

Supplementary information

Uranium-Hydrogen Interactions. Synthesis and Crystal Structure of Tris(*N,N*-Dimethylaminodiboranato)uranium(III)

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Experimental Section

All operations were carried out in vacuum or under argon using standard Schlenk techniques. All glassware was dried in an oven at 150 °C, assembled hot, and allowed to cool under vacuum before use. Tetrahydrofuran and pentane were distilled under nitrogen from sodium/benzophenone and degassed with argon immediately before use. Toluene was dried similarly over molten sodium. The compounds UCl_4 and $\text{Na}(\text{H}_3\text{BNMe}_2\text{BH}_3)$ were prepared by literature routes.^{1,2}

Elemental analyses were carried out by the University of Illinois Microanalytical Laboratory. The IR spectra were recorded on a Nicolet Impact 410 infrared spectrometer as Nujol mulls between KBr plates. The ^1H data were obtained on a Varian Unity U500 instrument at 500 MHz. The ^{11}B NMR data were collected on a General Electric GN300WB instrument at 96 MHz. Chemical shifts are reported in δ units (positive shifts to high frequency) relative to TMS (^1H) or $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (^{11}B). Decomposition temperatures were determined in closed capillaries under argon on a Thomas-Hoover Unimelt apparatus. Powder X-ray diffraction measurements were carried out on a Bruker P4RA/GADDS wide angle diffractometer using a $\text{Cu K}\alpha$ radiation source.

■ CAUTION: Uranium salts are alpha emitters and are known nephrotoxins. Inhalation should be avoided by conducting all operations of dry materials in an approved fume hood and with proper safety equipment. Complexes **1a** and **1b** enflame upon exposure to air.

Tris(*N,N*-dimethylaminodiboranato)uranium(III), **U(H₃BNMe₂BH₃)₃,**
structural isomer 1a. To a suspension of UCl₄ (0.27 g, 0.71 mmol) in diethyl ether (20 mL) at 0 °C was added a solution of sodium *N,N*-dimethylaminodiboranate (0.27 g, 2.9 mmol) in diethyl ether (20 mL). The mixture was warmed to room temperature and stirred for 17 h. Gas slowly evolved and the bright green solution gradually turned dark brown. The brown mixture was evaporated to dryness under vacuum and the brown residue was extracted with pentane (6 × 50 mL). The light brown extracts were combined, concentrated to 45 mL, and cooled to -20 °C to yield light brown crystals. Yield: ca. 30 mg (9 %). NMR and IR data were identical to those for isomer **1b**. The low yield can be attributed to the poor solubility of **1a** in pentane. Addition of toluene after the pentane extractions resulted in the formation of dark red solutions indicative of **1b**. The ¹H and ¹¹B NMR spectra of the dried red solids obtained from these toluene extractions match those reported for **1b**.

Structural isomer 1b. To a suspension of UCl₄ (0.50 g, 1.3 mmol) in diethyl ether (15 mL) at 0 °C was added a solution of sodium *N,N*-dimethylaminodiboranate (0.51 g, 5.4 mmol) in diethyl ether (15 mL). The mixture was warmed to room temperature and stirred for 13 h. Gas slowly evolved and the bright green solution gradually turned dark brown. The brown mixture was evaporated to dryness under vacuum and the brown residue was extracted with toluene (2 × 25 mL). The red extracts

were combined and evaporated to dryness under vacuum to yield a dark reddish-brown residue. The residue was washed with pentane (10 mL) and evaporated to dryness under vacuum to yield a powdery, burnt orange solid. Yield: 0.32 g (53 %). In another reaction, the residue was extracted with toluene (2×25 mL), concentrated to ca. 20 mL, and cooled to -20 °C to yield red microcrystals. Yield: 0.14 g, (26 %). M.p. 156 °C (dec). Anal. Calcd for $C_6H_{36}B_6N_3U$: C, 15.9; H, 8.01; N, 9.27. Found: C, 15.7; H, 7.50; N, 9.06. 1H NMR (C_7D_8 , 20 °C): δ 3.76 (br s, fwhm = 60 Hz, NMe_2 , 36 H), 91.3 (br s, fwhm = 1100 Hz, BH_3). ^{11}B NMR (C_7D_8 , 20 °C): δ 163.4 (br s, fwhm = 510 Hz). IR (cm^{-1}): 2399 vs, 2331 m, 2270 s, 2202 vs, 2168 s, 2094 sh, 1402 w, 1327 sh, 1265 s, 1238 s, 1215 s, 1182 m, 1166 s, 1161 s, 1132 m, 1032 m, 928 m, 902 w, 808 w, 760 w, 451 m.

Crystallographic Studies.³ Single crystals of **1a** obtained from pentane and **1b** obtained from toluene, were mounted on glass fibers with Paratone-N oil (Exxon) and immediately cooled to -80 °C in a cold nitrogen gas stream on the diffractometer. Standard peak search and indexing procedures, followed by least-square refinement yielded the cell dimensions given in Table S1. The monoclinic lattice and systematic absences $0k0$ ($k \neq 2n$) and $h0l$ ($l \neq 2n$) for **1a** and **1b** were uniquely consistent with the space group $P2_1/c$, which was confirmed by the success of the subsequent refinements. The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background and Lorentz and polarization effects. No corrections for crystal decay were necessary but a face-indexed absorption correction was applied. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of unique data. All unique data were used in the least-squares refinements. The analytical approximations to the scattering factors were

used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion. The correct positions for the uranium atoms were deduced from the E-maps (SHELX). Least-squares refinement and difference Fourier calculations were used to locate atoms not found in the initial solutions. In the final cycle of least squares, independent anisotropic displacement factors were refined for the non-hydrogen atoms. The quantity minimized by the least-squares program was $\Sigma w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.0318P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$ for **1a** [$w = \{[\sigma(F_o^2)]^2 + (0.374P)^2\}^{-1}$ for **1b**]. Hydrogen atoms on the anionic ligands of **1a** were placed in idealized positions with C-H (methyl) = 0.98 Å and B-H = 1.15 Å; idealized methyl and boranyl groups were allowed to rotate about their respective axis to find the best least-squares positions. The displacement parameters for the boranyl hydrogens were set equal to 1.2 times U_{eq} for the attached carbon and boron, respectively; those for methyl hydrogens were set to 1.5 times U_{eq} for the attached carbon. For **1b**, the boranyl hydrogen atoms were located in the difference maps, and their positions were refined with independent isotropic displacement parameters. Chemically equivalent B–H distances within the BH₃ units were constrained to be equal within a standard deviation of 0.01 Å. The methyl hydrogen atoms in **1b** were placed in idealized positions similar to those in **1a**. No correction for isotropic extinction was necessary. Successful convergence was indicated by the maximum shift/error of 0.000 for the last cycles. The largest peak in the final Fourier difference map (2.90 eÅ⁻³) for **1a** was located 0.96 Å from U1 and the largest peak in the final Fourier difference map (4.18 eÅ⁻³) for **1b** was located 0.96 Å from U1. A final analysis of variance between observed and calculated structure factors showed no apparent errors.

Table S1. Crystallographic data for structural isomers of $\text{U}(\text{H}_3\text{BNMe}_2\text{BH}_3)_3$, **1a** and **1b**, at 193 K

	1a	1b
formula	$\text{C}_6\text{H}_{36}\text{B}_6\text{N}_3\text{U}$	$\text{C}_6\text{H}_{36}\text{B}_6\text{N}_3\text{U}$
FW (g mol ⁻¹)	453.27	453.27
λ (Å)	0.71073	0.71073
crystal system	Monoclinic	Monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	15.9392(4)	12.3571(6)
b (Å)	10.2456(3)	10.8128(6)
c (Å)	11.4154(3)	14.6145(7)
α (deg)	90	90
β (deg)	97.192(1)	96.116(3)
γ (deg)	90	90
V (Å ³)	1849.54(9)	1941.6(2)
Z	4	4
ρ_{calc} (g cm ⁻³)	1.628	1.551
R_{int}	0.1043	0.0910
μ (mm ⁻¹)	8.757	8.342
absorption correction	Face-indexed	Face-indexed
max., min. transm. factors	0.843, 0.190	0.754, 0.456
data/restraints/parameters	4251/0/151	5035/49/223
goodness-of-fit on F^2	0.925	0.904
R_1 [$I > 2\sigma(I)$] ^a	0.0318	0.0345
wR_2 (all data) ^b	0.0701	0.0776
largest diff. peak and hole (e ⁻ Å ⁻³)	2.905/-2.556	4.175/-1.927

^a $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ for reflections with $F_o^2 > 2 \sigma(F_o^2)$.

^b $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum (F_o^2)^2]^{1/2}$ for all reflections.

Table S2. Selected Bond Lengths and Angles for $U(H_3BNMe_2BH_3)_3$, **1a**.^a

Bond Lengths (Å)			
U(1)-B(1)	2.953(4)	U(1)-H(6D)	2.48
U(1)-B(2)	2.957(3)	U(1)-H(6E)	2.60
U(1)-B(3)	2.939(4)	U(1)-H(6F)'	2.50
U(1)-B(4)	2.943(3)	B(1)-N(1)	1.569(8)
U(1)-B(5)	2.944(3)	B(2)-N(1)	1.583(7)
U(1)-B(6)	2.949(4)	B(3)-N(2)	1.581(7)
U(1)-H(1D)	2.57	B(4)-N(2)	1.562(8)
U(1)-H(1E)	2.37	B(5)-N(3)	1.576(7)
U(1)-H(2D)	2.42	B(6)-N(3)	1.562(7)
U(1)-H(2E)	2.53	N(1)-C(1)	1.483(7)
U(1)-H(3D)	2.46	N(1)-C(2)	1.477(7)
U(1)-H(3E)	2.44	N(2)-C(3)	1.491(7)
U(1)-H(4D)	2.50	N(2)-C(4)	1.486(7)
U(1)-H(4E)	2.56	N(3)-C(5)	1.487(7)
U(1)-H(5D)	2.52	N(3)-C(6)	1.490(6)
U(1)-H(5E)	2.48		
Bond Angles (deg)			
B(1)-U(1)-B(2)	53.4(2)	C(3)-N(2)-B(4)	109.9(5)
B(3)-U(1)-B(4)	53.0(2)	C(4)-N(2)-B(3)	109.4(4)
B(5)-U(1)-B(6)	51.9(2)	C(4)-N(2)-B(4)	110.1(4)
B(1)-N(1)-B(2)	109.4(4)	C(5)-N(3)-B(5)	110.1(4)
B(3)-N(2)-B(4)	109.8(4)	C(5)-N(3)-B(6)	110.7(4)

B(5)-N(3)-B(6)	108.8(4)	C(6)-N(3)-B(5)	108.8(4)
C(1)-N(1)-B(1)	109.1(5)	C(6)-N(3)-B(6)	110.3(4)
C(1)-N(1)-B(2)	109.3(2)	C(1)-N(1)-C(2)	108.3(4)
C(2)-N(1)-B(1)	110.8(4)	C(3)-N(2)-C(4)	108.4(4)
C(2)-N(1)-B(2)	109.9(5)	C(5)-N(3)-C(6)	108.2(4)
C(3)-N(2)-B(3)	109.2(4)		

^aSymmetry transformations used to generate equivalent atoms: ' = x, -y+½, z-½

Table S3. Selected Bond Lengths and Angles for $U(H_3BNMe_2BH_3)_3$, **1b**.^a

Bond Lengths (Å)			
U(1)-B(1)	2.902(6)	U(1)-H(52)	2.51(5)
U(1)-B(2)	2.862(7)	U(1)-H(53)	2.46(5)
U(1)-B(3)	2.861(7)	B(1)-N(1)	1.581(8)
U(1)-B(4)	2.889(6)	B(2)-N(1)	1.583(8)
U(1)-B(5)	2.670(6)	B(3)-N(2)	1.593(8)
U(1)-B(6)'	2.665(6)	B(4)-N(2)	1.572(7)
U(1)-H(11)	2.59(5)	B(5)-N(3)	1.540(7)
U(1)-H(12)	2.46(7)	B(6)-N(3)	1.553(7)
U(1)-H(21)	2.57(6)	N(1)-C(1)	1.495(7)
U(1)-H(22)	2.48(6)	N(1)-C(2)	1.480(7)
U(1)-H(31)	2.46(5)	N(2)-C(3)	1.484(7)
U(1)-H(32)	2.47(5)	N(2)-C(4)	1.473(7)
U(1)-H(41)	2.47(6)	N(3)-C(5)	1.491(7)
U(1)-H(42)	2.40(5)	N(3)-C(6)	1.484(7)
U(1)-H(51)	2.31(5)		
Bond Angles (deg)			
B(1)-U(1)-B(2)	53.2(2)	C(2)-N(1)-B(2)	110.2(5)
B(3)-U(1)-B(4)	53.0(2)	C(3)-N(2)-B(3)	109.4(5)
B(1)-U(1)-B(4)	104.0(2)	C(3)-N(2)-B(4)	109.4(5)
B(1)-U(1)-B(5)	139.1(2)	C(4)-N(2)-B(3)	110.2(5)

B(2)-U(1)-B(5)	86.2(2)	C(4)-N(2)-B(4)	110.3(5)
B(3)-U(1)-B(5)	118.3(2)	C(5)-N(3)-B(5)	108.7(4)
B(4)-U(1)-B(5)	89.8(2)	C(5)-N(3)-B(6)	109.1(4)
B(1)-N(1)-B(2)	109.2(4)	C(6)-N(3)-B(5)	108.2(4)
B(3)-N(2)-B(4)	108.4(4)	C(6)-N(3)-B(6)	109.3(4)
B(5)-N(3)-B(6)	112.7(4)	C(1)-N(1)-C(2)	109.7(5)
C(1)-N(1)-B(1)	109.0(5)	C(3)-N(2)-C(4)	109.2(5)
C(1)-N(1)-B(2)	109.0(5)	C(5)-N(3)-C(6)	108.8(5)
C(2)-N(1)-B(1)	109.7(5)		

^aSymmetry transformations used to generate equivalent atoms: ' = -x, y+1/2, -z+1/2

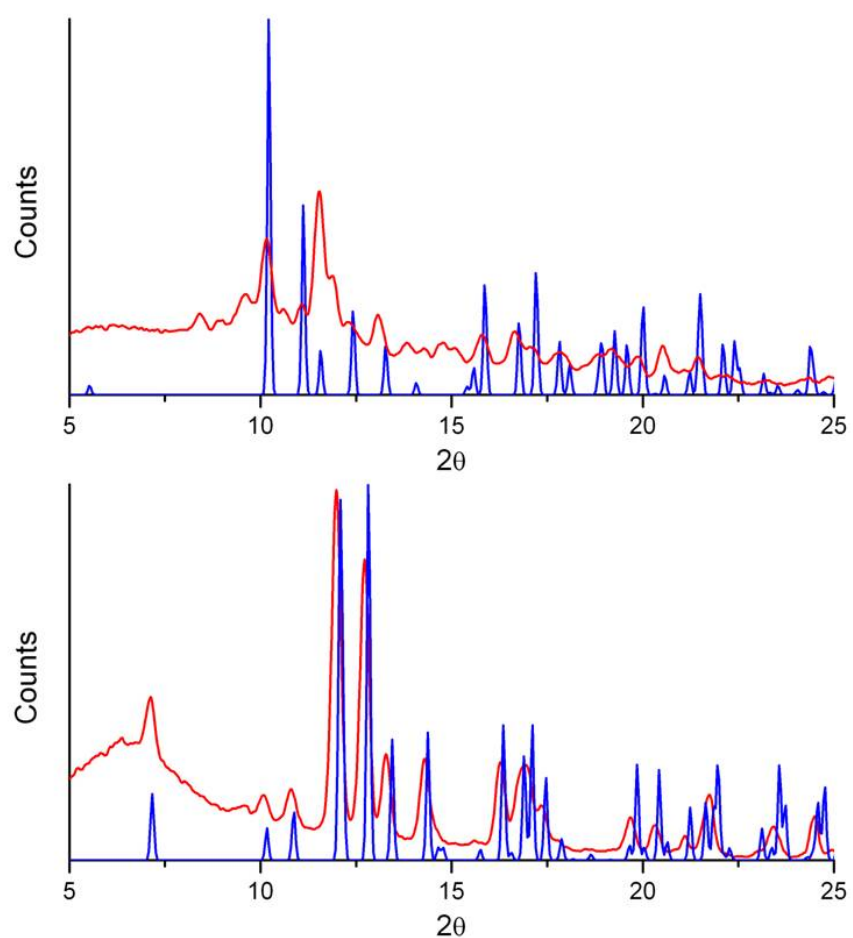


Figure S1. Top: Experimental powder XRD pattern of material obtained from pentane extract (red) and calculated powder XRD pattern from the single crystal diffraction data for **1a**. Bottom: Experimental powder XRD pattern of material obtained from toluene extract (red) and calculated powder XRD pattern from the single crystal diffraction data for **1b** (blue).

Supplementary References

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- (3) Brumaghim, J. L.; Priepot, J. G.; Girolami, G. S. *Organometallics* **1999**, *18*, 2139-2144.