Lewis Acid Capping of a Uranium(V) Nitride via a Uranium(III) Azide Molecular Square

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Supporting Information

Experimental Procedures

General Considerations: Unless otherwise noted, all reactions were performed using standard Schlenk line techniques under an atmosphere of nitrogen or argon or in an MBraun inert atmosphere glove box under an atmosphere of nitrogen. Glassware and Celite® were stored in an oven at *ca*. 150 °C for at least 3 h prior to use. Molecular sieves (4 Å) were activated by heating to 200 °C overnight under vacuum prior to storage in a glove box. NMR spectra were recorded at room temperature unless noted otherwise on Bruker AV-300, AVB-400, AVQ-400, DRX-500, AV-500, or AV-600 spectrometers. ^{13}C NMR chemical shifts (δ) are given relative to residual solvent peaks and are recorded in units of parts per million (ppm). ^{11}B NMR chemical shifts (δ) were referenced to an external standard ($BF_3 \cdot OEt_2$, δ = 0). ^{19}F NMR chemical shifts (δ) are reported in ppm and referenced to an external standard ($CFCl_3$ in $CDCl_3$). FT-IR samples were prepared as Nujol mulls pressed between KBr plates, with data collected with a Nicolet iS10 FT-IR spectrometer. Melting points were determined using sealed capillaries prepared under nitrogen on an OptiMelt automated melting point system. Elemental analyses were determined at the Microanalytical Facility at the College of Chemistry, University of California, Berkeley. Photolysis experiments were conducted in a Rayonet reactor, model RPR-100, centered at 253 nm.

Materials: Diethyl ether, *n*-hexane, *n*-pentane, THF, 1,2-dimethoxyethane (DME), benzene, and toluene were purified by passage through columns of activated alumina and degassed by sparging with nitrogen. C_6D_6, and pyridine-d_5 were vacuum-transferred from flasks containing sodium/benzophenone (C_6D_6) or calcium hydride (pyridine-d_5), degassed with three freeze-pump-thaw cycles, and stored over molecular sieves. $(Cp^{iPr4})_2UI$,[1] $[(Cp^{iPr4})_2U][B(C_6F_5)_4]$,[1] and $B(C_6F_5)_3$,[2] were synthesized according to literature procedures. All other chemicals were purchased from commercial sources and used as received.

Synthesis of $[(Cp^{iPr4})_2U(\mu\text{-}\eta^1\text{:}\eta^1\text{-}N_3)]_4$ (1)

THF (4 mL) was added to a mixture of $(Cp^{iPr4})_2UI$ (95 mg, 0.11 mmol, 1.0 equiv) and NaN_3 (7.7 mg, 0.12 mmol, 1.0 equiv), and the resulting green suspension was stirred in the dark for 18 h at room temperature. Volatiles were removed *in vacuo*, and the product was extracted into 6 mL of hexane (added quickly to ensure the product did not begin crystallizing in a smaller volume of solvent), filtered through Celite, concentrated to a volume of 1 mL, and allowed to crystallize at room temperature overnight. The product was isolated as green crystals after washing with 1 mL of pentane and drying *in vacuo* (70 mg, 0.023 mmol, 82% yield). X-ray quality crystals of **1** were grown from pentane at room temperature. Note that while the crude material could be extracted into hydrocarbon or ethereal solvents, the crystalline product formed upon filtration and concentration were subsequently not soluble in any solvents tested, including hexane, toluene, THF, DME, and pyridine. As such, X-ray quality crystals of **1** were formed by recrystallization of the crude material as opposed to isolated product. Mp ca. 134 °C (decomp.); IR: 2100 (*v*(N_3), vs), 1364 (m), 1302 (m), 1274 (w), 1188 (w), 1177 (m), 1146 (m), 1103 (m), 1061 (w), 983 (m), 919 (w), 794 (w), 779 (m), 723 (m) 670 (w), 632 (w), 616 (w), 602 (w) cm^{-1}. Anal. Calcd. (%) for $C_{136}H_{232}N_{12}U_4$ (**1**): C, 54.68; H, 7.83; N, 5.63. Found: C, 53.99; H, 7.60; N, 5.39.

Synthesis of $(Cp^{iPr4})_2U(\mu\text{-}N)B(C_6F_5)_3$ (2)

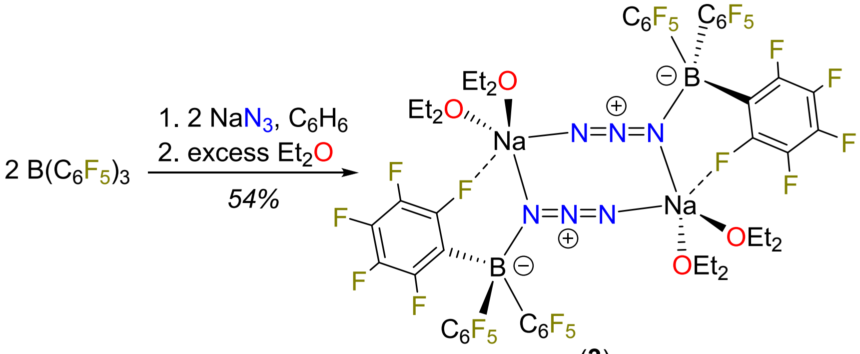
Benzene (2 mL) was added to a mixture of **1** (99 mg, 0.033 mmol, 1.0 equiv) and $B(C_6F_5)_3$ (68 mg, 0.13 mmol, 4.0 equiv), and the resulting suspension was stirred in the dark for 45 min at room temperature. During this time, the reaction mixture changed from a green suspension to a clear, dark red-orange solution. Volatiles were removed by lyophilization (to ensure the product did not begin crystallizing in a small volume of solvent), and the product was extracted into 3 mL of toluene, filtered through Celite, concentrated, and cooled to –40 °C. The product was isolated as dark red crystals after washing with 1 mL of hexane and drying *in vacuo*. Concentration and cooling of the supernatant yielded a second crop of product in a similar fashion (104 mg combined, 0.085 mmol, 64% yield). X-ray quality crystals of **2** were grown from toluene at –40 °C. Mp ca. 154 °C (decomp.). Due to very low solubility in hydrocarbon solvents and instability in more coordinating solvents such as THF or pyridine, it was not possible to acquire adequate NMR spectroscopic data for **2**. IR: 1640 (m), 1515 (s), 1305 (w), 1274 (m), 1180 (w), 1147 (w), 1086 (s), 973 (s), 951 (s), 839 (w), 805 (w), 748 (w), 771 (w), 762 (w), 744 (w), 734 (m), 727 (m), 696 (w), 681 (m), 657 (w), 624 (w), 601 (w) cm^{-1}. Anal. Calcd. (%) for $C_{52}H_{58}BF_{15}NU$ (**2**): C, 50.74; H, 4.75; N, 1.14. Found: C, 51.14; H, 4.56; N, 1.24.

Synthesis of $[(C_6F_5)_3B(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}N_3)Na(OEt_2)_2]_2$ (3)

Based on the reported synthesis of $[N(^nBu)_4][\{(C_6F_5)_3BN\}U\{N(^tBu)(3,5\text{-}Me_2C_6H_3)\}_3]$,[3] we sought to determine if we could prepare **2** by reaction of an azidoborate salt with a uranium(III) precursor. The reaction of a 1:1 mixture of NaN_3 and $B(C_6F_5)_3$ in benzene, followed by crystallization from diethyl ether, yielded the novel azidoborate species $[(C_6F_5)_3B(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}N_3)Na(OEt_2)_2]_2$ (**3**) (See Scheme S1 and Figure S5; selected structural metrics are shown in Table S3). Reactions between **3** and either $(Cp^{iPr4})_2UI$ or $[(Cp^{iPr4})_2U][B(C_6F_5)_4]$[1] yielded intractable mixtures.

Benzene (2 mL) was added to a mixture of $B(C_6F_5)_3$ (108 mg, 0.21 mmol, 1.0 equiv) and NaN_3 (15 mg, 0.22 mmol, 1.1 equiv), and the resulting colorless suspension was stirred for 24 h at room temperature. Volatiles were removed from the colorless, cloudy mixture *in vacuo*, and the product was extracted with 2 mL of ether, filtered through Celite, concentrated, and cooled to –40 °C. The product was isolated as colorless crystals after washing with 1 mL of hexane and drying *in vacuo* (82 mg, 0.11 mmol, 54% yield). X-ray quality crystals of **3** were grown from ether at –40 °C. Mp ca. 137 °C (decomp.); ^{11}B NMR (193 MHz, $(CH_3CH_2)_2O$): δ −6.99 (s); ^{13}C (151 MHz, $(CH_3CH_2)_2O$): δ 148.13 (m, $^1J_{C,F}$ = 243 Hz), 139.12 (m, $^1J_{C,F}$ = 248 Hz), 136.74 (m, $^1J_{C,F}$ = 244 Hz), 120.10 (broad, *ipso*-C_6F_5); ^{19}F NMR (376 MHz, $(CH_3CH_2)_2O$): δ −133.87 (dd, $^3J_{F,F}$ = 23.8, $^4J_{F,F}$ = 8.6 Hz, 12F, *o*-F), −160.29 (t, $^3J_{F,F}$ = 20.0 Hz, 6F, *p*-F), −165.32 (m, 12F, *m*-F); IR: 2148 ($\nu(N_3)$, vs), 1645 (s), 1601 (w) 1518 (s), 1331 (m), 1301 (w), 1281 (s), 1183 (w), 1153 (w), 1093 (s), 1067 (m), 1014 (w), 974 (s), 914 (w), 884 (w), 867 (m), 835 (w), 801 (m), 769 (m), 746 (m), 733 (w), 692 (s), 670 (m), 652 (w), 618 (m), 604 (w) cm^{-1}. Anal. Calcd. (%) for $C_{52}H_{40}B_2F_{30}N_6Na_2O_4$ (**3**): C, 43.06; H, 2.78; N, 5.79. Found: C, 42.91; H, 2.89; N, 6.24.

Scheme S1. Synthesis of $[(C_6F_5)_3B(\mu_3\text{-}\eta^1{:}\eta^1{:}\eta^1\text{-}N_3)Na(OEt_2)_2]_2$ (**3**)



(**3**)

NMR Spectroscopy

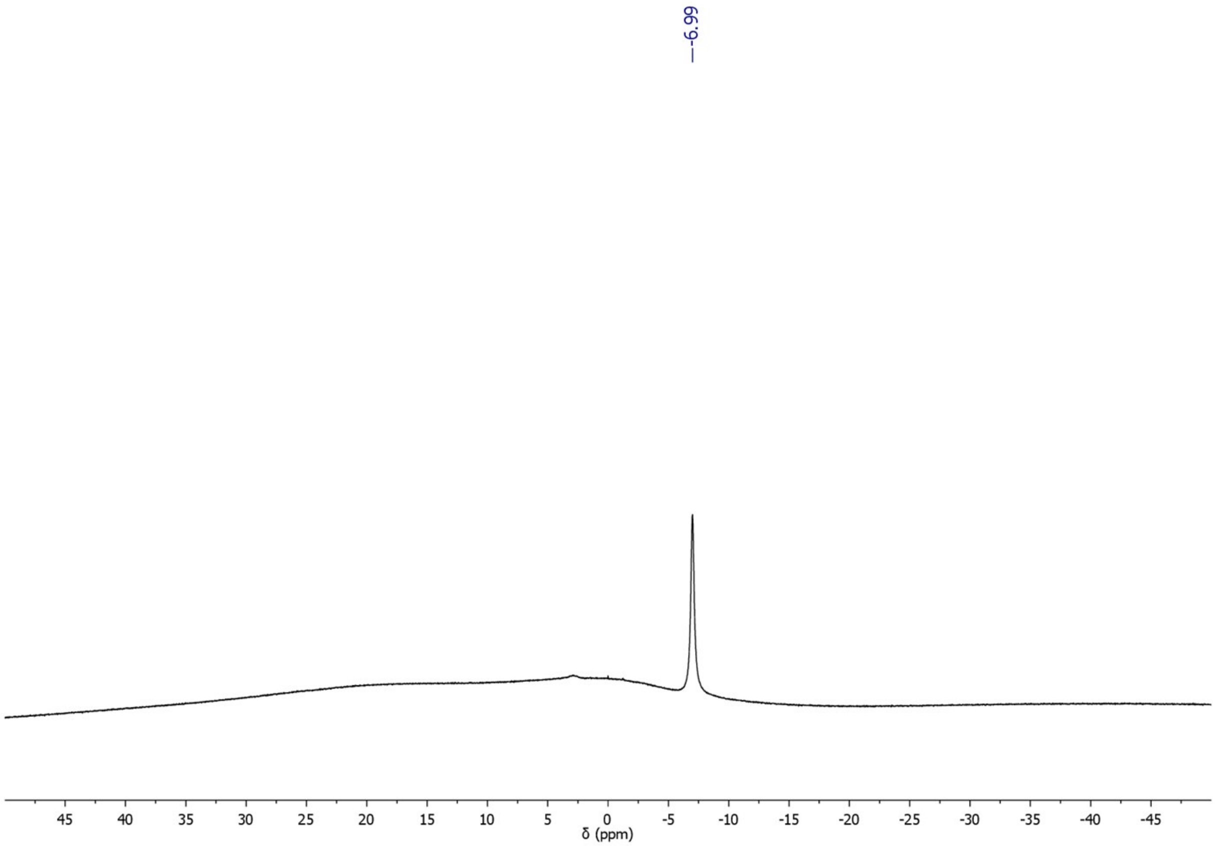


Figure S1. Room temperature ^{11}B NMR spectrum of $[(C_6F_5)_3B(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}N_3)Na(OEt_2)_2]_2$ (**3**) in $(CH_3CH_2)_2O$. The broad resonance centered at about δ = 10 ppm originates from borosilicate glass in the sample tube and spectrometer probe.

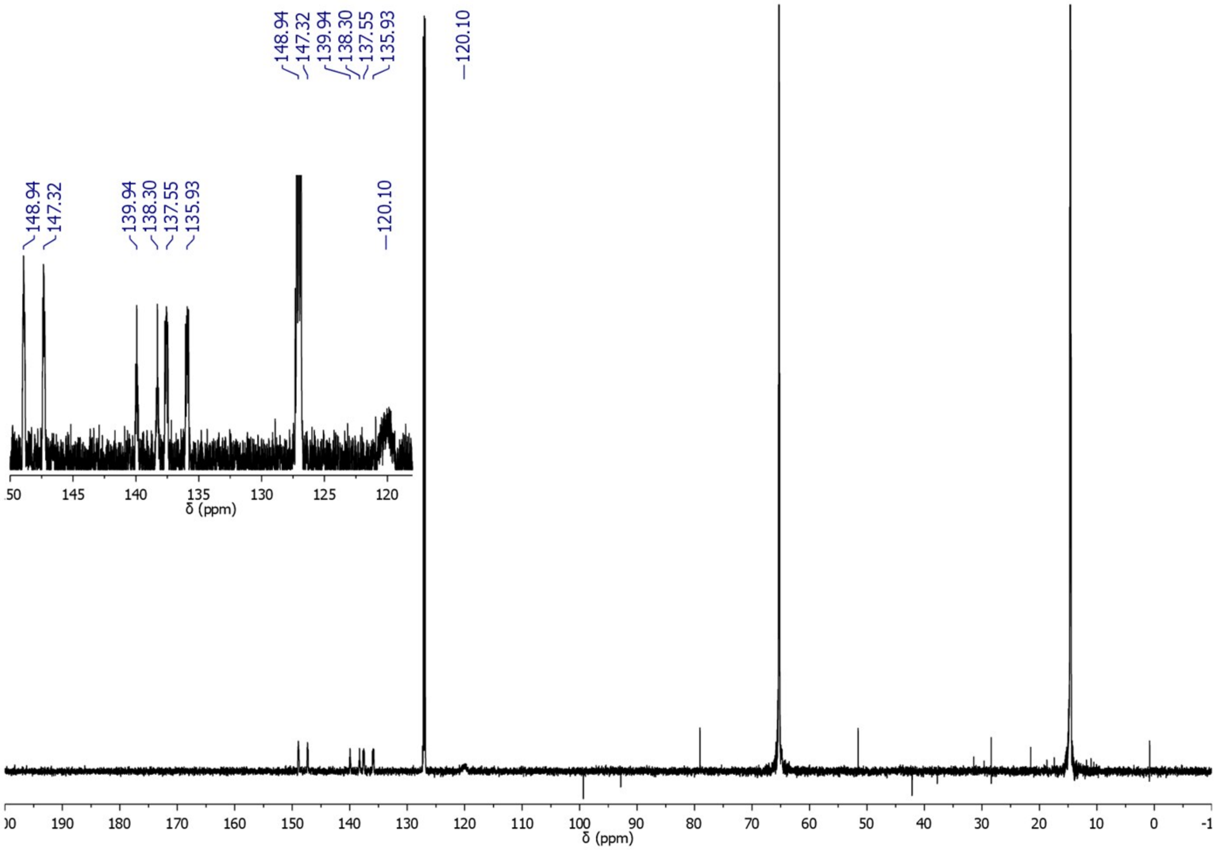


Figure S2. Room temperature ^{13}C NMR spectrum of $[(C_6F_5)_3B(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}N_3)Na(OEt_2)_2]_2$ (**3**) in $(CH_3CH_2)_2O$. The inset spectrum highlights the resonances attributable to **3**. In addition to the residual diethyl ether signals at δ 65.3 and 14.6, the signal at δ = 127 ppm is from a sealed capillary of C_6D_6 added to facilitate locking and shimming.

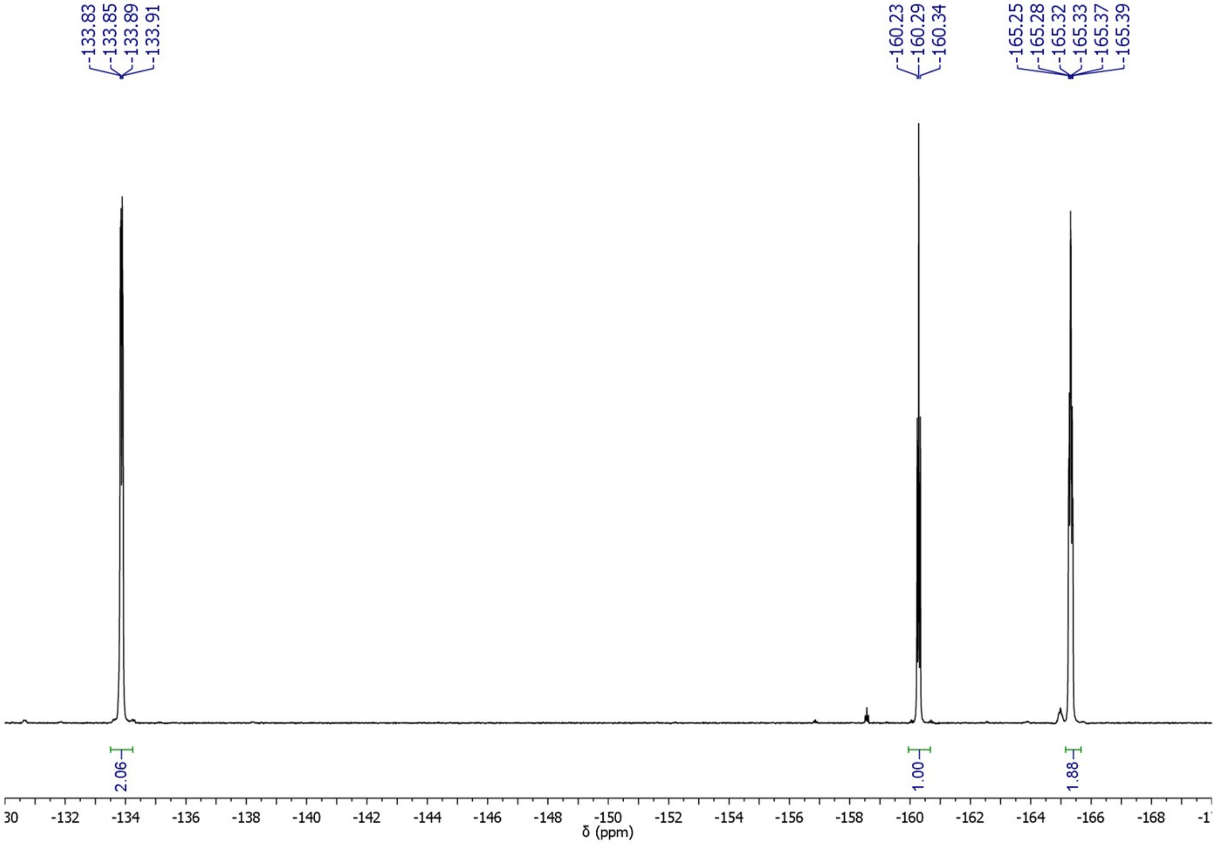


Figure S3. Room temperature ^{19}F NMR spectrum of $[(C_6F_5)_3B(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}N_3)Na(OEt_2)_2]_2$ (**3**) in $(CH_3CH_2)_2O$.

X-ray Crystallography

In a dry nitrogen glovebox, samples of single crystals of **1**, **2**, and **3** were coated in Paratone-N oil prior to transport to diffraction facilities, where they were evaluated by polarized light microscopy and mounted on a Kaptan loop (for **1**) or on a MiTeGen 10 µm aperture Dual-Thickness MicroMount (for **2** and **3**). X-ray diffraction data for **1** were collected at CheXray, Berkeley, CA, using a Bruker APEX II QUAZAR instrument outfitted with a monochromated Mo Kα radiation source (λ = 0.71073 Å). X-ray diffraction data for **2** and **3** were collected at the Advanced Light Source (ALS), Lawrence Berkeley National Lab, Berkeley, CA, station 12.2.1 using a silicon monochromated beam of 17 keV (λ = 0.7288 Å) synchrotron radiation. All data collections were conducted at 100 K, with the crystals cooled by a stream of dry nitrogen. Bruker APEX2 or APEX3 software was used for the data collections, Bruker SAINT V8.37A or V8.38A software was used to conduct the cell refinement and data reduction procedures,[4] and absorption corrections were carried out by a multi-scan method utilizing the SADABS program.[5] Initial structure solutions were found using direct methods (SHELXT),[6] and refinements were carried out using SHELXL-2014.[7–9] Thermal parameters for all non-hydrogen atoms were refined anisotropically. Thermal ellipsoid plots were made using Mercury.[10] Complex **1** possessed highly disordered outer sphere solvent molecules; the data for this structures were treated with the BYPASS routine included in the OLEX2 software package.[11] All structures have been deposited to the Cambridge Crystallographic Data Centre (CCDC), with deposition numbers 1984940 (**1**), 1984941 (**2**), and 1984942 (**3**).

Table S1. Selected distances (Å) and angles (°) for **1**.

	1
U–N	2.487(8)–2.526(8)
N–N	1.159(8)–1.175(9)
U–N–N	160.8(6)–177.0(7)
N–U–N	91.6(2)–100.8(2)
Cp(cent)–U[a]	2.511(4)–2.540(4)
Cp(cent)–U–Cp(cent)[a]	137.8(1)

[a] One of the Cp rings was modeled over two positions; as the AFIX 56 command was used to fix both rings into a regular pentagon (the model was not stable upon refinement when this command was removed), metrics involving these Cp ring centroids were not included for either component.

Table S2. Selected distances (Å) and angles (°) for **2**.

	2
U(1)–N(1)	1.893(2)
B(1)–N(1)	1.557(5)
U(1)–F(1)	2.597(2)
C(36)–F(1)	1.394(3)
All other C–F	1.338(3)–1.354(4)
U(1)–N(1)–B(1)	159.9(2)
F(1)–U(1)–N(1)	69.19(8)
Cp(cent)–U	2.511(1), 2.520(1)
Cp(cent)–U–Cp(cent)	129.60(4)

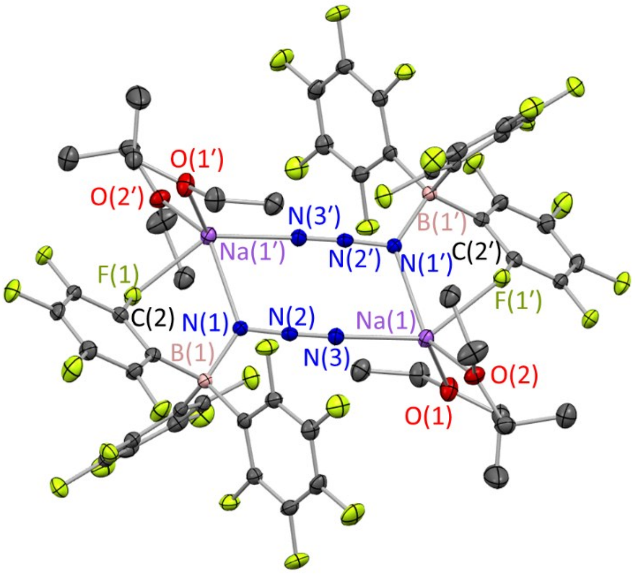


Figure S5. X-ray crystal structure of $[(C_6F_5)_3B(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}N_3)Na(OEt_2)_2]_2$ (**3**) with 50% probability ellipsoids. Hydrogen atoms and positional disorder are omitted for clarity. Selected structural metrics are listed in Table S3.

Table S3. Selected distances (Å) and angles (°) for **3**.

	3
B(1)–N(1)	1.606(2)
Na(1)–N(3)	2.425(1)
Na(1)–N(1′)	2.571(1)
N(1)–N(2)	1.216(1)
N(2)–N(3)	1.140(1)
Na(1)–O(1)	2.311(1)
Na(1)–O(2)	2.297(1)
Na(1)–F(1′)	2.3976(8)
C(2)–F(1)	1.363(2)
All other C–F	1.340(2)–1.354(2)
B(1)–N(1)–N(2)	117.9(1)
Na(1)–N(3)–N(2)	160.7(1)
Na(1)–N(1′)–N(2′)	111.30(9)

Table S4. Crystallographic data for $[(\mathrm{Cp}^{\mathrm{iPr4}})_2\mathrm{U}(\mu\text{-}\eta^1{:}\eta^1\text{-}\mathrm{N}_3)]_4$ (**1**)

Empirical formula	$C_{141}H_{244}N_{12}U_4$	
Formula weight	3059.59	
Color, habit	Green, block	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	$P4_22_12$	
Unit cell dimensions	a = 20.7855(5) Å	$\alpha = 90°$.
	b = 20.7855(5) Å	$\beta = 90°$.
	c = 35.3744(10) Å	$\gamma = 90°$.
Volume	15283.0(9) $Å^3$	
Z / Z″	8 / 4	
Density (calculated)	1.330 Mg/m^3	
Absorption coefficient	4.272 mm^{-1}	
F(000)	6168.0	
Crystal size	0.24 × 0.20 × 0.16 mm^3	
Theta range for data collection	1.500 to 25.379°	
Index ranges	$-24 \le h \le 25$, $-25 \le k \le 24$, $-42 \le l \le 39$	
Reflections collected	104285	
Independent reflections	14035 [$R_{int} = 0.0690$]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0. 4901 and 0.3804	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14035 / 61 / 817	
Goodness-of-fit on F^2	1.030	
Final R indices [I > 2σ(I)]	$R_1 = 0.0356$, $wR_2 = 0.0670$	
R indices (all data)	$R_1 = 0.0501$, $wR_2 = 0.0712$	
Flack parameter	0.029(9)	
Largest diff. peak and hole	0.76 and –0.60 $e \cdot Å^{-3}$	

Table S5. Crystallographic data for $(\mathrm{Cp}^{\mathrm{iPr4}})_2\mathrm{U}(\mu\text{-N})\mathrm{B}(\mathrm{C}_6\mathrm{F}_5)_3$ (**2**)

Empirical formula	$C_{55.5}H_{62}BF_{15}NU$	
Formula weight	1276.90	
Color, habit	Orange, plate	
Temperature	100(2) K	
Wavelength	0.7288 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.5562(5) Å	α = 100.421(2)°.
	b = 13.4735(6) Å	β = 97.392(2)°.
	c = 18.1929(8) Å	γ = 116.686(2)°.
Volume	2626.3(2) $Å^3$	
Z	2	
Density (calculated)	1.615 Mg/m^3	
Absorption coefficient	1.516 mm^{-1}	
F(000)	1268.0	
Crystal size	0.150 × 0.150 × 0.020 mm^3	
Theta range for data collection	1.877 to 26.042°	
Index ranges	$-15 \leq h \leq 15, -16 \leq k \leq 16, -21 \leq l \leq 21$	
Reflections collected	34714	
Independent reflections	9599 [R_{int} = 0.0302]	
Completeness to theta = 25.930°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7462 and 0.5399	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9599 / 0 / 690	
Goodness-of-fit on F^2	1.068	
Final R indices [I > 2σ(I)]	$R_1 = 0.0218$, $wR_2 = 0.0477$	
R indices (all data)	$R_1 = 0.0244$, $wR_2 = 0.0488$	
Largest diff. peak and hole	1.07 and –1.09 $e \cdot Å^{-3}$	

Table S6. Crystallographic data for $[(C_6F_5)_3B(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-}N_3)Na(OEt_2)_2]_2$ (**3**)

Empirical formula	$C_{52}H_{40}B_2F_{30}N_6Na_2O_4$	
Formula weight	1450.50	
Color, habit	Colorless, block	
Temperature	100(2) K	
Wavelength	0.7288 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.1153(4) Å	α = 70.9380(10)°.
	b = 11.7453(4) Å	β = 81.4520(10)°.
	c = 12.4529(4) Å	γ = 72.2550(10)°.
Volume	1461.32(9) $Å^3$	
Z / Z″	2 / 1	
Density (calculated)	1.648 Mg/m^3	
Absorption coefficient	0.191 mm^{-1}	
F(000)	728.0	
Crystal size	0.15 × 0.15 × 0.12 mm^3	
Theta range for data collection	1.976 to 27.097°	
Index ranges	$-13 \leq h \leq 13$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$	
Reflections collected	20441	
Independent reflections	5943 [$R_{int} = 0.0539$]	
Completeness to theta = 25.930°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7462 and 0.6657	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5943 / 1 / 451	
Goodness-of-fit on F^2	1.048	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0331$, $wR_2 = 0.0855$	
R indices (all data)	$R_1 = 0.0355$, $wR_2 = 0.0877$	
Largest diff. peak and hole	0.34 and –0.33 $e \cdot Å^{-3}$	

EPR Spectroscopy

EPR spectroscopy was performed in the CalEPR center in the University of California, Davis. X-band continuous wave EPR spectra were recorded on the Bruker Biospin EleXsys E500 spectrometer with a super high Q resonator (ER4122SHQE). Cryogenic temperatures were achieved by using an ESR900 liquid helium cryostat with a temperature controller (Oxford Instrument ITC503). Spectrometer settings were: conversion time, 40 ms; modulation amplitude, 0.5 mT; modulation frequency, 100 kHz; and other settings as indicated in figure captions. Spectral simulations were performed in Matlab 2018a (MathWorks Inc.) with Easyspin 5.2.28 toolbox.[12]

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