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Oxidative Elimination of H_2 from $[Cp'_2U(\mu\text{-}OH)]_2$ to form $[Cp'_2U(\mu\text{-}O)]_2$, where Cp′ is 1,3-$(Me_3C)_2C_5H_3$ or 1,3-$(Me_3Si)_2C_5H_3$

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November 1995

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Oxidative Elimination of H_2 from $[Cp'_2U(\mu\text{-}OH)]_2$ to form $[Cp'_2U(\mu\text{-}O)]_2$, where Cp′ is 1,3-$(Me_3C)_2C_5H_3$ or 1,3-$(Me_3Si)_2C_5H_3$

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Abstract

The thermal decomposition of the dimeric trivalent uranium metallocene hydroxides, $(R_2C_5H_3)_4U_2(\mu\text{-}OH)_2$, where R is Me_3C or Me_3Si, gives the dimeric tetravalent uranium metallocene oxides, $(R_2C_5H_3)_4U_2(\mu\text{-}O)_2$ and dihydrogen. The net reaction is an oxidative-elimination. The reaction is intramolecular and does not involve free radicals. The mechanism is postulated to involve an α-elimination as the rate determining step, giving $(R_2C_5H_3)_4U_2(\mu\text{-}O)(\mu\text{-}OH)(H)$ as an intermediate which then eliminates dihydrogen in a subsequent fast step.

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.

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

$$Cp' = 1,3\text{-}(Me_3Si)_2C_5H_3 \text{ or } 1,3\text{-}(Me_3C)_2C_5H_3$$

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_3UOH, 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 equivalents of water to Cp_3Ti gives $Cp_4Ti_2(\mu\text{-}O)$ presumably *via* a titanocene hydroxide intermediate.[3] This is not a general reaction since addition of water to Cp_3Zr results in oxidation of the zirconium center and yields Cp_3ZrH and $[Cp_2ZrO]_3$.[4]

Adding one equivalent of water to Cp''_3U ($Cp'' = 1,3\text{-}(Me_3Si)_2C_5H_3$) produces the bridging hydroxide $Cp''_4U_2(\mu\text{-}OH)_2$ (**I-OH**), eq 2.[5] Since the related tris-cyclopentadienyluranium complex $Cp^{\ddagger}_3U$ ($Cp^{\ddagger} = 1,3\ (Me_3C)_2C_5H_3$) is difficult to prepare, the hydroxide $Cp^{\ddagger}_4U_2(\mu\text{-}OH)_2$ (**II-OH**) was prepared from the hydride $Cp^{\ddagger}_4U_2(\mu\text{-}H)_2$, eq 3.[6] The hydroxides are soluble in hexane from which they were crystallized.

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

$$Cp^{\ddagger}_4U_2(\mu\text{-}H)_2 + 2\ H_2O \rightarrow Cp^{\ddagger}_4U_2(\mu\text{-}OH)_2 + 2\ H_2 \quad (3)$$

The ^1H 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 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,1c]

Insert Figure 1 here

While examining the variable temperature ^1H 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 $Cp''_4U_2(\mu\text{-}O)_2$ (**I-O**) as shown by independent synthesis, eq 4.[8]

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

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

The other hydroxide **II-OH** also decomposes to the analogous dimeric oxide $Cp^{\ddagger}_4U_2(\mu\text{-}O)_2$ (**II-O**).[9] Both **I-O** and **II-O** are soluble in toluene and tetrahydrofuran from which they were crystallized. The variable temperature ^1H 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 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]

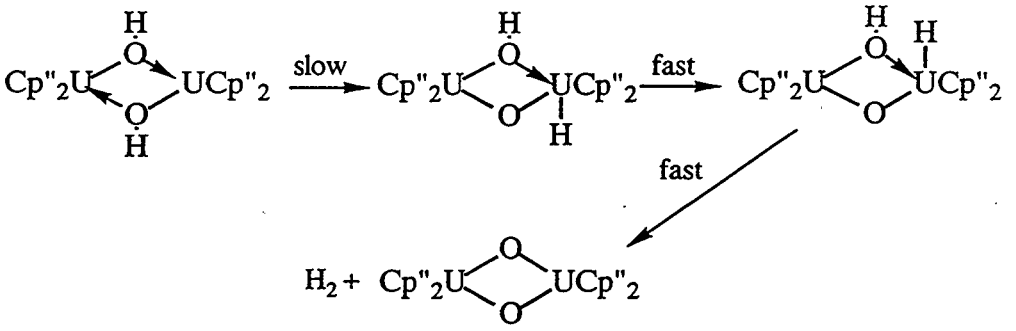
The reaction shown in eq 1 was investigated in several ways, and the results are shown in Table 1. The quantitative experiments were done using **I-OH** rather than **II-OH** since **I-OH** decomposed over a more convenient temperature range. The origin of the slower decomposition rate of **II-OH** is not known, but is likely due to its $Cp^{\ddagger}$ ring conformation. The low temperature NMR spectrum of **II-OH** shows that the molecule exists as a mixture of conformers, some of which can not have C_{2h} symmetry. Since **II-O** has C_{2h} symmetry, the $Cp^{\ddagger}$ 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.

Insert Table 1 Here

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 ^1H NMR spectroscopy.[12]

Insert Figure 2 Here

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 is 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 step-wise 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.



(5)

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 $[(Me_3SiNCH_2CH_2)_3N]W(CH_3)$, $\Delta S^{\ddagger}$ 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_4C from $CpTa(CH_2CMe_3)_2Cl_2$, $\Delta S^{\ddagger}$ varies from -4 eu to -36 eu , and the KIE is 5.4 at 36 °C.[13] For the closely related migration of the hydroxyl proton of L_3ReOH (L = 3-hexyne) to form $L_2Re(O)H$, 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 approximately 60 to 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.

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Supplementary Material Available: Synthetic details and results, crystallographic details, atomic positions and a list of bond distances and angles in **I-OH** (16 pages). Table of structure factors for **I-OH** si available from the authors upon request. Ordering information is given on any current masthead.

References

(1) a) Gilje, J. W.; Roesky, H. W. *Chem. Rev.* **1994**, *94*, 895.
b) Beletskaya, I. P.; Voskoboynikov, A. Z.; Chuklanova, E. B.; Kirillova, N. I.; Shestakova, A. K.; Parshina, I. N.; Gusev, A. I.; Magomedov, G. K. *J. Am. Chem. Soc.* **1993**, *115*, 3156-3166.
c) Hitchcock, P. B.; Lappert, M. F.; Prashar, S. *J. Organomet. Chem.* **1991**, *413*, 79-90.

(2) a) Kannellakopolous, B. In *Organometallics of the f-Elements*; T. J. Marks and R. D. Fischer, Ed.; D. Reidel Publishing Company: Dordrecht: Holland, 1978; pp 1-36.
b) Berthet, J.-C.; Ephritikhine, M.; Lance, M.; Nierlich, M.; Vigner, J. *J. Organomet. Chem.* **1993**, *460*, 47-53.

(3) Lukens Jr., W. W.; Andersen, R. A. *Inorg. Chem.* **1995**, *34*, 3440-3443.

(4) Lukens Jr., W. W.; Andersen, R. A. *Organometallics* **1995**, *14*, 3435-3439.

(5) a) **I-OH**: ^{1}H NMR (C_6D_6 30° C): δ -9.18 ($\nu_{1/2}$ = 26 Hz, $SiMe_3$) ppm. 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 $C_{22}H_{43}OSi_4U$: C, 39.2; H, 6.43. Found C, 39.0; H, 6.42.
b) The preparation of Cp''_3U is in the Supplementary Material

(6) a) **II-OH:** ^{1}H NMR (C_6D_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 $Cp^{\ddagger}_4U_2(\mu\text{-}H)_2$ is given in the Supplementary Material.

(7) Crystal Data for **I-OH**: Space Group: P1(bar); a = 11.499(2), b = 11.999(3), c = 12.969 (2) Å, α = 118.90(2)°, β = 105.81(2)°, γ = 90.62(2)°, V = 1486(1) $Å^3$, Z = 1, D_c = 1.51 gcm^{-3}, T = -95° C; 14751 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 techniqes. Hydroxide hydrogen atoms were not located.

(8) **I-O:** ^{1}H NMR (C_7D_8, 30° C): δ 82.5 (2 H, $\nu_{1/2}$ = 97 Hz, A_2), 79.9 (1 H, $\nu_{1/2}$ = 46 Hz, B), -0.73 (18 H, $\nu_{1/2}$ = 16 Hz, $SiMe_3$), -13.2 (18 H, $\nu_{1/2}$ = 21 Hz, $SiMe_3$), -81.8 (2 H, $\nu_{1/2}$ = 41 Hz, A_2), -85.3 (1 H, $\nu_{1/2}$ = 144 Hz, B). IR: 582(U-O-U; 548, U-^{18}O-U) cm^{-1}. MS *m/z* 1344 (M^+). Anal. Calcd for $C_{22}H_{42}OSi_4U$: C, 39.3; H, 6.29. Found: C, 39.3; H, 6.15.

(9) **II-O:** ^{1}H NMR (C_7D_8, 30° C): δ 78.6 (2 H, $\nu_{1/2}$ = 24 Hz, A_2), 75.7 (1 H, $\nu_{1/2}$ = 19 Hz, B), 1.0 (18 H, $\nu_{1/2}$ = 6 Hz, CMe_3), -16.4 (18 H, $\nu_{1/2}$ = 7 Hz, CMe_3), -85.8 (1 H, $\nu_{1/2}$ = 20 Hz, B), -94.5 (2 H, $\nu_{1/2}$ = 20 Hz, A_2). IR 572 (U-O-U; 540 , U-18O-U) cm^{-1}. MS*m/z* 1216 (M^+). Anal. Calcd for $C_{52}H_{84}O_2U_2$: C, 51.3; H, 6.96. Found: C, 51.0; H, 7.03.

(10) Crystal Data for **II-O**: Space Group: P1(bar); a = 10.6985(8) Å, b = 11.0246(8) Å, c = 12.2575(9) Å, α = 64.522(1)°, β = 73.698(1)°, γ = 89.962(1), V = 1261.9(1) $Å^3$, Z = 1, D_c = 1.602 gcm^{-3}, T = -95° C; 5485 data collected, 3906 unique (R_{int} = 0.071), 3543 observed [I > 3σ(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.

(11) Zalkin, A.; Beshouri, S. *Acta Cryst.* **1988**, *C44*, 1826-1827.

(12) The origin of the HD is most reasonably ascribed to the presence of H_2O 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 consitent with this hypothesis.

(13) a) Shih, K.-Y.; Toland, K.; Seidel, S. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 12103-12014.
b) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282-4291.
c) Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210 - 3222.

(14) Tahmassebi, S. K.; Conry, R. R.; Mayer, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 7553-7554.

(15) McMillen, D. F.; Golden, D. M. *Rev. Phys. Chem.* **1982**, *33*, 493-532.

(16) a) Bruno, J. W.; Stecher, H. A.; Morss, L. R.; Sonnenberger, D. C.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7275-7280.
b) Jemine, X.; Goffart, J.; Berthet, J.-C.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1992**, 2439-2440.

(17) Sonnenberger, D. C.; Gaudeillo, J. G. *Inorg. Chem.* **1988**, *27*, 2747-2748.

Captions for figures in "Oxidative Elimination of H_2 from $[Cp'_2U(\mu\text{-}OH)]_2$ to form $[Cp'_2U(\mu\text{-}O)]_2$, where Cp' is 1,3-$(Me_3C)_2C_5H_3$ or 1,3-$(Me_3Si)_2C_5H_3$"

Figure 1: On ORTEP drawing of $[Cp''_2U(\mu\text{-}OH)]_2$ with 50% thermal ellipsoids. U···U = 3.717(1) Å, U-O = 2.295(3) Å, U-O' = 2.299(3) Å, U-C_{ave} = 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°.

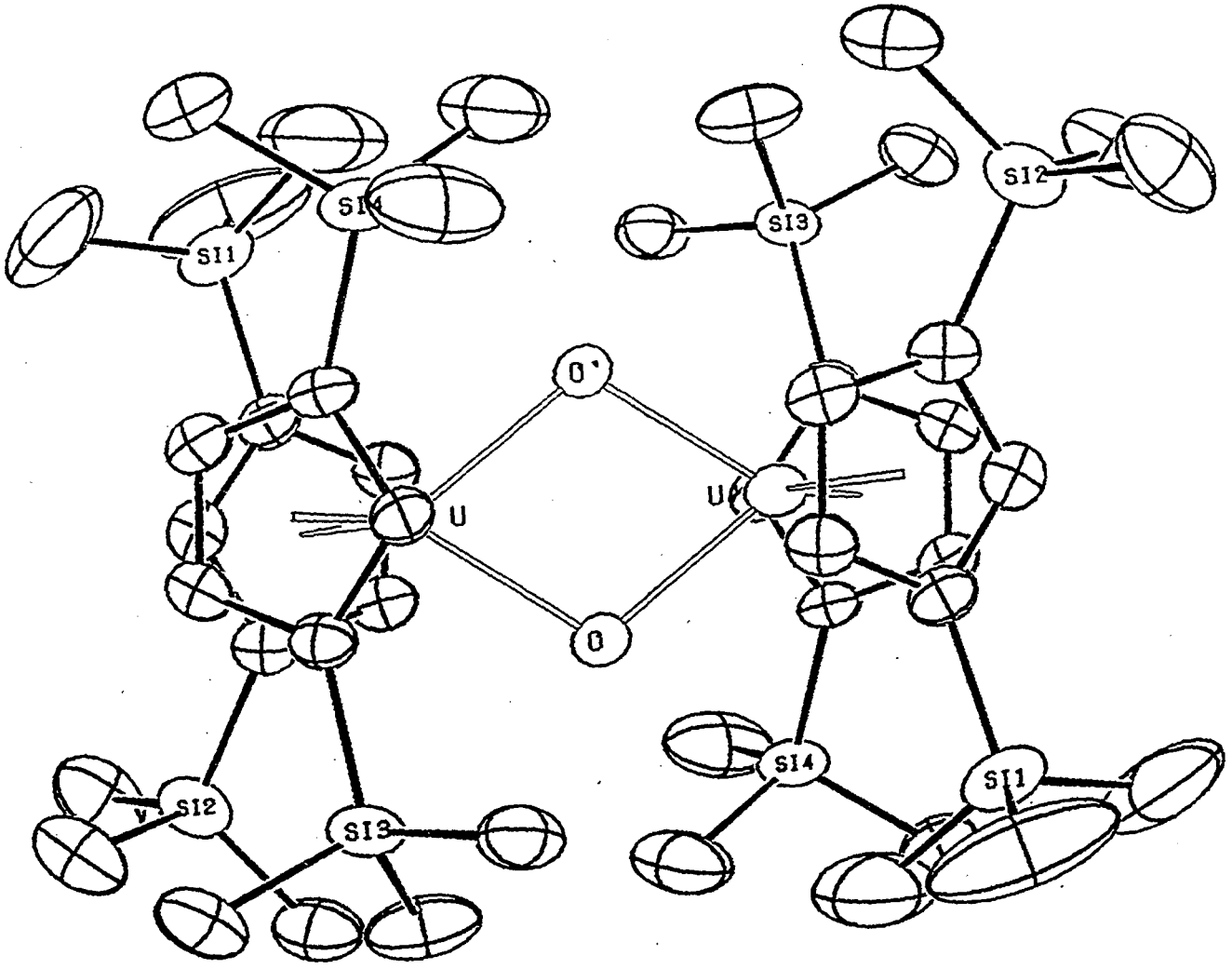
Figure 2: Eyring plot for the decomposition of $[Cp''_2U(\mu\text{-}OH)]_2$ from 30 °C to 107 °C.

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

Compound	T	k (10^{-4} s^{-1})
$[Cp''_2UOH]_2$	380	36.6
	373	17.7
	371	14.6
	362	5.82
	353	2.63
	341	0.837
	319	0.0580
	303	0.00796
$[Cp''_2UOH]_2$+ DHA[b]	373	16.5
$[Cp''_2UOD]_2$	380	8.99
$[Cp^{\ddagger}_2UOH]_2$	373	2.82

a)The kinetic data was obtained by following the disappearance of the ^1H NMR resonances of **I-OH** as a function of time. The details are given in the Supplementary Material.

b) DHA is dihydroanthracene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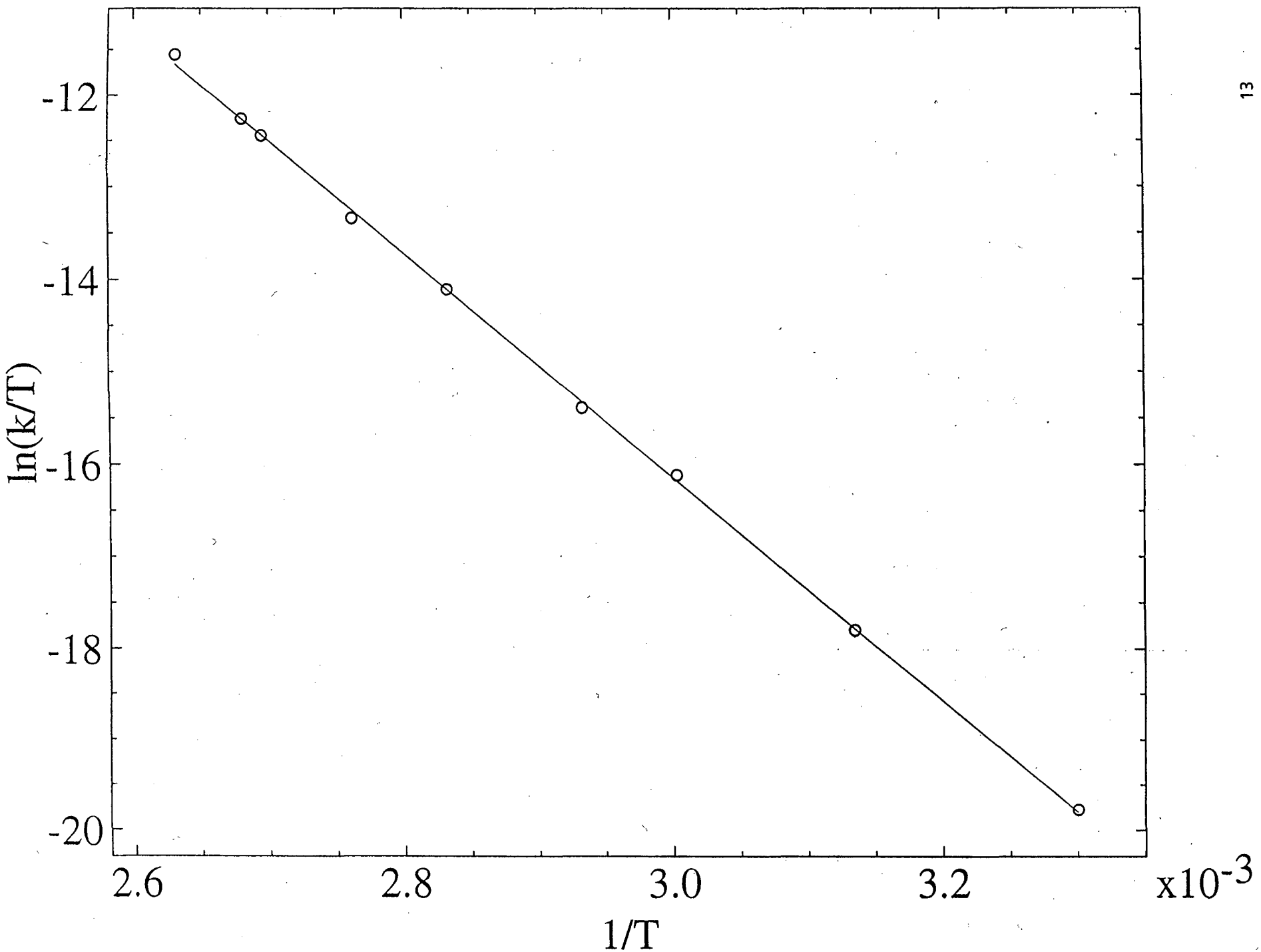
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x10-3
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Supplementary Material for

Oxidative Elimination of H_2 from $[Cp'_2U(\mu\text{-}OH)]_2$ to form $[Cp'_2U(\mu\text{-}O)]_2$, where Cp' is 1,3-$(Me_3C)_2C_5H_3$ or 1,3-$(Me_3Si)_2C_5H_3$

Experimental Details (6 pages)

Crystallography Details, Atom Numbering Scheme, and Tables of Positions, Distances, Angles,
and Anisotropic Thermal Parameters for $[Cp''_2U(\mu\text{-}OH)]_2$ (11 pages)

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Experimental.

All reactions and manipulations were carried out in an inert atmosphere using standard Schlenk and dry box techniques. Hexane, diethyl ether, and tetrahydrofuran were dried over sodium benzophenone ketyl and distilled and degassed immediately prior to use. Deuterated NMR solvents were dried over and distilled from potassium or sodium. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer as Nujol mulls between CsI plates. Melting points were measured on a Buchi melting point apparatus in sealed capillaries and are uncorrected. NMR spectra collected on a JEOL FX-90Q spectrometer at 30° C. Electron impact mass spectra were determined by the mass spectroscopy laboratory and microanalyses were performed by the microanalytical laboratories, both at the University of California, Berkeley.

Kinetics Data. The rates of the decomposition of $[Cp''_2U(\mu\text{-}OH)]_2$ was determined by monitoring the log of the ratio of the peak height of the $SiMe_3$ protons of the Cp" ligand over the peak height of the residual protons of the solvent versus time. The peak height was used because the data obtained from the log of the ratio of the integrals was not satisfactory for two reasons. First, the $SiMe_3$ peak is very broad, and second, the baseline rolls near the $SiMe_3$ peak. The kinetics data are the average of 3 separate runs except for the 46 °C and 30 °C points which are the average of 2 separate runs, and the last two temperatures are only over 2 half-lives since the rate at this temperature was so slow. The data was collected both in the NMR probe at a fixed temperature and by using a heating bath; both sets of data fit the same line. The rates are reported to $\pm 2\sigma$, and the activation parameters are given with 95% confidence limits corrected for small sample size using Student's t values.

Decomposition with added Dihydroanthracene. A mixture of $[Cp''_2UOH]_2$ with 3-7 equivalents of DHA was dissolved in C_7D_8 and the decomposition was monitored in the NMR probe at 100° C.

$[Cp''_2UOH]_2 + [Cp''_2UOD]_2$ crossing experiment. A mixture of equal amounts $[Cp''_2UOH]_2$ and $[Cp''_2UOD]_2$ was dissolved in C_7D_8 and the decomposition was monitored in the NMR probe at 107° C. By NMR, the gas evolved was $H_2$with very little HD (some HD is always seen in the decomposition of $[Cp''_2UOD]_2$ presumably due to adventitious water in the solvent or NMR tube).

$Cp^{\ddagger}_2UMe_2$. $Cp^{\ddagger}_2UCl_2$ (1.00g, 1.51 mmol) was dissolved in 50 mL of diethyl ether, and methyllithium (4.2 mL, 0.72 M in diethyl ether, 3.01 mmol) was added by syringe. The solution immediately turned orange. After stirring for one hour, the ether was removed under reduced pressure. The solid residue was suspended in 25 mL of hexane then filtered giving a deep orange solution. The volume of the solution was reduced to *ca* 3 mL. Cooling to -20° C gave orange brown blocks (0.73 g, 78 %). MP 120 -125 °C. ^1H NMR(C_6D_6): δ 18.81 (1H, B), -0.64 (18H, t-Bu), -35.43 (2H, A_2), -39.02(3H, Me) ppm. IR: 1250(s), 1200(m), 1165(m), 1110(s), 1055(m), 1025(m), 935(m), 845(m), 825(s), 810(m), 765(s), 675(m), 655(m), 405(m) cm^{-1}. MS $(M-CH_3)^+$ *m/z* = 659. Anal. Calcd for $C_{28}H_{48}U$: C, 54.0, H:7.71; Found C:53.7; H:7.83.

$[Cp^{\ddagger}_2UH]_2$. $Cp^{\ddagger}_2UMe_2$ (0.45 g, 0.72 mmol) was dissolved in 20 mL diethyl ether and transferred to a heavy-walled pressure bottle by cannula. The bottle was pressurized to 225 psi with hydrogen. After stirring for eight hours, the solution was transferred to a Schlenk tube by cannula. The ether was removed under reduced pressure and the black solid residue was dissolved in 50 mL of warm diethyl ether. Cooling to -80°C produced small black crystals (0.21 g, 49 %). MP: 263 - 265 °C. ^1H NMR(C_6D_6): δ = -18 ($\nu_{1/2}$ =

600 Hz, t-Bu) ppm. The A_2 and B hydrogens were not observed. IR: 3070(w), 2920(w), 1290(w), 1250(s), 1230(w), 1200(m), 1150(s) (U-H; 825(shoulder), U-D), 1050(w), 1020(w), 925(m), 800(s), 740(s), 670(m), 655(m), 605(w), 555(w), 425(w), 350(w) cm^{-1}. MS: M^+ *m/z*(calc, found): 1187(100,100), 1188(58,57), 1189(17,17), 1190(3,4). Anal. Calcd for $C_{26}H_{43}U$: C, 52.6 ; H, 7.30. Found: C, 52.3; H, 7.28.

$[Cp^{\ddagger}_2U(\mu\text{-}OH)]_2$ $[Cp^{\ddagger}_2UH]_2$ (0.50 g, 0.42 mmol) was suspended in 30 mL of diethyl ether. Degassed water (15 μL, 0.84 mmol) was added by syringe. The solution immediately turned blue-green, and blue-green solid precipitated. After stirring for one hour, the solid was allowed to settle, and the mother liquor was removed. The resulting blue-green powder was dried under reduced pressure (0.46 g, 89 %). The compound does not melt to 300 °C. ^1H NMR (C_6D_6) : δ -9.96($\nu_{1/2}$ = 500 Hz, CMe_3). The A_2 and B protons were not observed. IR: 3620(m) (O-H; 2785, O-D), 1251(s), 1022(w), 793(s), 739(s), 644(m), 361(m) cm^{-1}. MS $(M\text{-}2)^+$*m/z*(calc, found) 1217(100,100), 1216(58,57), 1215(17,18), 1214(3,5). Anal Calcd for $C_{26}H_{43}OU$: C, 51.2; H, 7.11; Found: C, 51.1; H, 7.22.

$[Cp''_2U(\mu\text{-}OH)]_2$. A solution of degassed water (20.8 μL, 1.2 mmol) in 10 mL of tetrahydrofuran was added dropwise to a solution of Cp''_3U (1.00 g, 1.2 mmol) in 25 mL of tetrahydrofuran. The dark green solution immediately became bright blue-green. After stirring for 30 min., the solvent was removed under reduced pressure, and the green solid residue was dissolved in 100 mL of hexane. The hexane solution was filtered, and the volume of the filtrate was reduced to *ca.* 60 mL. Slow cooling to -80 °C produced dark green crystals (0.68 g, 87 %). The compound did not melt to 250° C. ^1H NMR (C_6D_6): δ -9.18 ($\nu_{1/2}$ = 26 Hz, $SiMe_3$). The A_2 and B hydrogen resonances were not observed. IR: 3630(OH; 2680, OD)(m), 3070 (w), 3040(w), 1315(m), 1240(s), 1205(m), 1075(s), 1055(w), 915(s) 830(s), 770(m), 750(s), 690(m), 630(s), 615(w), 575(w),

475(m), 370(m), 350(s), 300(s), 275(w), 240(w) cm^{-1}. MS $(M)^+$ *m/z* (calc, found): 1347 (100, 100), 1348 (90, 91), 1349 (66, 64), 1350 (34, 33). Anal. Calcd for $C_{22}H_{43}OSi_4U$: C, 39.2; H, 6.43. Found C, 39.0; H, 6.42.

Cp''_2UMe_2. Methyllithium (4.2 mL , 0.72 M solution in diethyl ether, 3.0 mmol) was added by syringe to a stirring, orange solution of Cp''_2UCl_2[1] (1.0 g, 1.5 mmol) in diethyl ether (50 mL). Upon completion of the addition, white precipitate formed and the solution became red-orange. After stirring for 16 hours at room temperature, the volatile materials were removed under reduced pressure; the resulting red solid residue was extracted with hexane (2 x 25 mL). The filtrate was concentrated (5 mL) and cooled to -20° C yielding red-orange prisms (0.73 g, 78 %). MP 120-125° C. ^1H NMR (C_6D_6 30°C): δ 7.7 (2 H, $\nu_{1/2}$ = 9 Hz, B), -1.0 (36 H, $\nu_{1/2}$ = 4 Hz, $SiMe_3$), -21.2 (4 H, $\nu_{1/2}$ = 10 Hz, A_2), -28.0 (6 H, $\nu_{1/2}$ = 8 Hz, U-Me). IR: 1250(s), 1200(m), 1165(m), 1110(s), 1055(m), 1025(m), 935(m), 845(m), 825(s), 810(m), 765(s), 675(m), 655(m), 405(m) cm^{-1}. MS $(M-CH_3)^+$ *m/e* = 659. Anal. Calcd for $C_{24}H_{48}Si_4U$: C, 54.0; H, 7.71. Found: C, 53.7; H, 7.83.

$[Cp''_2U(\mu\text{-}O)]_2$. A solution of degassed water (14.9 μL, 0.83 mmol) in 10 mL of tetrahydrofuran was added dropwise to a solution of Cp''_2UMe_2 (0.57 g, 0.83 mmol) in 25 mL of tetrahydrofuran. The orange solution foamed and turned brown. After stirring for three hours, the solution was filtered, and the volume of the filtrate was reduced to *ca.* 2 mL. Cooling to -20° C produced red blocks (0.17 g, 30 %). The compound does not melt to 250° C. ^1H NMR (C_7D_8): δ 82.5 (2 H, $\nu_{1/2}$ = 97 Hz, A_2), 79.9 (1 H, $\nu_{1/2}$ = 46 Hz, B), -0.73 (18 H, $\nu_{1/2}$ = 16 Hz, $SiMe_3$), -13.2 (18 H, $\nu_{1/2}$ = 21 Hz, $SiMe_3$), -81.8 (2 H, $\nu_{1/2}$ = 41 Hz, A_2), -85.3 (1 H, $\nu_{1/2}$ = 144 Hz, B). IR: 3108(w), 3081(w), 3062(w), 1413(w), 1329(m), 1265(s), 1218(m), 1084(s), 1070(m), 926(s), 842(s), 793(s), 762(s), 701(m), 644(s), 627(w), 582 (U-O-U; 548, U-^{18}O-U)(s), 493(m), 486(m), 382(m), 322(m),

289(w), 252(w), 233(w) cm^{-1}. MS $(M)^+$ *m/z* (calc, found) 1344 (100, 100), 1345 (90.6, 73.8), 1346 (66.9, 55.0), 1347 (34.6, 29.3), 1348 (15.3, 8.0), 1349 (5.6, 3.6). Anal. Calcd for $C_{22}H_{42}OSi_4U$: C, 39.3; H, 6.29. Found: C, 39.3; H, 6.15.

$[Cp^{‡}_2U(\mu\text{-}O)]_2$. Degassed water (63 μL, 3.6 mmol) was added by syringe to a stirring, red, tetrahydrofuran (90 mL) solution of $Cp^{‡}_2UMe_2$ (2.1 g, 3.3 mmol). Vigorous evolution of a colorless gas occurred immediately upon addition. The solution gradually darkened to brown as the reaction mixture stirred for 8 hours at room temperature. The volatile materials were removed under reduced pressure; the remaining dark brown solid residue was washed with hexane (2 x 20 mL), extracted into hot toluene (3 x 50 mL) and filtered. The filtrate was concentrated (70 mL) and cooled to -20° C, yielding a brown microcrystalline solid (1.1 g, 54 %). The compound did not melt to 300° C. ^1H NMR (C_7D_8): δ 78.6 (2 H, $\nu_{1/2}$ = 24 Hz, A_2), 75.7 (1 H, $\nu_{1/2}$ = 19 Hz, B), 1.0 (18 H, $\nu_{1/2}$ = 6 Hz, CMe_3), -16.4 (18 H, $\nu_{1/2}$ = 7 Hz, CMe_3), -85.8 (1 H, $\nu_{1/2}$ = 20 Hz, B), -94.5 (2 H, $\nu_{1/2}$ = 20 Hz, A_2). IR: 3079(w), 1635(w), 1561(w), 1307(w), 1292(w), 1253(m), 1202(m), 1168(m), 1086(w), 1059(m), 1025(m), 923(m), 809(s), 751(s), 672(m), 659(m), 572(s)Ê(U-O-U; 540, U-^{18}O-U), 488(m), 428(m), 349(m), 255(m) cm^{-1} .MS $(M)^+$ *m/z* (calc, found) 1216 (100, 100), 1217 (59, 58), 1218 (18, 17), 1219 (3, 2). Anal. Calcd for $C_{26}H_{42}OU$: C, 51.3; H, 6.96. Found: C, 51.0; H, 7.03.

Kinetics Data

Compound	T	k (s^{-1})
$[Cp''_2UOH]_2$	380	$3.66 \times 10^{-3} \pm 2.5 \times 10^{-5}$
$[Cp''_2UOH]_2$	373	$1.77 \times 10^{-3} \pm 1.2 \times 10^{-5}$
$[Cp''_2UOH]_2$	371	$1.46 \times 10^{-3} \pm 7.8 \times 10^{-5}$
$[Cp''_2UOH]_2$	362	$5.82 \times 10^{-4} \pm 3.2 \times 10^{-5}$
$[Cp''_2UOH]_2$	353	$2.63 \times 10^{-4} \pm 1.6 \times 10^{-5}$
$[Cp''_2UOH]_2$	341	$8.37 \times 10^{-5} \pm 8.8 \times 10^{-6}$
$[Cp''_2UOH]_2$	319	$5.80 \times 10^{-6} \pm 6.1 \times 10^{-7}$
$[Cp''_2UOH]_2$	303	$7.96 \times 10^{-7} \pm 2.6 \times 10^{-8}$
$[Cp''_2UOH]_2$+ DHA	373	$1.65 \times 10^{-3} \pm 2.4 \times 10^{-4}$
$[Cp''_2UOD]_2$	380	$8.99 \times 10^{-4} \pm 1.2 \times 10^{-5}$

$k_H/k_D = 4.1(1)$ 107°C

$k_H/k_D = 6.0(2)$ at 25°C (calculated from 107° C data)

$\Delta H^{\ddagger} = 24.2 \pm 0.10$ kcal/mol

$\Delta S^{\ddagger} = -6.8 \pm 0.29$ eu.

DHA is dihydroanthracene

$[Cp''_2UOH]_2$

A crystal measuring 0.18 mm x 0.25 mm x 0.28 mm was mounted in a thin walled quartz capillary. The crystal was transferred to an Enraf-Nonius CAD-diffractometer and cooled to -95 °C under a cold stream previously calibrated by a thermocouple placed in the sample position. The crystal was centered in the beam. Automatic peak search and indexing procedures indicated that the crystal was possessed a triclinic cell and yielded the unit cell parameters. The cell parameters and data collection parameters are given in Table I.

The 14751 raw intensity data were converted to structure factor amplitudes and their esds by correction for scan speed, background, and Lorentz-polarization effects. [2,3] Inspection of the intensity standards showed no decrease in intensity over the duration of data collection. Inspection of the azimuthal scan data showed a variation with $I_{min}/I_{max} = 0.69$ for the average curve. An empirical correction based on the average curve was applied. Averaging of redundant data left 9960 unique data.

The uranium atom positions were obtained by solving the Patterson map. Refinement on the uranium position followed by a difference Fourier search yielded the other heavy atom positions. The heavy atom structure was refined by standard least squares and Fourier techniques. The heavy atoms were refined isotropically. The hydroxide hydrogen atoms were not located or used in structure factor calculations. Positional parameters of all of the hydrogen atoms except those on O1, O2, C6, C7, and C8 were refined. Those hydrogen atoms were assigned idealized locations ad B_{iso} approximately 1.15 times that of the B_{eq} of the carbon atom to which they were attached, and these hydrogen atoms were not refined. Thermal parameters for the hydrogen atoms were constrained to be equal for all hydrogen atoms attached to the same carbon atom. In the final cycle of the least squares refinement, 28 reflections appeared to be suffering from multiple diffraction and were given zero weight.

The final residuals for 363 variables refined against the 7005 unique data for which $F^2 > 3\sigma(F^2)$ were R = 3.31%, R_w = 3.71%, and GOF = 1.09. The R value for all data (including unobserved reflections) was 7.30%. The quantity minimized by the least squares refinements was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weight given to a particular reflection. The p-factor used to reduce the weight of intense reflections, was set to 0.03 initially, but later changed to 0.04. [4] The analytical form of the scattering factor tables for neutral atoms were used and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion. [5]

Inspection of the residuals ordered in the ranges of $\sin(\theta/\lambda)$, $|F_o|$, and parity and values of the individual indexes showed no trends. The largest positive and negative peaks in the final difference Fourier map had electron densities of 2.03 e/Å^3 and -1.25 e/Å^3 respectively.

Crystal Data for $[Cp''_2UOH]_2$

Space group:	$P\bar{1}$
a, Å	11.499(2)
b, Å	11.999(3)
c, Å	12.969(2)
α, deg.	118.90(2)
β, deg.	105.81(2)
γ, deg.	90.62(2)
V, $Å^3$	1486(1)
Z	1
fw	1384
d_{calc} g/cm^3	1.51
μ_{calc} 1/cm	53.5
radiation	MoKα(λ= 0.71073 Å)
monochrometer	highly oriented graphite
scan range, type	$3° \leq 2\theta \leq 64°$, θ-2θ
scan speed, deg/min	6.7 → 2.01 (θ, deg/min)
scan width, deg	$\Delta\theta = 0.70 + 0.35\tan\theta$
reflections collected	14751
unique reflections	9960
reflections $F_o^2 > 3ß(F_o^2)$	7005
R, %	3.31
R_w, %	3.71
R_{all}, %	7.30
GOF	1.09
Largest Δ/σ in final least squares cycle	0

Intensity standards: (0,7,-7); (0,3,6); (7,-2, 0); measured every hour of X-ray exposure time. The data showed no decay.

Orientation Standards: 3 reflections were checked after every 200 measurements. Crystal orientation was redetermined if any of the reflections were offset from their predicted positions by more than 0.1°. Reorientation was required twice over the course of the data collection. The cell constants and errors are listed as their final values.

References

(1) Blake, P. C.; Lappert, M. F.; Taylor, R. G. In 1990; Vol. 27; pp 172.

(2) The data reduction formulas are:

$$F_o^2 = \frac{\omega}{Lp}(C\text{-}2B) \qquad \sigma_o(F_o^2) = \frac{\omega}{Lp}(C + 4B)^{1/2}$$

$$F_o = (F_o^2)^{1/2} \qquad \omega_o(F) = [F_o^2 + \sigma_o(F_o^2)]^{1/2} - F_o$$

where C is the total count of the scan, B is the sum of the two background counts, ω is the scan speed used in deg/min, and

$$\frac{1}{Lp} = \frac{\sin 2\theta \ (1 + \cos^2 2\theta_m)}{1 + \cos^2 2\theta_m - \sin^2 2\theta}$$

is the correction for Lorentz and polarization effects for a reflection with scattering angle 2θ and radiation monochromatized with a 50% perfect single crystal monochrometer with scattering angle $2\theta_m$.

(3) Calculations were performed on a DEC Microvax II using locally modified Molen software operating under Micro-VMS operating system.

(4) $$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} \qquad wR = \left[\frac{\Sigma(|F_o| - |F_c|)^2}{\Sigma wF_o^2}\right]^{1/2}$$

$$GOF = \left[\frac{\Sigma(|F_o| - |F_c|)^2}{(n_o - n_v)}\right]^{1/2}$$

where n_o is the number of observations and n_v is the number of variable parameters, and the weights were given by

$$w = \frac{1}{\sigma^2(F_o)} \qquad \sigma(F_o^2) = [\sigma_o^2(F_o^2) + (pF^2)^2]^{1/2}$$

where $\sigma^2(F_o)$ is calculated as above from $\sigma(F_o^2)$ and where p is the factor use to lower the weight of intense reflections.

(5) Cromer, D. T.; Waber, J. T. In *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

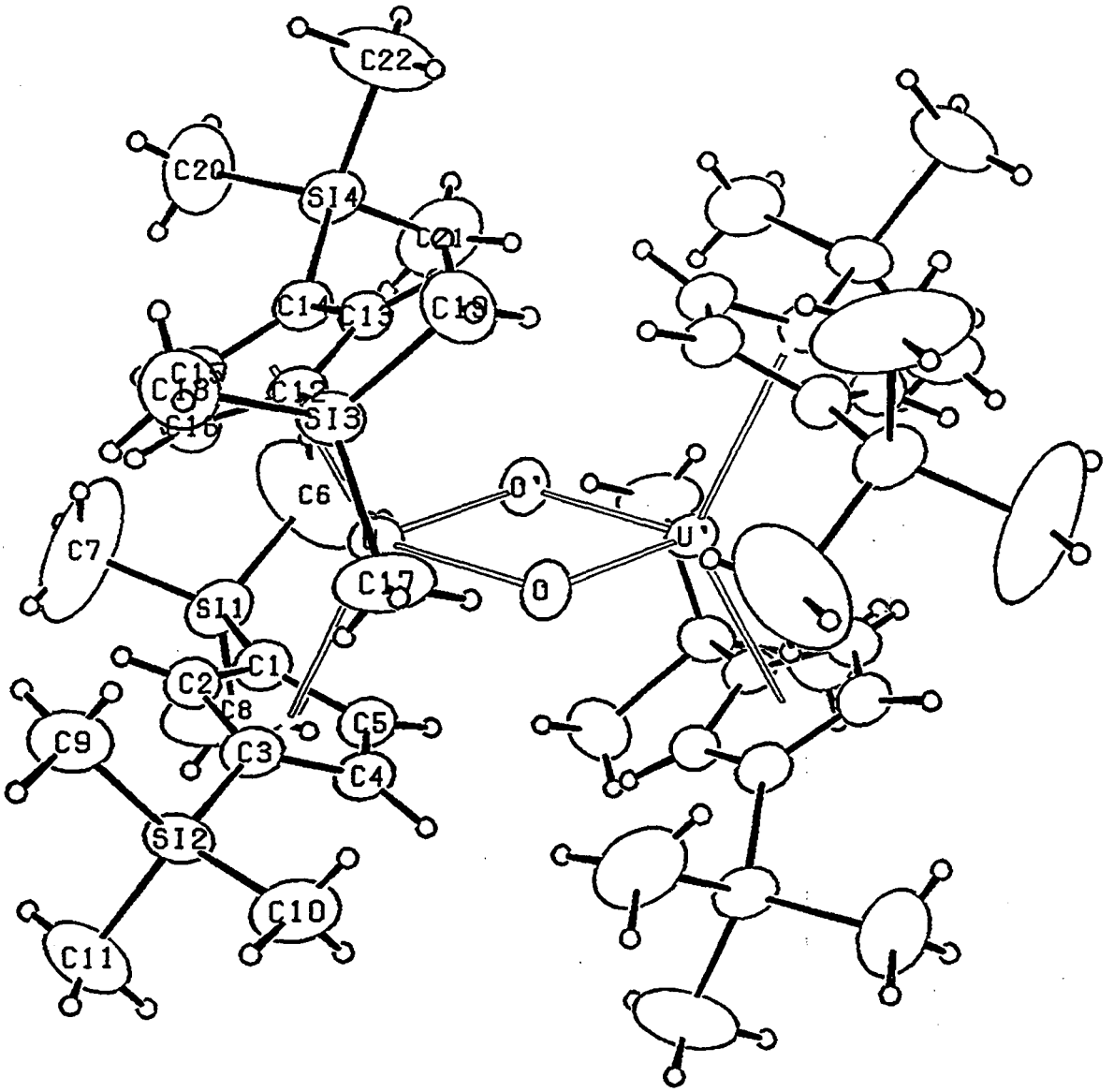
C22
C20
SI4
C21
C14
C13
C18
C15
C19
C12
SI3
C16
C6
O'
U
U'
C7
C17
O
SI1
C1
C2
C8
C5
C9
C3
C4
SI2
C10
C11

Table of Positional Parameters and Their Estimated Standard Deviations

Atom	x	y	z	B(Å²)
U	0.01029(1)	-0.00152(1)	0.14482(1)	2.354(3)
SI1	-0.2958(1)	-0.2022(1)	0.1223(1)	3.68(3)
SI2	0.2172(1)	-0.2495(1)	0.2445(1)	3.40(3)
SI3	0.3352(1)	0.2433(1)	0.3755(1)	2.78(2)
SI4	-0.1735(1)	0.3189(1)	0.2915(1)	3.21(3)
O	0.1192(2)	-0.0127(3)	0.0167(2)	2.76(6)
C1	-0.1364(4)	-0.2044(4)	0.1164(4)	2.86(9)
C2	-0.0276(4)	-0.1821(4)	0.2126(4)	3.03(9)
C3	0.0727(4)	-0.2166(4)	0.1662(4)	3.01(9)
C4	0.0229(4)	-0.2626(4)	0.0355(4)	2.85(9)
C5	-0.1029(4)	-0.2551(4)	0.0062(4)	2.91(9)
C6	-0.3694(7)	-0.0917(9)	0.0708(9)	11.8(3)
C7	-0.2934(7)	-0.136(1)	0.2820(7)	12.3(4)
C8	-0.3874(6)	-0.3617(7)	0.015(1)	12.2(3)
C9	0.2839(6)	-0.1188(5)	0.4091(5)	5.2(2)
C10	0.3300(5)	-0.2738(5)	0.1603(6)	5.0(2)
C11	0.1769(6)	-0.4004(5)	0.2442(6)	6.1(2)
C12	0.1677(3)	0.2135(3)	0.3503(3)	2.55(8)
C13	0.0752(3)	0.2656(3)	0.2963(3)	2.39(8)
C14	-0.0387(3)	0.2390(3)	0.3113(4)	2.59(8)
C15	-0.0145(4)	0.1692(4)	0.3755(4)	2.85(9)
C16	0.1093(4)	0.1539(4)	0.3990(4)	2.83(9)
C17	0.3924(5)	0.0969(5)	0.2765(6)	5.2(2)
C18	0.4189(5)	0.2975(5)	0.5397(5)	4.6(1)
C19	0.3676(4)	0.3696(4)	0.3395(5)	4.0(1)
C20	-0.2568(5)	0.3217(7)	0.3944(5)	6.6(2)
C21	-0.2798(6)	0.2450(7)	0.1315(6)	6.6(2)
C22	-0.1193(6)	0.4874(5)	0.3363(7)	6.9(2)

Starred atoms were included with isotropic thermal parameters.
The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter defined as:

$$(4/3) * [a^2*\beta(1,1) + b^2*\beta(2,2) + c^2*\beta(3,3) + ab(\cos\gamma)*\beta(1,2) + ac(\cos\beta)*\beta(1,3) + bc(\cos\alpha)*\beta(2,3)]$$

where a,b,c are real cell parameters, and $\beta(i,j)$ are anisotropic betas.

Table of Positional Parameters and Their Estimated Standard Deviations (cont.)

Atom	x	y	z	B(A2)
H2	-0.024(4)	-0.152(4)	0.290(4)	0.9(5)*
H4	0.063(4)	-0.301(4)	-0.028(4)	0.9*
H5	-0.153(4)	-0.281(4)	-0.078(4)	0.9*
H9A	0.368(6)	-0.138(6)	0.460(6)	6(1)*
H9B	0.306(6)	-0.056(6)	0.408(6)	5.5*
H9C	0.224(6)	-0.090(6)	0.452(6)	5.5*
H10A	0.415(6)	-0.280(6)	0.213(6)	5(1)*
H10B	0.291(6)	-0.336(6)	0.083(6)	4.9*
H10C	0.362(6)	-0.202(6)	0.159(5)	4.9*
H11A	0.244(7)	-0.422(6)	0.261(6)	6(1)*
H11B	0.116(7)	-0.379(6)	0.294(6)	6.2*
H11C	0.133(7)	-0.477(6)	0.149(6)	6.2*
H13	0.084(4)	0.309(4)	0.258(3)	0.2(5)*
H15	-0.085(4)	0.140(4)	0.396(3)	0.2*
H16	0.150(4)	0.132(4)	0.444(3)	0.2*
H17A	0.477(5)	0.115(5)	0.295(5)	3.2(8)*
H17B	0.374(5)	0.033(5)	0.275(5)	3.2*
H17C	0.343(5)	0.062(5)	0.177(5)	3.2*
H18A	0.503(5)	0.315(5)	0.562(5)	2.7(8)*
H18B	0.403(5)	0.370(5)	0.587(5)	2.7*
H18C	0.399(5)	0.227(5)	0.557(5)	2.7*
H19A	0.460(5)	0.394(5)	0.363(5)	3.4(8)*
H19B	0.318(5)	0.344(5)	0.257(5)	3.4*
H19C	0.335(5)	0.427(5)	0.372(5)	3.4*
H20A	-0.330(7)	0.354(6)	0.382(6)	6(1)*
H20B	-0.268(7)	0.247(7)	0.395(6)	6.5*
H20C	-0.210(7)	0.365(6)	0.479(6)	6.5*
H21A	-0.345(5)	0.290(5)	0.126(5)	3.8(9)*
H21B	-0.223(6)	0.258(5)	0.085(5)	3.8*
H21C	-0.309(6)	0.173(5)	0.140(5)	3.8*
H22A	-0.185(8)	0.519(8)	0.321(7)	9(2)*
H22B	-0.073(8)	0.532(7)	0.444(7)	8.6*
H22C	-0.074(8)	0.490(7)	0.304(7)	8.6*
H6A	-0.4504	-0.0908	0.0751	15.4**
H6B	-0.3231	-0.0062	0.1250	15.4**
H6C	-0.3705	-0.1198	-0.0111	15.4**
H7A	-0.3750	-0.1350	0.2848	15.8**
H7B	-0.2553	-0.1882	0.3132	15.8**
H7C	-0.2486	-0.0506	0.3308	15.8**
H8A	-0.4691	-0.3604	0.0169	16.1**
H8B	-0.3885	-0.3867	-0.0682	16.1**
H8C	-0.3533	-0.4226	0.0349	16.1**

Starred atoms were included with isotropic thermal parameters. Hydrogen thermal parameters were refined in groups, with all hydrogens in the group having a common thermal parameter. Double-starred atoms were included but not refined.

Table of Anisotropic Thermal Parameters - B's

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
U	2.111(4)	1.930(3)	2.499(4)	0.287(3)	0.737(3)	0.732(3)	2.354(3)
SI1	2.61(4)	3.33(4)	4.15(4)	-0.14(3)	1.52(3)	0.96(3)	3.68(3)
SI2	3.21(5)	2.46(3)	3.76(4)	0.83(3)	0.39(4)	1.36(3)	3.40(3)
SI3	1.77(3)	2.57(3)	3.46(4)	0.37(3)	0.41(3)	1.35(2)	2.78(2)
SI4	2.14(4)	3.37(4)	3.59(4)	1.04(3)	1.08(3)	1.28(3)	3.21(3)
O	2.16(9)	3.57(9)	2.60(8)	0.45(8)	0.84(7)	1.55(6)	2.76(6)
C1	2.5(1)	2.6(1)	3.2(1)	0.2(1)	1.1(1)	1.15(9)	2.86(9)
C2	3.4(2)	2.5(1)	3.1(1)	0.5(1)	1.2(1)	1.27(9)	3.03(9)
C3	2.7(1)	2.4(1)	3.1(1)	0.3(1)	0.7(1)	0.98(9)	3.01(9)
C4	2.6(1)	2.2(1)	3.0(1)	0.3(1)	0.9(1)	0.76(9)	2.85(9)
C5	2.6(1)	2.5(1)	2.7(1)	0.2(1)	0.5(1)	0.79(9)	2.91(9)
C6	5.3(3)	17.0(4)	21.4(5)	5.0(3)	5.4(3)	15.2(3)	11.8(3)
C7	4.6(3)	23.3(9)	5.6(3)	-1.7(4)	2.4(2)	4.5(4)	12.3(4)
C8	5.9(3)	4.9(3)	19.5(7)	-1.4(2)	6.7(3)	0.1(4)	12.2(3)
C9	5.2(3)	3.6(2)	4.4(2)	1.2(2)	-0.4(2)	1.3(1)	5.2(2)
C10	3.7(2)	4.6(2)	5.6(2)	1.7(2)	1.2(2)	1.9(2)	5.0(2)
C11	6.3(3)	4.2(2)	7.1(2)	0.5(2)	0.0(2)	3.6(1)	6.1(2)
C12	2.3(1)	2.3(1)	2.5(1)	0.5(1)	0.7(1)	0.86(8)	2.55(8)
C13	2.3(1)	2.2(1)	2.6(1)	0.43(9)	0.90(9)	1.07(8)	2.39(8)
C14	1.8(1)	2.6(1)	2.9(1)	0.33(9)	0.81(9)	1.01(9)	2.59(8)
C15	2.5(1)	2.7(1)	2.9(1)	0.2(1)	1.1(1)	1.07(9)	2.85(9)
C16	2.5(1)	2.7(1)	2.8(1)	0.5(1)	0.4(1)	1.33(9)	2.83(9)
C17	3.1(2)	3.4(2)	7.6(3)	1.0(1)	2.1(2)	1.4(2)	5.2(2)
C18	3.0(2)	5.1(2)	4.5(2)	0.2(2)	-0.4(2)	2.4(1)	4.6(1)
C19	2.5(2)	4.5(1)	5.4(2)	0.4(1)	0.7(1)	2.9(1)	4.0(1)
C20	4.9(2)	10.9(3)	7.7(2)	4.6(2)	4.5(1)	6.0(2)	6.6(2)
C21	4.1(2)	8.2(3)	5.6(3)	2.8(2)	1.0(2)	2.3(2)	6.6(2)
C22	4.6(2)	4.6(2)	11.5(4)	1.9(2)	1.8(3)	4.3(2)	6.9(2)

The form of the anisotropic temperature factor is:
$\exp[-\frac{1}{4}\{h^2a^{*2}B(1,1) + k^2b^{*2}B(2,2) + l^2c^{*2}B(3,3) + 2hka^*b^*B(1,2) + 2hla^*c^*B(1,3) + 2klb^*c^*B(2,3)\}]$ where a^*, b^*, and c^* are reciprocal lattice constants.

UOHDIM

Intramolecular Distances

ATOM 1	ATOM 2	DISTANCE
U	U'	3.717(1)
U	O	2.295(3)
U	O'	2.299(3)
U	C1	2.760(4)
U	C2	2.772(5)
U	C3	2.806(4)
U	C4	2.770(4)
U	C5	2.745(4)
U	CP1	2.493
U	C12	2.768(4)
U	C13	2.785(4)
U	C14	2.825(4)
U	C15	2.790(4)
U	C16	2.758(4)
U	CP2	2.509
C1	C2	1.419(6)
C1	C5	1.424(6)
C2	C3	1.418(6)
C3	C4	1.437(6)
C4	C5	1.407(6)
C1	SI1	1.855(4)
SI1	C6	1.869(10)
SI1	C7	1.817(9)
SI1	C8	1.815(8)
C3	SI2	1.853(5)
SI2	C9	1.857(6)
SI2	C10	1.852(7)
SI2	C11	1.863(7)
C12	C13	1.430(6)
C12	C16	1.421(6)
C13	C14	1.431(5)
C14	C15	1.423(6)
C15	C16	1.406(6)
C12	SI3	1.863(4)
SI3	C17	1.863(6)
SI3	C18	1.848(6)
SI3	C19	1.851(6)
C14	SI4	1.855(4)
SI4	C20	1.832(7)
SI4	C21	1.843(8)
SI4	C22	1.858(7)

Primed atoms are related to unprimed atoms by the inversion center at (0,0,0)

UOHDIM

Intramolecular Angles

ATOM 1	ATOM 2	ATOM 3	ANGLE
O	U	O'	72.01(11)
U	O	U'	107.99(11)
O	U	CP1	107.11
O	U	CP2	115.14
O'	U	CP1	109.05
O'	U	CP2	111.77
CP1	U	CP2	127.96
C2	C1	C5	105.7(4)
C1	C2	C3	111.1(4)
C2	C3	C4	105.1(4)
C3	C4	C5	109.0(4)
C1	C5	C4	109.0(4)
C1	SI1	C6	110.3(3)
C1	SI1	C7	109.4(3)
C1	SI1	C8	110.0(3)
C6	SI1	C7	106.0(7)
C6	SI1	C8	106.4(6)
C7	SI1	C8	114.7(6)
C3	SI2	C9	111.4(2)
C3	SI2	C10	111.3(3)
C3	SI2	C11	106.6(3)
C9	SI2	C10	110.6(3)
C9	SI2	C11	107.5(4)
C10	SI2	C11	109.3(4)
C13	C12	C16	106.0(3)
C12	C13	C14	110.0(4)
C13	C14	C15	105.5(3)
C14	C15	C16	109.5(4)
C12	C16	C15	109.0(4)
C12	SI3	C17	113.2(2)
C12	SI3	C18	108.5(3)
C12	SI3	C19	109.1(2)
C17	SI3	C18	108.0(3)
C17	SI3	C19	107.9(3)
C18	SI3	C19	110.1(3)
C14	SI4	C20	108.3(3)
C14	SI4	C21	115.3(3)
C14	SI4	C22	109.0(3)
C20	SI4	C21	109.5(4)
C20	SI4	C22	109.2(5)
C21	SI4	C22	105.4(5)

Primed atoms are related to unprimed atoms by the inversion center at (0,0,0)

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