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Synthesis of Cationic Cyclooctatetraene Uranium Complexes by Protonolysis of Borohydride Precursors: The First Cationic Organometallic Borohydride and the First Organometallic Dication of an f Element

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*Summary: Reaction of (COT)U(BH_4)$_2$(THF) (COT = η-C_8H_8, THF = tetrahydrofuran) with NEt_3HBPh_4 afforded [(COT)U(BH_4)(THF)$_2$][BPh_4] (**1**), which further reacted with the ammonium salt in the presence of HMPA to give [(COT)U(HMPA)$_3$][BPh_4]$_2$ (**2**); the crystal structure of a pyridine solvate of **2** has been determined.*

Cationic complexes of d transition metals and f elements currently deserve special attention since they are potential precursors in inorganic and organometallic synthesis as well as efficient catalysts in a number of organic reactions. While several pathways allow the preparation of such compounds,[1] a large number of uranium cations have been recently obtained by protonolysis of a U−NR_2 bond with the ammonium salt $NHEt_3BPh_4$.[2] The cationic amide compounds [(Cp*)$_2$U(NMe_2)(THF)][BPh_4][3] and [(COT)U(NEt_2)(THF)$_2$][BPh_4][4] (Cp* = η-C_5Me_5, COT = η-C_8H_8, THF = tetrahydrofuran) served to prepare a variety of bis(pentamethylcyclopentadienyl) and mono(cyclooctatetraene) uranium derivatives, whereas [U(NEt_2)$_3$][BPh_4][5] proved to be very active in the selective dimerization, hydroamination, and hydrosilylation of terminal alkynes.[6] Protonation of a U−NR_2 bond also enabled access to rare examples of uranium dications: [UCl_2(THF)$_4$]$^{2+}$ and [U(NEt_2)$_2$(THF)$_3$]$^{2+}$.[5] Thereafter, we found that borohydride complexes of 4f and 5f metals could also be conveniently transformed into cationic species by protonolytic cleavage of the M−BH_4 bond with acidic ammonium salts. Thus the uranium(III) cation [U(BH_4)$_2$(THF)$_5$][BPh_4][7] and [(COT)Nd(THF)$_4$][BPh_4], a first example of a cyclooctatetraene lanthanide cation, were obtained.[8] This protonolysis reaction was also used for the preparation of the zirconium borohydride complexes [(C_5H_4R)$_2$Zr(BH_4)(THF)][BPh_4].[9] Here we report on the cyclooctatetraene uranium compounds [(COT)U(BH_4)(THF)$_2$][BPh_4] (**1**) and [(COT)U(HMPA)$_3$][BPh_4]$_2$ (**2**) (HMPA = hexamethylphosphoramide), which have been prepared from (COT)U(BH_4)$_2$(THF). These represent the first cationic organometallic borohydride and the first organometallic dication of an f element, respectively. We also present the X-ray crystal structure of a pyridine solvate of **2**.

The monocationic compound **1** was prepared by treating (COT)U(BH_4)$_2$(THF)[10] with 0.87 equiv of NEt_3HBPh_4 in THF, as shown in eq 1. After refluxing

$$\mathrm{(COT)U(BH_4)_2(THF) + NEt_3HBPh_4 \xrightarrow{THF} \underset{\mathbf{1}}{[(COT)U(BH_4)(THF)_2][BPh_4]} + BH_3{\cdot}NEt_3 + 0.5H_2} \qquad (1)$$

for 3 h and evaporating to dryness, the excess of (COT)U(BH_4)$_2$(THF) was removed with toluene and **1** was isolated as a golden brown powder (87% yield based on the ammonium salt). In the synthesis of **1**, it is essential to use a default of NEt_3HBPh_4 in order to avoid the formation of the dication [(COT)U(THF)$_x$]$^{2+}$ (vide infra). Complex **1** could be obtained in quantitative yield by using a 2-fold excess of the ammonium salt at room temperature (NMR experiment); however, the reaction required 3 weeks to go to completion, and the similar solubility of **1** and NEt_3HBPh_4 in THF precluded any further purification.

Complex **1** was characterized by its elemental analyses (C, H, B) and its ^{1}H NMR spectrum, which exhibits signals at δ 221.0 and −33.64 corresponding to the BH_4 and COT ligands, respectively. In the IR spectrum, the strong broad band centered at 2462 cm^{-1} is diagnostic of a bidentate borohydride ligand.[11]

Treatment of **1** with L = $OPPh_3$ and HMPA in THF led to the immediate and quantitative formation

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[1] Organo-f-element cations have been most generally prepared either by (a) heterolytic cleavage of a metal−halogen bond: Aslan, H.; Yünlü, K.; Fischer, R. D.; Bombieri, G.; Benetollo, F. *J. Organomet. Chem*. **1988**, *354*, 63, or (b) protonolysis of a metal−carbon bond: Lin, Z.; Le Maréchal, J. F.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 4127.

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of the Lewis base adducts $[(COT)U(BH_4)L_3][BPh_4]$, which are quite stable in solution (NMR experiments).[12] However, **1** was found to be unstable in pyridine, being slowly transformed into the dication $[(COT)U(pyridine)_x]^{2+}$ and other unidentified species.[13] Similarly, the monocation $[(COT)U(BH_4)(HMPA)_3]^+$ was converted into the dication $[(COT)U(HMPA)_3]^{2+}$ in pyridine (vide infra). It is likely that pyridine reacted with **1** to give the corresponding hydride $[(COT)UH(pyridine)_x]^+$ by abstraction of BH_3.[14] This cationic hydride could then disproportionate into the dication and the putative dihydride $(COT)UH_2$, which decomposed in solution. Such a disproportionation reaction was previously observed with the cationic zirconium hydride $[(C_5H_4R)_2ZrH(PMe_2Ph)_2][BPh_4]$[9] and was invoked to explain the deactivation of catalytic cationic systems.[9,15] No uranium hydride was, however, detected during the reaction.

Further reaction of **1** and NEt_3HBPh_4 in refluxing THF afforded the dication $[(COT)U(THF)_x]^{2+}$. However, an excess of the ammonium salt was necessary to observe the complete formation of the organometallic product, which could not be then isolated pure from the reaction mixture. Protonation of $[(COT)U(BH_4)L_3][BPh_4]$ (L = $OPPh_3$ and HMPA) was much more rapid than that of **1** at 20 °C, giving the dication $[(COT)UL_3]^{2+}$ with evolution of gas, presumably dihydrogen, according to eq 2. The HMPA adduct $[(COT)U(HMPA)_3][BPh_4]_2$ (**2**),

$$[(COT)U(BH_4)L_3][BPh_4] + NEt_3HBPh_4 \xrightarrow{THF} [(COT)UL_3][BPh_4]_2 + BH_3{\cdot}NEt_3 + 0.5H_2 \quad (2)$$

$$L = OPPh_3 \text{ or HMPA, } \mathbf{2}$$

being poorly soluble in THF, could be easily separated by filtration. The dicationic complex **2** was synthesized directly from $(COT)U(BH_4)_2(THF)$, by treatment in THF with 2 equiv of NEt_3HBPh_4 in the presence of HMPA, and was isolated as an orange microcrystalline powder in 75% yield. The ^{1}H NMR spectrum of **2** in pyridine-d_5 shows the COT signal at δ −32.48.

The crystals of **2**·pyridine are composed of discrete cations and anions. The BPh_4 anions display the expected structural parameters; a view of one of the two independent and quite identical dications is shown in Figure 1, while selected bond distances and angles are listed in Table 1. The dications adopt a three-legged piano-stool configuration in which the O−U−O angles vary from 84.0° to 88.2°, with a mean value of 87(3)°, and the COT−U−O angles (COT = centroid of the C_8H_8 ring) range between 127.2° and 128.7°, averaging 127(1)°. The uranium atom is 1.92(2) Å from the planar cyclooctatetraene ring (within ±0.01 Å), and the mean U−C bond distance is 2.65(3) Å; these values compare well with those determined in the monocationic cyclooctatetraene complexes $[(COT)U(NEt_2)(THF)_3]^+$ (2.02(2) and 2.71(4) Å),[3] $[(COT)U(S_2CNEt_2)(THF)_2]^+$ (1.93(3) and 2.64(4) Å),[3] and $[(COT)(C_5H_5)U(THF)_2]^+$ (1.96(2) and 2.65(2) Å).[16] The structure of the dication $[(COT)U(HMPA)_3]^{2+}$ strongly resembles that of the samarium monocation $[(COT)Sm(HMPA)_3]^+$, which exhibits the same oxygen−metal−oxygen angles and metal−carbon bond lengths.[17] However, the U−O bond distances, which average 2.22(2) Å, are significantly shorter than the Sm−O bond distances, by 0.1 Å. Such a difference, which was also observed between the U−O(HMPA) bond distances of $U(S^iPr)_4(HMPA)_2$[18] and $[U(S^iPr)_2(HMPA)_4]^{2+}$,[19] respectively equal to 2.31(1) and 2.2(2) Å, would reflect the stronger interaction of the Lewis base with the more electropositive uranium center.

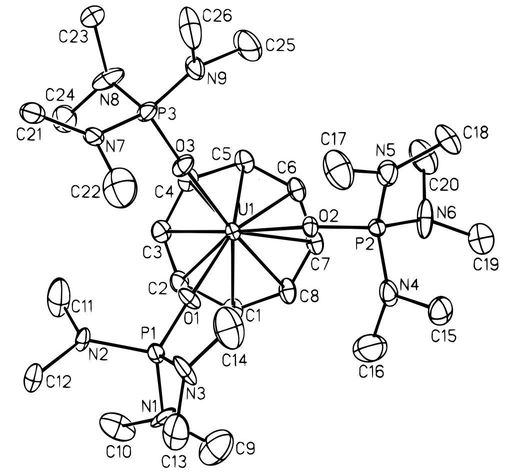

Figure 1. View of the crystal structure of one of the two independent dications $[(COT)U(HMPA)_3]^{2+}$ with thermal ellipsoids drawn at the 30% level.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $[(COT)U(HMPA)_3][BPh_4]_2$·pyridine

U(1)−C(1)	2.692(14)	U(1)−C(2)	2.627(14)
U(1)−C(3)	2.678(14)	U(1)−C(4)	2.628(14)
U(1)−C(5)	2.642(14)	U(1)−C(6)	2.612(14)
U(1)−COT[a]	1.92(2)	U(1)−O(1)	2.227(8)
U(1)−O(2)	2.236(7)	U(1)−O(3)	2.205(9)
COT−U(1)−O(1)	127.2(5)	COT−U(1)−O(2)	127.3(5)
COT−U(1)−O(3)	128.7(6)	O(1)−U(1)−O(2)	87.1(3)
O(2)−U(1)−O(3)	88.2(3)	O(1)−U(1)−O(3)	84.0(3)
U(1)−O(1)−P(1)	169.6(6)	U(1)−O(2)−P(2)	162.9(5)
U(1)−O(3)−P(3)	173.6(6)		

[a] COT is the centroid of the cyclooctatetraene ring.

The results presented here fully illustrate the major utility of borohydride compounds as precursors for the synthesis of cationic species. Noteworthily, protonolysis of $(COT)U(BH_4)_2(THF)$ allowed the successive formation of the mono- and dications **1** and **2**, whereas similar treatment of the amide analogue $(COT)U(NEt_2)_2(THF)$ gave only $[(COT)U(NEt_2)(THF)_2][BPh_4]$, which remains inert toward an excess of the ammonium salt.[4] [(COT)U-

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[12] The Lewis base adducts have not been isolated, and it is possible that in solution these are actually $[(COT)U(BH_4)L_2]^+$ with rapid exchange between free and coordinated L; in the presence of excess HMPA, only one signal corresponding to free and coordinated ligand is observed.

[13] $(COT)U(BH_4)_2(THF)$ was also found to decompose in pyridine-d_5 to give unidentified products (δ −3.50, −15.76, and −47.2) which are different from those issued from **1** (δ −12.98 and −28.46).

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$(BH_4)(THF)_2][BPh_4]$ (**1**) and $[(COT)U(HMPA)_3][BPh_4]_2$ (**2**) are very valuable for the preparation of new derivatives; these will be presented in a forthcoming paper.

Experimental Section

All preparations and reactions were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a glovebox. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately before use. Deuterated solvents were dried over Na−K alloy.

Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany). The ^1H NMR spectra were recorded on a Bruker DPX 200 instrument and were referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). IR spectra were obtained on a Perkin-Elmer 1725X spectrometer. The salt NEt_3HBPh_4 precipitated by mixing NEt_3HCl and $NaBPh_4$ in water; $(COT)U(BH_4)_2(THF)$ was prepared as previously described.[10]

$[(COT)U(BH_4)(THF)_2]][BPh_4]$ (1). A flask was charged with $(COT)U(BH_4)_2(THF)$ (0.364 g, 0.82 mmol) and NEt_3HBPh_4 (0.299 g, 0.71 mmol), and THF (50 mL) was condensed into it under vacuum at −78 °C. After heating at 65 °C for 3 h, the dark brown solution was filtered and evaporated to dryness. The red brown solid was washed with toluene (50 mL) in order to eliminate the excess of $(COT)U(BH_4)_2(THF)$, and **1** was extracted in THF (50 mL); after filtration (to eliminate a white unidentified solid), evaporation, and drying under vacuum, **1** was isolated as a golden brown powder (0.507 mg, 87% based on the ammonium salt). Anal. Calcd for $C_{40}H_{48}B_2O_2U$: C, 58.56; H, 5.90; B, 2.63. Found: C, 58.94; H, 6.07; B, 2.54. ^1H NMR (THF-d_8): δ 221.0 (br q, $w_{1/2} = 270$ Hz, $J = 90$ Hz, 4 H, BH_4), 6.48 (br m, 20 H, BPh_4), −33.64 (s, 8 H, COT); (pyridine-d_5) δ 260.5 (br s, $w_{1/2} = 230$ Hz, 4 H, BH_4), 7.19 (br t, 8 H, *o*-BPh_4), 7.05 (t, $J = 6$ Hz, 8 H, *m*-BPh_4), 6.91 (t, $J = 7$ Hz, 4 H, *p*-BPh_4), 3.51 (br s, 8 H, THF), 1.47 (br s, 8 H, THF), −33.40 (s, 8 H, COT). IR (Nujol): 2462 s, 2182 w, 2108 w cm^{-1}.

$[(COT)U(BH_4)L_3][BPh_4]$ (L = $OPPh_3$ and HMPA). An NMR tube was charged with **1** (ca. 5 mg) in THF-d_8 (0.4 mL), and 3 equiv of L were added. The spectrum of the red-orange solution showed the immediate and quantitative formation of the Lewis base adduct. ^1H NMR (THF-d_8): L = $OPPh_3$, δ 92.1 (br s, $w_{1/2} = 80$ Hz, 4 H, BH_4), 6.94 and 6.51 (br m, 47 H, *m*-$OPPh_3$ and *p*-PPh_3 and BPh_4), 4.79 (br s, 18 H, *o*-PPh_3), −32.77 (s, 8 H, COT); L = HMPA, δ 61.7 (br s, $w_{1/2} = 280$ Hz, 4 H, BH_4), 6.82 (br t, 8 H, *o*-BPh_4), 6.48 (t, $J = 7$ Hz, 8 H, *m*-BPh_4), 6.41 (t, $J = 7$ Hz, 4 H, *p*-BPh_4), 1.82 (s, 54 H, HMPA), −32.09 (s, 8 H, COT).

$[(COT)U(HMPA)_3][BPh_4]_2$ (2). In the glovebox, THF (30 mL) was added to $(COT)U(BH_4)_2(THF)$ (0.272 g, 0.61 mmol) and NEt_3HBPh_4 (0.541 g, 1.28 mmol) in a flask, and HMPA (0.6 mL, 3.45 mmol) was introduced via a syringe. The reaction mixture was stirred for 4 h at 20 °C; evolution of gas was observed, and an orange powder was deposited from the dark red solution. After evaporation and drying under vacuum, the solid was washed with THF (30 mL) and extracted with pyridine (30 mL). The solution was filtered, and the solvent was evaporated off, leaving **2** as a bright orange powder (0.697 g, 75%). Anal. Calcd for $C_{74}H_{102}B_2N_9O_3P_3U$: C, 58.54; H, 6.77; N, 8.30. Found: C, 58.35; H, 6.90; N, 8.48. ^1H NMR (pyridine-d_5): δ 7.80 (br m, 16 H, *o*-BPh_4), 7.09 (t, $J = 7$ Hz, 16 H, *m*-BPh_4), 6.95 (t, $J = 7$ Hz, 8 H, *p*-BPh_4), 0.29 (s, 54 H, HMPA), −32.48 (s, 8 H, COT).

Table 2. Experimental Data for the X-ray Diffraction Studies of $[(COT)U(HMPA)_3][BPh_4]_2$·pyridine

formula	$C_{79}H_{107}B_2N_{10}O_3P_3U$
fw	1597.31
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	32.147(3)
b (Å)	17.805(2)
c (Å)	30.766(1)
β (deg)	117.610(4)
V (Å^3)	15604(2)
Z	8
D(calcd) (g/cm^3)	1.360
μ (cm^{-1})	2.195
cryst size (mm)	0.30 × 0.20 × 0.15
radiation type	Mo Kα
temp (K)	123
θ range, deg	5.0−20.8
no. of reflns collected	56 685
no of reflns merged	15 451
no of reflns observed	7962
observn criterion	$I > 2\sigma(I)$
no of params refined	1329
R^a	0.060
$R_w{}^b$	0.11
goodness of fit	0.965

^{a} $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. ^{b} $R_w = [\sum w(||F_o) - |F_c||)^2/\sum w(|F_o|)^2]^{1/2}$.

X-ray Crystal Structure of $[(COT)U(HMPA)_3][BPh_4]_2$·pyridine. Red-orange crystals were obtained within 1 week upon layering a pyridine solution of **2** with pentane. Diffraction data were collected with a Nonius Kappa-CCD area-detector diffractometer. The crystal-to-detector distance was fixed at 30 cm, and the unit cell was determined from all the reflections measured on 10 frames with Φ rotation steps of 1°. A 180° Φ range was scanned during data recording (90 frames, Φ rotation = 2°, exposure time = 30 s per frame). The data were processed with the HKL package,[20] and the structure was solved by direct methods and subsequent Fourier differences with SHELXS86[21] and refined on F^2 with SHELXTL[22] with anisotropic thermal parameters for all non hydrogen atoms for cations and solvent molecules. H atoms were introduced at calculated positions as riding atoms with an anisotropic displacement parameter equal to 1.2 (CH) or 1.5 (CH_2) times that of the parent atom. Data were corrected for absorption.[23] Crystal data and details of data collection and structure refinements are given in Table 2. Further details are included in the Supporting Information.

The crystal structure of a THF solvate of **2** has also been determined at 123 K; it is isostructural with that of the pyridine solvate: $P2_1/c$, $a = 31.9479(4)$ Å, $b = 17.8007(3)$ Å, $c = 30.6404(4)$ Å, $\beta = 116.867(1)$°.

Supporting Information Available: Tables giving data collection and refinement details, atomic coordinates, thermal parameters, and bond lengths and bond angles of the crystallographically characterized complex. This material is available free of charge via the Internet at http://pubs.acs.org.

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