New chemistry from an old reagent

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New Chemistry from an Old Reagent: Mono- and Dinuclear Macrocyclic Uranium(III) Complexes from $[U(BH_4)_3(THF)_2]$**

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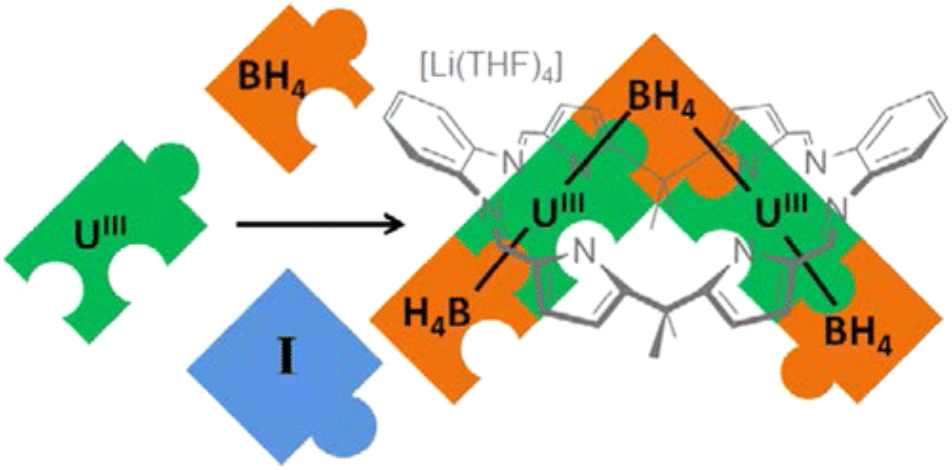
Experimental details, characterization data and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org. X-ray structural CCDC codes 999591-999594.

Graphical abstract:



Abstract

A new robust and high-yielding synthesis of the valuable U^{III} synthon $[U(BH_4)_3(THF)_2]$ is reported. Reactivity in ligand exchange reactions is found to contrast significantly to that of uranium triiodide. This is exemplified by the synthesis and characterization of azamacrocyclic U^{III} complexes, including mononuclear $[U(BH_4)(L)]$ and dinuclear $[Li(THF)_4][\{U(BH_4)\}_2(\mu\text{-}BH_4)(L^{Me})]$ and $[Na(THF)_4][\{U(BH_4)\}_2(\mu\text{-}BH_4)(L^{A})(THF)_2]$. The structures of all complexes have been determined by single-crystal X-ray diffraction and display two new $U^{III}{}_2(BH_4)_3$ motifs.

Introduction

The highly reducing nature of U^{III} and its many accessible frontier bonding orbitals enable a wide range of impressive small molecule activation chemistry with substrates including N_2, NO, CO, CO_2, arenes and alkynes.[1] The encapsulation of one or more of these large ions in a defined macrocyclic microenvironment would be expected to result in significantly better control over the activation and subsequent substrate reactivities compared with simple, flexible supporting ligand sets. An illustrative U^{III} example is that the tetradentate triamido tren-based ligand enabled the isolation of the first uranium dinitrogen complex,[2] while a complex of a more rigid polypyrrolic framework enabled the only f-block example of the complete cleavage of the triple bond in N_2.[3]

Pyrrolic macrocyclic ligands are well known in uranium chemistry and the coordination chemistry of uranyl and neptunyl cations[4] relevant to separations chemistry[5] and actinide sensing applications[6] has been extensively studied. The majority of our work in this area using the octadentate, tetraanionic Pacman calixpyrroles ($H_4L^{R/A}$ Fig. 1) has explored the reduction and functionalization of the uranyl dication.[7] However, there are very few examples of low oxidation state complexes of these ligands known.[8] In the last ten years, we have been able to synthesize the mononuclear complex $[U^{IV}(L^{Et})]$,[9] and the magnetically interesting oligomeric U^{III} and Np^{III} iodides $[(An^{III}I)_2(L^{Et})]_n$, for which no structural information was obtainable from standard crystallographic techniques.[10] Very recently, we also reported the first actinide complexes of the conformationally flexible, small-cavity macrocycle *trans*-calix[2]benzene[2]pyrrolide $(L)^{2-}$ (H_2L in Fig. 1).[11] This ligand is competent for the stabilization of one or two U^{III} cations as $[UI(THF)(L)]$ and the very unusual dinuclear $[U_2I_4(L)]$, respectively,[12] but the chemistry is highly dependent on reaction conditions.

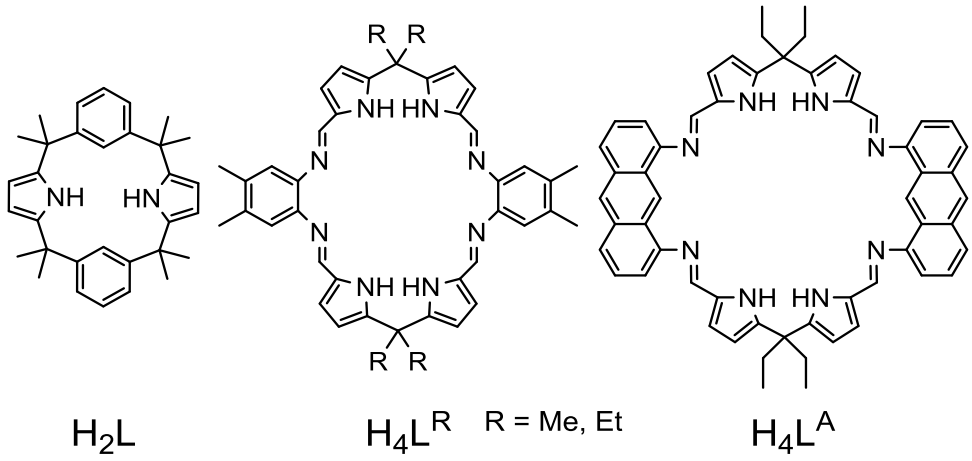


Figure 1. Azamacrocyclic ligands used in this work.

The non-trivial role of solvent,[13] choice of alkali metal salt[14] and U-precursor[15] in U^{III} chemistry is well precedented if not well understood and often yields dramatic differences in reaction chemistry. We have found considerable synthetic difficulties in the reactions of UI_3 with $(L)^{2-}$, $(L^R)^{4-}$ R= Me, Et and $(L^A)^{4-}$, observing the formation of multiple products, unstable complexes and poorly soluble materials that were difficult to characterize (see below). This led us to investigate borohydrides as alternative U^{III} precursors.

Borohydride compounds of uranium were targeted during the Manhattan project because of their volatility, and extensive $U(BH_4)_4$ chemistry was reported in spite of its non-trivial synthesis.[16] The thermal instability of these U^{IV} complexes with respect to U^{III} underlines the attractiveness of borohydride as a supporting ligand for U^{III} chemistry:[17] Ephritikhine and co-workers demonstrated the thermal decomposition of $U(BH_4)_4$ to $[U(BH_4)_3(\eta\text{-}C_6H_3Me_3)]$[18] and the subsequent protonation to $[U(BH_4)_2(THF)_5][BPh_4]$, a rare example of a U^{III} cation.[19] Prior to this work the only report of $U(BH_4)_3$ from a U^{III} precursor was the reaction of UH_3 with diborane.[20] This reaction allowed the structural characterisation of the *tris*(THF) adduct $[U(BH_4)_3(THF)_3]$ but in a 4 % yield. The reaction between UCl_3 and 3 equivalents of $NaBH_4$ yielded a red solid which was not fully characterised. [21]

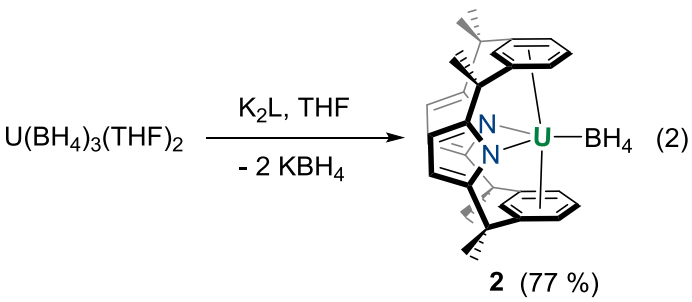
$$UI_3(THF)_4 \xrightarrow[\text{- 3 NaI}]{\text{3 NaBH}_4\text{, THF}} \underset{\textbf{1}\ (90\ \%)}{U(BH_4)_3(THF)_2} \quad (1)$$

In contrast, we have found that the reaction between UI_3 and three equivalents of $NaBH_4$ reproducibly yields $[U(BH_4)_3(THF)_2]$ **1** (Eq. 1) as an analytically pure, red microcrystalline material in greater than 90 % yield after removal of volatiles and soxhlet extraction of the crude reaction product with Et_2O. The degree of solvation has been determined by NMR spectroscopy (see SI) and elemental analysis. Unfortunately, crystals of **1** isolated from a variety of solvents could not be analysed by X-ray diffraction due to rapid and destructive

desolvation during crystal mounting. The formal low coordination number of U^{III} in $[U(BH_4)_3(THF)_2]$ may well be augmented in the solid state by oligomerisation. The ^1H and ^{11}B NMR spectra of **1** in d_8-THF at ambient temperature exhibit very broad resonances assigned to BH_4^- at 85 and 230 ppm, respectively.

The development of a routine and reproducible route to **1** has allowed us to probe the low oxidation state uranium chemistry of the mono- and dinucleating macrocycles shown in Fig. 1. The reaction between **1** and K_2L in THF at ambient temperature gives $[U(BH_4)(L)]$ **2** as a dark brown solid in 77 % yield after workup (Eq. 2). Unlike the synthesis of the iodide derivatives [UI(THF)(L)] and $[U_2I_4(L)]$, this reaction is high yielding and selective, and the mono(borohydride) **2** has improved thermal stability and solubility compared to the mono(iodide) analogue. It also does not require the use of Li_2L (which generates unwanted, soluble by-products) or a reduction step.

The ^1H NMR spectrum of **2** in d_8-toluene is consistent with a C_{2v} symmetric macrocyclic environment and η^6:κ^1:η^6:κ^1 metal-ligand binding, with the geminal methyl groups observed as two magnetically non-equivalent, contact-shifted singlets of equal intensity at 3.14 and −0.69 ppm. The $(BH_4)^-$ protons are seen as a very broad resonance at 113 ppm ($W_{1/2}$ = 994 Hz) in the ^1H NMR spectrum and as a singlet at 170 ppm in the $^{11}B\{^1H\}$ NMR spectrum, consistent with an averaged BH_4 proton environment on the NMR timescale; there was no resolution of the coupling in the ^{11}B spectrum (Fig. 3). The IR spectrum of **2** displays strong absorptions in the region of 2500-2000 cm^{-1} consistent with $(\mu\text{-H})_2BH_2$ binding: $\nu(B\text{-}H_t)$ 2414 and 2384 cm^{-1} and $\nu(B\text{-}H_\mu)$ 2120 cm^{-1}.[22]



Single crystals of **2** were grown by vapor diffusion of hexanes into a saturated THF solution at ambient temperature. The uranium macrocycle binding in the molecular structure (Fig. 2) of **2** is directly analogous to that seen in the unsolvated iodide complex [UI(L)].[12] The interplanar arene angle, which gives a measure of uranium-arene interaction, of 14.32° is even smaller than the 15.52° found in [UI(L)]. However, the U1···B1 separation of 2.927(7) Å is much longer than those found in $U(BH_4)_3(THF)_3$ (2.625-2.699 Å)[20] and other examples of U^{III} borohydrides.[16c] In $[U(BH_4)_3(DMPE)_2]$ (DMPE = dimethylphospinoethane),[23] two distinct U···B separations were seen, with the shorter (2.68(4) Å) axial ligand assigned as $(\mu\text{-H})_3BH$ and the longer (2.84(3) Å) equatorial ligands as $(\mu\text{-H})_2BH_2$. While the bridging mode of the borohydride in **2** could not be determined in the solid-state structure, it is likely to be $(\mu\text{-H})_2BH_2$ based on the U1···B1 separation,[24] which is consistent with the IR data.

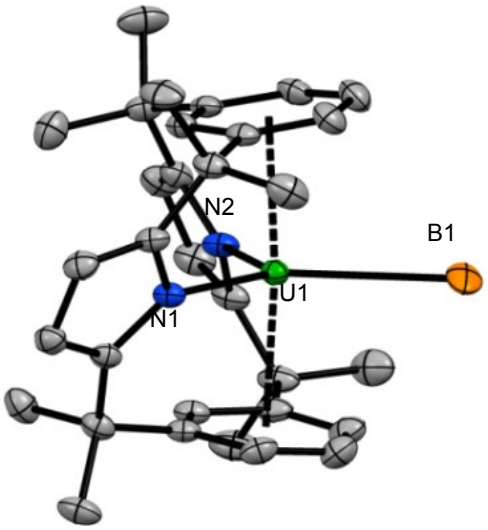
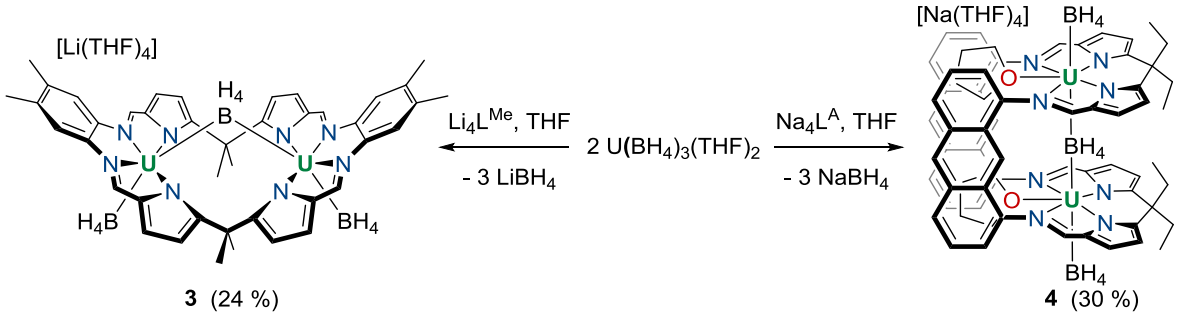


Figure 2. Solid-state structure of **2** (displacement ellipsoids are drawn at 50 % probability). For clarity all H atoms are omitted. Selected bond distances (Å) and angles (°) for **2**: U1–N1 2.452(4), U1–N2 2.476(4), U1···B1 2.927(7), N1–U1–N2 118.94(14), $[aryl1]_{cent}$–U1– $[aryl2]_{cent}$ 174.73.

The Pacman family of Schiff-base calixpyrroles was developed to provide bimetallic ligands for the cooperative activation of small molecules within the intermetallic cleft.[25] In light of this, we have long sought to exploit the combined reducing power of two U^{III} centers bound within such a framework. However, reactions of UI_3 as the U^{III} source with the *ortho*-phenylene hinged macrocycle H_4L^{Et} result in poorly-soluble, oligomeric materials and reactions with the anthracenyl macrocycle H_4L^{A} form unstable species which could not be isolated cleanly (see SI).[10]

The reactions between two equivalents of **1** and the alkali metal salts of the Pacman macrocycles H_4L^{Me} and H_4L^{A} in THF yield the ionic dinuclear products $[M(THF)_4][\{U(BH_4)\}_2(\mu\text{-}BH_4)(L)(THF)_x]$ **3** and **4** respectively, where M = Li, L = L^{Me}, x = 0, (**3**), and M = Na, L = L^{A}, x = 2, (**4**) as crystalline solids in moderate isolated yields of 24 % and 30 % (Scheme 1). These are highly unusual dinuclear U^{III}/U^{III} complexes of a single ligand, the only previous example of which is $[U_2I_4(L)]$.[12] While the solid-state structures of $U^{IV}(BH_4)_4$ are oligomeric with bridging BH_4 groups,[26] **3** and **4** are molecular and the first compounds to contain the $\{U^{III}\text{-}(\mu\text{-}BH_4)\text{-}U^{III}\}$ moiety. Indeed, the ability of BH_4 to effectively bridge two U^{III} centers in the intermetallic cleft appears to provide important stabilization to these dinuclear complexes and may explain their improved kinetic stability compared to the iodide analogues.



Scheme 1. Synthesis of $[Li(THF)_4][(UBH_4)_2(\mu\text{-}BH_4)(L^{Me})]$ **3** and $[Na(THF)_4][(UBH_4)_2(\mu\text{-}BH_4)(L^{A})(THF)_2]$ **4**

The ^{1}H NMR spectra of **3** and **4** display paramagnetically contact-shifted resonances corresponding to symmetric ligand environments in which the two N_4 metal binding pockets are identical. The alkyl groups at the *meso* carbons, which are equivalent in the spectra of the free macrocycles, become desymmetrized in the metallated products and appear as two sets of resonances corresponding to the two groups oriented towards the intermetallic cavity and the two pointing away from the cavity. Broad resonances are observed in the ^{1}H NMR spectra of **3** at 63 ppm ($W_{1/2}$ = 702 Hz) and **4** at −73 ppm ($W_{1/2}$ = 498 Hz) which are assigned to the protons of the terminal borohydride ligands. No resonances are observed for the bridging borohydride protons of either complex, even in the ^{1}H{^{11}B} spectra.

The ^{11}B NMR spectra show two different boron environments in a 1:2 ratio (Fig. 3). In the spectrum of **3** broad resonances are observed at 325 ppm (μ-BH_4) and 212 ppm (terminal BH_4) whilst for **4** they appear at 212 ppm (μ-BH_4) and 207 ppm (terminal BH_4). Coupling to the H atoms is not resolved on the NMR timescale. The IR spectra of **3** and **4** display several overlapping bands in the region from 2500 to 2100 cm^{-1} consistent with multiple BH_4 binding modes.[22]

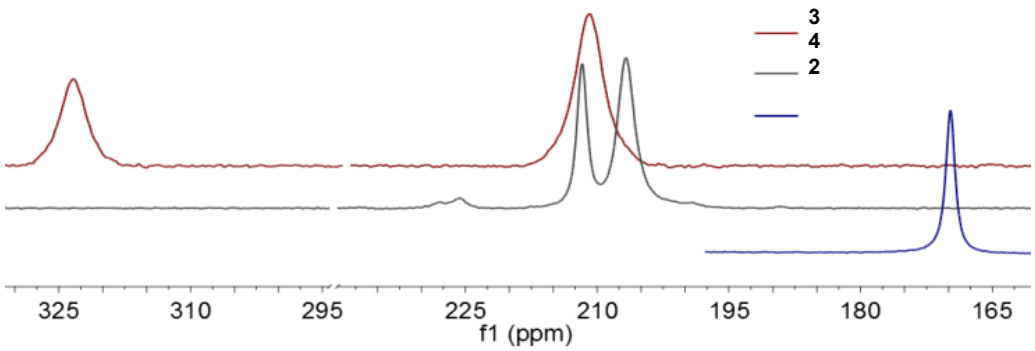


Figure 3. ^{11}B NMR spectra (d_8-THF) of the complexes **2** (lower, blue), **3** (upper, red) and **4** (middle, grey). Spectra of **3** and **4** were acquired over the range 60 – 340 ppm; that of **2** was acquired over the range −20 – 200 ppm.

Single crystals of **3** were grown from a saturated THF solution at ambient temperature. In the solid state (Fig. 4) the complex does not adopt the classic Pacman geometry where the *ortho*-phenylene rings of the macrocycle act as hinges, but instead the ligand flexes at the *meso* carbons so adopting a bowl-shaped geometry.[4b] Each U^{III} is pseudo-octahedral and bound in the equatorial macrocyclic plane to the two *ortho* imine nitrogens of one aryl ring and to two adjacent pyrrolide nitrogens whilst two BH_4 ligands, one terminal (B1/B2) and one bridging (B3), occupy the axial sites. The BH_4 protons could not be located crystallographically but the U1···B1 and U2···B2 distances of 2.630(9) Å and 2.640(9) Å, respectively (Table 1), are consistent with $(\mu\text{-H})_3BH$ binding modes for the *exo* BH_4 ligands (B1 and B2) whilst the *endo* BH_4 protons bridge the two metal centers with longer U1/2···B3 separations of 2.915(7) Å and 2.911(7) Å. This would agree with an *endo*-$(\mu\text{-H})_2BH(\mu\text{-H})$ interaction averaged over the two U^{III} centers. By adopting the bowl conformation, the U1···B3···U2 interaction is optimized since the two U^{III} centers can achieve greater separation (U1···U2 = 4.7884(3) Å) than is seen in archetypal Pacman complexes of this ligand (M···M 3.1 – 4.2 Å).[27]

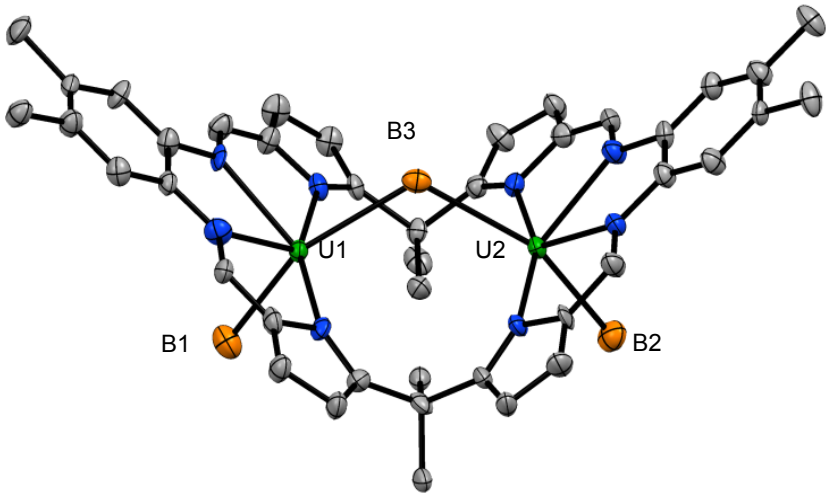


Figure 4. Solid state structure of the anionic portion of **3** (displacement ellipsoids are drawn at 50 % probability). For clarity, H atoms, lattice solvent and the $[Li(THF)_4]^+$ cation are omitted.

Single crystals of the pyridine solvate **4py** were grown from a pyridine/hexane solution of **4** at ambient temperature. In contrast to **3**, in the solid-state the anthracenyl macrocycle adopts the classic Pacman geometry (Fig. 5) since the separation between the two metal binding pockets is much greater than for the *ortho*-phenylene macrocycle. For the pentagonal bipyramidal U^{III} centers, four of the equatorial donors are provided by the two imine nitrogens (attached to different anthracene rings) and two pyrrolide nitrogens of the ligand with the fifth site occupied by a pyridine solvent molecule, having displaced the less strongly coordinating THF. One terminal and one bridging BH_4 occupy the axial sites. The borohydride protons were

located from the difference Fourier map and their positions refined (see SI). The terminal BH_4 groups (B1 and B2) are bound in a $(\mu\text{-H})_3BH$ fashion while the central bridging BH_4 (B3) binds to each U^{III} center through two bridging $(\mu\text{-H})_2B(\mu\text{-H})_2$ consistent with the U···B separations (Table 1). The sodium cation is coordinated to the remaining H of one terminal BH_4 group, and four pyridine molecules in the solid-state structure but this does not persist in solution where the NMR spectra show a symmetric ligand environment. The terminal and bridging B_t···U and B_μ···U separations observed in **3** and **4py** are similar (Table 1) but the geometries of the $\{BH_4\text{-U-}(\mu\text{-}BH_4)\text{-U-}BH_4\}$ cores of the two complexes differ due to the constraints imposed by the two macrocycles. Whilst this core is essentially linear in **4py**, the metal-borohydride unit in **3** has a significant bend at the bridging BH_4 (U1-B3-U2 = 110.5(3)°) and the $\{BH_4\text{-U-}(\mu\text{-}BH_4)\}$ units deviate from linearity. The U···U separation is also 1.14 Å longer in **4py** (5.9243(3) Å) than in **3** (4.7884(3) Å).

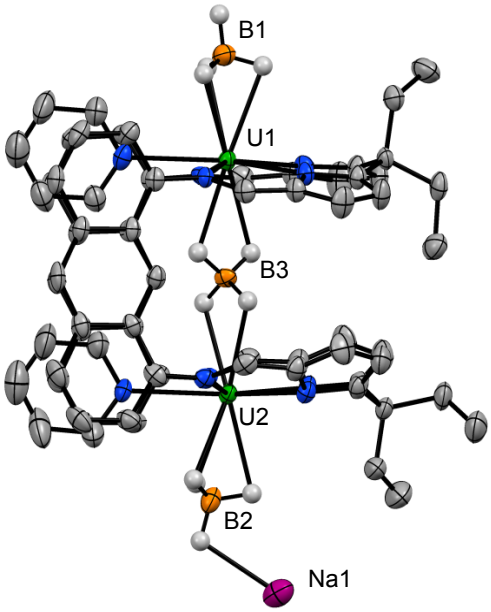


Figure 5. Solid state structure of **4py** (displacement ellipsoids are drawn at 50 % probability). For clarity, all H atoms except those of the BH_4 ligands, the four pyridine molecules ligating the Na^+ cation, and lattice solvent are omitted.

Table 1. Selected distances (Å), angles (°) for **3** and **4py**

	3	**4py**
U···U	4.7884(3)	5.9243(3)
U···B_t	2.630(9), 2.640(9)	2.681(9), 2.723(8)
U···B_μ	2.915(7), 2.911(7)	2.949(7), 2.977(7)
mean U–N_{pyr}	2.59	2.49
mean U–N_{im}	2.50	2.62
B_t–U–B_μ	158.6(3), 158.7(3)	175.5(2), 169.3(2)
U–B_μ–U	110.5(3)	177.8(3)

We have demonstrated a new and straightforward synthesis of $[U(BH_4)_3(THF)_2]$, the first directly from U^{III}. This well-defined U^{III} precursor has greater use than UI_3 in the formation of mono- and dinuclear U^{III} complexes. This is only the second report of dinuclear U^{III} complexes of a single ligand for which structural information has been obtained, and the first incorporating a $\{U^{III}\text{-}(\mu\text{-}BH_4)\text{-}U^{III}\}$ unit. These complexes combine the reducing potentials of two U^{III} metal cations with the chemical versatility of the borohydride anion and present unique opportunities to explore the chemistry of low oxidation state uranium confined within different macrocyclic frameworks.

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