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Actinide Chemistry

Reductive Coupling of Acetonitrile by Uranium and Thorium Hydride Complexes To Give Cyanopentadienyl Dianion $(C_6N_3H_7)^{2-}$**

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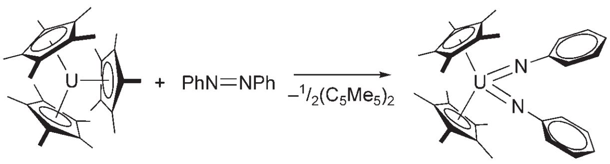
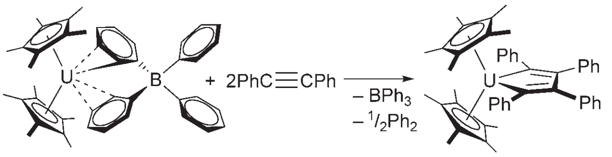
Recent studies of reductive organoactinide chemistry have shown that multielectron reductions can be achieved by combining ligand-based reduction with traditional metal-based reduction.[1–5] This ligand-based reduction is available not only in sterically crowded complexes such as $[(C_5Me_5)_3U]$ [Eq. (1)][1,2] and $[\{(C_5Me_5)_2U\}_2(C_6H_6)]$,[3] but also in compounds with normal bond lengths such as $[(C_5Me_4R)_2U(\mu\text{-}Ph)_2BPh_2]$ (R = Me,[4] H[5]) [Eq. (2)]. Hence, in Equation (1) the $(C_5Me_5)^-$ ligand delivers an electron and forms $(C_5Me_5)_2$ as a by-product in a sterically induced reduction process,[4] but in Equation (2) $(BPh_4)^-$ acts as a reductant without apparent steric inducement.[4]



(1)

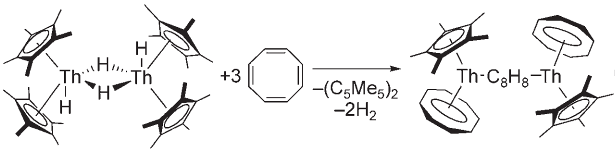
$$\mathrm{PhN{=}NPh} + 4e^- \longrightarrow 2(\mathrm{PhN})^{2-}$$
$$[(C_5Me_5)_2U]^{1+} \longrightarrow [(C_5Me_5)_2U]^{4+} + 3e^-$$
$$(C_5Me_5)^- \longrightarrow {}^{1}\!/_{2}\,(C_5Me_5)_2 + 1e^-$$



(2)

$$2\mathrm{PhC{\equiv}CPh} + 2e^- \longrightarrow (C_4Ph_4)^{2-}$$
$$[(C_5Me_5)_2U]^{1+} \longrightarrow [(C_5Me_5)_2U]^{2+} + 1e^-$$
$$(BPh_4)^- \longrightarrow BPh_3 + {}^{1}\!/_{2}\,Ph_2 + 1e^-$$

In search of other ligands that would function like $(BPh_4)^-$ in Equation (2), we examined the actinide hydrides $[\{(C_5Me_5)_2UH\}_2]$ and $[\{(C_5Me_5)_2ThH_2\}_2]$.[6] With substrates such as PhEEPh (E = S, Se), PhNNPh, and C_8H_8, each hydride ligand in $[\{(C_5Me_5)_2UH\}_2]$ and $[\{(C_5Me_5)_2ThH_2\}_2]$ can deliver one electron and generate hydrogen gas as an easily separable by-product [Eq. (3)]. Although these hydride 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.



(3)

$$3(C_8H_8) + 6e^- \longrightarrow 3(C_8H_8)^{2-}$$
$$4H^- \longrightarrow 2H_2 + 4e^-$$
$$2(C_5Me_5)^- \longrightarrow (C_5Me_5)_2 + 2e^-$$

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 CH_3CN to a brown-green solution of the trivalent uranium hydride $[\{(C_5Me_5)_2UH\}_2]$ (**1**) in toluene forms a dark red solution, from which $[\{(C_5Me_5)_2U(CH_3C(NH){=}CHC(NH){=}CHCN)\}_2]$ (**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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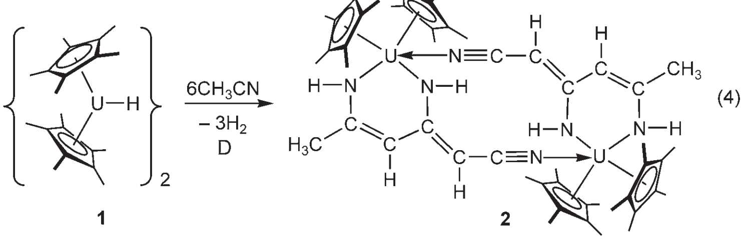


initiated by alkyl and amide metal complexes,[18–23] the combination of reduction, insertion, deprotonation, and rearrangement that contributes to the formation of this diaminocyanopentadienyl dianion unit appears to be unique.

The analogous reaction of **1** and CD_3CN suggested that none of the hydrogen atoms in $(C_6N_3H_7)^{2-}$ arose from the hydride ligands in **1**, as the ^1H NMR resonances attributable to the $(C_6N_3H_7)^{2-}$ ligand in the spectrum of **2** were absent in the ^1H NMR spectrum of the CD_3CN product.

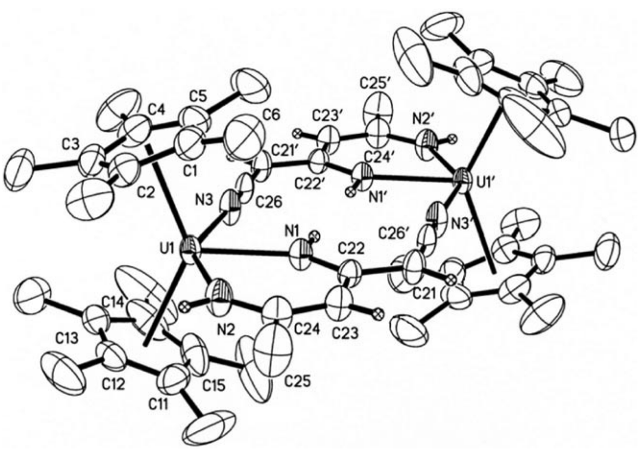
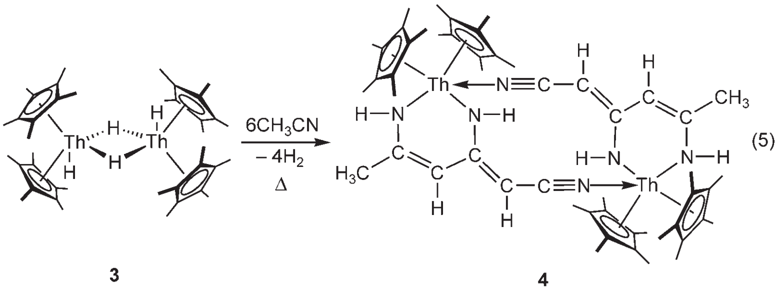


Figure 1. A thermal ellipsoid plot of **2** drawn at the 50% probability level. Selected bond lengths [Å]: U1–N1 2.332(3), U1–N2 2.331(4), U1–N3 2.461(4), U1–(C1–C5)$_{centroid}$ 2.480, U1–(C11–C15)$_{centroid}$ 2.494, N1–C22 1.350(5), N2–C24 1.349(6), N3–C26 1.160(6), C21–C26′ 1.381(6), C21–C22 1.415(5),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

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 $[\{(C_5Me_5)_2ThH_2\}_2]$ (**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 CH_3CN 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 $(C_6N_3H_7)^{2-}$ 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]



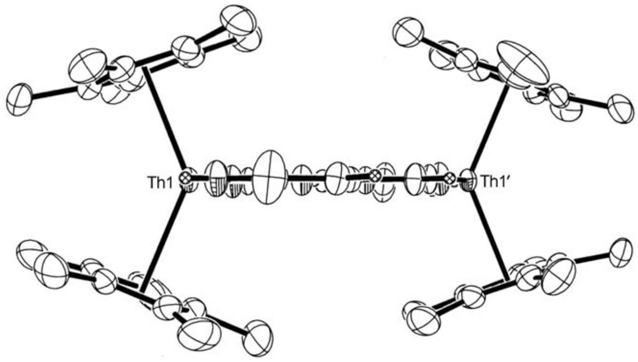


Figure 2. A thermal ellipsoid plot of **4** drawn at the 50% probability level. Selected bond lengths [Å] (numbering scheme analogous to that in Figure 1): Th1–N1 2.389(3), Th1–N2 2.387(2), Th1–N3 2.505(2), Th1–(C1–C5)$_{centroid}$ 2.548, Th1–(C11–15)$_{centroid}$ 2.556, N1–C22 1.349(3), N2–C24 1.340(4), 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 $(C_6N_3H_7)^{2-}$ ligand is nearly planar; the maximum deviation from the An-$(C_6N_3H_7)$-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-(C_5Me_5) 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 $(C_6N_3H_7)^{2-}$ 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–

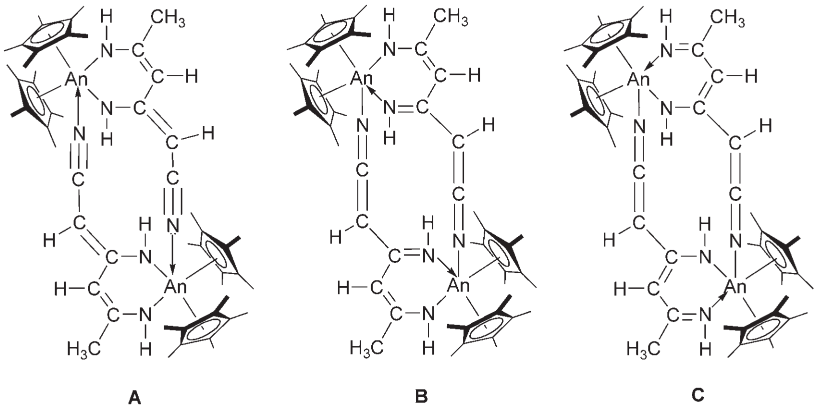


Figure 3. Possible resonance structures for **2** and **4** (An = U, Th).

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(NR$_2$) single bond lengths in the U^{IV} metallocenes [(C$_5$Me$_5$)$_2$U{NH(2,6-Me$_2$C$_6$H$_3$)}$_2$] (2.267(6) Å),[30] [(C$_5$Me$_5$)$_2$U(NMe$_2$)(CNCMe$_3$)$_2$][BPh$_4$] (2.22(1) Å),[31] and [(C$_5$Me$_5$)$_2$U(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(NR$_2$) bond lengths in [(C$_5$Me$_5$)$_2$Th(N=CPh$_2$)$_2$] (2.259(4), 2.265(5) Å),[12] [(C$_5$Me$_5$)$_2$Th(N=CPhBz)$_2$] (2.256(8) Å),[12] and [(C$_9$Me$_7$)$_2$Th(NMe$_2$)$_2$] (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 [(C$_5$Me$_5$)$_2$UI$_2$(N≡CPh)] (2.53(1) Å)[33] and [(C$_5$Me$_5$)$_2$U(N≡CMe)$_5$][BPh$_4$]$_2$ (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, CH$_3$CN (1 mL) was added to a solution of brown-green [{(C$_5$Me$_5$)$_2$UH}$_2$] (**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/CH$_3$CN. ^{1}H NMR (500 MHz, C$_6$D$_6$): $\delta = 4.1$ (s, 30H, C$_5$Me$_5$, $\Delta\nu_{1/2} = 11$ Hz), −16.6 (s, 1H, CH), −18.1 (s, 3H, CH$_3$), −26.5 (s, 1H, CH), −135.4 (s, 1H, NH), −213.4 ppm (s, 1H, NH). ^{13}C NMR (125.5 MHz, C$_6$D$_6$): $\delta = -22.1$ (C$_5$*Me*$_5$), 126.0 (*C*$_5$Me$_5$), 36.3 (CH), 66.7 (CH$_3$), 164.8 ppm (CH). APCI-MS: [*M*$^+$], *m/z* 1258.7; [*M*+H]$^+$, *m/z* 1259.7. IR (KBr): $\tilde{\nu} = 2972$m, 2899m, 2855m, 2722w, 2442w, 2365w, 2275w, 2208w, 2115vs, 1531vs, 1463 s, 1417vs, 1302m, 1211w, 1090w, 1021w, 998w, 918w, 901m, 870m, 730m, 696w, 544w cm^{-1}. Anal. calcd (%) for C$_{52}$H$_{74}$N$_6$U$_2$: 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 CH$_3$CN (1 mL) and [{(C$_5$Me$_5$)$_2$ThH}$_2$] (**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/CH$_3$CN. ^{1}H NMR (500 MHz, C$_6$D$_6$): $\delta = 2.05$ (s, 30H, C$_5$Me$_5$, $\Delta\nu_{1/2} = 2$ Hz), 3.63 (s, 1H, CH), 0.88 (s, 3H, CH$_3$), 4.67 (s, 1H, CH), 4.58 (s, 1H, NH), 6.20 ppm (s, 1H, NH). ^{13}C NMR (125.5 MHz, C$_6$D$_6$): $\delta = 11.8$ (C$_5$*Me*$_5$), 124.3 (*C*$_5$Me$_5$), 20.2 (CH$_3$), 45.1 (CH), 95.1 ppm (CH). APCI-MS: [*M*$^+$], *m/z* 1246.7; [*M*+H]$^+$, *m/z* 1247.7. IR (KBr): $\tilde{\nu} = 2963$s, 2906s, 2857s, 2185m, 2112m, 1597vs, 1550vs, 1438vs, 1378s, 1292s, 1262m, 1151m, 1020m, 862w, 802w, 766w, 636w cm^{-1}. Anal. calcd (%) for C$_{52}$H$_{74}$N$_6$Th$_2$: 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 $P2_1/c$, $a = 14.811(3)$, $b = 13.838(3)$, $c = 16.318(4)$ Å, $\beta = 112.553(3)°$, $V = 3088.8(12)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.552$ Mg m^{-3}, $R1 = 0.0315$ [$I > 2\sigma(I)$], $wR2 = 0.0844$, GOF = 1.044. Compound **4** crystallizes in space group $P2_1/c$, $a = 14.8389(14)$, $b = 13.8689(12)$, $c = 16.3543(15)$ Å, $\beta = 112.0130(10)°$, $V = 3120.3(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.524$ Mg m^{-3}, $R1 = 0.0187$ [$I > 2\sigma(I)$], $wR2 = 0.0487$, 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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