Oxidative Elimination of H$_2$ from [Cp′$_2$U(μ-OH)]$_2$ To Form [Cp′$_2$U(μ-O)]$_2$, Where Cp′ Is 1,3-(Me$_3$C)$_2$C$_5$H$_3$ or 1,3-(Me$_3$Si)$_2$C$_5$H$_3$

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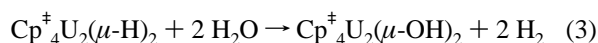
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This paper describes the unprecedented thermal decomposition reaction of a dimeric metal hydroxide shown in eq 1. Since the net transformation involves elimination of hydrogen along with oxidation of the uranium metallocene from U(III) to U(IV), the reaction is an oxidative elimination.

$$Cp′_4U_2(\mu\text{-OH})_2 \rightarrow Cp′_4U_2(\mu\text{-O})_2 + H_2 \quad (1)$$

$$Cp′ = 1,3\text{-(Me}_3\text{Si)}_2\text{C}_5\text{H}_3 \text{ or } 1,3\text{-(Me}_3\text{C)}_2\text{C}_5\text{H}_3$$
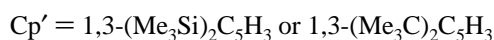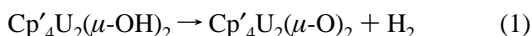
Few metallocene hydroxides of the lanthanide metals have been prepared, and none have been described for the trivalent actinide metals.[1] Among the tetravalent actinide metals, a few metallocene hydroxides, of the type Cp$_3$UOH, have been described.[2] The preparation of metal hydroxides generally involves the addition of water to a suitable precursor. We have shown recently that addition of 0.5 equiv of water to Cp$_3$Ti gives Cp$_4$Ti$_2$(μ-O) presumably *via* a titanocene hydroxide intermediate.[3] This is not a general reaction since addition of water to Cp$_3$Zr results in oxidation of the zirconium center and yields Cp$_3$ZrH and [Cp$_2$ZrO]$_3$.[4]

Adding 1 equiv of water to Cp′′$_3$U (Cp′′ = 1,3-(Me$_3$Si)$_2$C$_5$H$_3$) produces the bridging hydroxide Cp′′$_4$U$_2$(μ-OH)$_2$ (**I**-OH), eq 2.[5] Since the related tris(cyclopentadienyl)uranium complex Cp‡$_3$U (Cp‡ = 1,3 (Me$_3$C)$_2$C$_5$H$_3$) is difficult to prepare, the hydroxide Cp‡$_4$U$_2$(μ-OH)$_2$ (**II**-OH) was prepared from the hydride Cp‡$_4$U$_2$-(μ-H)$_2$, eq 3.[6] The hydroxides are soluble in hexane, from which

$$2 \, Cp′′_3U + 2H_2O \rightarrow Cp′′_4U_2(\mu\text{-OH})_2 + 2 \, Cp′′H \quad (2)$$

$$Cp^\ddagger_4U_2(\mu\text{-H})_2 + 2 \, H_2O \rightarrow Cp^\ddagger_4U_2(\mu\text{-OH})_2 + 2 \, H_2 \quad (3)$$

they were crystallized. The ^{1}H NMR spectra of both hydroxide compounds are temperature dependent. For **II**-OH, five CMe$_3$ resonances, which coalesce to a single resonance at 25 °C, are observed at low temperature. The low-temperature spectrum

Figure 1. ORTEP drawing of [Cp′′$_2$U(μ-OH)]$_2$ with 50% thermal ellipsoids. U$\cdots$U, 3.717(1) Å; U−O, 2.295(3) Å; U−O′, 2.299(3) Å; U−C$_{av}$, 2.78(2) Å; U−Cp, 2.50 Å; U−O−U, 108.0(1)°; O−U−O′, 72.0(1)°; Cp−U−Cp, 128°.

of **II**-OH is believed to be due to at least two isomers with different ring conformations. For **I**-OH, two SiMe$_3$ resonances of equal area are observed below 0 °C. These peaks coalesce at 0 °C, with $\Delta G^\ddagger = 12$ kcal/mol. The low-temperature NMR spectrum of **I**-OH can be explained by its crystal structure, Figure 1.[7] In the solid state, **I**-OH has inversion symmetry but idealized C_{2h} symmetry. The structurally characterized lanthanide analogues have a similar structure.[1b,c]

While examining the variable-temperature ^{1}H NMR spectra of **I**-OH, we noticed that this compound decomposes at a reasonable rate at 100 °C to give a new set of resonances due to a U(IV) metallocene. The new resonances are due to the dimeric uranium oxide compound Cp′′$_4$U$_2$(μ-O)$_2$ (**I**-O), as shown by independent synthesis, eq 4.[8] The other hydroxide, **II**-OH,

$$2Cp′_2UMe_2 + 2H_2O \rightarrow Cp′_4U_2(\mu\text{-O})_2 + 2MeH \quad (4)$$

$$Cp′ = Me_3Si \, (\text{I-O}) \text{ or } Me_3C \, (\text{II-O})$$

also decomposes to the analogous dimeric oxide Cp‡$_4$U$_2$(μ-O)$_2$ (**II**-O).[9] Both **I**-O and **II**-O are soluble in toluene and tetrahydrofuran, from which they were crystallized. The variable-temperature ^{1}H NMR spectra of **I**-O and **II**-O are similar. At room temperature, the spectra of both compounds show inequivalent R groups, A$_2$, and B hydrogens. The SiMe$_3$ groups of **I**-O coalesce at 110 °C, with $\Delta G^\ddagger = 17$ kcal/mol. Coalesence of the other inequivalent A$_2$ and B hydrogens is not observed due to their very large chemical shift differences. The coalescence temperature for the CMe$_3$ resonances of **II**-O is greater than 110 °C, and coalescence is not observed. The solid state structures **I**-O and **II**-O are very similar; both have idealized C_{2h} symmetric structures, as found for **I**-OH.[10] The

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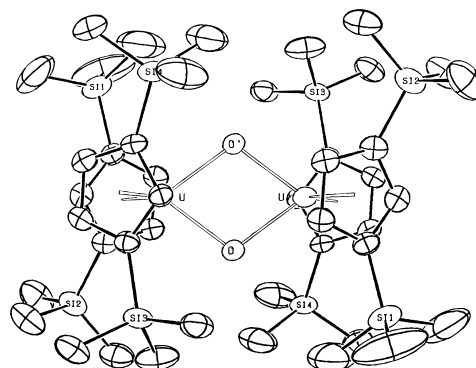(2) (a) Kannellakopolous, B. In *Organometallics of the f-Elements*; Marks, T. J., Fischer, R. D., Eds.; D. Reidel Publishing Co.: Dordrecht, 1978; pp 1−36. (b) Berthet, J.-C.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1993**, *460*, 47−53.
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(4) Lukens, W. W., Jr.; Andersen, R. A. *Organometallics* **1995**, *14*, 3435−3439.
(5) (a) **I**-OH: ^{1}H NMR (C$_6$D$_6$, 30 °C) δ −9.18 ($\nu_{1/2}$ = 26 Hz, SiMe$_3$) (the A$_2$ and B hydrogens were not observed); IR 3630 (m) (OH; 2680, OD) cm^{-1}; MS *m/z* 1347 (M$^+$). Anal. Calcd for C$_{22}$H$_{43}$OSi$_4$U: C, 39.2; H, 6.43. Found: C, 39.0; H, 6.42. (b) The preparation of Cp′′$_3$U is in the supporting information.
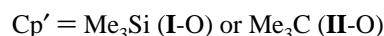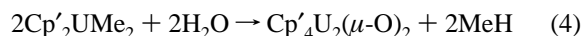(6) (a) **II**-OH: ^{1}H NMR (C$_6$D$_6$, 30 °C) δ −9.96 ($\nu_{1/2}$ = 500 Hz, CMe$_3$) ppm (the A$_2$ and B hydrogens were not observed); IR 3620 (O−H; 2675, O−D) cm^{-1}; MS *m/z* 1217 (M$^+$ − 2). Anal. Calcd for C$_{26}$H$_{43}$OU: C, 51.2; H, 7.11. Found: C, 51.1; H, 7.22. (b) The preparation of Cp‡$_4$U$_2$-(μ-H)$_2$ is given in the supporting information.

(7) Crystal data for **I**-OH: space group $P\bar{1}$; $a = 11.499(2)$, $b = 11.999$-(3), and $c = 12.969(2)$ Å; $\alpha = 118.90(2)°$, $\beta = 105.81(2)°$; $\gamma = 90.62(2)°$; $V = 1486(1)$ Å^3, $Z = 1$, $D_c = 1.51$ g cm^{-3}, $T = -95$ °C; 14 751 data collected, 9960 unique, 7005 observed [$F^2 > 3\sigma(F^2)$]; $R = 0.033$, $R_W = 0.037$, GOF = 1.09. Structure solved by Patterson and Fourier techniques. Hydroxide hydrogen atoms were not located.
(8) **I**-O: ^{1}H NMR (C$_7$D$_8$, 30 °C) δ 82.5 (2H, $\nu_{1/2}$ = 97 Hz, A$_2$), 79.9 (1H, $\nu_{1/2}$ = 46 Hz, B), −0.73 (18H, $\nu_{1.2}$ = 16 Hz, SiMe$_3$), −13.2 (18H, $\nu_{1/2}$ = 21 Hz, SiMe$_3$), −81.8 (2H, $\nu_{1/2}$ = 41 Hz, A$_2$), −85.3 (1H, $\nu_{1/2}$ = 144 Hz, B); IR 582 (U−O−U; 548, U−^{18}O−U) cm^{-1}; MS *m/z* 1344 (M$^+$). Anal. Calcd for C$_{22}$H$_{42}$OSi$_4$U: C, 39.3; H, 6.29. Found: C, 39.3; H, 6.15.
(9) **II**-O: ^{1}H NMR (C$_7$D$_8$, 30 °C) δ 78.6 (2H, $\nu_{1/2}$ = 24 Hz, A$_2$), 75.7 (1H, $\nu_{1/2}$ = 19 Hz, B), 1.0 (18H, $\nu_{1/2}$ = 6 Hz, CMe$_3$), −16.4 (18H, $\nu_{1/2}$ = 7 Hz, CMe$_3$), −85.8 (1H, $\nu_{1/2}$ = 20 Hz, A$_2$), −94.5 (2H, $\nu_{1/2}$ = 20 Hz, A$_2$); IR 572 (U−O−U; 540, U−^{18}O−U) cm^{-1}; MS *m/z* 1216 (M$^+$). Anal. Calcd for C$_{26}$H$_{42}$OU: C, 51.3; H, 6.96. Found: C, 51.0; H, 7.03.
(10) Crystal data for **II**-O: space group $P\bar{1}$; $a = 10.6985(8)$, $b = 11.0246$-(8), and $c = 12.2575(9)$ Å; $\alpha = 64.522(1)°$, $\beta = 73.698(1)°$; $\gamma = 89.962$-(1); $V = 1261.9(1)$ Å^3, $Z = 1$, $D_c = 1.602$ g cm^{-3}, $T = -95$ °C; 5485 data collected, 3906 unique ($R_{int} = 0.071$), 3543 observed [$I > 3\sigma(I)$]; $R = 0.052$, $R_W = 0.073$, GOF = 3.12. Structure solved by direct methods and Fourier techniques. One of the CMe$_3$ groups is disordered. Details of the structure will be published later.

Table 1. Kinetic Data for the Decomposition of Bridging Hydroxides[a]

compound	T (°C)	k (10^{-4} s^{-1})
[Cp″$_2$UOH]$_2$	380	36.6
	373	17.7
	371	14.6
	362	5.82
	353	2.63
	341	0.837
	319	0.0580
	303	0.00796
[Cp″$_2$UOH]$_2$ + DHA[b]	373	16.5
[Cp″$_2$UOD]$_2$	380	8.99
[Cp‡$_2$UOH]$_2$	373	2.82

[a] The kinetic data were obtained by following the disappearance of the ^{1}H NMR resonances of **I**-OH as a function of time. The details are given in the supporting information. [b] DHA is dihydroanthracene.
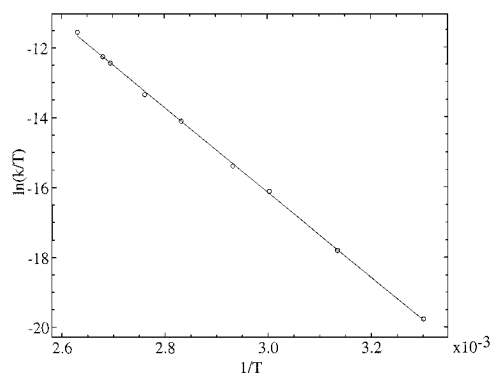
**Figure 2.** Eyring plot for the decomposition of [Cp″$_2$U(μ-OH)]$_2$ from 30 °C to 107 °C.

origin of the high barrier to SiMe$_3$ site exchange in **I**-O as compared to **I**-OH is likely the result of the shorter U–U distance of 3.393(1) Å in **I**-O versus 3.717(1) Å in **I**-OH.[11]

The reaction shown in eq 1 was investigated in several ways, and the results are shown in Table 1. The quantitative experiments were done using **I**-OH rather than **II**-OH, since **I**-OH decomposed over a more convenient temperature range. The origin of the slower decomposition rate of **II**-OH is not known but is likely due to its Cp‡ ring conformation. The low-temperature NMR spectrum of **II**-OH shows that the molecule exists as a mixture of conformers, some of which cannot have C_{2h} symmetry. Since **II**-O has C_{2h} symmetry, the Cp‡ ring conformation must change during the reaction, and this reorganization energy gives rise to a higher barrier. In **I**-OH and **I**-O, the rings have the same conformation, so no reorganization is needed, resulting in a faster rate of decomposition.

The rate of disappearance of **I**-OH was followed over 3 half-lives (only >2 half-lives at 30 °C and 46 °C) and obeyed first-order kinetics at all temperatures investigated. No induction period was observed in the appearance of **I**-O, and the rate of appearance of **I**-O was the same as the rate of disappearance of **I**-OH. Addition of excess dihydroanthracene did not change the reaction rate, and no anthracene was formed during the reaction. From the rate data in Table 1, the activation parameters, $\Delta H^{\ddagger} = 24.2 \pm 0.1$ kcal/mol and $\Delta S^{\ddagger} = -6.8 \pm 0.3$ eu, were obtained (Figure 2). The rate of disappearance of **I**-OD also obeyed first-order kinetics, and $k_H/k_D = 4.1(1)$ at 107 °C (this corresponds to a k_H/k_D of 6.0 at 25 °C). The decomposition of a 1:1 mixture of **I**-OH and **I**-OD gave mainly H$_2$ and D$_2$ (which was not quantitatively measured), with only a trace of HD detected by ^{1}H NMR spectroscopy.[12]

These data show that the decomposition of **I**-OH is intramolecular. The observations that a trivial amount of HD was observed in the cross-over experiment and that no anthracene

was observed when dihydroanthracene was added to the reaction mixture are strong evidence against a free-radical mechanism. Two possible pathways remain: a concerted or a step-wise elimination of H$_2$. The concerted process seems unreasonable since, in order eliminate H$_2$, the planar U$_2$(OH)$_2$ unit would have to bend so that the hydrogen atoms are close enough to form a bond. A stepwise mechanism with the O–H bond cleavage and oxidation of the two uranium centers to U(IV) as the rate-determining step, followed by the rapid elimination of H$_2$ (eq 5), is consistent with all of the observations.
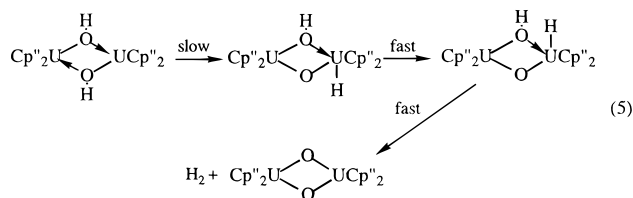
The observed kinetic isotope effect (KIE) and activation entropies are similar to those known for α-elimination reactions. For the elimination of H$_2$ from [(Me$_3$SiNCH$_2$CH$_2$)$_3$N]W(CH$_3$), $\Delta S^{\ddagger}$ is -16 eu, and the KIE is 5.6 at 47 °C; for the elimination of CH$_4$ from Cp*WMe$_5$, $\Delta S^{\ddagger}$ is -1 eu, and the KIE is 6 at 25 °C; and for the elimination of Me$_4$C from CpTa(CH$_2$CMe$_3$)$_2$Cl$_2$, $\Delta S^{\ddagger}$ varies from -4 to -36 eu, and the KIE is 5.4 at 36 °C.[13] For the closely related migration of the hydroxyl proton of L$_3$ReOH (L = 3 hexyne) to form L$_2$Re(O)H, the KIE is 5, and $\Delta S^{\ddagger}$ is -25 eu.[14] The similarity of the parameters observed for the decomposition of **I**-OH to those observed for other α-elimination and migration reactions implies that this process occurs in the decomposition of **I**-OH.

The elimination of H$_2$ from two hydroxide ligands at first glance seems thermodynamically unreasonable since, in the first step of the reaction, an O–H bond of 119 kcal/mol[15] is broken and a U–H bond of ~60–80 kcal/mol[16] is formed. However, both uranium atoms are oxidized from U(III) to U(IV) in the first step of the net reaction. Since this oxidation potential is ~1.8 V,[17] the oxidation adds about 80 kcal/mol to the reaction, making it exothermic.

Supporting Information Available: Synthetic details and results, crystallographic details, atomic positions, and a list of bond distances and angles in **I**-OH (16 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions. Structure factors for **I**-OH are available from the authors upon request.

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(12) The origin of the HD is most reasonably ascribed to the presence of H$_2$O on the glassware or in the NMR solvent. The glassware was silylated prior to use. The amount of HD varied from experiment to experiment, which is also consistent with this hypothesis.

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