957 | 2.759284 | 0.012826 |
| H | 6.704367 | -1.53902 | -0.05985 |
| H | 6.762006 | 0.108639 | 0.89569 |

Sum of electronic and thermal Free Energies $=-3593.919695$ Hartrees.
Table 6.8.3. Geometry optimized coordinates of compound 6.2-Me.

| Atomic Number | x | y | z |
| :--- | ---: | ---: | ---: |
| U | -0.8341 | -0.04069 | 0.016972 |
| O | -2.62167 | -0.19236 | 0.082313 |
| N | -0.74324 | -1.5144 | -1.66016 |
| N | -1.00843 | 2.144105 | -0.42682 |


| N | -0.67123 | -0.73776 | 2.134794 |
| :---: | :---: | :---: | :---: |
| Si | -2.29996 | 2.73464 | -1.51604 |
| Si | 0.315439 | -1.29979 | -3.08459 |
| Si | -1.82696 | -2.93789 | -1.64985 |
| Si | 0.051929 | 3.370508 | 0.322214 |
| Si | -1.86913 | -0.18684 | 3.344494 |
| Si | 0.57691 | -1.89167 | 2.684004 |
| C | 1.191435 | -3.00111 | 1.268566 |
| C | -2.82575 | 1.354056 | 2.784911 |
| C | 0.76349 | 0.519742 | -3.38819 |
| C | -2.52962 | -3.3116 | 0.073773 |
| C | 1.923378 | -2.28812 | -2.9175 |
| C | 0.771775 | 2.78198 | 1.977478 |
| C | -3.76739 | 3.453827 | -0.55672 |
| C | -3.33461 | -2.69948 | -2.77382 |
| C | 1.48001 | 3.846735 | -0.82944 |
| C | -3.02672 | 1.364943 | -2.61106 |
| C | -1.63304 | 4.039484 | -2.72757 |
| C | -0.52751 | -1.82711 | -4.70681 |
| C | -0.89555 | -4.51373 | -2.16425 |
| C | -0.87122 | 4.969297 | 0.783814 |
| C | -1.01706 | 0.31452 | 4.9689 |
| C | -3.18556 | -1.50393 | 3.696093 |
| C | -0.08092 | -3.13326 | 3.965729 |
| C | 2.063001 | -1.0061 | 3.456558 |
| H | 0.44184 | -3.7481 | 0.984538 |
| H | 2.070137 | -3.54907 | 1.636494 |
| H | 1.495498 | -2.46291 | 0.368189 |
| H | -2.20248 | 2.14465 | 2.356679 |
| H | -3.32151 | 1.77533 | 3.669964 |
| H | -3.59808 | 1.106256 | 2.05179 |
| H | 1.239852 | 1.011284 | -2.53753 |
| H | -0.10408 | 1.115935 | -3.69044 |
| H | 1.478314 | 0.543744 | -4.22251 |
| H | -1.79372 | -3.2725 | 0.882583 |
| H | -2.93487 | -4.3323 | 0.05303 |
| H | -3.34453 | -2.63012 | 0.332296 |
| H | 2.519117 | -1.93103 | -2.07163 |
| H | 2.52979 | -2.17224 | -3.82533 |
| H | 1.737461 | -3.35776 | -2.77517 |
| H | 1.296686 | 1.82548 | 1.929535 |
| H | 0.002282 | 2.714338 | 2.754083 |
| H | 1.497404 | 3.538011 | 2.308198 |
| H | -4.15642 | 2.719505 | 0.157486 |
| H | -4.57831 | 3.699554 | -1.25506 |
| H | -3.51857 | 4.363458 | -0.00258 |


| H | -3.86182 | -1.77397 | -2.51665 |
| :---: | :---: | :---: | :---: |
| H | -4.03498 | -3.53219 | -2.62662 |
| H | -3.08372 | -2.65938 | -3.83806 |
| H | 2.072507 | 2.96893 | -1.10585 |
| H | 2.144755 | 4.564005 | -0.32993 |
| H | 1.122473 | 4.313686 | -1.75319 |
| H | -2.28036 | 0.746594 | -3.11893 |
| H | -3.62869 | 1.851609 | -3.39057 |
| H | -3.68356 | 0.698485 | -2.04627 |
| H | -1.24236 | 4.940054 | -2.24413 |
| H | -2.44629 | 4.353651 | -3.39493 |
| H | -0.83497 | 3.625097 | -3.35513 |
| H | -0.79874 | -2.88608 | -4.75451 |
| H | 0.171316 | -1.63185 | -5.53116 |
| H | -1.43174 | -1.23904 | -4.90102 |
| H | -0.48863 | -4.48071 | -3.17967 |
| H | -1.58505 | -5.36681 | -2.11574 |
| H | -0.06549 | -4.72327 | -1.47888 |
| H | -1.30521 | 5.503741 | -0.06662 |
| H | -0.1528 | 5.648032 | 1.262839 |
| H | -1.67212 | 4.781302 | 1.508092 |
| H | -0.4808 | -0.50193 | 5.462227 |
| H | -1.77589 | 0.680028 | 5.673112 |
| H | -0.30254 | 1.129795 | 4.803582 |
| H | -3.6509 | -1.83724 | 2.761653 |
| H | -3.97646 | -1.07448 | 4.325193 |
| H | -2.79328 | -2.38624 | 4.210536 |
| H | -0.41812 | -2.67967 | 4.902645 |
| H | 0.733157 | -3.82737 | 4.214374 |
| H | -0.90712 | -3.73135 | 3.564792 |
| H | 2.558048 | -0.34821 | 2.735705 |
| H | 2.80155 | -1.74202 | 3.80103 |
| H | 1.771406 | -0.40052 | 4.321111 |
| C | 1.485922 | 0.142952 | -0.07 |
| C | 2.717966 | 0.193076 | -0.0849 |
| C | 4.143373 | 0.225577 | -0.09977 |
| C | 4.842594 | 1.447975 | -0.15947 |
| C | 4.886852 | -0.97215 | -0.05748 |
| H | 4.285286 | 2.378536 | -0.19727 |
| H | 4.36231 | -1.9215 | -0.01276 |
| C | 6.233171 | 1.463221 | -0.17647 |
| C | 6.276664 | -0.93977 | -0.07628 |
| H | 6.754313 | 2.416444 | -0.22703 |
| H | 6.831401 | -1.87484 | -0.04757 |
| C | 6.976356 | 0.274672 | -0.13252 |
| C | 8.48557 | 0.301686 | -0.11888 |

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| H | 8.870923 | 0.329865 | 0.909424 |
| :--- | ---: | ---: | ---: |
| H | 8.90686 | -0.58829 | -0.5985 |
| H | 8.875691 | 1.184578 | -0.63618 |

Sum of electronic and thermal Free Energies $=-3518.719195$ Hartrees.
Table 6.8.4. Geometry optimized coordinates of compound 6.2-Ph.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | 1.551936 | -0.03353 | 0.002745 |
| O | 3.341099 | -0.17694 | 0.010551 |
| N | 1.500976 | -0.25007 | 2.226075 |
| N | 1.689765 | 2.000463 | -0.9132 |
| N | 1.388001 | -1.83105 | -1.31853 |
| Si | 2.981808 | 3.122944 | -0.39112 |
| Si | 0.437381 | 0.732895 | 3.273903 |
| Si | 2.616793 | -1.39765 | 3.026662 |
| Si | 0.596506 | 2.560037 | -2.20981 |
| Si | 2.562531 | -2.06996 | -2.6461 |
| Si | 0.171924 | -3.11231 | -1.06123 |
| C | -0.39442 | -3.19919 | 0.751279 |
| C | 3.484133 | -0.47659 | -3.10886 |
| C | -0.03089 | 2.388183 | 2.471042 |
| C | 3.331771 | -2.68012 | 1.822894 |
| C | -1.15501 | -0.1926 | 3.71735 |
| C | -0.13818 | 1.11933 | -3.20431 |
| C | 4.424486 | 3.171947 | -1.6183 |
| C | 4.112076 | -0.52503 | 3.796539 |
| C | -0.82307 | 3.598881 | -1.50442 |
| C | 3.739221 | 2.643875 | 1.282164 |
| C | 2.307068 | 4.883037 | -0.13968 |
| C | 1.279324 | 1.247734 | 4.901133 |
| C | 1.715906 | -2.40749 | 4.362081 |
| C | 1.480072 | 3.6007 | -3.53535 |
| C | 1.690822 | -2.62491 | -4.24226 |
| C | 3.911685 | -3.32019 | -2.18957 |
| C | 0.851065 | -4.85935 | -1.38901 |
| C | -1.34665 | -2.86918 | -2.1674 |
| H | 0.383392 | -3.62329 | 1.395812 |
| H | -1.2558 | -3.88037 | 0.795469 |
| H | -0.71092 | -2.24561 | 1.18004 |
| H | 2.839356 | 0.396194 | -3.24815 |
| H | 3.996361 | -0.65734 | -4.06366 |
| H | -0.241731 | -0.21631 | -2.36493 |
|  | 0.825101 | 2.294315 | 1.481733 |
|  |  | 3.067812 | 2.396768 |
|  |  |  |  |
|  |  |  |  |
|  |  |  |  |

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| H | -0.77165 | 2.870169 | 3.123977 |
| :---: | :---: | :---: | :---: |
| H | 2.607073 | -3.08814 | 1.112058 |
| H | 3.713735 | -3.52137 | 2.416822 |
| H | 4.163738 | -2.26773 | 1.245441 |
| H | -1.74377 | -0.42153 | 2.823496 |
| H | -1.77693 | 0.425988 | 4.377615 |
| H | -0.95087 | -1.13362 | 4.239197 |
| H | -0.63901 | 0.358507 | -2.60181 |
| H | 0.618563 | 0.625784 | -3.82364 |
| H | -0.88874 | 1.541314 | -3.88707 |
| H | 4.83045 | 2.166756 | -1.7777 |
| H | 5.23153 | 3.794896 | -1.21055 |
| H | 4.149237 | 3.581687 | -2.59465 |
| H | 4.620608 | 0.096295 | 3.050793 |
| H | 4.831824 | -1.27563 | 4.149043 |
| H | 3.853323 | 0.112584 | 4.646775 |
| H | -1.39514 | 3.023552 | -0.76957 |
| H | -1.50787 | 3.903814 | -2.30666 |
| H | -0.46201 | 4.507475 | -1.01135 |
| H | 3.00474 | 2.402264 | 2.056761 |
| H | 4.31794 | 3.505303 | 1.642274 |
| H | 4.420862 | 1.794001 | 1.192265 |
| H | 1.88928 | 5.338667 | -1.04269 |
| H | 3.125455 | 5.52955 | 0.203409 |
| H | 1.529204 | 4.90071 | 0.633114 |
| H | 1.553444 | 0.41293 | 5.553418 |
| H | 0.575963 | 1.879595 | 5.459921 |
| H | 2.181045 | 1.844573 | 4.72194 |
| H | 1.2821 | -1.80151 | 5.163397 |
| H | 2.428673 | -3.10186 | 4.826254 |
| H | 0.90907 | -3.00901 | 3.926297 |
| H | 1.914227 | 4.536026 | -3.16945 |
| H | 0.741691 | 3.863747 | -4.30473 |
| H | 2.275283 | 3.031049 | -4.02988 |
| H | 1.176787 | -3.58796 | -4.16193 |
| H | 2.43835 | -2.72004 | -5.0408 |
| H | 0.954534 | -1.88106 | -4.56969 |
| H | 4.393239 | -3.03673 | -1.24679 |
| H | 4.685135 | -3.32476 | -2.96884 |
| H | 3.539807 | -4.34345 | -2.08435 |
| H | 1.15557 | -5.04115 | -2.42429 |
| H | 0.056746 | -5.58014 | -1.15235 |
| H | 1.703729 | -5.09157 | -0.74085 |
| H | -1.85424 | -1.92528 | -1.94624 |
| H | -2.06473 | -3.68406 | -2.00668 |
| H | -1.08055 | -2.86718 | -3.22986 |

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| C | -0.77218 | 0.137536 | 0.001978 |
| :--- | :---: | :---: | :---: |
| C | -2.00525 | 0.162078 | 0.001938 |
| C | -3.4303 | 0.160073 | 0.005434 |
| C | -4.16271 | 1.2856 | -0.42436 |
| C | -4.14293 | -0.97875 | 0.435487 |
| H | -3.63067 | 2.166703 | -0.76852 |
| H | -3.5934 | -1.85033 | 0.776908 |
| C | -5.55178 | 1.266507 | -0.42343 |
| C | -5.53209 | -0.98619 | 0.432476 |
| H | -6.0935 | 2.135242 | -0.78587 |
| H | -6.05812 | -1.86518 | 0.793255 |
| C | -6.26799 | 0.133042 | 0.002749 |
| C | -7.75086 | 0.117783 | -0.00353 |
| C | -8.45939 | -1.046 | -0.35002 |
| C | -8.48602 | 1.267048 | 0.335335 |
| H | -7.91264 | -1.93775 | -0.64324 |
| C | -7.9603 | 2.169766 | 0.633496 |
| C | -9.85341 | -1.05982 | -0.358 |
| H | -9.88008 | 1.252909 | 0.328587 |
| H | -10.3804 | -1.96792 | -0.63844 |
| C | -10.4281 | 2.150354 | 0.603071 |
| H | -10.5702 | 0.089563 | -0.01844 |

Sum of electronic and thermal Free Energies $=-3710.405029$ Hartrees.
Table 6.8.5. Geometry optimized coordinates of compound 6.2-H.

| Atomic Number | x | y | z |
| :---: | :---: | :---: | :---: |
| U | -0.66733 | -0.06746 | 0.015758 |
| O | -2.43968 | -0.34294 | 0.081552 |
| N | -0.50689 | -1.37881 | -1.78624 |
| N | -0.98863 | 2.132761 | -0.21793 |
| N | -0.42374 | -0.9575 | 2.052859 |
| Si | -2.32587 | 2.73897 | -1.24081 |
| Si | 0.524541 | -0.98405 | -3.1922 |
| Si | -1.50622 | -2.85982 | -1.89344 |
| Si | -0.00289 | 3.346269 | 0.645992 |
| Si | -1.63301 | -0.61928 | 3.327013 |
| Si | 0.913974 | -2.0672 | 2.467642 |
| C | 1.558947 | -3.00028 | 0.943166 |
| C | -2.71868 | 0.885748 | 2.925838 |
| C | 0.845066 | 0.880699 | -3.33928 |
| C | -2.17742 | -3.41444 | -0.2065 |
| C | 2.191662 | -1.88032 | -3.10822 |
| C | 0.751494 | 2.644672 | 2.240441 |

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| C | -3.81667 | 3.290918 | -0.20955 |
| :---: | :---: | :---: | :---: |
| C | -3.03003 | -2.61289 | -2.99323 |
| C | 1.39158 | 4.007364 | -0.45335 |
| C | -2.99082 | 1.425418 | -2.4384 |
| C | -1.74587 | 4.175945 | -2.34324 |
| C | -0.29237 | -1.42756 | -4.85216 |
| C | -0.4872 | -4.33011 | -2.53697 |
| C | -1.01876 | 4.836315 | 1.250952 |
| C | -0.78828 | -0.20852 | 4.980347 |
| C | -2.83404 | -2.0639 | 3.576131 |
| C | 0.385663 | -3.47243 | 3.638266 |
| C | 2.353746 | -1.15783 | 3.297258 |
| H | 0.844332 | -3.76004 | 0.608119 |
| H | 2.474883 | -3.52858 | 1.242785 |
| H | 1.811321 | -2.36793 | 0.089418 |
| H | -2.17249 | 1.755874 | 2.548879 |
| H | -3.2166 | 1.193556 | 3.855314 |
| H | -3.49273 | 0.63828 | 2.194331 |
| H | 1.294906 | 1.327539 | -2.45019 |
| H | -0.0674 | 1.436036 | -3.58163 |
| H | 1.546376 | 1.030192 | -4.17179 |
| H | -1.44562 | -3.38042 | 0.606029 |
| H | -2.50718 | -4.45761 | -0.30428 |
| H | -3.03886 | -2.8145 | 0.099021 |
| H | 2.771387 | -1.55632 | -2.2383 |
| H | 2.784292 | -1.65806 | -4.00529 |
| H | 2.071169 | -2.96728 | -3.05013 |
| H | 1.341561 | 1.736083 | 2.102222 |
| H | -0.01429 | 2.445676 | 2.99808 |
| H | 1.422555 | 3.410268 | 2.65394 |
| H | -4.14119 | 2.484055 | 0.457324 |
| H | -4.65636 | 3.528947 | -0.87571 |
| H | -3.61738 | 4.174459 | 0.403693 |
| H | -3.59904 | -1.73552 | -2.66556 |
| H | -3.68903 | -3.48687 | -2.90751 |
| H | -2.78733 | -2.48128 | -4.05175 |
| H | 2.028909 | 3.191041 | -0.80746 |
| H | 2.018929 | 4.711009 | 0.109647 |
| H | 1.006064 | 4.535425 | -1.33185 |
| H | -2.21854 | 0.884159 | -2.99319 |
| H | -3.61955 | 1.94076 | -3.17716 |
| H | -3.61143 | 0.687307 | -1.92356 |
| H | -1.41485 | 5.059437 | -1.7884 |
| H | -2.57726 | 4.48896 | -2.98849 |
| H | -0.9221 | 3.865593 | -2.99722 |
| H | -0.49622 | -2.49377 | -4.98957 |

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| H | 0.388652 | -1.1197 | -5.65689 |
| :---: | :---: | :---: | :---: |
| H | -1.23295 | -0.88388 | -4.99655 |
| H | -0.07937 | -4.18627 | -3.54229 |
| H | -1.12921 | -5.22022 | -2.56865 |
| H | 0.350665 | -4.55323 | -1.86562 |
| H | -1.48954 | 5.417631 | 0.452359 |
| H | -0.3414 | 5.512248 | 1.790014 |
| H | -1.80363 | 4.534281 | 1.953917 |
| H | -0.18063 | -1.02411 | 5.384697 |
| H | -1.55986 | 0.024461 | 5.725911 |
| H | -0.14321 | 0.673503 | 4.888475 |
| H | -3.2961 | -2.35027 | 2.624655 |
| H | -3.63897 | -1.75708 | 4.256896 |
| H | -2.36024 | -2.95348 | 4.001404 |
| H | 0.048608 | -3.14019 | 4.624836 |
| H | 1.257841 | -4.12153 | 3.794624 |
| H | -0.40625 | -4.09191 | 3.202136 |
| H | 2.805533 | -0.41882 | 2.629021 |
| H | 3.134925 | -1.87441 | 3.583314 |
| H | 2.033249 | -0.63785 | 4.206323 |
| C | 1.636663 | 0.282108 | -0.07372 |
| C | 2.863306 | 0.402604 | -0.09973 |
| C | 4.285702 | 0.513639 | -0.1272 |
| C | 4.91181 | 1.7762 | -0.176 |
| C | 5.087754 | -0.64674 | -0.10503 |
| H | 4.299571 | 2.67211 | -0.19205 |
| H | 4.609572 | -1.62033 | -0.06455 |
| C | 6.300648 | 1.86977 | -0.2036 |
| C | 6.475679 | -0.54193 | -0.1335 |
| H | 6.772115 | 2.847925 | -0.24168 |
| H | 7.082963 | -1.44271 | -0.11657 |
| C | 7.086322 | 0.71413 | -0.18288 |
| H | 8.169787 | 0.792159 | -0.20466 |

Sum of electronic and thermal Free Energies $=-3479.428918$ Hartrees.
Table 6.8.6. Geometry optimized coordinates of compound 6.2-CI.

| Atomic Number | X | y | z |
| :---: | :---: | :---: | :---: |
| U | 0.996474 | -0.03809 | 0.000216 |
| 0 | 2.785716 | -0.18474 | 0.005374 |
| N | 0.888215 | -0.92179 | 2.046847 |
| N | 1.148768 | 2.174936 | -0.24475 |
| N | 0.866894 | -1.35172 | -1.80397 |
| Si | 2.42646 | 3.080307 | 0.624055 |
| Si | -0.18674 | -0.28446 | 3.326176 |

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| Si | 1.977645 | -2.27305 | 2.486489 |
| :---: | :---: | :---: | :---: |
| Si | 0.093548 | 3.110235 | -1.34271 |
| Si | 2.079668 | -1.18511 | -3.10958 |
| Si | -0.35854 | -2.63791 | -1.9827 |
| C | -0.99033 | -3.25818 | -0.30064 |
| C | 3.00591 | 0.470355 | -3.04153 |
| C | -0.63876 | 1.536386 | 3.038741 |
| C | 2.708141 | -3.14133 | 0.964351 |
| C | -1.78537 | -1.29132 | 3.460527 |
| C | -0.61801 | 2.042301 | -2.74145 |
| C | 3.894734 | 3.502804 | -0.4968 |
| C | 3.466828 | -1.69556 | 3.506269 |
| C | -1.34668 | 3.902065 | -0.3987 |
| C | 3.156587 | 2.102061 | 2.078113 |
| C | 1.731414 | 4.67731 | 1.385264 |
| C | 0.641024 | -0.27474 | 5.038789 |
| C | 1.044813 | -3.62197 | 3.447257 |
| C | 1.022926 | 4.490634 | -2.26232 |
| C | 1.25439 | -1.23146 | -4.82131 |
| C | 3.417914 | -2.52336 | -3.0155 |
| C | 0.328504 | -4.21319 | -2.79788 |
| C | -1.84161 | -2.0593 | -3.01055 |
| H | -0.23809 | -3.86274 | 0.217776 |
| H | -1.85075 | -3.91418 | -0.49422 |
| H | -1.32593 | -2.47292 | 0.380192 |
| H | 2.363759 | 1.345314 | -2.90264 |
| H | 3.525587 | 0.598435 | -4.00076 |
| H | 3.7574 | 0.479319 | -2.24758 |
| H | -1.07502 | 1.741985 | 2.058993 |
| H | 0.221729 | 2.198953 | 3.18092 |
| H | -1.38769 | 1.811749 | 3.794101 |
| H | 1.994987 | -3.3186 | 0.153967 |
| H | 3.084648 | -4.12124 | 1.287422 |
| H | 3.547654 | -2.57745 | 0.548331 |
| H | -2.36032 | -1.24936 | 2.530165 |
| H | -2.41674 | -0.88636 | 4.262132 |
| H | -1.58886 | -2.34355 | 3.691453 |
| H | -1.16682 | 1.16094 | -2.40238 |
| H | 0.154605 | 1.71655 | -3.44634 |
| H | -1.32285 | 2.670462 | -3.30363 |
| H | 4.281572 | 2.599432 | -0.98157 |
| H | 4.706075 | 3.925376 | 0.110578 |
| H | 3.653776 | 4.228014 | -1.27958 |
| H | 3.993715 | -0.88258 | 2.994318 |
| H | 4.173467 | -2.52844 | 3.619525 |
| H | 3.201062 | -1.34701 | 4.508544 |

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| H | -1.9309 | 3.14027 | 0.127133 |
| :---: | :---: | :---: | :---: |
| H | -2.01529 | 4.424402 | -1.0956 |
| H | -1.00167 | 4.629981 | 0.343078 |
| H | 2.415845 | 1.589876 | 2.699297 |
| H | 3.687477 | 2.812914 | 2.725566 |
| H | 3.876737 | 1.353711 | 1.736173 |
| H | 1.341235 | 5.388056 | 0.650079 |
| H | 2.532242 | 5.18569 | 1.938051 |
| H | 0.927108 | 4.459708 | 2.098016 |
| H | 0.911171 | -1.26538 | 5.416655 |
| H | -0.06624 | 0.164641 | 5.75496 |
| H | 1.543118 | 0.347542 | 5.050171 |
| H | 0.626135 | -3.28187 | 4.399579 |
| H | 1.739847 | -4.44211 | 3.670904 |
| H | 0.224087 | -4.04099 | 2.852863 |
| H | 1.443286 | 5.265252 | -1.61402 |
| H | 0.31541 | 4.983765 | -2.9423 |
| H | 1.835996 | 4.087047 | -2.8766 |
| H | 0.734676 | -2.16928 | -5.04128 |
| H | 2.025335 | -1.09755 | -5.59145 |
| H | 0.531429 | -0.4149 | -4.93554 |
| H | 3.873542 | -2.54195 | -2.01906 |
| H | 4.212046 | -2.29827 | -3.73941 |
| H | 3.043882 | -3.52784 | -3.2342 |
| H | 0.670599 | -4.08068 | -3.82882 |
| H | -0.47613 | -4.96059 | -2.81645 |
| H | 1.156095 | -4.64069 | -2.22052 |
| H | -2.35828 | -1.22149 | -2.5322 |
| H | -2.56268 | -2.87977 | -3.12236 |
| H | -1.54451 | -1.74153 | -4.01556 |
| C | -1.33902 | 0.141537 | -0.00115 |
| C | -2.57089 | 0.181227 | -0.00404 |
| C | -3.99702 | 0.195983 | -0.00492 |
| C | -4.71096 | 1.409656 | -0.07479 |
| C | -4.72167 | -1.01206 | 0.063635 |
| H | -4.16656 | 2.346611 | -0.12953 |
| H | -4.18344 | -1.95289 | 0.116056 |
| C | -6.10217 | 1.417878 | -0.07523 |
| C | -6.11288 | -1.00938 | 0.063169 |
| H | -6.64843 | 2.353554 | -0.12887 |
| H | -6.66694 | -1.9405 | 0.115895 |
| C | -6.79408 | 0.207193 | -0.0062 |
| Cl | -8.54898 | 0.214837 | -0.00724 |

Sum of electronic and thermal Free Energies $=-3939.029965$ Hartrees.

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## Chapter 7:

## Concluding Remarks

### 7.1 Conclusions and Overview.

In this dissertation, several areas of inorganic and synthetic actinide chemistry have been expanded. First, uranium-nitrogen multiple bonds have been synthesized in two ancillary ligand frameworks and with varying substitution at the imido nitrogen atom. We have observed differences in the reactivities and electronic structures of these compounds compared with uranium-oxygen multiply bonded complexes reported in the literature. ${ }^{1,2}$ Also, uranium complexes bearing novel redox-active ligands have been synthesized. The electronic structures of these compounds have been investigated using computational and experimental methods, and reactivity was explored in some cases. Previously, $\alpha$-diiminies, ${ }^{3,4} 2,2^{\prime}$-bipyridine, ${ }^{5-7} \eta^{6}$-arenes, ${ }^{8,9}$ iminoquinones, ${ }^{10,11}$ pyridine(diimines), ${ }^{12,13}$ and benzophenone ${ }^{14}$ had been used as redox-active ligands for uranium. However, the use of imido ligands with redox-active substituents and organic amides, such as $N, N$-dimethylbenzamide were novel. More broadly, while the $N, N-$ dimethylbenzamide radical anion had been transiently generated ${ }^{15-17}$ and recently proposed as an intermediate in the reduction of organic amides by $\mathrm{SmI}_{2}$-amine- $\mathrm{H}_{2} \mathrm{O},{ }^{18}$ it had not previously been isolated and characterized. We were able to exploit the $\mathrm{U}(\mathrm{III} / \mathrm{IV})$ couple to stabilize this intermediate proposed in $\operatorname{Ln}(I I / I I I)$ chemistry. In the context of our work on ketyl radical complexes of uranium, we also observed unprecedented reactivity of uranium(III) with esters, in which the ester methoxy group was transferred to the uranium center. Last, we synthesized a series of uranium(VI) oxo acetylide complexes and observed the extreme downfield shift of the ${ }^{13} \mathrm{C}$ acetylide resonance as a result of temperature independent paramagnetism (TIP) of the uranium (VI) center.

### 7.2 Future Opportunities.

A goal of the work in this dissertation that remained elusive was the synthesis and stabilization of reactive uranium-ligand bonds and multiple bonds. We were particularly interested
in synthesizing terminal $U=C$ bonds. Uranium chalcogen ${ }^{19-21}$ and pnictogen ${ }^{22,23}$ multiple bonds have now been isolated, and nucleophilic carbene complexes of uranium stabilized by ylidic structures have been known for almost a decade (Scheme 7.2.1). ${ }^{24}$ However, unsupported uranium alkylidenes have been inaccessible using the traditional routes. ${ }^{25}$


Scheme 7.2.1 Resonance structures contributing to the bonding in previously reported nucleophilic uranium carbene ${ }_{24.25}$ complex, $\left[(\mathrm{SCS}) \cup\left(\mathrm{BH}_{4}\right)_{2}(\mathrm{THF})_{2}\right] \quad(\mathrm{SCS}=$ bis(diphenylthiophosphinoyl)methane). ${ }^{24}$

We pursued routes to support terminal $\mathrm{U}=\mathrm{C}$ bonds using many of the ligand frameworks presented in this dissertation (Scheme 7.2.2). We hypothesized that the thermodynamic stability afforded by the inverse trans influence could support these reactive bonds and designed reactions to install the $U=C$ bond trans to a strong donor ligand. One example of a reaction that was attempted was $\mathrm{K}\left[\mathrm{U}^{\prime \mathrm{V}}\left(=\mathrm{NSiMe}_{3}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]$ (2.1-K) with $\mathrm{Ph}_{2} \mathrm{CN}_{2}$ (Scheme 7.2.2a). However, instead of elimination of nitrogen gas and installation of $\mathrm{a}=\mathrm{CPh}_{2}$ ligand trans to the imido ligand proceeding, no reaction occurred. We reasoned that $\mathbf{2 . 1} \mathbf{- K}$ was not reducing enough to react with $\mathrm{Ph}_{2} \mathrm{CN}_{2}$. A similar approach was attempted with $\mathrm{K}_{2}\left[\mathrm{U}^{\mathrm{V}}\left[=\mathrm{NC}(2-\mathrm{naph}) \mathrm{Ph}_{2}\right]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right](\mathbf{3 . 4 - 2 K})$ (Scheme 7.2.2b). However, 3.4-2K was unstable and unable to be isolated. If reactions with 3.4$\mathbf{2 K}$ with $\mathrm{Ph}_{2} \mathrm{CN}_{2}$ were attempted without isolating $\mathbf{3 . 4 - 2 K}$ only diamagnetic products were observed by ${ }^{1} \mathrm{H}$ NMR spectroscopy.
a)



b)


2-

c)

[TMPH][pyrrole]

d)



$$
\mathbf{N}^{*}=\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}
$$

Scheme 7.2.2 Selected proposals for installing U=C bond trans to a strong imido or oxo donor ligands. These reactions failed for the following reasons: a) there was no reaction b) the starting material was unstable and unable to be isolated, and in situ reactions resulted in only diamagnetic product c) reduction occurred d) in the PN framework, only U (III) and $\mathrm{U}(\mathrm{IV})$ products were able to be isolated.

Uranium $(\mathrm{VI})$ organometallic complexes such as $\mathrm{U}^{\mathrm{V1}}(=\mathrm{O})(\mathrm{CCPh})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ had been synthesized previously by our group. ${ }^{26}$ We attempted reactions of this complex with nucleophiles, with the goal of promoting nucleophilic attack at the carbon-carbon triple bond to synthesize
complexes of the general type $\left[\mathrm{U}^{\mathrm{VI}}(=\mathrm{O})[=\mathrm{C}=\mathrm{C}(\mathrm{Ph})(\mathrm{R})]\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\right]^{-}$(Scheme 7.2.2c). Reaction with superbases, such as methyllithium, instead resulted in reduction. Hoping to avoid reduction of the complex, we tried using nucleophiles that would not have such a high basicity. In this context we reacted 2,2,6,6-tetramethylpiperidine (TMP) with pyrrole and added the resulting product, $[T M P H][p y r r o l e]$, to $\mathrm{U}^{\mathrm{VI}}(=\mathrm{O})(\mathrm{CCPh})\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$. However, we still observed primarily paramagnetically shifted peaks in the ${ }^{1} \mathrm{H}$ NMR spectrum, implying that reduction had occurred.

The organometallic complex, $\mathrm{U}^{\mathrm{VI}}(=\mathrm{O}) \mathrm{Me}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$, had also been synthesized by our group previously. ${ }^{26}$ Deprotonation reactions of the methyl group trans to the oxo were unsuccessful and often similarly resulted in reduction of the complex. We reasoned that the tris(bis(trimethylsilylamide) ligand framework may not be ideal for this chemistry since it competes with the axial ligands for covalent interaction with the metal center. This equatorial competition for covalencey can undermine the axial stability garnered from the inverse trans influence. We hypothesized that an electron poor ligand, such as the PN ligand, would compete less with the axial ligands for bonding. However, the PN ligand was not effective in stabilizing the higher +5 and +6 oxidation states of uranium, and the analogous organometallic compound, $(\mathrm{PN})_{2} \mathrm{U}^{\mathrm{V}}(=\mathrm{O}) \mathrm{Me}$, was not able to be synthesized in our hands (Scheme 7.2.2d).

Given the challenges associated with both strong and weak equatorial ligands, and the propensity of uranium complexes with monodentate ligands to decompose to HL or $\mathrm{ML}(\mathrm{M}=\mathrm{Li}$, $\mathrm{Na}, \mathrm{K}$ ) if proton sources are available or alkali metals are used in reaction conditions, a multidentate ligand may solve some of the problems previously mentioned. The first example of a crystallographically characterized uranium-nitride was supported by ( $\operatorname{Tren}^{\text {TIPS }}$ ) ${ }^{3-}$, a tetradentate ligand (TrenTIPS $\left.=\left[\mathrm{N}_{( }\left(\mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{NSi}^{\prime} \mathrm{Pr}_{3}\right)_{3}\right]^{3-}\right)\left(\right.$ Scheme 7.2.3a) ${ }^{23}$ While there are many advantages to the $\operatorname{Tren}^{\text {TIPS }}$ ligand framework, including its chelating ability and sterically protected coordination sphere, the apical nitrogen donor is a weak axial donor. Potentially, a strong axial donor, such as an imido, could replace this apical nitrogen so that otherwise reactive $U-L$ bonds could be further stabilized through the inverse trans influence (Scheme 7.2.3b).
a)


$\mathrm{R}=\mathrm{Ar},{ }^{i} \mathrm{Pr}, \mathrm{SiMe}_{3}$

Scheme 7.2.3 Multidentate ligands used to support uranium-ligand multiple bonds. a) The previously reported uranium(VI) nitride supported by the Tren ${ }^{\text {TTPS }}$ ligand framework. b) A proposed multidentate ligand for supporting reactive $\mathrm{U}=\mathrm{C}$ bonds.

### 7.3 Miscellaneous Results.

In parallel to the work described in Chapters 2-6, other compounds were prepared and reactions attempted that were not directly related to the content of those chapters. Some interesting results from these reactions are included here.

### 7.3.1 Attempts at Synthesizing Uranium-Carbon Multiple Bonds.

As mentioned in Section 7.2, we were interested in synthesizing uranium-carbon multiple bonds, since unsupported uranium alkylidene complexes are not yet known. In this context, we tried reactions with simple uranium starting materials and known carbene transfer reagents. Previously, $\mathrm{U}^{I I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ was reacted with $\mathrm{Ph}_{2} \mathrm{CN}_{2}$ in a hexanes/pyridine solvent mixture to yield $\left[\mathrm{Na}(\mathrm{py})_{2}\right]\left[\mathrm{U}^{1 \mathrm{~V}}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(\eta^{2}-\mathrm{N}_{2} \mathrm{CPh}_{2}\right)\right] .{ }^{27}$ This compound featured a $\mathrm{Ph}_{2} \mathrm{CN}_{2}$ ligand that had been reduced by two electrons. While one electron involved in this reduction came from the uranium ion, the second came from adventitious Nal , which is difficult to remove from the $U^{\text {III }}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ starting material. The same reaction carried out in diethyl ether and crystallized from a concentrated THF solution layered with hexanes yielded $[\mathrm{Na}(\mathrm{THF})]\left[\mathrm{U}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(\eta^{2}-\right.\right.$ $\left.\mathrm{N}_{2} \mathrm{CPh}_{2}\right)$ ] (7.1) (Scheme 7.3.1).


Scheme 7.3.1 Reaction of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with diphenyldiazomethane.
The uranium-ligand bond lengths in 7.1 were identical to those found in the previously synthesized compound, $\left[\mathrm{Na}(\mathrm{py})_{2}\right]\left[\mathrm{U}^{\mathrm{V}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(\eta^{2}-\mathrm{N}_{2} \mathrm{CPh}_{2}\right)\right]$ (Figure 7.3.1). However, because this product is formed in part from impurities in the starting material, we attempted to reduce the amount of Nal carried by $\left.\mathrm{U}^{\mathrm{IIII}} \mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$. The standard preparation of $\mathrm{U}^{\mathrm{III}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ consists of stirring $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$ and $\mathrm{Na}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]$ in THF overnight, filtering the crude reaction mixture, and removing volatiles under reduced pressure. The residue is then dissolved in hexanes and the volatiles are removed again under reduced pressure. This step is performed with the aim of desolvating the Nal, which has THF coordinated, increasing its solubility in organic solvents. The residue is then dissolved in hexanes again, the Nal is filtered off, and the volatiles are removed from the filtrate, which contains the product. ${ }^{28}$ This procedure is effective in making $\left.\mathrm{U}^{\text {III }} \mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$. However, NaI remains with the uranium product and is not completely filtered off during the extraction with hexanes. We were able to reduce, to some degree, the amount of Nal carried through to the product by conducting the reaction of $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$ and $\mathrm{Na}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]$ in a suspension in pentane overnight. The process of removing volatiles, extracting with noncoordinating solvents such as pentane or hexanes, filtering, and removing the volatiles was then repeated 3-5 times, until negligible white solid was left on the frit at the filtration step. In these cases 7.1 persisted but was not the major product by ${ }^{1} \mathrm{H}$ NMR. Another compound with paramagnetically shifted peaks was present in these cases, but was not identified.


Figure 7.3.1 Thermal ellipsoid plot of 7.1 at $50 \%$ probability. Bond lengths (Å) and angles $\left({ }^{\circ}\right)$ : $\mathrm{U}(1)-\mathrm{N}(1) 2.179(3), \mathrm{U}(1)-\mathrm{N}(2) 2.330(2), \mathrm{U}(1)-\mathrm{N}(3) 2.330(3), \mathrm{U}(1)-\mathrm{N}(4) 2.342(3), \mathrm{U}(1)-\mathrm{N}(5)$ 2.343(3), N(1)-N(2) 1.347(3), $\mathrm{Na}(1)-\mathrm{N}(1)$ 2.346(3).

To supersede the need to remove Na from the starting material, we also reacted $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$ directly with $\mathrm{Ph}_{2} \mathrm{CN}_{2}$. This resulted in an immediate color change from dark blue to pale orange. The crude ${ }^{1} \mathrm{H}$ NMR was very clean and showed ten unique aryl protons ranging from 67.52 to 13.45 ppm . There were also two broad peaks at -6.89 and -10.00 ppm . Potentially these signals could correspond to coordinated THF. However, the integration is very high relative to the aryl protons and may correspond to another product. When $\mathrm{KC}_{8}$ was added to this unidentified product the reaction mixture bubbled and became dark. The ${ }^{1} \mathrm{H}$ NMR was no longer paramagnetically shifted, which may imply that a uranium $(\mathrm{VI})$ product was formed. In the aryl region of the NMR, peaks ranged from 7.93 to 7.09 ppm . Additionally, there were two broad peaks at 2.74 and 0.90 ppm , which may correspond to coordinated THF. The goal of performing these reactions was to synthesize $\mathrm{U}^{\mathrm{VI}}\left(=\mathrm{CPh}_{2}\right)_{3}(\mathrm{THF})_{3}$; however, the products of these reactions were not able to be crystallized in our hands. The Bart group used a similar method to synthesize
the uranium tris(imido) complex, $\mathrm{U}^{\mathrm{Vl}}(=\mathrm{NDipp})_{3}(\mathrm{THF})_{3}$, in which they added potassium graphite portionwise to a mixture of $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$ with 2,6-diisopropylphenyl azide. ${ }^{29}$

### 7.3.2 Varied Ancillary Ligand Frameworks.

We considered that the bis(trimethylsilyl)amide ligand framework may be competing for covalent interactions at the expense of axial bonding (see Section 7.2). So, we reasoned that varying the substitution of the amide ligands: $U^{\mathrm{V1}}(=\mathrm{O}) \mathrm{Me}\left[\mathrm{NR}_{2}\right]_{3}$, with less donating equatorial ligands, would contribute to the goal of isolating $\mathrm{U}^{\mathrm{VI}}=\mathrm{CH}_{2}$ moieties. Once synthesized, we planned to deprotonate the axial methyl group to form a $\mathrm{U}=\mathrm{C}$ bond (Scheme 7.3.2).



Scheme7.3.2 Target compounds with equatorial amide ligands.
Previously, our group had reported the uranium(III) amide complex, $U^{\prime \prime \prime}\left[\mathrm{N}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{2}\right]_{3}(\mathrm{THF})_{2}{ }^{30}$ When this was reacted with MeLi, none of the desired compound, $\mathrm{MeU}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{2}\right]_{3}$, was observed. We then targeted the uranium(IV) chloride compound, $\mathrm{CIU}^{1 \mathrm{~V}}\left[\mathrm{~N}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{2}\right]_{3}$, since we expected it to have increased stability to decomposition when reacted with MeLi. However, upon reaction with $\mathrm{CuCl}, \mathrm{U}^{1 \mathrm{~V}} \mathrm{Cl}_{2}\left[\mathrm{~N}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{2}\right]_{2}(\mathrm{THF})_{2}$ (7.2) was formed. Compound 7.2 was crystallized from toluene at $-21^{\circ} \mathrm{C}$ (Scheme 7.3 .3 , Figure 7.3.2). This reaction was facilitated by transmetallation of the amide ligand to copper. Further reaction of this complex with MeLi resulted in decomposition to $\operatorname{LiN}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{2}$.


$$
N^{\dagger}=N\left(C_{6} F_{5}\right)_{2}
$$

Scheme 7.3.3 Reaction of $U^{I I I}\left[N\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{2}\right]_{3}$ with CuCl .


Figure 7.3.2 Thermal ellipsoid plot of 7.2 at $50 \%$ probability. Hydrogen atoms are omitted for clarity. Bond lengths ( $\AA$ ) and angles $\left({ }^{\circ}\right): \mathrm{U}(1)-\mathrm{N}(1) 2.318(2), \mathrm{U}(1)-\mathrm{N}(2) 2.329(2), \mathrm{U}(1)-\mathrm{Cl}(1)$ $2.5919(7), \mathrm{U}(1)-\mathrm{Cl}(2) 2.5892, \mathrm{Cl}(1)-\mathrm{U}(1)-\mathrm{Cl}(2) 176.10(3), \mathrm{N}(1)-\mathrm{U}(1)-\mathrm{N}(2) 178.36(8)$.

We then synthesized the ligand $\mathrm{HN}\left[\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]$ ( $\mathrm{Ar}=3,5$-dimethylphenyl), drawing inspiration from the other known uranium(IV) methyl compound in an amide ligand framework, $\mathrm{MeU}^{\mathrm{IV}}\left[\mathrm{N}\left({ }^{t} \mathrm{Bu}\right)(\mathrm{Ar})\right]_{3} .{ }^{31}$ The ligand was synthesized by deprotonation of 3,5-dimethylaniline by $n$ butyllithium. The deprotonated product was then reacted with $\mathrm{SiMe}_{3} \mathrm{Cl}$ in situ, to yield $\mathrm{HN}\left[\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]$ in $89 \%$ yield. The amine was easily deprotonated by $\mathrm{Na}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]$ to yield
$\mathrm{Na}\left[\mathrm{N}\left[\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]\right]$, which could then be submitted to salt metathesis reactions with uranium starting materials, $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$ and $\mathrm{UCl}_{4}$. When $\mathrm{Na}\left[\mathrm{N}\left[\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]\right]$ was reacted with $\mathrm{UCl}_{4}$ at room temperature, the tetrakis amide complex, $U^{I V}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{4}(7.3)$, was formed cleanly and was crystallized from a small volume of pentane at $-21^{\circ} \mathrm{C}$ (Scheme 7.3.4, Figure 7.3.3). The $\mathrm{U}-\mathrm{N}_{\text {amide }}$ bond lengths of 7.3 were similar to the average $U-N_{\text {amide }}$ bond lengths of $U^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{4}$ at 2.2435 (17) and $2.2987(2) \AA$, respectively.

(7.3)

(7.4)


Scheme7.3.4 Reaction of $\mathrm{UCl}_{4}$ with $\mathrm{Na}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]$ at room temperature and $-21^{\circ} \mathrm{C}$.


Figure 7.3.3 Thermal ellipsoid plot of 7.3 at $50 \%$ probability. Hydrogen atoms are omitted for clarity. Bond lengths $(\AA)$ : $\mathrm{U}(1)-\mathrm{N}(1) 2.2435(17)$.

If the reaction of $\mathrm{UCl}_{4}$ with $\mathrm{Na}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]$ was cooled to $-21^{\circ} \mathrm{C}$, however, the uranium chloride cluster, $\mathrm{Na}\left[\mathrm{U}_{2}{ }^{\mathrm{VV}} \mathrm{Cl}_{5}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{4}\right]$ (7.4), was formed in a mixture with 7.3 (Scheme 7.3.4, Figure 7.3.4). The structure of 7.4 showed a dinuclear complex in which uranium centers were bridged by five chloride ligands and a cation that was not able to be refined. Additionally, each uranium center coordinated only two amide ligands, instead of yielding the desired tris(amide) complex, $\mathrm{ClU}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{3}$.


Figure 7.3.4 Preliminary thermal ellipsoid plot of 7.4 at $50 \%$ probability. Hydrogen atoms are omitted for clarity. The non-positive definite in this structure was not able to be refined as a sodium atom. Bond lengths ( A ) and angles ( ${ }^{\circ}$ ): $\mathrm{U}(1)-\mathrm{N}(1) 2.285(3), \mathrm{U}(1)-\mathrm{N}(2) 2.281(3), \mathrm{U}(1)-\mathrm{P}(1)$ $3.0544(10), \quad \mathrm{U}(1)-\mathrm{P}(2) \quad 3.0897(9), \quad \mathrm{U}(1)-\mathrm{N}(3) 2.20(4), \quad \mathrm{U}(1)-\mathrm{N}(6) \quad 2.273(3), \quad \mathrm{N}(3)-\mathrm{U}(1)-\mathrm{N}(6)$ 170.6(8) N(1)-U(1)-N(2) 141.51(11), N(1)-U(1)-P(2) 151.02(8).

Because our reactions with $\mathrm{UCl}_{4}$ in this ligand framework resulted in either tetrakis or bis(amide) complexes, we attempted salt metathesis reactions with the uranium(III) starting material, $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$, with the aim of synthesizing the tris(amide) complex, $\mathrm{U}^{I I I}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{3}$ (Scheme 7.3.5). However, when $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$ was reacted with three equivalents of $\mathrm{Na}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]$ at room temperature, the uranium(III) tetrakis(amide) complex, $\mathrm{Na}(\mathrm{THF})_{4} \mathrm{U}^{\mathrm{ll}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{4}$ (7.5), was formed and was able to be crystallized from minimal pentane at $-21^{\circ} \mathrm{C}$ (Figure 4.3.6).

(7.6)


(7.7)

Scheme 7.3.5 Reaction of $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$ with $\mathrm{Na}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]$ at room temperature and $-196{ }^{\circ} \mathrm{C}$ and synthesis of $\mathrm{MeU}^{1 \mathrm{~V}}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{3}$.


Figure 7.3.5 Thermal ellipsoid plot of 7.5 at $50 \%$ probability. Hydrogen atoms are omitted for clarity. This structure was not of high quality and a .cif file was not generated. Bond lengths $(\AA)$ : $\mathrm{U}(1)-\mathrm{N}(1)$ 2.373, $\mathrm{U}(1)-\mathrm{N}(2)$ 2.386, $\mathrm{U}(1)-\mathrm{N}(3) 2.413, \mathrm{U}(1)-\mathrm{N}(4) 2.322$.

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To avoid formation of the tetrakis(amide) we cooled the reaction mixture to $-196^{\circ} \mathrm{C}$, by freezing solutions of $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$ and $\mathrm{Na}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]$, and adding the sodium salt to $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$ upon thawing (Scheme 7.3.5). Additionally, we used an excess of $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$, as the Cummins group had done in their synthesis of $\mathrm{IU}^{\mathrm{IV}}[\mathrm{N}(\mathrm{Ad})(\mathrm{Ar})]_{3} .{ }^{9}$ These reaction conditions resulted in the analogous uranium(IV) product in our ligand framework, $\mathrm{IU}^{1 \mathrm{~V}}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{3}$ (7.6) (Figure 4.3.7). Due to the reduced steric demand of the ligands in 7.6 compared with the tetrakis(amide) complex, 7.3, the average $U-\mathrm{N}_{\text {amide }}$ bond lengths were considerably shorter at 2.209(2) and 2.2435 (17) Å for 7.6 and 7.3, respectively.


Figure 7.3.6 Thermal ellipsoid plot of $\mathbf{7 . 6}$ at $50 \%$ probability. Hydrogen atoms are omitted for clarity. Bond lengths $(\AA)$ : $\mathrm{U}(1)-\mathrm{l}(1) 3.0360(3), \mathrm{U}(1)-\mathrm{N}(1) 2.215(2), \mathrm{U}(1)-\mathrm{N}(2) 2.197(2), \mathrm{U}(1)-\mathrm{N}(3)$ 2.214(2).

When 7.6 was reacted with MeLi at $-21^{\circ} \mathrm{C}$, the desired product, $\mathrm{MeU}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{3}$ (7.7), was formed (Scheme 7.3.5, Figure 7.3.7). Unfortunately, 7.7 crystallized with two equivalents of $\mathrm{Li}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]$, resulting from partial decomposition of the compounds in the reaction mixture. Despite the impurity present in the crystal structure, the bond lengths compared well with the previously reported uranium(IV) methyl compounds in amide ligand frameworks, $\mathrm{MeU}^{\mathrm{IV}}\left[\mathrm{N}\left({ }^{t} \mathrm{Bu}\right)(\mathrm{Ar})\right]_{3}$ and $\mathrm{MeU}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} .{ }^{26,31}$ The U-C bond length was slightly shorter in 7.7 than in $\mathrm{MeU}^{\mathrm{IV}}\left[\mathrm{N}\left({ }^{\dagger} \mathrm{Bu}\right)(\mathrm{Ar})\right]_{3}$, with bond lengths of $2.422(14)$ and $2.446(7) \AA$, respectively. However,
the U-C bond length was not statistically different from that of $\mathrm{MeU}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}{ }^{26,31}$ Future directions for 7.7 include purification from $\mathrm{Li}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]$ and reaction with O -atom donors to yield the uranium $(\mathrm{VI})$ compound, $\mathrm{U}^{\mathrm{VI}}(=\mathrm{O}) \mathrm{Me}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{3}$.


Figure 7.3.7 Thermal ellipsoid plot of 7.7 at $50 \%$ probability. Hydrogen atoms and $\left[\mathrm{Li}\left(\mathrm{OEt}_{2}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{2}\right.$ are omitted for clarity. Bond lengths $(\AA): \mathrm{U}(1)-\mathrm{C}(34) 2.422(14), \mathrm{U}(1)-\mathrm{N}(1)$ 2.226(10), U(1)-N(2) 2.216(10), U(1)-N(3) 2.218(10).

### 7.3.3 Tetranuclear Uranium Compounds with Alternating Nitride and Azide Bridges.

We reacted $U^{\text {III }}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with sodium azide in a solution of THF (Scheme 7.3.6). This resulted in a tetranuclear uranium complex bridged by azide and nitride ligands, $\mathrm{Na}(\mathrm{THF})_{5}\left\{\left[\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} \mathrm{U}^{\mathrm{IV}}(\mathrm{N}) \mathrm{U}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{2}\right]_{2}\left(\mathrm{~N}_{3}\right)\right\}$ (7.8-Na). There are now several examples of uranium complexes with bridging nitride ligands. ${ }^{32-34}$ However, the only examples of multinuclear uranium complexes with bridging nitride and azide ligands were two structurally related 24membered rings with eight uranium centers reported by Evans and coworkers. ${ }^{35}$ Similarly, these complexes were synthesized from a uranium(III) starting material, $\left(\mathrm{C}_{5} \mathrm{Me}_{4} \mathrm{R}\right)_{2} \mathrm{U}^{\text {II }}\left[\mathrm{B}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)_{4}\right](\mathrm{R}=$ $\mathrm{Me}, \mathrm{H})$, which was reacted with sodium azide.

(7.8-Na)


Scheme 7.3.6 Reactions to yield tetranuclear uranium complexes bridged by nitride and azide ligands.

We crystallized $7.8-\mathrm{Na}$ from minimal THF at $-21^{\circ} \mathrm{C}$ (Figure 7.3.8). Compared with the compounds reported by Evans and coworkers, we had a larger range of $\mathrm{U}-\mathrm{N}_{\text {nitride }}$ bond distances, ranging from 1.99(2)-2.14(2) $\AA$, while their $U-N_{\text {nitride }}$ bond distances ranged from 2.012(16)$2.090(8)$ Å. Conversely, both of the $\mathrm{U}-\mathrm{N}_{\text {azide }}$ bond lengths in 7.8-Na were indistinguishable at 2.42(3) and 2.43(3) $\AA$, while the Evans compounds have large ranges for their $U-N_{\text {azide }}$ bond lengths, from 2.449(14) to $2.525(7) \AA \AA^{35}$


Figure 7.3.8 Thermal ellipsoid plot of $7.8-\mathrm{Na}$ as a dimer at $50 \%$ probability. Hydrogen atoms are omitted for clarity and only one molecule is shown from the asymmetric unit. Bond lengths $(\AA)$ ): $\mathrm{U}(1)-\mathrm{N}(1) 2.33(2), \mathrm{U}(1)-\mathrm{N}(2) 2.36(3), \mathrm{U}(1)-\mathrm{N}(3) 2.31(2), \mathrm{U}(1)-\mathrm{N}(11) 2.14(2), \mathrm{U}(2)-\mathrm{N}(11) 1.99(2)$, $\mathrm{U}(2)-\mathrm{N}(4) 2.31(3), \mathrm{U}(2)-\mathrm{N}(5) 2.31(2), \mathrm{U}(2)-\mathrm{N}(12)$ 2.42(3), U(3)-N(14) 2.43(3), U(3)-N(6) 2.32(2), $\mathrm{U}(3)-\mathrm{N}(7) 2.35(2), \mathrm{U}(3)-\mathrm{N}(15) 2.00(3), \mathrm{U}(4)-\mathrm{N}(15) 2.11(3), \mathrm{U}(4)-\mathrm{N}(8) 2.33(2), \mathrm{U}(4)-\mathrm{N}(9) 2.28(2)$, $\mathrm{U}(4)-\mathrm{N}(10) 2.31$ (2).

We also reacted the uranium $(\mathrm{V})$ compound, $\mathrm{U}^{\mathrm{V}}\left(\mathrm{N}_{3}\right)_{2}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ with potassium graphite in THF (Scheme 7.3.6). This resulted in the analogous potassium compound, $\mathrm{K}(\mathrm{THF})_{x}\left\{\left[\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} \mathrm{U}^{\mathrm{IV}}(\mathrm{N}) \mathrm{U}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{2}\right]_{2}\left(\mathrm{~N}_{3}\right)\right\}(7.8-\mathrm{K})$. This may imply that in the reaction to synthesize $7.8-\mathrm{Na}$, the uranium(V) bis(azide) complex is formed as an intermediate and is reduced by $\mathrm{U}^{\mathrm{II}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ to yield $7.8-\mathrm{Na}$.

### 7.4 Experimental.

### 7.4.1 Methods.

All reactions and manipulations were performed under an inert atmosphere $\left(\mathrm{N}_{2}\right)$ using standard Schlenk techniques or in a Vacuum Atmospheres, Inc. Nexus II drybox equipped with a molecular sieves 13X / Q5 Cu-0226S catalyst purifier system. Glassware was oven-dried overnight at $150{ }^{\circ} \mathrm{C}$ prior to use. Unless otherwise noted, reactions were conducted in 20 mL scintillation vials in approximately $5-10 \mathrm{~mL}$ of solvent. ${ }^{1} \mathrm{H}$ NMR were obtained on a Bruker DMX300 Fourier transform NMR spectrometer at 300 MHz . Chemical shifts were recorded in units of
parts per million downfield from residual proteo solvent peaks. The infrared spectra were obtained from $400-4000 \mathrm{~cm}^{-1}$ using a Perkin Elmer 1600 series infrared spectrometer.

### 7.4.2 Materials.

Tetrahydrofuran, $\mathrm{Et}_{2} \mathrm{O}$, hexanes, and pentane were purchased from Fisher Scientific. These solvents were sparged for 20 min with dry argon and dried using a commercial two-column solvent purification system comprising columns packed with Q5 reactant and neutral alumina, respectively (for hexanes and pentane), or two columns of neutral alumina (for THF, $\mathrm{Et}_{2} \mathrm{O}$ and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ). All solvents were stored over $3 \AA$ molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. and stored over potassium mirror overnight prior to use. Starting materials: $\mathrm{Ul}_{3}(\mathrm{THF})_{4}{ }^{36}, \quad \mathrm{UCl}_{4}{ }^{37}, \quad \mathrm{U}\left[\mathrm{N}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{2}\right]_{3}(\mathrm{THF})_{2}{ }^{30}, \quad \mathrm{U}\left(\mathrm{N}_{3}\right)_{2}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}{ }^{38}$, $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}{ }^{28}$, and $\mathrm{Ph}_{2} \mathrm{CN}_{2}{ }^{39}$ were prepared according to the reported procedures unless otherwise noted. $\mathrm{NaN}_{3}$ was dried under vacuum at room temperature overnight. Subsequently it was stirred in THF, toluene, and pentane in series for 24 hours each.

### 7.4.3 $[\mathrm{Na}(\mathrm{THF})]\left[\mathrm{U}^{1 \mathrm{~V}}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(\boldsymbol{\eta}^{2}-\mathrm{N}_{2} \mathrm{CPh}_{2}\right)\right]$ (7.1).

To a solution of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}\left(50 \mathrm{mg}, 0.07\right.$ mmol, 1 equiv) in $\mathrm{Et}_{2} \mathrm{O}$ was added $\mathrm{Ph}_{2} \mathrm{CN}_{2}$ $(14 \mathrm{mg}, 0.07 \mathrm{mmol}, 1$ equiv). The reaction mixture immediately turned from purple to red. Volatiles were removed under reduced pressure, and the residue was extracted with pentane. The pentane solution was filtered over Celite, reduced to a small volume and crystallized at $21^{\circ} \mathrm{C}$, giving 7.1 as red crystals. ${ }^{1} \mathrm{H}$ NMR (benzene-d6): $\delta 34.39(1 \mathrm{H}), 16.89(2 \mathrm{H}), 12.17(1 \mathrm{H})$, $11.54(1 \mathrm{H}), 10.47(1 \mathrm{H}), 8.99(4 \mathrm{H}),-5.19(54 \mathrm{H})$.

### 7.4.4 $\mathrm{U}^{\mathrm{IV}} \mathrm{Cl}_{2}\left[\mathrm{~N}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{2}\right]_{2}(\mathrm{THF})_{2}$ (7.2).

To a solution of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{2}\right]_{3}(\mathrm{THF})_{2}(150 \mathrm{mg}, 0.11 \mathrm{mmol}, 1$ equiv) in toluene was added $\mathrm{CuCl}(42 \mathrm{mg}, 0.42 \mathrm{mmol}, 4$ equiv). The reaction mixture was stirred for 1 h and filtered over Celite. The solution was reduced to a small volume and crystallized at $-21^{\circ} \mathrm{C}$ to yield 7.2 as pale orange crystals. ${ }^{19}$ F NMR (THF): $\delta-160.42$ (3F), -166.68 (6F), -290.47 (6F).

### 7.4.5 (3,5-Dimethylphenyl)(trimethylsilyl)amine.

To a 3-neck round-bottom flask equipped with addition funnel and condenser was added 3,5-dimethylaniline ( $9.74 \mathrm{~g}, 80.00 \mathrm{mmol}$, 1 equiv) in a solution of $\mathrm{Et}_{2} \mathrm{O}(50 \mathrm{~mL})$ under nitrogen. At room temperature $n$-butyllithium ( $1.5 \mathrm{M}, 52 \mathrm{~mL}, 80.00 \mathrm{mmol}, 1$ equiv) was added dropwise. The reaction mixture was then cooled to $-78^{\circ} \mathrm{C}$. A solution of $\mathrm{SiMe}_{3} \mathrm{Cl}(10.15 \mathrm{~mL}, 80.00 \mathrm{mmol}, 1$ equiv) in $\mathrm{Et}_{2} \mathrm{O}(50 \mathrm{~mL})$ was then added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 1 h . The volatiles were removed under reduced pressure, and in the glovebox, hexanes was used to extract the product. The suspension was filtered over Celite, and the volatiles were removed to yield ( 3,5 -dimethylphenyl)-trimethylsilylamine as a white solid. Yield: $13.78 \mathrm{~g}, 71.26 \mathrm{mmol}, 89 \%{ }^{1} \mathrm{H}$ NMR (benzene- $\mathrm{d}_{6}$ ): $\delta 6.43(\mathrm{~d}, 1 \mathrm{H}, J=0.56 \mathrm{~Hz}), 6.30(\mathrm{~d}, 2 \mathrm{H}$, $J=0.49 \mathrm{~Hz}$ ), $3.02(\mathrm{~s}, 1 \mathrm{H}), 7.53(\mathrm{~s}, 6 \mathrm{H}), 0.18(\mathrm{~s}, 9 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (benzene- $\left.d_{6}\right): \delta 147.60,138.75$, 120.25, 114.93, 21.66, 0.18.

### 7.4.6 Sodium (3,5-dimethylphenyl)(trimethylsilyl)amide.

To a solution of ( 3,5 -dimethylphenyl)(trimethylsilyl)amine ( $13.78 \mathrm{~g}, 71.26 \mathrm{mmol}, 1$ equiv) in $\mathrm{Et}_{2} \mathrm{O}(70 \mathrm{~mL})$ was added $\mathrm{Na}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]$ ( $13.07 \mathrm{~g}, 71.26 \mathrm{mmol}, 1$ equiv) in $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$. The reaction mixture was stirred for 6 h , and subsequently the solid was collected by filtration. Additional product was collected from the filtrate by crystallization from a small volume of $\mathrm{Et}_{2} \mathrm{O}$ layered with hexanes, giving sodium (3,5-dimethylphenyl)(trimethylsilyl)amide as a white solid. Yield: $15.00 \mathrm{~g}, 69.65 \mathrm{mmol}, 98 \%{ }^{1}{ }^{1} \mathrm{H}$ NMR (benzene- $\mathrm{d}_{6}$ ): $\delta 6.20(\mathrm{~s}, 1 \mathrm{H}), 6.16(\mathrm{~s}, 2 \mathrm{H}), 2.27(\mathrm{~s}, 6 \mathrm{H})$, 0.22 (s, 9H). ${ }^{13} \mathrm{C}$ NMR (benzene- $d_{6}$ ): $\delta 161.73,139.45,119.48,115.26,21.94,2.89$.

### 7.4.7 $\mathrm{U}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{4}(7.3)$.

To a solution of $\mathrm{UCl}_{4}(1.00 \mathrm{~g}, 2.63 \mathrm{mmol}, 1$ equiv) in THF was added dropwise a solution of sodium ( 3,5 -dimethylphenyl)(trimethylsilyl)amide ( $1.70 \mathrm{~g}, 7.90 \mathrm{mmol}, 3$ equiv) in THF. The reaction mixture was stirred for 1 h , filtered over Celite, and the volatiles were removed under reduced pressure. The residue was extracted with hexanes, filtered over Celite, and crystallized at $-21^{\circ} \mathrm{C}$ to give 7.3 as green crystals. ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $\delta 10.01(36 \mathrm{H}),-1.63(4 \mathrm{H}),-6.19$ (24H), -13.21 (8H).

### 7.4.8 ( THF$\left.)_{2} \mathrm{Na}^{2} \mathrm{U}_{2}{ }^{1 \mathrm{~V}} \mathrm{Cl}_{5}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{4}\right]$ (7.4).

Separate solutions of $\mathrm{UCl}_{4}(100 \mathrm{mg}, 0.263 \mathrm{mmol}, 1$ equiv) and sodium (3,5dimethylphenyl)(trimethylsilyl)amide (128 mg, $0.594,2.26$ equiv) in THF were cooled to $-21^{\circ} \mathrm{C}$. Sodium (3,5-dimethylphenyl)(trimethylsilyl)amide was then added to $\mathrm{UCl}_{4}$, and the volatiles were immediately removed from the reaction mixture under reduced pressure. The residue was extracted with hexanes and filtered over Celite, giving a mixture of 7.3 and 7.4. Compound 7.4 was selectively crystallized from the solution of hexanes at $-21^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $\delta$ $10.68(36 \mathrm{H}),-1.09(4 \mathrm{H}),-2.13(4 \mathrm{H}),-5.73(4 \mathrm{H})$. The methyl peaks were too broad to be observed at room temperature.

### 7.4.9 $\mathrm{Na}(\mathrm{THF})_{4}\left[\mathrm{U}^{\mathrm{II}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{4}\right]$ (7.5).

To a solution of $\mathrm{Ul}_{3}(\mathrm{THF})_{4}(50 \mathrm{mg}, 0.06 \mathrm{mmol}, 1$ equiv $)$ in THF was added dropwise a solution of sodium (3,5-dimethylphenyl)(trimethylsilyl)amide ( $36 \mathrm{mg}, 0.17 \mathrm{mmol}, 3$ equiv) in THF. The reaction mixture was stirred for 1 h and the volatiles were removed under reduced pressure. The residue was extracted with hexanes, filtered over Celite, and crystallized at $-21^{\circ} \mathrm{C}$ to yield black crystals of 7.5. ${ }^{1} \mathrm{H}$ NMR (benzene- $\left.d_{6}\right): \delta 1.59(36 \mathrm{H}),-0.51(4 \mathrm{H}),-1.03(24 \mathrm{H}),-2.66(8 \mathrm{H})$.

### 7.4.8 $\mathrm{IU}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{3}(7.6)$.

Separate solutions of $\mathrm{UI}_{3}(\mathrm{THF})_{4}(1.00 \mathrm{~g}, 1.11 \mathrm{mmol}, 1$ equiv) and sodium $(3,5-$ dimethylphenyl)(trimethylsilyl)amide ( $0.54 \mathrm{~g}, 2.50 \mathrm{mmol}, 2.25$ equiv) were prepared in toluene. The solutions were frozen at $-196 \quad{ }^{\circ} \mathrm{C}$. Upon thawing, sodium (3,5dimethylphenyl)(trimethylsilyl)amide was added to the solution of $\mathrm{UI}_{3}(\mathrm{THF})_{4}$, and the volatiles were removed immediately. The residue was extracted with hexanes, filtered over Celite, and volatiles were removed. The residue was extracted with $\mathrm{Et}_{2} \mathrm{O}$ and crystallized at $-21^{\circ} \mathrm{C}$ to yield 7.6 as pale brown crystals. Yield: $300 \mathrm{mg}, 0.32 \mathrm{mmol}, 29 \% .{ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $\delta 7.83(27 \mathrm{H})$, $0.10(3 \mathrm{H}),-2.22(6 \mathrm{H}),-5.55(18 \mathrm{H})$.

### 7.4.9 $\mathrm{MeU}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{3}(7.7)$.

To a solution of 7.6 ( $32 \mathrm{mg}, 0.03 \mathrm{mmol}, 1$ equiv) in $\mathrm{Et}_{2} \mathrm{O}$ at $-21^{\circ} \mathrm{C}$ was added a solution of MeLi in $\mathrm{Et}_{2} \mathrm{O}$ ( $23 \mu \mathrm{~L}, 0.04 \mathrm{mmol}, 1.1$ equiv). The reaction mixture was stirred for 5 min before the volatiles were removed under reduced pressure. The residue was extracted with hexanes,
filtered over Celite, and crystallized at $-21{ }^{\circ} \mathrm{C}$ to yield brown crystals of 7.7- $\left[\mathrm{Li}\left(\mathrm{OEt}_{2}\right)\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)(\mathrm{Ar})\right]_{2}\right.$. Compound 7.7 was never able to be purified, so a yield was not determined. ${ }^{1} \mathrm{H}$ NMR (benzene $\left.-d_{6}\right): \delta 7.01(27 \mathrm{H}),-0.79(3 \mathrm{H}),-4.85(18 \mathrm{H}),-5.51(6 \mathrm{H})$.

### 7.4.10 $\mathrm{Na}(\mathrm{THF})_{5}\left\{\left[\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} \mathrm{U}^{\mathrm{IV}}(\mathrm{N}) \mathrm{U}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{2}\right]_{2}\left(\mathrm{~N}_{3}\right)\right\}(7.8-\mathrm{Na})$.

To a solution of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(25 \mathrm{mg}, 0.04 \mathrm{mmol}, 1$ equiv) in THF was added sodium azide ( $3 \mathrm{mg}, 0.05 \mathrm{mmol}, 1.5$ equiv). The reaction mixture was stirred for 5 min , over the course of which a color change from dark purple to light brown occurred, before it was filtered over Celite. The solution was reduced to a small volume and $7.8-\mathrm{Na}$ was crystallized at $-21^{\circ} \mathrm{C}$ as pale brown crystals. ${ }^{1} \mathrm{H}$ NMR (benzene- $d_{6}$ ): $\delta 51.91(9 \mathrm{H}),-1.64(18 \mathrm{H}),-2.62(126 \mathrm{H}),-9.07(18 \mathrm{H}),-14.88$ (9H).

### 7.4.11 K(THF $)_{x}\left\{\left[\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3} \mathrm{U}^{\mathrm{IV}}(\mathrm{N}) \mathrm{U}^{\mathrm{IV}}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{2}\right]_{2}\left(\mathrm{~N}_{3}\right)\right\}$ (7.8-K).

To a solution of $\mathrm{U}\left(\mathrm{N}_{3}\right)_{2}\left[\mathrm{~N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}(15 \mathrm{mg}, 0.02 \mathrm{mmol}$, 1 equiv) in THF was added potassium graphite ( $10 \mathrm{mg}, 0.08 \mathrm{mmol}, 4$ equiv). The reaction mixture turned purple and was filtered over Celite. When the volatiles were removed, the residue turned brown, giving 7.8-K and a mixture of other products. ${ }^{1} \mathrm{H}$ NMR (benzene $\left.-d_{6}\right): \delta 50.83(9 \mathrm{H}),-2.29(144 \mathrm{H}),-8.15(18 \mathrm{H}),-$ 14.98 (9H).

### 7.5 Crystallographic Analysis.

X-ray intensity data were collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Ka radiation ( $\lambda=0.71073 \AA$ ) at a temperature of $143(1) \mathrm{K}$. In all cases, rotation frames were integrated using SAINT, ${ }^{40}$ producing a listing of unaveraged $\mathrm{F}^{2}$ and $\sigma\left(F^{2}\right)$ values, which were then passed to the SHELXTL ${ }^{41}$ program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using TWINABS ${ }^{42}$ or SADABS. ${ }^{43}$ The structures were solved by direct methods (SHELXS-97). ${ }^{44}$ Refinement was by full-matrix least squares based on $F^{2}$ using SHELXL-97. ${ }^{44}$ All reflections were used during refinements. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

### 7.6 Spectroscopic Analysis.

${ }^{1} \mathrm{H}$ NMR spectra were obtained on a Bruker DMX-300 Fourier transform NMR spectrometer at 300 MHz . Chemical shifts were recorded in units of parts per million referenced to residual solvent peaks ( ${ }^{1} \mathrm{H}$ ). The UV-Visible absorption spectra were obtained from 2000-290 nm using a Perkin Elmer 950 UV-Vis/NIR Spectrophotometer, and all samples were prepared under an $\mathrm{N}_{2}$ environment. 1 mm pathlength screw cap quartz cells were used with a blank measured before each run.


Figure 7.6.1. ${ }^{1} \mathrm{H}$ NMR reaction of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ synthesized in THF with $\mathrm{Ph}_{2} \mathrm{CN}_{2}$ in benzene- $\mathrm{d}_{6}$.


Figure 7.6.2. ${ }^{1} \mathrm{H}$ NMR reaction of $\mathrm{U}\left[\mathrm{N}\left(\mathrm{SiMe}_{3}\right)_{2}\right]_{3}$ synthesized in pentane with $\mathrm{Ph}_{2} \mathrm{CN}_{2}$ in benzene$d_{6}$. Starred peaks ( ${ }^{*}$ ) indicate 7.1 present in product mixture with unknown paramagnetic product.


Figure 7.6.2. Crude ${ }^{1} \mathrm{H}$ NMR of reaction of $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$ with $\mathrm{Ph}_{2} \mathrm{CN}_{2}$.


Figure 7.6.4. ${ }^{1} \mathrm{H}$ NMR of reaction of $\mathrm{Ul}_{3}(\mathrm{THF})_{4}$ with $\mathrm{Ph}_{2} \mathrm{CN}_{2}$ and potassium graphite in benzene$d_{6}$.


(7.2)
$\begin{array}{llllllll}-150 & -170 & -190 & -210 & -230 & -250 & -270 & -290\end{array}$

Figure 7.6.5. ${ }^{19} \mathrm{~F}$ NMR of 7.2 in THF.


Figure 7.6.6. ${ }^{1} \mathrm{H}$ NMR of (3,5-dimethylphenyl)(trimethylsilyl)amine in benzene- $d_{6}$.
$\stackrel{\circ}{\circ} \stackrel{\text { Nom }}{\sim}$ $\stackrel{\infty}{\stackrel{\circ}{-}} \underset{\stackrel{\infty}{\div}}{\stackrel{\circ}{\circ}}$

$\begin{array}{lllllllllllll}150 & 130 & 110 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0\end{array}$

Figure 7.6.7. ${ }^{13} \mathrm{C}$ NMR of (3,5-dimethylphenyl)(trimethylsilyl)amine in benzene- $d_{6}$.


Figure 7.6.8. ${ }^{1} \mathrm{H}$ NMR of sodium ( 3,5 -dimethylphenyl)(trimethylsilyl)amide in benzene- $d_{6}$.


Figure 7.6.9. ${ }^{13} \mathrm{C}$ NMR of sodium (3,5-dimethylphenyl)(trimethylsilyl)amide in benzene- $d_{6}$.


Figure 7.6.10. ${ }^{1} \mathrm{H}$ NMR of 7.3 in benzene- $d_{6}$.


Figure 7.6.11. ${ }^{1} \mathrm{H}$ NMR of 7.4 in benzene- $d_{6}$.


Figure 7.6.12. ${ }^{1} \mathrm{H}$ NMR of 7.5 in benzene- $d_{6}$.
-7.83
-7.16
$\begin{array}{ll}0 & \text { N } \\ \cdots & \text { N } \\ \vdots & 1\end{array}$
م

(7.6)


Figure 7.6.13. ${ }^{1} \mathrm{H}$ NMR of 7.6 in benzene- $d_{6}$.


Figure 7.6.14. ${ }^{1} \mathrm{H}$ NMR of 7.7 in benzene- $d_{6}$.


Figure 7.6.15. ${ }^{1} \mathrm{H}$ NMR of $7.8-\mathrm{Na}$ in benzene- $\mathrm{d}_{6}$.


Figure 7.6.16. ${ }^{1} \mathrm{H}$ NMR of $7.8-\mathrm{K}$ in benzene- $d_{6}$.

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