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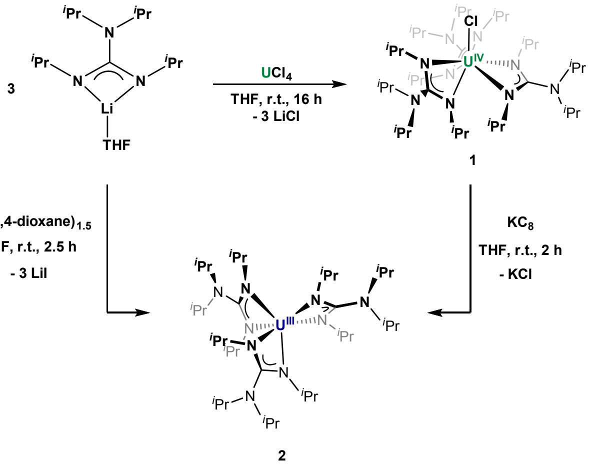
Reaction of the first homoleptic U(III) guanidinate complex with diphenyldiazomethane results in two-electron oxidation of U(III) to U(V) and isolation of the first U(V) hydrazido complex. Corresponding U(V) imido, U(V) oxo, and U(IV) azido complexes were also synthesized for structural comparison.

With the redox chemistry of uranium primarily governed by one-electron processes, effecting two-electron transformations similar to those seen with transition-metals is an ongoing challenge.[1,2] Two-electron oxidation at uranium is generally facilitated by reactions with organic azides or oxygen-atom transfer reagents, resulting in terminal imido and oxo complexes, respectively.[3,4] Diphenyldiazomethane has been shown to act as both a one-[5] and two-electron[6-8] oxidant towards uranium, forming amido- and imido-type bonds, with these oxidative transformations limited to U(III) to U(IV) or U(IV) to U(VI). However, no stable U(V) diphenyldiazomethane complexes have been isolated; putative U(V) species are presumed to undergo disproportionation or comproportionation.[7]

Our group has recently focused on the utility of amidinates[9-13] as ancillary ligands to support actinide metal centers, effect unique reactivity, and provide new metal-atom linkages.[14-16] Here we turn our attention to guanidinate-supported actinide complexes. Although rare,[17,18] they should provide an avenue to perform comparative reactivity studies relative to the amidinate systems, and we envisioned the greater electron-richness[19] might help support a variety of uranium-ligand multiple bonds. Here we present the synthesis and characterization of both U(IV) (**1**) and U(III) (**2**) guanidinate complexes, the latter being the first homoleptic U(III) guanidinate species reported. Complex **2** undergoes two-electron oxidation upon reaction with diphenyldiazomethane, generating the tris-guanidinate U(V) hydrazido product (**3**), which contains a short, terminal U-N bond indicative of uranium-nitrogen multiple bonding. Additionally, two-electron oxidation of **2** with either an organic azide or an oxygen-atom transfer reagent leads to the corresponding U(V) imido (**4**) or U(V) oxo (**5**) complexes, respectively.

After screening a number of guanidinate ligands, we settled on the *N,N,N′,N′′*-tetraisopropylguanidinate (TIG) ligand for its ease of synthesis and ability to generate isolable actinide complexes in high yield. Treatment of UCl_4[20] with 3 equiv. of Li(TIG)(THF)[21] afforded $UCl(TIG)_3$ (**1**) as green crystals in 93% yield upon crystallization from toluene. Reduction of **1** with KC_8 in THF led to a color change from green to dark blue; the resulting U(III) guanidinate complex $U(TIG)_3$ (**2**) was isolated in 81% yield upon workup and crystallization from HMDSO. Alternatively, reaction of $UI_3(1,4\text{-dioxane})_{1.5}$[22] with 3.5 equiv. of Li(TIG)(THF) afforded **2** in 73% yield (Scheme 1).



Scheme 1 Syntheses of complexes **1** and **2**

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Complexes **1** and **2** are rare examples of uranium guanidinate species, and **2** is the first homoleptic U(III) guanidinate complex isolated and characterized. The solid-state molecular structures of **1** and **2** were determined by single-crystal X-ray diffraction studies (Figures S23, S24). The U1-Cl1 bond length in **1** is 2.662(1) Å, while the U-N_{guan} bond lengths average 2.44 Å; this average increases to 2.49 Å in **2**, consistent with the larger size of U(III) vs. U(IV). The C-N bond lengths of the NCN chelating fragment of the guanidinate ligands fall within the range of 1.33-1.35 Å in both **1** and **2**, indicating delocalization of electron density. ^{1}H NMR spectroscopy reveals paramagnetically shifted resonances in both complexes; however, while **1** displays broad, overlapping resonances, **2** exhibits six sharp resonances ranging from 30 to -10 ppm integrating to a ratio of 1:1:3:3:3:3, reflecting averaged C_3 symmetry of the molecule in solution.

With **2** in hand, we investigated the ability of the tris-guanidinate framework to support uranium-ligand multiple bonds. Upon combining a magenta solution of diphenyldiazomethane[23] in hexane with dark blue **2** in hexane, an immediate color change to dark red-brown occurred, with no apparent gas evolution. Subsequent workup and crystallization from pentane afforded $U(N_2CPh_2)(TIG)_3$ (**3**) as dark red-brown crystals in 72% yield (Scheme 2). The solid-state molecular structure of **3** was determined by single-crystal X-ray diffraction studies, which revealed a short U1-N10 bond distance of 2.060(3) Å, and a near-linear U1-N10-N11 bond angle of 165.8(3)°. This information, coupled with the elongation of the N10-N11 bond length to 1.299(4) Å (compared to ~1.13 Å for free diphenyldiazomethanes[24]), is consistent with a two-electron reduction of the diphenyldiazomethane moiety by the uranium center, resulting in a U(V) hydrazido complex, featuring a short U-N_{imido} bond (Figure 1). To the best of our knowledge, this is the first example of a U(V) imido complex bearing diphenyldiazomethane as a multiply-bonded ligand.

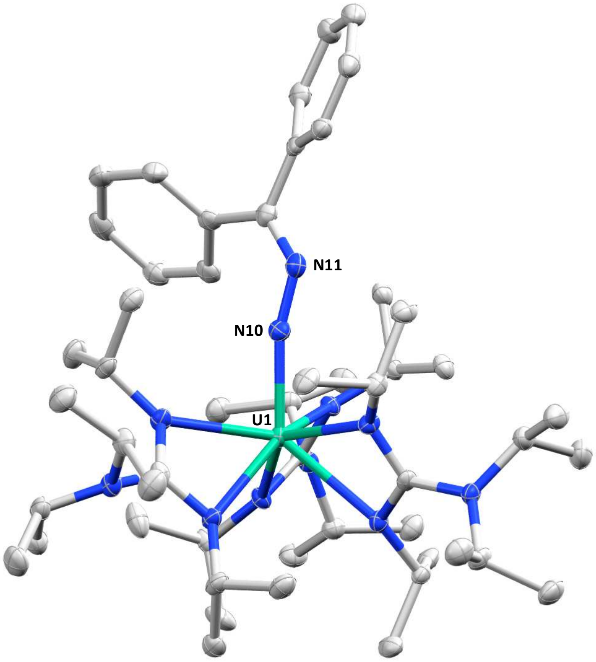
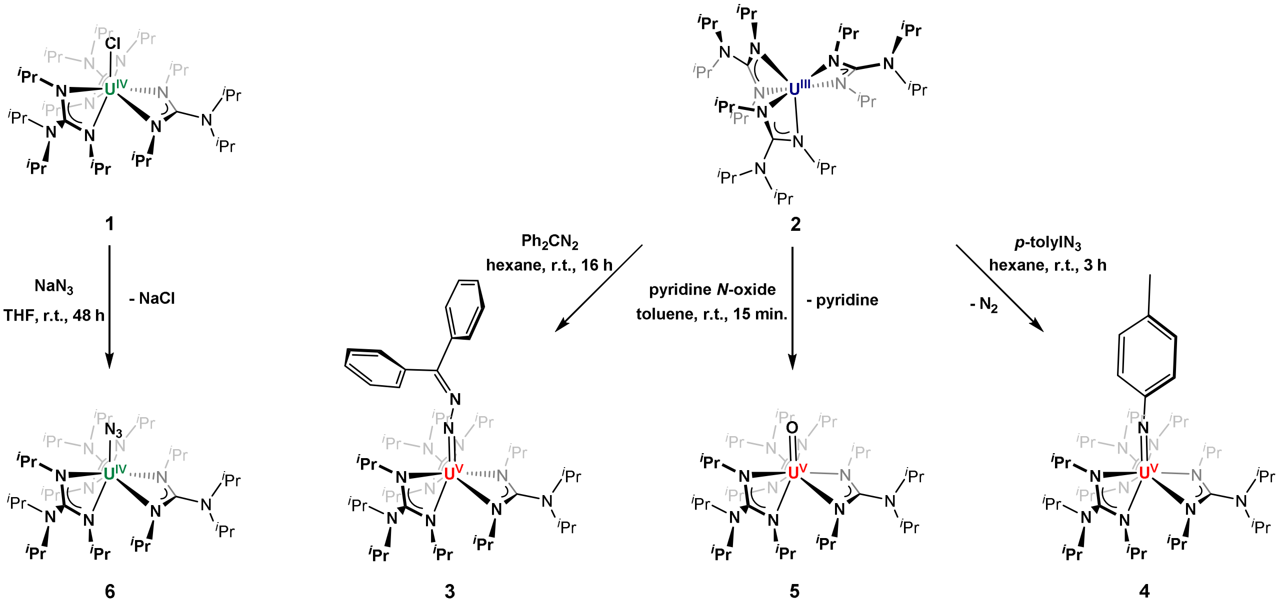


Fig. 1 Molecular structure of **3** (thermal ellipsoids drawn at the 50% probability level). Pentane solvent molecule and hydrogen atoms omitted for clarity.

Although the U-N_{imido} bond length is longer than typically observed with U(V) monoimido systems (average 1.97 Å[25]), it agrees well with the imido bonds observed in other U(IV) and U(VI) systems with diphenyldiazomethane.[6,7] The U-N_{guan} bond lengths average 2.47 Å, and the C-N bond distances in the NCN chelating fragment of the guanidinate ligands fall in the range of 1.32-1.34 Å, indicating no reduction of any of the guanidinate ligands. The room-temperature magnetic moment



Scheme 2 Syntheses of complexes **3-6**

(determined by Evans NMR method) of **3** is μ_{eff} = 2.68 μ_B, whereas the magnetic moments of **1** and **2** are μ_{eff} = 2.93 μ_B and μ_{eff} = 3.34 μ_B, respectively, all consistent with oxidation state assignments of **1** – U(IV), **2** – U(III), and **3** – U(V).[26] However, the possibility of a U(IV) complex with a ligand-centered radical cannot be discounted; Meyer and co-workers observed one-electron oxidation of their $[((^{tBu}ArO)_3tacn)U^{III}]$ species with diphenyldiazomethane, generating a U(IV) complex with an η^2-bound hydrazonato ligand which was observed to contain a ligand-centered radical.[5] We do not believe this is the case with **3**, as the U-N bond length in **3** is ~0.20 Å shorter than that of the analogous bond observed by Meyer, and the near-linear nature of the U-N-N linkage, as well as the lack of an η^2-bonding motif, indicate the ligand does not possess radical character. Attempts to eliminate N_2 from **3**, via photolysis or heating, to generate a uranium carbene species resulted in decomposition.

To definitively assign the short U-N bond distance in **3** as a uranium-nitrogen multiple bond, we assembled a variety of complexes for structural comparison. First, an authentic U(V)-imido complex was accessed through the two-electron oxidation of **2** with an organic azide. Next, to further probe the ability of the $U(TIG)_3$ framework to form stable U(V) complexes through two-electron oxidation processes, we targeted a terminal U(V) oxo. Lastly, we sought a U(IV) analog containing an amido or azido moiety to demonstrate that the U-N_{imido} bond in **3** is significantly shorter than a genuine U(IV)-N single bond (Scheme 2). Treatment of a hexane solution of **2** with a hexane solution of *p*-tolyl azide[27] resulted in an immediate color change to dark red-brown, accompanied by obvious bubbling. Workup and crystallization from pentane afforded U(N-*p*tolyl)$(TIG)_3$ (**4**) as red-brown crystals in 76% yield. The identity of **4** as the U(V) imido complex was confirmed by X-ray diffraction studies, which revealed a U1-N10 bond length of 1.984(4) Å, as well as a U1-N10-C40 bond angle of 172.6(4)° (Figure S25). The U-N_{imido} bond lengths in **3** and **4** differ by 0.08 Å, which is likely the result of the larger steric profile of the diphenyldiazomethane ligand compared to the *p*-tolyl moiety. Bon d lengths and angles seen in **3** and **4** are consistent with that seen in other uranium-imido species.[3,25] The room-temperature magnetic moment of **4** is μ_{eff}=2.67 μ_B, which is nearly identical to that seen in **3**. Cyclic voltammograms were recorded for **3** and **4** in dichloromethane, using a 0.1 M $[Bu_4N][PF_6]$ electrolyte. The CV of compound **4** exhibits two reversible events (Figure S18). Both oxidative U(V)/U(VI) and reductive U(V)/U(IV) processes show negative $E_{1/2}$ values (V vs. Fc/Fc^+) of -0.83 and -2.7, respectively. Compared to $E_{1/2}$ values previously reported for metallocene[28] and amide[29] supported U(V) imido complexes, the potentials of the redox processes of **4** are shifted negatively by almost 800 mV, which is consistent with the strongly electron-donating nature of the TIG ligand. The CV of **3** shows no reversible redox processes. Attempts at chemical oxidation of both **3** and **4** to access the corresponding U(VI) species were not successful; IR spectra of crude reaction mixtures involving **3** contained characteristic stretching frequencies of free N_2CPh_2.

Reaction of **2** with pyridine *N*-oxide resulted in an immediate color change from dark blue to dark red; the corresponding U(V) terminal oxo complex U(O)$(TIG)_3$ (**5**) was isolated in 89% yield upon workup and isolation from pentane. The terminal nature of the oxo moiety, as well as the lack of coordinated pyridine, was confirmed by single-crystal X-ray diffraction studies. The U1-O1 bond length is 1.831(2) Å, which is typical of that seen in other U(V) terminal oxo species (Figure S26).[30-33] The U-N_{guan} and NCN bond lengths are similar to those observed in complexes **3** and **4**. The room-temperature magnetic moment is μ_{eff} = 2.31 μ_B, less than that seen with **3** and **4** but greater than that observed by Liddle and co-workers in their terminal U(V) nitride complex $[UN(Tren^{TIPS})][Na(12C4)_2]$,[34] and is in the range observed for other U(V) species.[26] Despite the lack of steric protection directly at the oxo moiety, the bulky nature of the tris-guanidinate framework is sufficient to prevent dimerization or decomposition. Moreover, **5** can also be generated from the reaction of **2** with trimethylamine *N*-oxide, as its identity was confirmed by ^1H NMR spectroscopy.

Having accessed a direct structural comparison to **3** through the synthesis of **4** and investigated the ability of **2** to support other two-electron oxidation processes through the generation of **5**, we looked to synthesize the corresponding U(IV) amido species to determine the typical U-N_{amido} single bond length in this tris-guanidinate system. However, the synthesis of a U(IV) amido analogue has proved challenging and we were unable to obtain crystals suitable for single-crystal X-ray diffraction studies. Therefore, we instead targeted an azido moiety since it would still provide a U-N single bond with uranium in the 4+ oxidation state. Salt metathesis of **1** with NaN_3 in THF over a period of two days cleanly afforded green crystals of $U(N_3)(TIG)_3$ (**6**) in 65% yield upon workup and crystallization from diethyl ether. Incorporation of the azido moiety in **6** was confirmed by the X-ray crystal structure, which displayed typical azide bond lengths and angles (1.189(3) Å, 1.154(3) Å, and 167.8(2)° for N10-N11, N11-N12, and U1-N10-N11, respectively), as well as a U1-N10 bond distance of 2.326(2) Å, consistent with other U(IV) azido species (Figure S27).[35,36] A strong peak at 2088 cm^{-1} in the FTIR spectrum is assigned to the azide stretch. Taken together, the data from these structural comparisons further support that **3** is best described as a U(V) imido; the U-N_{imido} bond length is much closer to that observed in **4** (difference of ~0.08 Å) than the U(IV)-N_{azido} bond length seen in **6** (difference of ~0.27 Å).

In summary, we have synthesized a number of unusual uranium guanidinate complexes, including the first homoleptic U(III) guanidinate and the first hydrazido complex of uranium in the 5+ oxidation state with diphenyldiazomethane. Comparative structural studies between other imido and azido analogues clearly demonstrate the multiple-bond character of the U-N linkage in **3**, with additional spectroscopic data supporting the U(V) assignment. The stabilization of this U(V) species, as well as the U(V) oxo complex, is tied to the encumbering steric profile provided by the tris-guanidinate framework. The electron richness of the TIG ligand is manifested in the cyclic voltammetry observed for **4** and is another important factor in the stability of these complexes. We are currently investigating the different reactivity profiles of the imido moieties in **3** and **4**, as well as conducting detailed analysis of their electronic properties.

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Conflicts of interest

There are no conflicts to declare.

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Use of a new homoleptic U(III) tris-guanidinate system stabilizes the formation of the first U(V) hydrazido complex.