Four-Electron Reduction Chemistry Using an Uranium(III) Phosphido Complex

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Four-Electron Reduction Chemistry Using an Uranium(III) Phosphido Complex

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The first uranium(III) phosphido complex is reported. Reaction of $(C_5Me_5)_2UI(THF)$ with $KP[(C_6H_2Me_3\text{-}2,4,6)(SiMe_3)]$ affords $(C_5Me_5)_2U[P(C_6H_2Me_3\text{-}2,4,6)(SiMe_3)](THF)$, 1. The reactivity of 1 was explored with two equivalents of N_3SiMe_3 and N_3Ad, Ad = adamantyl, both of which produce the U(VI) bis(imido) complexes via four-electron reduction of the azides.

The reductive chemistry of U(III) complexes has been an area of intense study due to its impressive small molecule activation[1] with substrates such as azides to form the imido functional group.[2-4] Imido ligands, in addition to other moieties,[5-10] have furthered our understanding of actinide-ligand bonding, which helps elucidate the involvement of the 5f- and 6d-orbitals when constructing a multiple bond.[11-15]

Reductive chemistry with uranium has been done in a variety of ways including redox-active ligands,[16] an uranium(III) precursor,[17, 18] or a combination of both the ligand and U(III) metal center.[19] Uranium(IV) can also be the starting oxidation state but this typically requires a redox-active ligand such as pyridine(diamine)[2] or ketyl radical,[20] or a reducing agent, most commonly an Na/Hg amalgam or potassium on graphite.[17,21-26] There are also examples with, what we will term here, pseudo redox-active ligands, or ligands which are traditionally not redox-active but undergo reductive coupling or transformation in the process of actinide-mediated redox chemistry. These would include tetraphenylborate,[27] benzyl,[28] pentamethylcyclopentadienyl,[29] and, recently, phosphido ligands.[30]

Since the coordination chemistry of the actinides is dominated by hard donor ligands, the number of U(III) complexes with the heavier congeners of the chalcogen group is limited,[31-41] and the only U(III) complexes known with any of the pnictogen group besides nitrogen is $(C_5Me_5)_2UH(dmpe)$,[42] $(CH_3BH_3)_3U(dmpe)_2$,[43] dmpe = 1,2-bis(dimethylphosphino)ethane, and $(C_5H_4Me)_3U[P(OCH_2)_3CEt$.[44] However, thorium(IV)[5, 30, 45-48] and uranium(IV)[49-51] complexes of phosphido, arsenido, antimony,[52] and bismuth[52] are known, but also rare.

Here, we report the first U(III) phosphido complex, $(C_5Me_5)_2U[P(Mes)(SiMe_3)](THF)$, Mes = $C_6H_2Me_3$-2,4,6. Our goal for this complex was to exploit the weak uranium-phosphorus bond as well as the reducing power of U(III) to perform both insertion and reduction chemistry. To study the reactivity, organic azides[53, 54] and isocyanide[46, 55] were chosen since these substrates are known to undergo both types of reactions.

The synthesis of $(C_5Me_5)_2U[P(Mes)(SiMe_3)](THF)$, **1**, was done by reacting $(C_5Me_5)_2UI(THF)$ with the bulky phosphido ligand, $KP(Mes)(SiMe_3)$, eq. 1, which resulted in an immediate color change from green to brown. The product was isolated as a dark brown powder. This complex appears to be NMR silent as no resonances could be definitively assigned in ^1H NMR spectrum of **1** and the ^{31}P NMR signal could not be located.

The structure was **1** was determined by X-ray crystallographic analysis, Figure 1. The U-P bond distance of 2.8903(9) Å is similar to the U(IV)-P bond distance of 2.883(2) Å in $U(Tren^{TIPS})(PH_2)$, $Tren^{TIPS}$ = $N\{CH_2CH_2NSi(^iPr)_3\}_3$. This is a result of the lack of steric crowding in the equatorial plane of **1**. The U-P bond distance in **1** is shorter than the 3.211 and 3.092 Å in $(C_5Me_5)_2UH(dmpe)$ due to phosphido versus phosphine character.[42]

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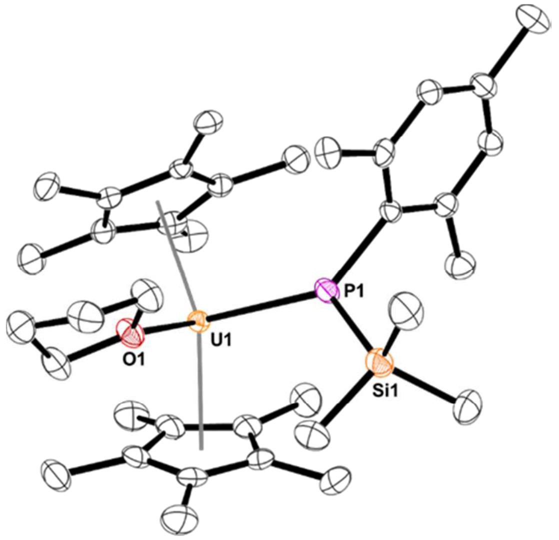
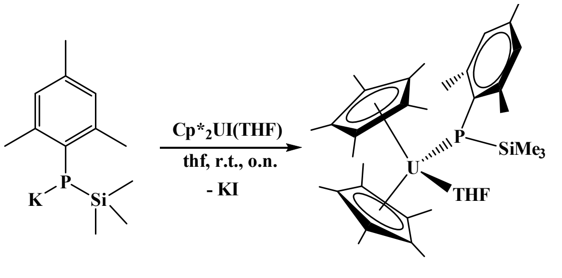


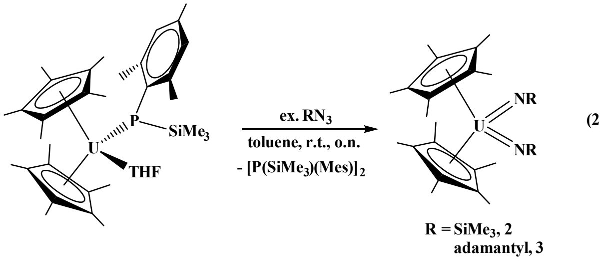
Figure 1. Thermal ellipsoid plot of $(C_5Me_5)_2U[P(C_6H_2Me_3$-2,4,6$)(SiMe_3)](THF)$, **1**, shown at 50% probability level. Hydrogen atoms were omitted for clarity.



(1)

1

The reactivity of **1** was examined with organic azides and *tert*-butyl isocyanide, which are known to undergo both insertion[46] and reduction chemistry.[55] Since U(III) is highly reducing, coupled with the weak uranium-phosphorus bond, we explored the possibility of both reaction types occurring with **1**. This was not the case. Organic azides such as 1-azidoadamantane (N_3Ad) and azidotrimethylsilane (Me_3SiN_3) react with **1** to form bis(imido) complexes, eq. 2. Both uranium(VI) products, $(C_5Me_5)_2U[=N(SiMe_3)]_2$, **2**, and $(C_5Me_5)_2U[=N(Ad)]_2$, **3**, can be isolated after recrystallization in low yield, eq. 2. While no color change occurred, gas evolution was observed. Complex **3** has been previously reported by Burns and co-workers from $(C_5Me_5)_2UCl_2$ with two equivalents of N_3Ad in the presence of excess potassium graphite. Complex **2** can be made from this route as well.



(2)

The ^1H NMR spectrum of **2** indicated a diamagnetic species with the $(C_5Me_5)^{1-}$ resonance at 4.40 ppm and the $SiMe_3$ group at 0.34 ppm. The resonance at -52.9 ppm for $SiMe_3$ in the ^{29}Si NMR spectrum is shifted considerably to higher frequency compared to other U(VI) complexes containing a silyl group previously reported.[56] For example, $(BIPM)UOCl_2$[57] and $(BIPM)U(NMes)(O)(DMAP)_2$[58] have ^{29}Si chemical shifts at -0.69 and -8.28 ppm, respectively. However, there are no uranium(VI) complexes with the $(=NSiMe_3)^{2-}$ functional group to compare directly. When compared to diamagnetic transition metal imido complexes, the ^{29}Si NMR chemical shift is also upfield shifted. For example, the ^{29}Si NMR resonance in $Ta(NMe_2)(=NSiMe_3)[CyNC(NMe_2)NCy]_2$ is found at -16.32 ppm.[59] Given the downfield shift of the $(C_5Me_5)^{1-}$ and upfield shift of the $SiMe_3$ in the ^1H and ^{29}Si NMR spectra, respectively, this is probably a result of temperature independent paramagnetism. A common observation in $(C_5Me_5)_2U(=NR)_2$ complexes.[49] For example, $(C_5Me_5)_2U(=N^tBu)_2$[60] and $(C_5Me_5)_2U(=NAd)_2$[61] have $(C_5Me_5)^{1-}$ resonances at 3.95 and 4.07 ppm, respectively.

The structure of **2** was determined by X-ray crystallographic analysis, Figure 2. The U-N bond distances in **2** are 1.948(5) and 1.957(5) Å. These bond lengths are similar to other metallocene bis(imido) complexes. For example, $(C_5Me_5)_2U(=NAd)_2$, **3**, has U-N bond distances of 1.94(2) and 1.96(2) Å,[17] while $(C_5Me_5)_2U(=NPh)_2$ are 1.952(7) Å.[22]

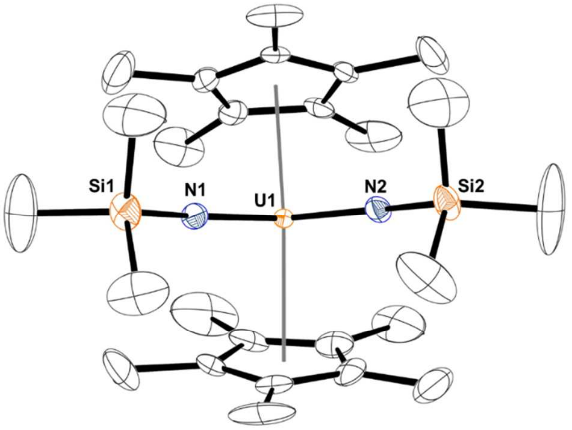
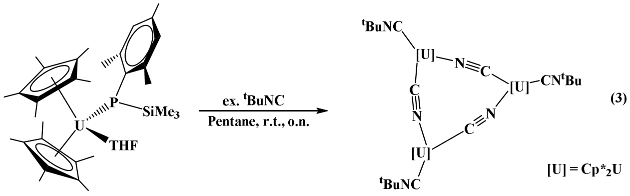


Figure **2**. Thermal ellipsoid plot of $(C_5Me_5)_2U[=N(SiMe_3)]_2$, **2**, shown at 50% probability level. Hydrogen atoms were omitted for clarity.

The reaction of **1** with two equivalents of an organic azide is a four-electron reduction. Three electrons from metal-based oxidation of U(III) to U(VI) and one-electron from the reductive coupling of the phosphido ligand to form half an equivalent of $(Mes)(SiMe_3)PP(SiMe_3)(Mes)$. This type of four-electron reactivity has been observed previously with $(C_5Me_5)_2U(BPh_4)$,[27] and $(C_5Me_5)_3U$.[27] While there is no direct comparison in reactivity of $(C_5Me_5)_2U(NR_2)$ with an organic azide, the reaction of $(C_5Me_5)_2U(hpp)$, hpp = 1,3,4,6,7,8-hexahydro-2*H*-pyrimido-[1,2-*a*]pyrimidinato, with Me_3SiN_3

produces the U(V) imido,[62] in contrast to here where reductive coupling of the phosphido is observed. However, the reduction of RN_3 to $(RN)^{2-}$ with U(III) commonly produces U(V) mono(imido) complexes.[63-68]

Reaction of **1** with ^{t}BuNC forms the previously known bridging cyanide product, $[(C_5Me_5)_2U(CNC(CH_3)_3)(\mu\text{-}CN)]_3$,[69] **4**, eq 3. The structure of **4** was determined by X-ray crystallographic analysis since it has a different unit cell than the one previously reported. This complex was previously synthesized from the reaction of $(C_5Me_5)_3U$ with an excess of ^{t}BuNC. In this case, the ligand-based redox chemistry of the phosphido acts as in a similar manner to the $(C_5Me_5)^{1-}$ ligand in the sterically crowded $(C_5Me_5)_3U$. Complex **4** maintains the +3 oxidation state and the byproduct of this reaction could not be determined, but no evidence of coupled phosphido product was found.



(3)

Conclusions

The synthesis and reactivity of the first U(III) phosphido complex has been conducted. With organic azides or ^{t}BuNC, the reactivity involves the elimination of the phosphido ligand either by reductive coupling or some other means. Unfortunately, our overall goal of combining functionalization and redox chemistry was not achieved, however, **1** can be used as a reducing agent through metal- and ligand-based reactivity.

Conflicts of interest

There are no conflicts to declare.

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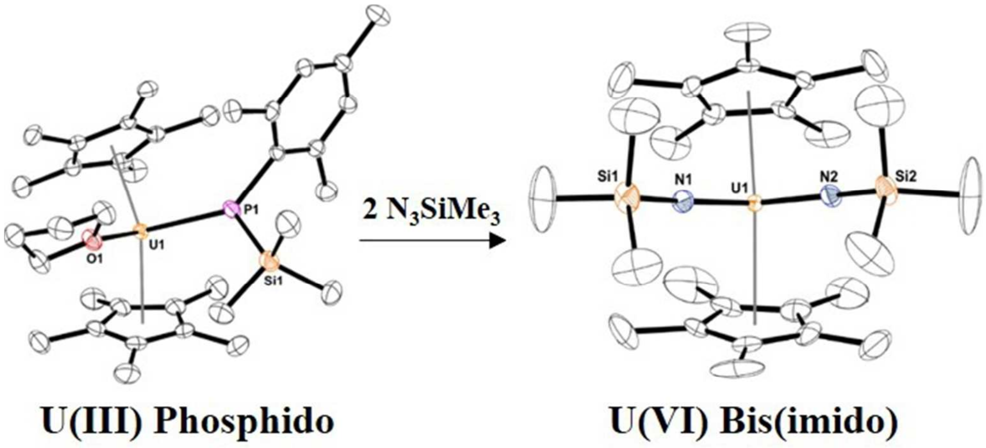

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