Electrochemical Properties of Bis(dicarbollide)uranium Dibromide

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Received October 10, 1997

The cyclic voltammogram of [(η^5-$C_2B_9H_{11}$)$_2$UBr$_2$]·2[Li(THF$_4$)] shows the electrochemical generation of a uranium(III) species. Subsequent Na/Hg reduction of [(η^5-$C_2B_9H_{11}$)$_2$UBr$_2$]·2[Li(THF$_4$)] leads to the new isolable uranium(III) species [(η^5-$C_2B_9H_{11}$)$_2$UBr(THF)]·2[Li(THF)$_x$] ($x = 2-4$). The green uranium(III) complex was characterized by NMR and elemental analysis and its structure determined by single-crystal X-ray crystallography. The coordination geometry around the dinegative uranium(III) moiety is pseudotetrahedral with two dicarbollide ligands, a bromide ligand, and a THF ligand. The electrochemical properties of the dicarbollide complex are discussed and compared to similar cyclopentadienyluranium complexes.

Introduction

The dicarbollide ligand has been of great interest to chemists since Hawthorne first prepared a transition metal dicarbollide complex 30 years ago.[1] Ostensibly, the dicarbollide ligand ($C_2B_9H_{11}^{2-}$) has many similarities to cyclopentadienyl ligands.[2] However, due to the dinegative charge,[3] the presence of boron, and the inward tilt of the HOMO orbitals, there are many structural features of metal dicarbollide complexes that are unique as compared to analogous cyclopentadienyl complexes.[4−6] Since our previous reports on the isolation of several new actinide dicarbollide complexes,[7] we have begun to investigate the redox behavior of these complexes. Our approach is to initially probe for interesting redox behavior using cyclic voltammetry followed by chemical synthesis and physical characterization of isolable products. We report herein the details of this approach on [(η^5-$C_2B_9H_{11}$)$_2$UBr$_2$]·2[Li(THF$_4$)] (**1**) with the cyclic voltammogram of **1** and its chemical reduction to a new, fully characterized uranium(III) compound. We also report an improvement of our previous method for the synthesis of **1**.[7a]

Experimental Section

All manipulations were carried out under a dry He atmosphere in a glovebox with less than 5 ppm oxygen. Solvents were deoxygenated and dried by refluxing under a nitrogen atmosphere over an appropriate drying agent (sodium, sodium/benzophenone, or CaH_2). Low temperatures (below −80 °C) were achieved in the glovebox using a cold well, cooled with liquid nitrogen and filled with sand.

Synthesis of [($C_2B_9H_{11}$)$_2$UBr$_2$]·2[Li(THF)$_4$] (1). A clear solution of [Me_3NH][$C_2B_9H_{12}$] (7.742 g, 40 mmol) in THF (250 mL) was cooled to below −80 °C using a cold well. The flask was then removed from the well, set to stir, and 50 mL of *n*-BuLi (1.6 M hexane solution, 80.0 mmol) was added via syringe to produce $Li_2C_2B_9H_{11}$ *in situ*. The reaction mixture was left to stir at room temperature for 1 h, after which time the flask was again cooled using the cold well. A separate solution consisting of UBr_4·4CH_3CN (14.438 g, 20 mmol) in 50 mL of THF was prepared and also placed in the cold well. After 15 min, the UBr_4·4CH_3CN solution was set to stir and the $Li_2C_2B_9H_{11}$ solution was slowly added. The reaction mixture was stirred at room temperature for 16 h. Removal of the solvents *in vacuo* afforded a viscous dark orange oil. The crude product was dissolved in 30 mL of THF, and a solid was precipitated from solution by the slow addition of pentane (20 mL). The solids were collected by filtration and washed with 10 mL of a THF/pentane (5/1) mixture and then 5 mL of cold THF giving a crystalline orange product **1** (19.752 g, 79% yield based on UBr_4·4CH_3CN). Yields varied (70−80%) between experiments. The ^{11}B NMR spectrum was identical to that previously reported.[7a]

Synthesis of [($C_2B_9H_{11}$)$_2$UBr(THF)]·2[Li(THF)$_2$] (2). A 50 mL flask was charged with **1** (0.563 g, 0.45 mmol) and 10 mL of THF. The orange solution was set to stir, and approximately 30 mg of Na (1.3 mmol, excess) and 100 mg of Hg were added. The reaction was allowed to proceed overnight, during which time the solution turned from orange to dark green. The green solution was decanted from the excess Na/Hg amalgam and filtered to remove a white precipitate. The filtrate was concentrated under vacuum leading to the precipitation of a green solid. The solid was collected by filtration and washed with minimal cold (−30 °C) THF, giving the crystalline green product (0.260 g, 46% yield). ^{11}B{^{1}H} NMR (THF): δ 548 (br s, 1 B), 435 (br s, 2 B), 62 (s, 2 B), 56 (s, 2 B), 14 (s, 2 B). Anal. Calcd for $C_{24}H_{62}B_{18}BrO_5Li_2U$: C, 30.1; H, 6.5. Found: C, 30.3; H, 6.4.

Electrochemistry Experiments. Electrochemical experiments were conducted on a BAS CV-40 instrument with the electrochemical cell

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(1) For a compilation of early work on the dicarbollide ligand see: Hawthorne, M. F.; Young, D. C.; Andrews, T. D.; Howe, D. V.; Pilling, R. L.; Pitts, A. D.; Reintjes, M.; Warren, L. F.; Wegner, P. A. *J. Am. Chem. Soc.* **1968**, *90*, 879.

(2) Hanusa, T. P. *Polyhedron* **1982**, *1*, 663.

(3) For charge-compensated dicarbollides see: Kang, H. C.; Lee, S. S.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1991**, *30*, 2024.

(4) For a review of carborane metal complexes see: Saxena, A. K.; Hosmane, N. S. *Chem. Rev.* **1993**, *93*, 1081.

(5) For some specific examples of unusual properties of the dicarbollide ligand see: (a) Viñas, C.; Pedrajas, J.; Bertran, J.; Teixidor, F.; Kivekäs, R.; Sillanpää, R. *Inorg. Chem.* **1997**, *36*, 2482. (b) Xie, Z.; Liu, Z.; Chiu, K.; Xue, F.; Mak, T. C. W. *Organometallics* **1997**, *16*, 2460. (c) Yoshida, M.; Crowther, D. J.; Jordan, R. F. *Organometallics* **1997**, *16*, 1349. (d) Anderson, S.; Mullica, D. F.; Sappenfield, E. L.; Stone, F. G. A. *Organometallics* **1996**, *15*, 1676. (e) Bazan, G. C.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1993**, *12*, 2126. (f) Kang, H. C.; Do, Y.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1988**, *27*, 1716. (g) Warren, L. F.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1970**, *92*, 1157.

(6) Three reports on uranium dicarbollide complexes precede our work: (a) Fronczek, F. R.; Halstead, G. W.; Raymond, K. N. *J. Chem. Soc., Chem. Commun.* **1976**, *8*, 279. (b) Fronczek, F. R.; Halstead, G. W.; Raymond, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 1769. (c) Shaw, K. F.; Reid, B. D.; Welch, A. J. *J. Organomet. Chem.* **1994**, *482*, 207.

(7) (a) Rabinovich, D.; Haswell, C. M.; Scott, B. L.; Miller, R. L.; Nielsen, J. B.; Abney, K. D. *Inorg. Chem.* **1996**, *35*, 1425. (b) Rabinovich, D.; Chamberlin, R. M.; Scott, B. L.; Nielsen, J. B.; Abney, K. D. *Inorg. Chem.* **1997**, *36*, 4216.

S0020-1669(97)01283-4 CCC: $15.00

in the glovebox. A single-cell compartment with a platinum working electrode, a platinum wire counter electrode, and silver wire reference electrode was used in the experiments. The $(TBA)PF_6$ (Aldrich) was crystallized three times in ethanol and dried at 100 °C under vacuum for 2 days. An electrolyte concentration of 0.1 M in THF was used in the experiments. Ferrocene was used as an external standard.

X-ray Structure Determination. Crystals of **2** were grown in THF at −30 °C over several days. A black, prism-shaped crystal was mounted on a glass fiber using silicone grease and placed under a liquid nitrogen cold stream on a Siemens P4/PC diffractometer. The mounting was performed under an argon air flow to eliminate crystal decomposition. The lattice parameters were optimized from a least-squares calculation on 25 carefully centered reflections of high Bragg angle. The data were collected using ω scans with a 1.84° scan range. Three check reflections monitored every 97 reflections showed no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS version 2.10b software. All data reduction, including Lorentz and polarization corrections and structure solution, and graphics were performed using SHELXTL PC version 4.2/360 software. The structure refinement was performed using SHELX 93 software.[8] The data were corrected for absorption using the XEMP facility in SHELXTL PC.

The structure was initially solved in the space group $P\bar{1}$ using Patterson and difference Fourier techniques. This solution yielded the uranium atom position and the majority of all other non-hydrogen atom positions. The assignment of the remaining atom positions from subsequent Fourier synthesis was problematic due to severe disorder, which resulted from the occupation of an inversion symmetry element by $[(C_2B_9H_{11})_2UBr(THF)]^{2-}$. Attempts were made to refine two disordered anions and two disordered cations. However, all atom positions in the $Li(THF)_4$ cations could not be assigned. The structure would not converge upon numerous cycles of least-squares refinement, and bond distances and angles of all moieties were anomalous. The best $R1$ value achieved was 0.083. At this time the space group was changed to $P1$, which eliminated the disorder problem and resulted in a smooth refinement. All non-hydrogen atoms were identified and all bond distances refined to reasonable values. The carbon atom positions in the dicarbollide ligands were assigned on the basis of temperature factors and bond distances. Hydrogen atoms were fixed in ideal positions using the HFIX facility and refined using the riding model. The C−H distances in the THF ligands were fixed at 0.97 Å, and the B−H and C−H distances of the dicarbollide ligands were fixed at 1.1 Å. The isotropic temperature factors of all hydrogen atoms were fixed at 1.2 times the equivalent isotropic U of the atom to which they were bound. The final refinement,[9] with all non-hydrogen atoms refined anisotropically, converged to $R1 = 0.0527$ and $R2_w = 0.1088$. Crystal data and structure refinement parameters are given in Table 1.

Results and Discussion

The cyclic voltammograms of **1** at a platinum electrode in 0.1 M $(TBA)PF_6$/THF show an irreversible reduction (Figure 1). The cathodic wave seen at approximately −1.4 V implies the electrochemical generation of a distinct U(III) species. In support of this, the cyclic voltammogram of **1** in CH_2Cl_2 showed only a reduction wave.[10] The general behavior of **1** contrasts with $Cp^*{}_2UCl_2$ (**3**),[11] which exhibits a completely reversible IV−III couple at −1.72 V *vs* $FeCp_2$ in 0.1 M $(TBA)BF_4$/THF.[12] In a similar electrolyte (0.1 M $(TBA)PF_6$/THF), the reduction wave observed for **1** has an onset around −1.56 V. Thus, it appears that whereas **3** is reduced to the stable anion $[Cp^*{}_2UCl_2]^-$, the reduction of **1** must lead to significant bond rearrangement.

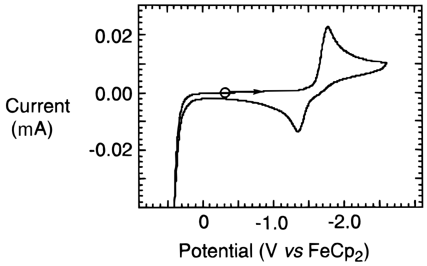

Figure 1. Cyclic voltammogram of **1** in 0.1 M $(TBA)PF_6$/THF at 200 mV/s.

Table 1. Crystal Data for $[(\eta^5\text{-}C_2B_9H_{11})_2U(Br)\cdot THF]\cdot 2[Li(THF)_4]$

formula	$C_{40}H_{94}B_{18}O_9BrLi_2U$
molwt	1245.55
T	198 K
λ	0.710 73
space group	$P1$
a	10.110(3) Å
b	11.718(2) Å
c	14.029(2) Å
α	11.546(5)°
β	103.65°
γ	93.97°
V	1479.6(5) Å^3
Z	1
ρ_{calc}	1.398 g/m^3
abs coeff	3.463 mm^{-1}
abs corr	empirical
T_{min}/T_{max}	0.34/10.57
$F(000)$	629
cryst size	0.16 × 0.21 × 0.31 mm
2θ	2.5−25.0°
index ranges	$-1 \le h \le 11$, $-12 \le k \le 12$, $-16 \le l \le 16$
reflcns collcd	5906
indepdt reflcns	5906 [R(int) = 0.000]
final R values	$R1 = 0.0527$, w$R_2 = 0.1088$
abs struct param	0.013(11)
largest diff peak/hole	1.846/−1.783 e Å^3 [near U(1)]

The interesting contrast between the cyclic voltammograms of **1** and **3** prompted us to perform a chemical reduction of **1** in order to isolate this new U(III) species. We found that treatment of **1** with excess Na/Hg amalgam in THF led to slow formation of a green solution and concomitant formation of a white NaBr precipitate. After 12 h, the ^{11}B NMR spectra of this solution showed a clean reaction to a new uranium dicarbollide compound with chemical shifts similar to the U(III) compound $[(\eta^5\text{-}C_2B_9H_{11})_2UI(THF)]\cdot 2[Li(TMEDA)_2]$, prepared by the reaction of UI_3 with 2 equiv of the dicarbollide ligand.[7a] The green powder that was isolated (50% yield, based on **1**) had an elemental analysis consistent with the formulation $[(\eta^5\text{-}C_2B_9H_{11})_2UBr(THF)]\cdot 2[Li(THF)_2]$. While Li^+ is typically solvated by four THF molecules, there have been instances when Li^+ coordinates with the electron-rich B−H bonds of the dicarbollide ligand, giving an unexpected number of THF molecules associated with the structure.[5e] On the basis of the evidence obtained thus far, we conclude that reduction of **1** leads to the loss of Br^- to give the green U(III) complex **2** (eq 1).

Confirmation of the predicted formulation for **2** was demonstrated by the single-crystal X-ray structure of the compound.

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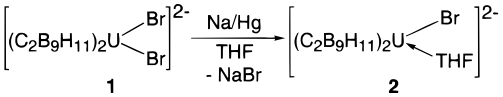
(8) XSCANS and SHELXTL PC are products of Siemens Analytical X-ray Instruments, Inc., 6300 Enterprise Lane, Madison, WI 53719. SHELX-93 is a program for crystal structure refinement written by G. M. Sheldrick (1993), Univ. of Göttingen, Germany.

(9) $R1 = \sum||F_o| - |F_c|/\sum|F_o|$ and $R2_w = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. The parameter $w = 1/[\sigma^2(F_o^2) + (0.0611P)^2]$.

(10) Alkyl halides react with U(III) organometallic complexes. See: Finke, R. G.; Schiraldi, D. A.; Hirose, Y. *J. Am. Chem. Soc.* **1981**, *103*, 1876.

(11) (a) Spirlet, M. R.; Rebiznat, J.; Apostolidis, C.; Kanellakopulos, B. *Acta Crystallogr. C.* **1992**, *C48*, 2135. (b) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650. (c) Finke, R. G.; Gaughan, G.; Voegeli, R. *J. Organomet. Chem.* **1982**, *229*, 179.

(12) We found that **3** in 0.1 $(TBA)BF_4$/THF gave a reversible wave at $E_{1/2}$ = −1.72 V *vs* $FeCp_2$, in agreement with ref 10c.



$$\left[(C_2B_9H_{11})_2U\begin{smallmatrix}Br\\Br\end{smallmatrix}\right]^{2-}\xrightarrow[\text{THF}\ -\text{NaBr}]{\text{Na/Hg}}\left[(C_2B_9H_{11})_2U\begin{smallmatrix}Br\\THF\end{smallmatrix}\right]^{2-}\quad (1)$$

1 **2**

Dark green prismatic crystals suitable for the structure determination were grown from a THF solution. The U(III) center in **2** adopts a tetrahedral coordination analogous to **1**, with one bromide ligand replaced by the oxygen of a THF molecule (Figure 2). The dianionic complex is compensated by two discrete Li(THF)$_4$ counterions (not shown), a result that seems to contradict our elemental analysis results of Li(THF)$_2$ but which is not completely surprising since the crystals were grown in THF. We were unable to find another suitable solvent for crystallization of **2**. The average U−dicarbollide centroid distance of 2.40 Å is equivalent to that in the U(III) complex [(η^5-$C_2(CH_3)_2B_9H_9$)U(I)$_2$(THF)$_2$]·PPN[7a] and longer than that of **1** (2.32 Å), consistent with the more electron rich uranium center. The U−Br bond length (2.883(2) Å) in **2** is also slightly longer than in **1** (2.830(2) Å). In **2** the dicarbollide−U−dicarbollide angle of 131.7° is significantly smaller than that found in **1** (143.1°). Since the cone angles, calculated from the crystal structures of **1** (121°) and **2** (119°) are almost identical,[13] steric interactions between the dicarbollide ligands cannot by themselves account for this difference in angles. Likewise, there does not appear to be a clear correlation for the Cp−U−Cp angles between U(III) and U(IV) complexes.[14] Finally, unlike **1** the carbon atoms of the dicarbollide ligand are not located on the adjacent side of this bent metallocene-like complex.

We have also begun to investigate the reactivity of the anionic uranium dicarbollide systems. Since neutral bis(cyclopentadienyl)uranium(III) complexes are known to couple alkynes in toluene,[15] we attempted to react **2** with excess diphenylacetylene in THF. No coupling products were detected from this reaction although **2** decomposes in CH_3CN. Attempts at coupling the diphenylacetylene in toluene also failed, possibly due to the negligible solubility of **2** in this solvent.

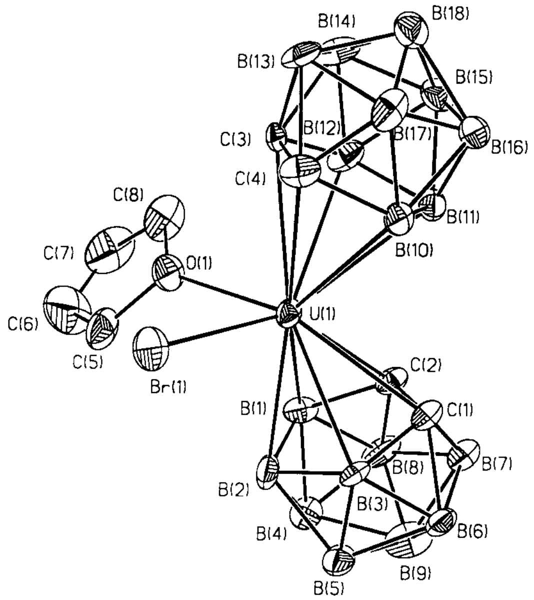


Figure 2. ORTEP view of **3** (thermal ellipsoids at 35% probability level).

In summary, reduction of **1** by electrolysis or Na/Hg amalgam leads to loss of bromide giving **2**. The coordination geometry of the uranium center for **2** is "pseudotetrahedral", similar to **1** and bis(cyclopentadienyl) analogues. The bond lengths and angles are consistent with a U(III) metal center. Contrasting with **3**, this new bis(dicarbollide) complex does not couple alkynes, a result that may be due to the limited solubility of **2** in most solvents.

Acknowledgment. This work was performed under the auspices of the Department of Energy, Los Alamos National Laboratory Nuclear Materials and Stockpile Management Program Office, and the Divisions of Chemical Science and Technology and Nuclear Materials Technology. Los Alamos National Laboratory is operated by the University of California for the U.S. Department of Energy under Contract W-7405-ENG-36.

Supporting Information Available: Text describing X-ray procedures, tables of crystal and intensity collection data, atomic coordinates, bond lengths, bond angles, cone angles, anisotropic displacement parameters, and hydrogen atomic coordinates, and ORTEP drawings for [(η^5-$C_2B_9H_{11}$)$_2$U(Br)·THF]·2[Li(THF)$_4$] (23 pages). Ordering information is given on any current masthead page.

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(13) The cone angles were calculated from an average of the 5 angles made from the centroid−U−H, where the H position was calculated and given a van der Waals radius of 1 Å. The cone angles are significantly smaller than those calculated for transition metals due to the much longer actinide−centroid bond lengths. See ref 2.

(14) For example, the centroid−U−centroid angle in systems containing the η^5-$C_5H_3(SiMe_3)_2$ ligand is sometimes smaller in the U(IV) complex than in the U(III) complexes: Blake, P. C.; Lappert, M. F.; Atwood, J. L.; Zhang, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1436.

(15) Fagan, P. J.; Manriquez, J. M.; Marks, T. J.; Day, C. S.; Vollmer, S. H.; Day, V. W. *Organometallics* **1982**, *1*, 170.