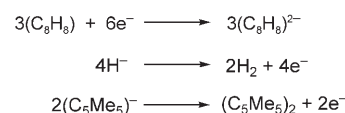
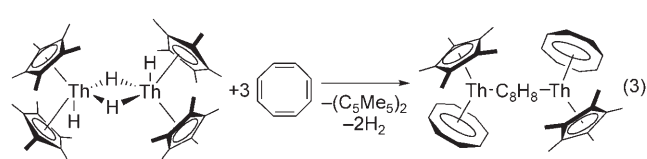
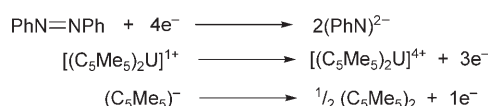
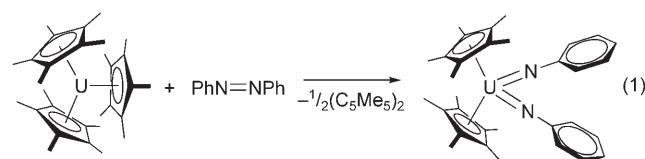


Reductive Coupling of Acetonitrile by Uranium and Thorium Hydride Complexes To Give Cyanopentadienyl Dianion (C₆N₃H₇)²⁻**

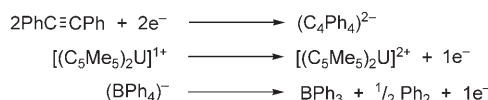
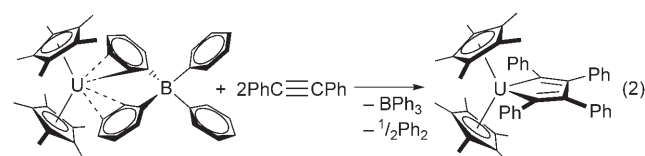
William J. Evans,* Kevin A. Miller, and Joseph W. Ziller

Recent studies of reductive organoactinide chemistry have shown that multielectron reductions can be achieved by combining ligand-based reduction with traditional metal-based reduction.^[1–5] This ligand-based reduction is available not only in sterically crowded complexes such as [(C₅Me₅)₃U] [Eq. (1)]^[1,2] and [(C₅Me₅)₂U]₂(C₆H₆),^[3] but also in com-

In search of other ligands that would function like (BPh₄)⁻ in Equation (2), we examined the actinide hydrides [(C₅Me₅)₂UH]₂ and [(C₅Me₅)₂ThH₂]₂.^[6] With substrates such as PhEPh (E = S, Se), PhNNPh, and C₈H₈, each hydride ligand in [(C₅Me₅)₂UH]₂ and [(C₅Me₅)₂ThH₂]₂ can deliver one electron and generate hydrogen gas as an easily separable by-product [Eq. (3)]. Although these hydride



pounds with normal bond lengths such as [(C₅Me₄R)₂U(μ-Ph)₂BPh₂] (R = Me,^[4] H^[5]) [Eq. (2)]. Hence, in Equation (1) the (C₅Me₅)⁻ ligand delivers an electron and forms (C₅Me₅)₂ as a by-product in a sterically induced reduction process,^[4] but in Equation (2) (BPh₄)⁻ acts as a reductant without apparent steric inducement.^[4]



ligands could function as one-electron reductants, it was conceivable that their reductive chemistry could be combined with other types of hydride-based transformations^[7–9] to achieve reaction sequences that are otherwise unavailable.

Herein, we show how these actinide hydrides can deliver a cascade of reactions involving not only reduction, but also insertion and deprotonation to assemble complicated products from simple precursors. In this case, the substrate is acetonitrile and the product is a dianion containing a six carbon atom chain. Nitriles are known to react in several ways with f elements, including metalation,^[10,11] insertion,^[12–14] and reduction.^[15,16] However, the capacity to effect reduction chemistry and traditional f-element hydride insertion and metalation chemistry with a single reagent has not been observed before.

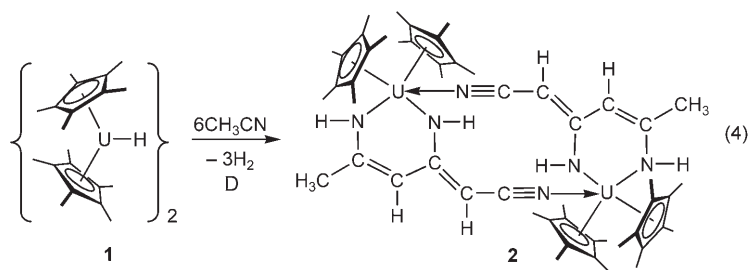
Addition of CH₃CN to a brown-green solution of the trivalent uranium hydride [(C₅Me₅)₂UH]₂ (**1**) in toluene forms a dark red solution, from which [(C₅Me₅)₂U-(CH₃C(NH)=CHC(NH)=CHCN)]₂ (**2**) could be isolated in 69% yield upon heating [Eq. (4)]. Complex **2** was identified by X-ray crystallography (Figure 1) and characterized by spectroscopic and analytical methods, including atmospheric pressure chemical ionization mass spectrometry (APCI-MS),^[17] which showed a mixture of [M]⁺ and [M+H]⁺ ions at m/z 1258.7 and 1259.7, respectively.

Overall, three molecules of acetonitrile have been coupled to give a dianionic tridentate ligand containing a six carbon atom chain with concomitant loss of six hydrogen atoms. Although nitriles have been condensed in many ways to monoanionic ligands by insertion and metalation reactions

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initiated by alkyl and amide metal complexes,^[18–23] the combination of reduction, insertion, deprotonation, and rearrangement that contributes to the formation of this diaminocyanopentadienyl dianion unit appears to be unique.

The analogous reaction of **1** and CD₃CN suggested that none of the hydrogen atoms in (C₆N₃H₇)^{2–} arose from the hydride ligands in **1**, as the ¹H NMR resonances attributable to the

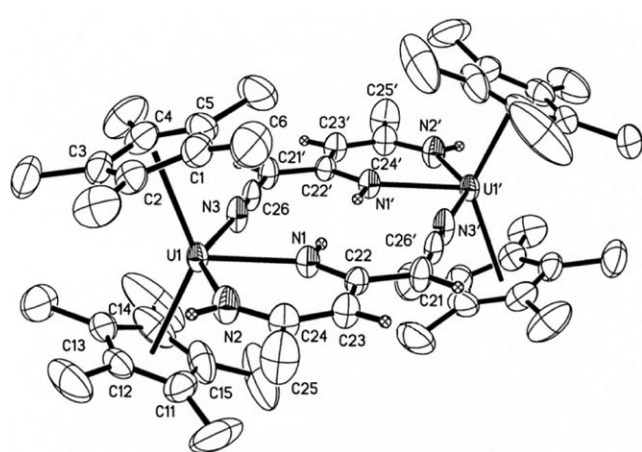
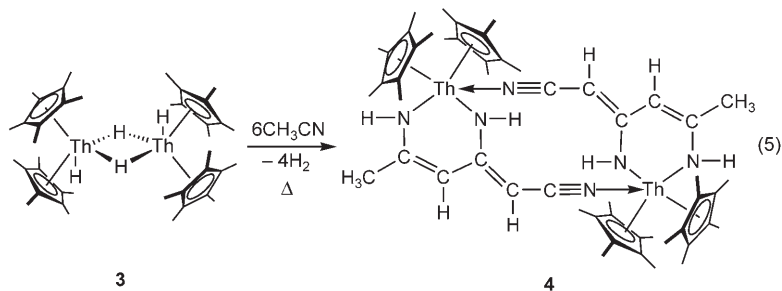


Figure 1. A thermal ellipsoid plot of **2** drawn at the 50% probability level. Selected bond lengths [Å]: U1–N1 2.332(3), U1–N2 2.331(4), U1–N3 2.461(4), U1–(C1–C5)_{centroid} 2.480, U1–(C11–C15)_{centroid} 2.494, N1–C22 1.350(5), N2–C24 1.349(6), N3–C26 1.160(6), C21–C26' 1.381(6), C21–C22 1.415(5), C22–C23 1.421(5), C23–C24 1.368(6), C24–C25 1.514(6).

(C₆N₃H₇)^{2–} ligand in the spectrum of **2** were absent in the ¹H NMR spectrum of the CD₃CN product.

Normally, it would not be possible to obtain reductive thorium chemistry analogous to that accessible from U^{III} complexes, as few Th^{III} compounds are known.^[24–27] For example, there is no thorium analogue of **1**. However, recently the tetravalent thorium hydride [(C₅Me₅)₂ThH₂]₂ (**3**) has been found to have chemistry similar to that of **1** in some cases.^[6] The four hydride ligands in **3** can provide the same reductive capacity generated from the two U^{III} and two hydride ions in **1**. Hence, the reaction of **3** with CH₃CN was also studied.

Despite the complexity of the reaction in Equation (4) and the presence of U^{III} in that case, Th^{IV} complex **3** gives an

analogous product [**4**; Eq. (5)]. Complex **4** was also identified by X-ray crystallography (Figure 2) and APCI-MS. This result indicated that a trivalent ion was not necessary to generate the (C₆N₃H₇)^{2–} ligand from acetonitrile and that the difference in the size of the metals did not change the course of the reaction. Th^{IV} is approximately 0.08 Å smaller than U^{III}, but 0.05 Å larger than U^{IV}.^[28]

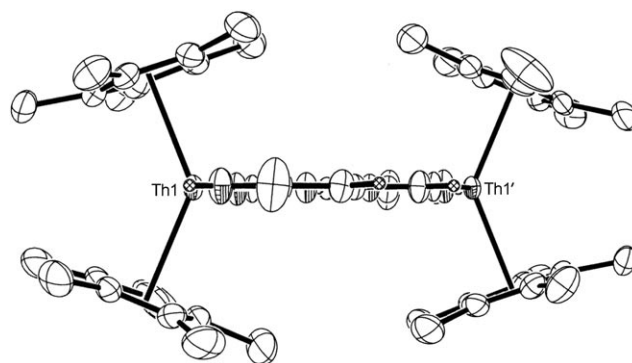


Figure 2. A thermal ellipsoid plot of **4** drawn at the 50% probability level. Selected bond lengths [Å] (numbering scheme analogous to that in Figure 1): Th1–N1 2.389(3), Th1–N2 2.387(2), Th1–N3 2.505(2), Th1–(C1–C5)_{centroid} 2.548, Th1–(C11–C15)_{centroid} 2.556, N1–C22 1.349(3), N2–C24 1.340(4), N3–C26 1.162(3), C21–C26' 1.372(4), C21–C22 1.415(4), C22–C23 1.423(3), C23–C24 1.371(4), C24–C25 1.510(4).

The structures of **2** and **4** are isomorphous. Their metal–ligand bond lengths differ by 0.044–0.068 Å, which correlates well with the 0.05 Å difference in the ionic radii of the tetravalent ions.^[28] As shown in Figure 2, the (C₆N₃H₇)^{2–} ligand is nearly planar; the maximum deviation from the An–(C₆N₃H₇)–An plane is 0.0770 and 0.0522 Å in **2** and **4**, respectively. The metallocene components of **2** and **4** have bond lengths and angles in the broad range common for tetravalent actinides.^[17] For example, the average U–C–(C₅Me₅) bond length in **2** of 2.75(3) Å is within the range of 2.74(5) to 2.80(5) Å observed for nine-coordinate tetravalent uranium metallocenes.^[17] The C–N and C–C bond lengths in the (C₆N₃H₇)^{2–} ligands in **2** and **4** suggest that resonance structures **A–C** in Figure 3 are all useful in understanding the structure, but that **A** is the major contributor. Hence, the C21–C22, C22–C23, and C23–C24 bond lengths are all in the range 1.368(6)–1.423(3) Å, which is intermediate between C–

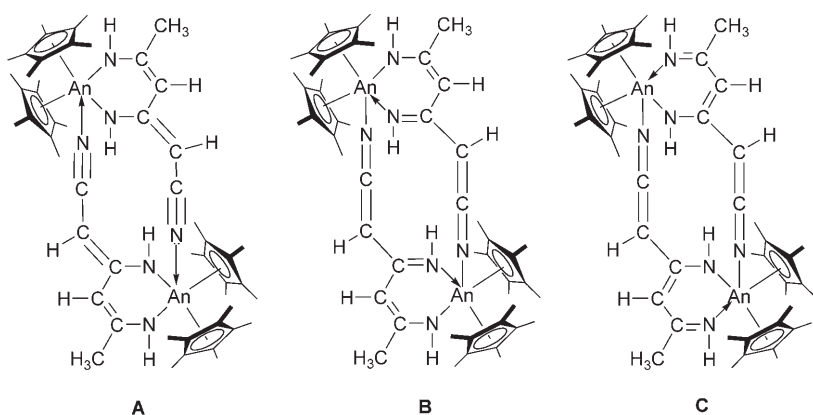


Figure 3. Possible resonance structures for **2** and **4** (An = U, Th).

C and C=C bonds.^[29] The C26–N3 bond lengths of 1.160(6) and 1.162(3) Å in **2** and **4**, respectively, are slightly longer than the typical bond lengths of 1.136–1.144 Å for C≡N bonds.^[23] The U–N1 (2.332(3) Å) and U–N2 (2.331(4) Å) bond lengths in **2** are equivalent and slightly longer than the U–N(NR₂) single bond lengths in the U^{IV} metallocenes [(C₅Me₅)₂U{NH(2,6-Me₂C₆H₃)₂}]₂ (2.267(6) Å),^[30] [(C₅Me₅)₂U(NMe₂)(CNCMe₃)₂][BPh₄]₂ (2.22(1) Å),^[31] and [(C₅Me₅)₂U(N=CPhBz)₂] (2.184(3) Å).^[12] Similarly, the Th–N(1) (2.389(2) Å) and Th–N(2) (2.387(2) Å) bond lengths are indistinguishable from each other and longer than the Th–N(NR₂) bond lengths in [(C₅Me₅)₂Th(N=CPh₂)₂] (2.259(4), 2.265(5) Å),^[12] [(C₅Me₅)₂Th(N=CPhBz)₂] (2.256(8) Å),^[12] and [(C₅Me₇)₂Th(NMe₂)₂] (2.24(2), 2.26(2) Å).^[32] The U–N3 bond length in **2** (2.461(4) Å) is longer than the U–N1 and U–N2 bond lengths, but is shorter than the U–N(neutral donor) bond lengths in the metallocenes [(C₅Me₅)₂UI₂(N≡CPh)] (2.53(1) Å)^[33] and [(C₅Me₅)₂U(N≡CMe)₅][BPh₄]₂ (2.547(8) Å).^[34]

Although the sequence of coordination, insertion, metalation, reduction, and hydride shift reactions that can combine to form **2** and **4** is not known, this system shows that actinide hydrides such as **1** and **3** can use the reduction reactivity shown in Equation (3) in concert with more traditional insertion and metalation chemistry to transform common substrates into complicated products. The hydride ligands in **1** and **3** can effect one-electron reductive reactivity along with other types of hydride reaction chemistry. As such, these actinide hydride reducing reagents can play unique roles in small molecule transformations. These reactions also show that a Th^{IV} hydride moiety can undergo chemistry equivalent to U^{III} in a complicated multistep reaction.

Experimental Section

2: In a nitrogen-filled glovebox, CH₃CN (1 mL) was added to a solution of brown-green [(C₅Me₅)₂UH]₂ (**1**, 163 mg, 0.152 mmol) in toluene (5 mL) to generate a dark red solution, which was heated at 100°C for 3 min and allowed to cool to room temperature. After 12 h, **2** was obtained as red crystals. The mother liquor was decanted and transferred to a vial, which was cooled to –35°C. Crystals grew after 12 h. A second crop of crystals was obtained after 12 h and combined with the first (139 mg, 69%). Crystals of **2** suitable for X-ray

diffraction were grown at 25°C from a concentrated solution in toluene/CH₃CN. ¹H NMR (500 MHz, C₆D₆): δ = 4.1 (s, 30H, C₅Me₅, Δν_{1/2} = 11 Hz), –16.6 (s, 1H, CH), –18.1 (s, 3H, CH₃), –26.5 (s, 1H, CH), –135.4 (s, 1H, NH), –213.4 ppm (s, 1H, NH). ¹³C NMR (125.5 MHz, C₆D₆): δ = –22.1 (C₅Me₅), 126.0 (C₅Me₅), 36.3 (CH), 66.7 (CH₃), 164.8 ppm (CH). APCI-MS: [M⁺], *m/z* 1258.7; [M+H]⁺, *m/z* 1259.7. IR (KBr): ν̄ = 2972m, 2899m, 2855m, 2722w, 2442w, 2365w, 2275w, 2208w, 2115vs, 1531vs, 1463s, 1417vs, 1302m, 1211w, 1090w, 1021w, 998w, 918w, 901m, 870m, 730m, 696w, 544w cm^{–1}. Anal. calcd (%) for C₅₂H₇₄N₆U₂: C 49.60, H 5.92, N 6.67, U 37.81; found: C 49.80, H 5.84, N 6.74, U 37.50.

4: **4** was obtained as described for **2** as yellow crystals (159 mg, 67%) from CH₃CN (1 mL) and [(C₅Me₅)₂ThH]₂ (**3**, 192 mg, 0.221 mmol). Crystals of **4** suitable for X-ray diffraction were grown at –35°C from a concentrated solution in toluene/CH₃CN. ¹H NMR (500 MHz, C₆D₆): δ = 2.05 (s, 30H, C₅Me₅, Δν_{1/2} = 2 Hz), 3.63 (s, 1H, CH), 0.88 (s, 3H, CH₃), 4.67 (s, 1H, CH), 4.58 (s, 1H, NH), 6.20 ppm (s, 1H, NH). ¹³C NMR (125.5 MHz, C₆D₆): δ = 11.8 (C₅Me₅), 124.3 (C₅Me₅), 20.2 (CH₃), 45.1 (CH), 95.1 ppm (CH). APCI-MS: [M⁺], *m/z* 1246.7; [M+H]⁺, *m/z* 1247.7. IR (KBr): ν̄ = 2963s, 2906s, 2857s, 2185m, 2112m, 1597vs, 1550vs, 1438vs, 1378s, 1292s, 1262m, 1151m, 1020m, 862w, 802w, 766w, 636w cm^{–1}. Anal. calcd (%) for C₅₂H₇₄N₆Th₂: C 50.07, H 5.98, N 6.74, Th 37.21; found: C 49.52, H 5.94, N 7.05, Th 37.00. Compound **2** crystallizes in space group *P*₂₁/*c*, *a* = 14.811(3), *b* = 13.838(3), *c* = 16.318(4) Å, β = 112.553(3)°, *V* = 3088.8(12) Å³, *Z* = 2, ρ_{calcd} = 1.552 Mg m^{–3}, *R*₁ = 0.0315 [*I* > 2σ(*I*)], *wR*₂ = 0.0844, GOF = 1.044. Compound **4** crystallizes in space group *P*₂₁/*c*, *a* = 14.8389(14), *b* = 13.8689(12), *c* = 16.3543(15) Å, β = 112.0130(10)°, *V* = 3120.3(5) Å³, *Z* = 2, ρ_{calcd} = 1.524 Mg m^{–3}, *R*₁ = 0.0187 [*I* > 2σ(*I*)], *wR*₂ = 0.0487, GOF = 1.047. CCDC-658798 (**2**) and CCDC-658799 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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