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Supporting Information

ABSTRACT: Deprotonation of [U(TrenTIPS)(NH2)] (1) [TrenTIPS = N(CH2CH2NSiPri3)2] with organoalkali metal reagents MR (M = Li, R = Bu); M = Na–Cs, R = CH2CH2H, afforded the imido-bridged dimers [{U–(TrenTIPS)(μ-N[H]M)}2] (M = Li–Cs (2a–e)). Treatment of 2c (M = K) with 2 equiv of 15-crown-5 ether (15CS) afforded the uranium terminal parent imido complex [U(TrenTIPS)(NH)]/[K(15CS)] (3c), which can also be viewed as a masked uranium(IV) nitride. The uranium–imido linkage was found to be essentially linear, and theoretical calculations suggested σπ4 polarized U–N multiple bonding. Attempts to oxidize 3c to afford the neutral uranium terminal parent imido complex [U(TrenTIPS)(NH)] (4) resulted in spontaneous disproportionation to give 1 and the uranium–nitride complex [U(TrenTIPS)(N)] (5); this reaction is a new way to prepare the terminal uranium–nitride linkage and was calculated to be exothermic by −3.25 kcal mol−1.

We recently reported the inadvertent formation of the uranium amide [U(TrenTIPS)(NH2)] (1) [TrenTIPS = N(CH2CH2NSiPri3)2].6b We have now prepared 1 deliberately in high yield, making it an attractive precursor from which to target U=−N multiple bonds. Here we show that deprotonation of 1 affords several uranium imido-bridged dimers, one of which can be converted into a uranium terminal parent imido complex. We also describe attempts to oxidize this complex that resulted in disproportionation to give 1 and a uranium(VI) nitride.

Complex 1 was previously isolated from the reaction of [U(TrenTIPS)] with [N3][NBun]4 in low yield (29%).6b We have now found that 1 can be routinely prepared from [U(TrenTIPS)-Cl]6a and NaNH2 and isolated in >90% yield,8 which renders 1 an attractive precursor to U=−N multiple bonds. Noting that a terminal molybdenum carbide was successfully prepared from its conjugate base by deprotonation and alkali metal sequestration8 and that closely related uranium nitrides are dimeric,6b we anticipated that deprotonation of 1 would give [{U(TrenTIPS)-(N[H]M)}2] (M = alkali metal), which could then undergo abstraction of M. Accordingly, treatment of 1 with tert-butyllithium or benzylsodium, potassium, or cesium afforded the alkali metal imido-bridged dimer complexes [{U(TrenTIPS)(μ-N[H]M)}2] (M = Li–Cs (2a–e)) in yields varying from 22 to 89% as pale-pink crystalline solids after workup and recrystallization (Scheme 1). The characterization data for 2a–e fully support the proposed formulations.

To confirm the molecular structures of 2a–e, we determined their structures by X-ray crystallography and found that the whole series adopts an essentially isostuctural dimeric formulation constructed around centrosymmetric M2N2 rings; the structure of the representative potassium complex 2c is illustrated in Figure 1.5 In 2a–e the imido centers adopt distorted tetrahedral geometries, and other than the expected expansion of the M2N2 ring size as the group-1 metal becomes larger, the basic structural unit varies little over the entire size range of the group-1 metals. The imido H atoms could be located in the Fourier transform difference maps but were then restrained during refinement of these heavy-atom structures. The U1−N5 bond lengths in 2a–e span the range 2.042(3) to 2.135(3) Å, with the longer U1−Nimido bond lengths observed in the lighter alkali metal complexes. This can be rationalized on the basis that lithium and...
sodium are more polarizing than the heavier alkali metals. Thus, the former polarize and lessen the electron density in the U−Namide linkage more than the latter, resulting in the observed trend. Notably, however, the U−Namide bond lengths in 2a−e are significantly shorter than the U−NH2 bond length in 1, reflecting the imido character of 2a−e compared with the amide character of 1. The U−Namide, U−Namine, and M−N bond lengths in 2a−e are unexceptional.11

With 2a−e in-hand, we attempted to abstract the alkali metal cations. Attempts to remove the Li, Na, Rb, and Cs ions from 2a, 2b, 2d, and 2e with crown ethers and cryptands gave intractable, oily product mixtures that could not be conclusively identified. However, treatment of 2c with 2 equiv of 15-crown-5 ether (15CS) and stirring of the resulting oil in hexane afforded [U(TrenTIPS)(NH)][K(15CS)2] (3c) as a pale-brown powder in 91% yield.2 The 1H NMR spectrum exhibits four resonances, consistent with a C3v-symmetric [U(TrenTIPS)(NH)]+ anion; however the imido hydrogen resonance could not be located. The UV/vis/NIR electronic absorption spectrum of 3c exhibits strong ligand-to-metal charge transfer bands that tail in from the UV region to around 15 000 cm−1 and weak (ε ≤ 100 M−1 cm−1) absorptions in the 15000−5000 cm−1 range that are characteristic of Laporte-forbidden f−f transitions of U(IV).12 The magnetic moment of 3c was found to be 2.8μB at 298 K; this decreased slowly upon cooling to ca. 80 K before falling more precipitously, reaching 1.5μB at 1.8 K and continuing to decrease. Although this is not classical U(IV) magnetism,13 similar behavior has been observed before for U(IV) in C3v symmetry with strongly donating axial ligands.14

The solid-state structure of 3c was determined by X-ray crystallography to confirm the separated ion pair formulation (Figure 2). The U1−NS bond length was determined to be 2.034(3) Å, which most likely reflects the anionic nature of [U(TrenTIPS)(NH)]+ in part counteracting the abstraction of an alkali metal to give a terminal U≡NH linkage. However, the U−Namide distance in 3c is 0.2 Å shorter than the U−NH2 bond length in 1,6b is only 0.07 Å longer than the sum of the double additive covalent radii of uranium and nitrogen,15 and compares well to terminal U(IV)≡NR bond lengths (1.95−2.01 Å).16 The U−Namide distances in 3c are indistinguishable from those of 2a−e, but the anionic and terminal nature of [U(TrenTIPS)(NH)]+ in 3c is apparent upon inspection of the U−Nmin bond, which is trans to the imido group and notably longer [2.749(3) Å] than the analogous distances in 2a−e [av 2.674(4) Å]. The imido H atom was located in the Fourier transform difference map and was refined with restraints, giving a U≡N−H angle of 172(3)°.

With 3c isolated, we reasoned that it might be straightforward to oxidize because of its “ate” formulation. This would in principle enable isolation of the unknown U(V) terminal parent imido linkage in [U(TrenTIPS)(N)] (4). We therefore treated 3c with 0.5 equiv of I2, since this method previously afforded a uranium(VI) nitride from a uranium(V) nitride separated ion pair precursor.6b However, although the I2 was consumed, [K(15CS)2][I] was eliminated, and oxidation of 3c appeared to occur, we found that spontaneous disproportionation occurred, as evidenced by inspection of the 1H NMR spectrum recorded within 10 min of a freshly prepared reaction between 3c and I2, which showed only 1 and [U(TrenTIPS)(N)] (5) in a 1:1 ratio. Despite numerous attempts to trap 4 by performing reactions and workup at low temperature or adding potential Lewis acid traps, we could not isolate it.9 Nevertheless, this reaction represents a new way to prepare terminal uranium(VI) nitrides, although it is intrinsically limited to a 50% maximum yield.

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2[U(TrenTIPS)(NH)] \rightarrow [U(TrenTIPS)(NH)]_2 + [U(TrenTIPS)(N)]
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In order to probe further the disproportionation reaction of 4 to give 1 and 5, we calculated the gas-phase enthalpy change (ΔH_g) for the reaction in eq 1 from single-point energy calculations on the geometry-optimized coordinates of 1, 4, and 5 and determined that this reaction is exothermic with ΔH_g = −5620
−3.25 kcal mol⁻¹. This value suggests that disproportionation of 4 to 1 and 5 is thermodynamically favorable, consistent with our experimental observations, and it is germane to note that although U(V) can be kinetically stabilized, it is fundamentally unstable with respect to disproportionation to U(IV) and U(VI);¹⁷ these observations may suggest one reason why the U(V)⇒NH linkage has never been isolated, since there is not a kinetically stabilizing NR group.

In order to probe the electronic structure of the uranium–imido linkage in 3c, we carried out density functional theory (DFT), natural bond orbital (NBO), and quantum theory of atoms in molecules (QTAIM) calculations on the anion of 3c and models of 1, 4, and 5 (Table 1). Known experimental structural data compare very well to the computed gas-phase structural data, indicating that the calculations provide qualitative models.

The calculated MDC-q charges and MDC-m spin densities for 1–5 are typical of Tren complexes of U(IV).¹⁸ The Mayer bond indices (BI) increase in going from 1 to 5, reflecting the progression from amide to U(IV)⇒imido to U(IV)⇒imido and finally to U(IV)⇒nitride. Although the BI for 5 is clearly consistent with a U≡N triple bond, the U≡N_{imido} BIs in 3c and 4 are substantially lower and are more consistent with the presence of formal double bonds. However, the linear U≡N≡H linkages in 3c and 4 are suggestive of triple-bonding interactions. Inspection of the Kohn–Sham frontier molecular orbitals (FMOs) for 1 and 3c² reveal the HOMO and HOMO−1 orbitals to be of essentially pure 5f character, consistent with the ⁵H₂ ground state of U(IV). For 4, only the HOMO is of essentially pure 5f character, consistent with the ⁷F₅/₂ ground state of U(IV). For the U≡NH₂ linkage in 1, a σ⁺π bonding combination could be identified. For 3c and 4, σ⁺π bonding combinations could be found for the U≡N_{imido} bonds, analogous to the U≡N triple-bond σ⁺π bonding interaction in 5. For 3c and 4, the expected orbital energy trend of σ > σ was found, whereas this is reversed in ⁵₆ because of the very short U≡N bond in this compound. The MOs representing the principal interactions that constitute the U⇒imido bonds in 3c and 4 are delocalized with significant Tren-N_{imido} contributions, and thus, we turned to NBO analysis to provide a chemically more intuitive description of the U≡N_{imido} bonds in 3c and 4 (Table 1).

The formal U≡NH₂ σ bond of 1 was returned by NBO as a N lone pair; however, a highly polarized π bond was reported. NBO identified one σ− and two π-bonding interactions for 3c–5. The imido N dominates the NBO breakdown of the U≡N_{imido} bonding interactions in 3c and 4, which suggests the presence of highly polarized U≡N_{imido} bonds, consistent with the calculated Mayer BIs. For the π bonds of 3c and 4, NBO suggests that the 5f orbitals dominate the U contribution, with the 6d orbitals playing only a modest role; in contrast, for the σ-bonding components, the 6d contribution dominates. The oxidation of 3c to 4 impacts on the nature of the U≡N_{imido} bond; specifically, upon moving from 3c to 4 the percentage contribution of U increases in both the σ and π bonds, and this trend continues upon moving to 5. However, since this trend could reflect an adjustment of the relative energies of the parent atomic orbitals in the U≡N_{imido} bonds in 3c and 4 rather than an increase in covalent overlap of the FMOs,¹⁹ we examined these linkages using QTAIM.

For 1–5, the calculations identified 3−1 bond critical points (BCPs) for the U≡amide, U≡imido, and U≡nitride linkages (Table 1). The topological electron densities [ρ(r)] of these BCPs vary from covalent (5) to polarized covalent (3c and 4) to predominantly electrostatic with a minor covalent contribution (1). The Laplacians of these BCP electron densities [Vρ(r)] for 1−5 are dominated by the heavy U center and consequently are uninformative. However, the increasingly negative BCP electronic energy density of the charge distribution [defined as H(r) = G(r) + V(r), where G(r) is the kinetic energy density and V(r) is the potential energy] in moving from 1 to 5 supports the increase in covalency in going from 1 to 5 as revealed by the ρ(r) data. The calculated BCP ellipticity parameters [ε(x)] for 3c–5 are close to zero, confirming the triple-bonding U≡N_{imido} and U≡N_{nitride} interactions in these linkages;¹⁹ σ bonds and triple (σ + π) bonds present a spherical distribution of electron density perpendicular to the bond path (ε = 0), whereas a double (σ + π) bond is asymmetric (ε > 0). The ellipticity of the U≡NH₂ BCP in 1 is consistent with a σ + π bond and is comparable to that of the C≡C BCP in ethylene (0.45).²⁰ Thus, the computational results suggest polarized, linear U≡N triple-bonding interactions in 3c and 4, in contrast to [U(Tren{Th}²)(PH)][K(B15CS)₃] (B15CS = benzo-15-crown-5 ether), which exhibits a bent U(IV)=PH double-bond interaction.²¹

We have reported the first f-block terminal parent imido complex, which can be viewed as a masked uranium(IV) nitride, and attempts to oxidize this complex to the neutral U(V) derivative resulted in disproportionation to the parent uranium(IV) amide and a uranium(IV) nitride. This reaction represents a new route to uranium nitrides and suggests one reason why U(IV)⇒NH linkages are unknown to date. Calculations suggested that σ⁺π triple-bonding interactions are present in the U≡N_{imido} linkages of 3c and putative 4.

ASSOCIATED CONTENT

S Supporting Information

Procedures and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.
COMMUNICATION

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Notes
The authors declare no competing financial interest.

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