While uranium imido complexes are well established in the literature, complexes featuring a uranium nitride functionality are rare. Data pertaining to terminal uranium nitrides are limited to the spectroscopic observation of the binary uranium nitrides UN and NUN and the ternary nitride NUF₃ under matrix conditions.¹,² We are interested in the uranium nitride functional group as it incorporates metal-ligand multiple bonding, valence f orbitals, and redox activity.³,⁴

One typical route to metal nitride species involves the reaction of azide anion with reducing metal complexes.⁵ In uranium chemistry, this approach had led to bi- and polymetallic complexes with μ-nitrido ligands bridging two or more uranium centers.⁶,⁷ We posited that use of an azide salt complexed by a simple Lewis acid would deliver a protected nitride ligand to uranium without bimetallic complex formation. Accordingly, we now report the synthesis and characterization of the first nitridoborate complexes of uranium, complexes that alternatively may be viewed as borane-capped uranium nitrides (Scheme 1).

The structurally characterized azidoborate salt [NMe₄][C₆F₅]B(3)Nₓ]3 (NMe₄)₁₀ seemed to be an ideal candidate to test our approach for delivery of a protected nitride fragment to uranium. For convenience, we prepared the tetra-n-butylammonium derivative [N(n-Bu)₄]₁[N(3)Bu]₁ in good yield by treating [N(n-Bu)₄]₁[N₃] with B(C₆F₅)₃ in C₆H₆.¹¹ Dropwise addition of a thawing Et₂O solution of purple-black (THF)U[N(n-Bu)₄]₁[N₃] (2, THF = tetrahydrofuran; Ar = 3,5-Me₆C₆H₃)¹² to a stirred thawing Et₂O solution of [N(n-Bu)₄]₁ resulted in evolution of N₂ and a change in color to dark brown. A brown solid was isolated in 80% yield after allowing the reaction mixture to stir for 2 h and workup. The isolated material exhibited a solution μeff of 1.98 μB at 20 °C in CDCl₃, as determined by Evans’s method,¹³ consistent with the formation of the uranium(V) complex [N(n-Bu)₄]₁[(C₆F₅)₃B(N₃)] (1) (vs. Fc/Fc +) assigned to the U⁵⁺/U⁶⁺ couple. Chemical oxidation of [N(n-Bu)₄]₁[N(3)Bu]₁ with I₂ (0.5 equiv) or AgOTf (1 equiv) in thawing Et₂O led to formation of the diamagnetic uranium(VI) complex [Me₃Si–NAr]₁ [(C₆F₅)₃B–NAr]₁ (3), which precipitated from solution upon concentrating the reaction mixture and adding n-pentane, and which was isolated in 82% yield.

The structure of 3, as determined by single crystal X-ray diffraction, features a B–N=U core that is again nearly linear (179.4(3)°) and a B–N=U bond distance of 1.592(6) Å, this being 0.05 Å longer than the corresponding distance in [3]¹. The U–N=U distance of 1.880(4) Å is ca. 0.04 Å shorter than the corresponding distance in [3] and is shorter than the U=N distances in the five-coordinate uranium(VI) imido(fluoride) complexes trans-U(NR)₂[N(SiMe₃)₂]F (R = SiMe₃, Ph).²⁵ For comparison, the terminal uranium nitrides UN, NUN, and NUF₃ have U–N distances of 1.746, 1.717 Å, and 1.759 Å, respectively.³⁶,³⁷ Lewis acid adducts of metal nitrides are known to display longer M–N distances than the corresponding free terminal nitrides.¹⁶,²⁸

To address the question of how the bonding in 3 compares to that of a free terminal uranium nitride or an organoimido uranium(VI) complex we turned to density functional theory and calculated U–N bond multiplicity (BM) indices based on Nalewajski-Mrozek valence indices.²⁷ This approach incorporates both covalent and ionic contributions to valency and yields BM indices, analogous to bond order, that correlate well with experimental observables such as interatomic distances and vibrational frequencies as well as chemically
Figure 1. ORTEP rendering of 3, ellipsoids displayed at 50% probability; hydrogen atoms and one molecule of co-crystallized Et₃O have been omitted for clarity. Selected bond lengths (Å) and angles (°): U1–N4, 1.880(4); N4–B1, 1.592(6); U1–N1, 2.193(3); U1–N2, 2.184(3); U1–N3, 2.194(4); B1–N4–U1, 179.4(3).

intuitive descriptions of bonding. This approach has recently been applied to metal-ligand and metal-metal multiply bonded systems with favorable results.27

Table 1 collects the calculated U–N distances and BM indices for the truncated model (C₆F₅)₃B–N(Me)[Ph] (3m) and several other relevant molecules (4-10).3,4,25,28-31 In all cases the calculated U–N distances agree well with the experimentally observed values and a linear relationship between BM and U–N distance is noted. Surprisingly, the calculated BM for the linear molecule 5 suggests a U–N quadruple bond, while the BM of the free terminal nitrides 6 and 7 are between that of a triple and quadruple bond.32

Table 1. A selection of calculated bond multiplicities.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Molecule</th>
<th>Bond</th>
<th>Distance [Å]</th>
<th>BM</th>
<th>(\rho_u)</th>
<th>(\rho_q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3m</td>
<td>(C₆F₅)₃B–N(Me)[Ph]</td>
<td>U–N</td>
<td>1.874 (1.868(2))</td>
<td>2.83</td>
<td>+3.18</td>
<td>−1.41</td>
</tr>
<tr>
<td>4</td>
<td>(C₆F₅)₃B[NMe]</td>
<td>U–N</td>
<td>2.193 (2.196)</td>
<td>1.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>N[N(Ph)]</td>
<td>U–N</td>
<td>1.590 (1.593(3))</td>
<td>0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>N[Ph]</td>
<td>U–N</td>
<td>1.755</td>
<td>3.71</td>
<td>+2.16</td>
<td>−0.61</td>
</tr>
<tr>
<td>7</td>
<td>N[N(N[Ph])]</td>
<td>U–N</td>
<td>1.769</td>
<td>3.67</td>
<td>+3.44</td>
<td>−1.24</td>
</tr>
<tr>
<td>8m</td>
<td>N[M–N(Ph)]</td>
<td>M–N</td>
<td>2.216</td>
<td>1.36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>U(N–Bu)</td>
<td>U–N</td>
<td>1.900 (1.964)</td>
<td>0.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>U[N–Bu]</td>
<td>U–N</td>
<td>1.882 (1.844)</td>
<td>2.70</td>
<td>+2.82</td>
<td>−1.47</td>
</tr>
<tr>
<td>11</td>
<td>U[N–Bu,N]</td>
<td>U–N</td>
<td>1.984 (1.972(3))</td>
<td>+3.71</td>
<td>−3.34</td>
<td></td>
</tr>
</tbody>
</table>

References

(11) Caution! Azide salts and covalent azides such as [N(Ph)-Bu][N3] and [N–Bu],[N3] are potentially explosive. Performing reactions with azide ions in dichloromethane may lead to the formation of diazidomethane, which is highly explosive.
(32) As NUN is isoelectronic to the well studied uranyl ion, one does not expect to find a quadruple bond here. It should be kept in mind that the Nalezewski-Mrozek method incorporates both covalent and ionic contributions, and so that it may not yet be optimized for challenging f element calculations.

Acknowledgments. We thank the National Science Foundation for supporting this research (CHE-0724158). ARF thanks MIT for the Alan Davison Graduate Fellowship and Dr. Theodore A. Betley for helpful discussions.

Supporting Information Available: Complete experimental details, characterization data, crystallographic and computational details, including crystallographic information files in CIF format and BM indices for several uranyl derivatives. This material is available free of charge via the Internet at http://pubs.acs.org.
Reaction of the azidoborate salt \([N(n-Bu)_4][(C_6F_5)_3B(N_3)]\) (1) with the uranium(III) tris(anilide) complex (THF)U(N[t-Bu]Ar)\(_3\) (2; THF = tetrahydrofuran; Ar = 3,5-Me\(_2\)C\(_6\)H\(_3\)) results in formation of the paramagnetic uranium(V) nitridoborate complex \([N(n-Bu)_4][(C_6F_5)_3B–N\(U(N[t-Bu]Ar)\))\(_3\)]\) (3). Chemical oxidation of \([N(n-Bu)_4]\)) (3) is facile and provides the diamagnetic uranium(VI) nitridoborate complex (C\(_6\)F\(_5\))\(_3\)B–N\(U(N[t-Bu]Ar)\))\(_3\) (4). \([N(n-Bu)_4]\)) (3) and 4 are the first nitridoborate complexes of uranium and were characterized by multinuclear NMR spectroscopy, single crystal X-ray diffraction methods, and elemental analysis. The X-ray crystal structures of \([N(n-Bu)_4]\)) (3) and 4 reveal extremely short U–N\(_{nitrido}\) distances (1.916(4) Å and 1.880(4) Å, respectively). Density functional theory was used to calculate the optimized structure of the truncated model (C\(_6\)F\(_5\))\(_3\)B–N\(U(N[Me]Ph)\))\(_3\); the procedure was carried out similarly for several other relevant complexes featuring U–N multiple bonds. Bond multiplicities based on Nalewajski-Mrozek valence indices were calculated, the results of which suggest that the U–N\(_{nitrido}\) interaction in 4 is close to a full triple bond.