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A General and Modular Synthesis of Monoimidouranium(IV) Dihalides

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Supporting Information

ABSTRACT: The conproportionation reaction between the dimeric diimidouranium(V) species $[\mathrm{U(N^tBu)_2(I)(^tBu_2bpy)}]_2$ ($^t\mathrm{Bu_2bpy}$ = 4,4′-di-*tert*-butyl-2,2′-bipyridyl) and $\mathrm{UI_3(THF)_4}$ in the presence of additional $^t\mathrm{Bu_2bpy}$ yields $\mathrm{U(N^tBu)(I)_2(^tBu_2bpy)(THF)_2}$ (**2**), an unprecedented example of a monoimidouranium(IV) dihalide complex. The general synthesis of this family of uranium(IV) derivatives can be achieved more readily by adding 2 equiv of MN(H)R (M = Li, K; R = ^{t}Bu, 2,6-$^i\mathrm{PrC_6H_3}$, 2-$^t\mathrm{BuC_6H_4}$) to $\mathrm{UX_4}$ in the presence of coordinating Lewis bases to give complexes with the general formula $\mathrm{U(NR)(X)_2(L)}_n$ (X = Cl, I; L = $^t\mathrm{Bu_2bpy}$, n = 1; L = THF, n = 2). The complexes were characterized by ^{1}H NMR spectroscopy and single-crystal X-ray diffraction analysis of compounds **2** and $\{\mathrm{U[N(2,6\text{-}^iPrC_6H_3)](Cl)_2(THF)_2}\}_2$ (**4**). (The X-ray structures of **5** and **6** are reported in the Supporting Information.)

Actinide complexes that possess multiple bonds to nitrogen continue to attract significant attention as a means to explore fundamental differences between d-block and actinide elements. Arguably the most well-studied of these derivatives are the monoimido metallocenes, $\mathrm{(C_5Me_5)_2U({=}NR)}$ (R = 2,4,6-$\mathrm{Me_3C_6H_2}$, 2,6-$^i\mathrm{Pr_2C_6H_3}$, 2,4,6-$^t\mathrm{Bu_3C_6H_2}$), which have provided important contrasts with analogous transition-metal complexes and critical insight into the unique chemical properties and behaviors that exist in U−N multiple bonds.[1] Surprisingly, nonmetallocene examples of monoimido derivatives are exceedingly rare and are limited to multinuclear examples that are predominantly amide-based in nature.[2,3] Noticeably missing from this family of compounds are the dihalide derivatives $\mathrm{U({=}NR')(X)_2}$ (R′ = alkyl, aryl; X = halide); these species possess significant potential to increase our general knowledge of organoimidouranium chemistry and provide important comparisons with analogous monoimido halide transition-metal species.[4] Of further importance, this family of complexes could serve as useful synthons for the generation of other monoimido derivatives, thus significantly expanding our knowledge of actinide chemistry. Herein, we report the general synthesis of monoimidouranium(IV) dihalide derivatives with the formula $\mathrm{U(NR')(X)_2(L)}_n$ [R′ = ^{t}Bu, 2,6-$^i\mathrm{PrC_6H_3}$, 2-$^t\mathrm{BuC_6H_4}$; X = Cl, I; L = $^t\mathrm{Bu_2bpy}$ ($^t\mathrm{Bu_2bpy}$ = 4,4′-di-*tert*-butyl-2,2′-bipyridyl), n = 1, L = tetrahydrofuran (THF), n = 2]. These interesting molecules can be prepared in one step from uranium tetrahalide precursors.

Our foray into the area of monoimidouranium(IV) chemistry began by investigating the conproportionation reaction between the diimidouranium(V) complex $[\mathrm{U(N^tBu)_2(I)(^tBu_2bpy)}]_2$ (**1**)[5] and $\mathrm{UI_3(THF)_4}$. A similar approach has proven successful in the synthesis of a uranium(IV) metallocene complex from uranium(III) and uranium(V) reagents.[6] In the presence of 2 equiv of $^t\mathrm{Bu_2bpy}$, the monoimidouranium(IV) species $\mathrm{U(N^tBu)(I)_2(^tBu_2bpy)(THF)_2}$ (**2**) is produced in 78% yield (Scheme 1). The ^{1}H NMR spectrum of **2** is consistent with a paramagnetic uranium(IV) complex, containing a broad resonance at 92.2 ppm attributable to the *tert*-butyl group of the imido ligand and bipyridyl aryl resonances at 7.37, 8.79, and 8.87 ppm.

A single-crystal X-ray diffraction study of **2** confirmed its identity as a monoimidouranium(IV) species; the solid-state molecular structure is shown in Figure 1. Complex **2** is mononuclear and features a distorted pentagonal-bipyramidal geometry at the uranium center with the imido moiety and one iodide ligand assuming the axial positions [N1−U1−I2 = 165.08(13)°]. Importantly, the coordinated bpy ligand possesses bond lengths that are typical of a coordinated, neutral bpy ligand and not those of a radical anion species.[7] In the case of the U═N(imido) bond distance [1.931(5) Å], this value is similar to the metallocene imidouranium(IV) complex $\mathrm{(C_5Me_5)_2U({=}N\text{-}2,4,6\text{-}^tBu_3C_6H_2)}$ [1.952(12) Å][1c] and the values reported for monoimidouranium(V) (1.940−2.019 Å)[8] and monoimidouranium(VI) (1.854 Å) derivatives.[9]

Intrigued by the possibility of a more direct synthesis of **2**, we investigated the reaction of $\mathrm{UI_4(OEt_2)_2}$ with 2 equiv of $\mathrm{LiNH^tBu}$ and 1 equiv of $^t\mathrm{Bu_2bpy}$. This procedure produces **2**, albeit in low yield (13%), which appears to be related to difficulties in removing LiI from the product. The dimeric dichloride derivative $[\mathrm{U(\mu\text{-}N^tBu)(Cl)_2(^tBu_2bpy)}]_2$ (**3**) can be obtained in 68% yield through the reaction of 2 equiv of $\mathrm{LiNH^tBu}$ with $\mathrm{UCl_4}$ in the presence of $^t\mathrm{Bu_2bpy}$.

We next investigated whether this general approach could be extended to include (arylimido)uranium(IV) complexes. Indeed, the addition of 2 equiv of LiN(H)R (R = Dipp = 2,6-$^i\mathrm{Pr_2C_6H_3}$, 2-$^t\mathrm{BuC_6H_4}$) to $\mathrm{UCl_4}$ in THF provides mono(arylimido) complexes with the general formula $[\mathrm{U(\mu\text{-}NR)(Cl)_2(THF)_2}]_2$ [R = Dipp (**4**), 2-$^t\mathrm{BuC_6H_4}$ (**6**)], as shown in Scheme 2. In the solid state, **4** and **6** exhibit nearly identical dimeric structures with bridging imido interactions (R = Dipp, Figure 1; R = 2-$^t\mathrm{BuC_6H_4}$, Figure S5 in the Supporting Information, SI) that are reminiscent

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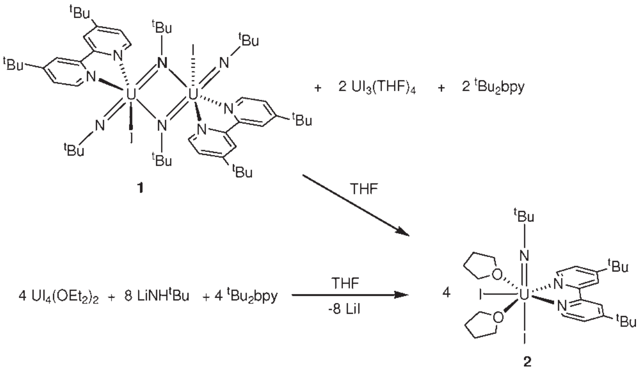
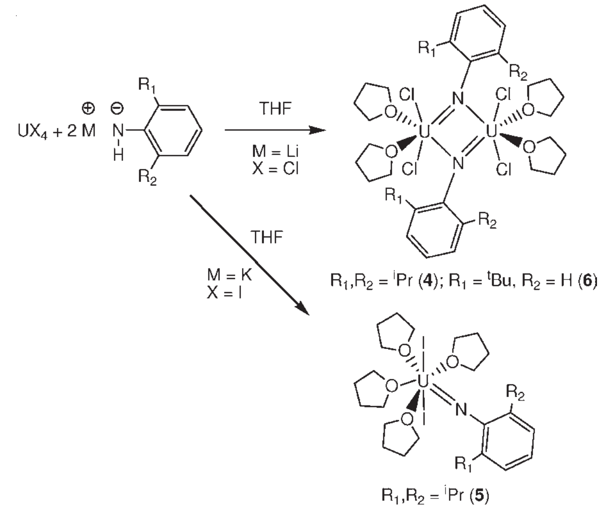
Scheme 1



Scheme 2



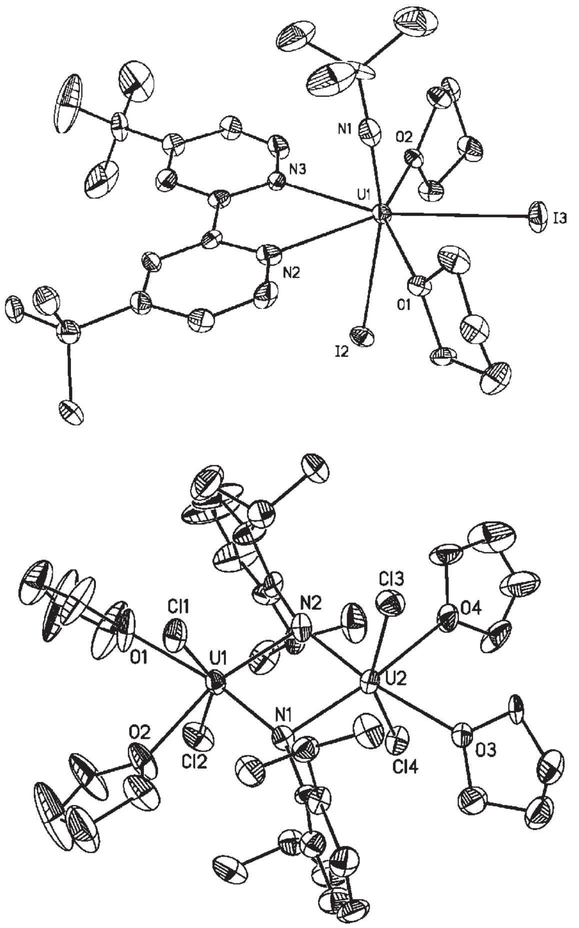


Figure 1. Solid-state molecular structures of **2** and **4** with thermal ellipsoids drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): **2**, U1−N1 = 1.931(5), U1−N2 = 2.631(6), U1−N3 = 2.648(6), U1−I1 = 3.2111(12), U1−I2 = 3.2028(11), U1−O1 = 2.521(3), U1−O2 = 2.531(3), N1−U1−I2 = 165.08(13), N1−U1−I3 = 98.79(13); **4**, U1−N1 = 2.125(8), U1−N2 = 2.349(9), U1−C21 = 2.847(10), U2−N2 = 2.125(9), U2−N1 = 2.328(8), U2−C9 = 3.014(10), U−Cl_{ave} = 2.657(3), U−O_{ave} = 2.495(8), N1−U1−N2 = 77.9(3), N1−U2−N2 = 78.4(3), U1−N1−U2 = 101.2(3), U1−N2−U2 = 101.5(4), Cl1−U1−Cl2 = 151.51(10), Cl3−U2−Cl4 = 155.73(9).

of complex **1** and contain U−N bond lengths that are similar to those found in other dimeric monoimidouranium(IV) complexes.[2] Treatment of $UI_4(OEt_2)_2$ with 2 equiv of KN(H)Dipp in THF yields the mono(arylimido)uranium(IV) product, **5**. The solid-state molecular structure of the diiodide **5** reveals a monomeric species (Figure S4 in the SI) with a short U−N bond length, similar to that found in **2**.[10]

Solution studies of **2**−**6** suggest that the nature of the halide ligand in combination with the coordinating ability of the solvent has a significant effect on the nuclearity of these complexes. In contrast to the diiodide species **2**, the ^{1}H NMR spectrum of **3** in pyridine-d_5 is devoid of any THF resonances. In light of this detail, we propose that complex **3** is a dimeric species in the solid state with a structure similar to that of compound **4**, having one coordinated bpy ligand in lieu of two THF molecules. This is consistent with the observation that crystals of the green compound, **2**, slowly lose THF to yield a brown product, which remains unchanged by ^{1}H NMR in pyridine-d_5. The spectrum of **2** in CD_2Cl_2 is significantly altered, suggesting that this compound may dimerize, while slowly losing coordinated THF. Similarly, ^{1}H NMR spectra of **4** and **6** vary dramatically depending on the identity of the solvent. For example, the methyl resonance of **4** shifts from −8.20 ppm in THF-d_8 to 13.96 ppm in pyridine-d_5, suggesting that pyridine coordinates to the dimeric complexes **3**, **4**, and **6**, breaking up any imido bridges and giving monomeric complexes in solution. Interestingly, the ^{1}H NMR spectrum of the monomeric species **5** remains constant in both THF-d_8 and pyridine-d_5, and its spectrum in pyridine-d_5 is nearly identical with that of its dichloride congener, **4**, consistent with the formation of the analogous pyridine adduct, U(N-2,6-^{i}Pr$_2$C$_6$H$_3$)(I)$_2$(pyridine)$_4$.[11]

Temperature- and field-dependent magnetic data were collected for analytically pure samples of **4** and **6**. The sensitivity of **2** toward the loss of THF prevented accurate measurements of this compound in four attempts. Temperature-dependent data for **4** are shown in Figure 2, with field-dependent data shown in the inset. Data for **6** are provided as SI (Figure S1).

At 300 K, the compounds achieve χT values of 0.88 (**4**) and 0.84 (**6**) emu K mol^{-1} per uranium ion. These χT values yield μ_{eff} = 2.65 (**4**) and 2.58 (**6**) μ_B per uranium ion at 300 K. The magnitudes of these moments are consistent with the reported values for uranium(IV) complexes.[12] The magnetic moments at 300 K reflect crystal-field splittings for **4** and **6** that are larger than

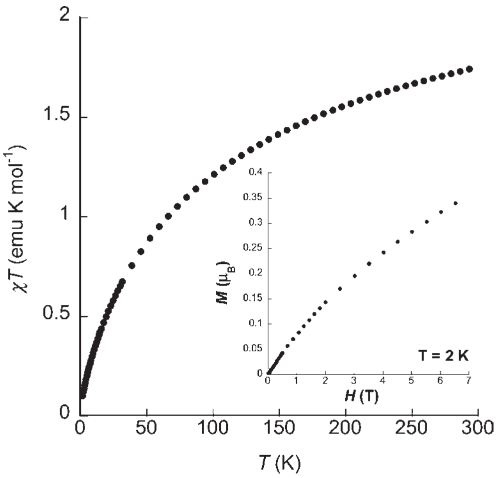


Figure 2. Magnetic data for **4** recorded from 2 to 300 K at 0.1 T and 0−7 T at 2 K (inset). The magnetic moments of **4** per uranium ion are 2.65 and 0.63 μ_B at 300 and 2 K, respectively.

kT. The low-symmetry crystal fields of **4** and **6** partially quench the orbital angular momentum of the formally ground-state $^3H_4$ term determined for the $5f^2$ ions using L−S coupling.[13]

The temperature-dependent data for **4** and **6**, collected at 0.1 T, are essentially identical. With decreasing temperature, both compounds show a monotonic decrease in their χT values, due to thermal depopulation of the crystal-field levels. At 2 K, the compounds attain χT values of 0.099 (**4**) and 0.094 (**6**) emu K mol^{-1} consistent with singlet ground states. Field-dependent data for **4** (inset, Figure 2) and **6** (inset, Figure S1 in the SI) do not saturate and attain values of 0.36 (**4**) and 0.34 (**6**) μ_B at 7 T. The field-dependent data are also consistent with the reported data for low-symmetry uranium(IV) complexes with singlet ground states.[14]

As was observed for other dimeric uranium(IV) complexes, there is no direct evidence of magnetic coupling in the temperature-dependent data for **4** and **6**. The dominance of the uranium(IV) crystal-field effects on their magnetic behavior prevents the simple detection of magnetic coupling in these complexes.[15]

In this Communication, we have demonstrated that monoimidouranium(IV) complexes with the general formula $U(NR)(X)_2(L)_n$ (R = ^{t}Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$, 2-^{t}BuC$_6$H$_4$; X = Cl, I; L = ^{t}Bu$_2$bpy, $n = 1$; L = THF, $n = 2, 4$) can be synthesized in a facile manner from UX_4 and 2 equiv of a primary amide. This simple approach promises to open up a new frontier in organoimidouranium chemistry, allowing for the synthesis of complexes that possess significant steric and electronic control at the metal center. Importantly, this methodology offers tremendous potential to generate imido complexes of other actinide elements, in particular transactinide derivatives, which could greatly expand our understanding of these multiply bonded heavy-element systems.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Complete details of the preparation and characterization of **2**−**6**, including X-ray crystallographic details (as a CIF file) of **2** and **4**−**6**, and magnetic data for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) The value of 1.958(8) Å for the U−N_{imido} distance in **5** compares quite favorably with the corresponding distance of 1.931(5) Å for **2**. For a more complete list of relevant bond lengths and angles, see the SI.

(11) Attempts to obtain X-ray-quality single crystals of **4**−**6** as pyridine or 4-*tert*-butylpyridine adducts have been unsuccessful.

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