Highly Reactive Uranium(III) Polypyrrolide Complexes: Intramolecular C−H Bond Activation, Ligand Isomerization, and Solvent Deoxygenation and Fragmentation

Ilia Korobkov, Sandro Gambarotta,* and Glenn P. A. Yap

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

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The reaction of $UX_3(THF)_4$ (X = Cl, I) with the tetraanion of $\{[(-CH_2-)_5]_4\text{-calix}[4]$-tetrapyrrole$\}$ gave different compounds depending on the uranium halide, the alkali-metal cation (Li vs K), the stoichiometric ratio of ligand to uranium, and the solvent used. Reaction of the potassium salt of the ligand with uranium iodide in THF and in the ratio 1:1 afforded the dinuclear, tetravalent species $\{[\{[(-CH_2-)_5]_4\text{-calix}[4]\text{tetrapyrrole}\}UK(THF)_3]_2(\mu_2\text{-O})\}\cdot$ 2THF (**1**). The source of the bridging oxygen atom is a THF deoxygenation process. A reaction carried out under identical conditions but with the tetralithium salt of the calix[4]tetrapyrrole afforded instead intractable material unless a stoichiometric ratio of two ligands per uranium was employed. In this event, a new species, the dinuclear tetravalent species $[\{[(-CH_2-)_5]_4\text{-calix}[4]\text{pyrrole}\}ULi(THF)_2]_2\cdot$hexane (**2**), was isolated. In this complex, the β-C atom of one of the pyrrole rings of the macrocycle was deprotonated and metalated by uranium of a second identical unit, thus assembling the dinuclear structure. The reaction is not accompanied by loss of hydrogen gas, while the excess ligand is acting as a Brønsted base. An identical reaction carried out by using uranium trichloride afforded instead the mononuclear tetravalent species $(\{[(-CH_2-)_5]_4\text{-calix}[4]\text{tetrapyrrole}\}ULi(OC_2H_5)(THF)_2)$ (**3**). In this compound one pyrrole ring was isomerized by shifting the attachment of the chain from the α- to the β-position. The $LiOCH_2CH_3$ unit was generated by another pathway of THF fragmentation. Finally, a reaction carried out in dimethoxyethane with the purpose of preventing oxidative attack to the metal center, afforded the mononuclear trivalent complex $[\{[(-CH_2-)_5]_4\text{-calix}[4]\text{tetrapyrrole}\}U(DME)][K(DME)]$ (**4**).

Introduction

A very high level of reactivity is a prerequisite for a metal complex to interact with an exceedingly inert molecule such as dinitrogen. Thus, the recent discoveries by Scott of a unique case of labile dinitrogen fixation performed by a trivalent uranium complex[1] and by Cummins of a stable heterodimetallic dinitrogen complex involving uranium[2] have opened new exciting perspectives in actinide chemistry and reiterated the great potential offered by their trivalent complexes for unprecedented transformations.

In contrast to the case of trivalent thorium, which is rare,[3] trivalent uranium is readily accessible[1,2,4] due to the availability in large scale of salts such as $UI_3(THF)_4$[5] and "UCl_3"[6] which may conveniently be used as starting

materials. However, delineating the chemical reactivity of trivalent uranium is rather difficult, given that the complexes reported to date are mainly cyclopentadienyl derivatives.[7] Information about trivalent uranium species of different ligand systems remains fragmentary and limited to a series of diversified derivatives.[1,2,8]

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Among the nitrogen donor ligands apparently capable of enhancing the reactivity of trivalent uranium,[1,2] di- and tetrapyrrolide polyanions seem also particularly promising. Their employment in lanthanide chemistry has been proven able to stabilize low-valent species[9] and to promote a variety of molecular activation processes,[10] including multielectron dinitrogen reduction[11] or labile coordination,[12] ethylene reversible fixation,[13] formation of dinuclear species with unusually short M−M contacts,[9a,14] and stabilization of exotic moieties.[10] A distinctive feature of complexes with this ligand system is an enhanced sensitivity of the reactivity to relatively minor features such as the nature of the alkali-metal cation retained in the structure or a minor modification of ligand substituents.[12,13] In addition, the pyrrolide ring may coordinate to the metal in a π-bonding fashion, thus preserving the salient characteristics of the Cp ligands. Also, the presence of the deprotonated N atom makes possible additional σ-bonding interactions which enhance the possibility of forming cluster structures.[9,11b,15] This characteristic may be particularly desirable in view of promoting molecular activation processes via cooperative attack of several reactive centers to the same substrate.[11]

In this first study of a series aimed at delineating the chemical behavior of trivalent uranium with a pyrrolide-based ligand system, we describe the results obtained from the reaction of trivalent uranium precursors with a macrocyclic tetrapyrrole tetraanion.

Experimental Section

All operations were performed under an inert atmosphere of a nitrogen-filled drybox or by using standard Schlenk-type glassware in combination with a nitrogen−vacuum line.

$UI_3(DME)_2$,[4] $UI_3(THF)_4$,[4] {[(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrole,[16] {[(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrolide}[K(THF)]$_4$, and {[(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrolide}[Li(THF)]$_4$ were prepared according to literature procedures.[13] $UCl_4(THF)_3$ was prepared by recrystallizing freshly prepared UCl_4[17] from THF. Solutions of "UCl_3" were prepared according to a literature procedure.[6] THF, toluene, and hexane were dried by passing through aluminum oxide columns and degassed in vacuo. DME was dried over $LiAlH_4$, distilled, and stored under an Ar atmosphere. Infrared spectra were recorded on a BOMEM MB-100 FTIR instrument from Nujol mulls on KBr pellets prepared inside the drybox. Samples for magnetic susceptibility measurements were carried out at room temperature using a Gouy balance (Johnson Matthey). Magnetic moments were calculated by following standard methods, and corrections for underlying diamagnetism were applied to the data.[18,19] Elemental analyses were carried out by using a Perkin-Elmer Series II CHN/O 2400 analyzer.

Preparation of {[{[(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrole}-UK(THF)$_3$]$_2$(μ$_2$-O)}·2THF (1). A solution of $UI_3(THF)_4$ (7.3 g, 8.1 mmol) in THF (100 mL) was treated with [(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrole]K$_4$(THF)$_2$ (7.2 g, 8.1 mmol) suspended in 50 mL of the same solvent. The initial dark blue color of the reaction mixture turned immediately dark green and finally dark brown. The resulting solution was stirred for 6 h, the solvent evaporated in vacuo, and the resulting solid material redissolved in toluene. A small amount of light-colored insoluble material was separated by centrifugation. The toluene solvent was removed in vacuo and the residue redissolved in THF and layered with hexane. Dark-orange prisms of **1** separated upon standing at room temperature for a few days (4.1 g, 1.8 mmol, 45%). IR (Nujol mull, cm^{-1}): ν 3088 (w), 3070 (w), 2671 (w), 1376 (s), 1344 (w), 1300 (w), 1275 (w), 1246 (m), 1182 (w), 1113 (w), 1050 (s), 902 (m), 878 (m), 795 (m), 740 (s), 628 (m), 550 (m). Anal. Calcd (found) for $C_{112}H_{160}N_8O_9U_2K_2$: C, 58.06 (58.95); H, 6.96 (7.13); N, 4.84 (4.85). $\mu_{eff} = 5.17$ μ_B.

Preparation of [μ$_2$-{[(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrole}-ULi(THF)$_2$]$_2$·hexane (2). A mixture of $UI_3(THF)_4$ (1.5 g, 1.6 mmol) and {[(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrole}{Li(THF)]$_4$ (1.9 g, 3.1 mmol) was dissolved in THF (50 mL). The initial dark blue color immediately turned dark brown. Stirring was continued for 6 h at room temperature. The solvent was evaporated in vacuo and the resulting dry solid redissolved in toluene. The insoluble residue was separated by centrifugation, and the solvent was evaporated in vacuo. The solid residue was redissolved in THF and layered with hexane, yielding dark brown orange crystals of **2** (0.6 g, 0.3 mmol, 38%). Anal. Calcd (found) for $C_{99}H_{134}N_8O_4U_2Li_2$: C, 59.75 (59.85); H, 6.79 (6.34); N, 5.63 (6.53). IR (Nujol mull, cm^{-1}): ν 3082 (m), 2657 (m), 1587 (w), 1462 (s), 1341 (m), 1293 (m), 1273 (s), 1246 (s), 1230 (m), 1203 (w), 1179 (w), 1138 (w), 1125 (w), 1036 (s), 991 (m), 970 (s), 875 (s, br), 830 (s), 795 (s, br), 738 (s), 702 (m), 618 (s, br), 554 (m). $\mu_{eff} = 3.60\mu_B$.

Preparation of {[(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrole*}-ULi(OC$_2$H$_5$)(THF)$_2$ (3). A freshly prepared dark green solution of potassium naphthalide prepared from potassium (0.3 g, 7.9 mmol) and naphthalene (1.0 g, 7.9 mmol) in THF (30 mL) was added to a solution of $UCl_4(THF)_3$ (6.8 g, 7.9 mmol) in THF (50 mL). The color of the solution immediately turned

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Table 1. Crystal Data and Structure Analysis Results

	1	**2**	**3**	**4**
formula	$C_{112}H_{160}K_2N_8O_9U_2$	$C_{99}H_{134}Li_2N_8O_4U_2$	$C_{50}H_{69}LiN_4O_3U$	$C_{48}H_{68}KN_4O_4U$
fw	2316.74	1990.15	1019.10	1042.22
space group	tetragonal, $P\bar{4}$	monoclinic, $P2_1/c$	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
a (Å)	19.437(1)	13.303(3)	20.751(3)	11.468(2)
b (Å)	19.437(1)	16.153(4)	10.861(1)	12.248(2)
c (Å)	14.112(1)	21.786(5)	20.648(3)	17.568(3)
α (deg)	90	90	90	82.784(3)
β (deg)	90	102.773(4)	94.989(2)	78.546(3)
γ (deg)	90	90	90	66.624(3)
V (Å^3)	5331.3(8)	4565(2)	4636(1)	2217.1(7)
Z	2	2	4	2
radiation (Kα, Å)	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	238(2)	231(2)	203(2	293(2)
D_{calcd} (g cm^{-3})	1.443	1.442	1.459	1.560
μ_{calcd} (cm^{-1})	3.171	3.597	3.546	3.803
R1, wR2	0.0288, 0.0693	0.0582, 0.1247	0.0453, 0.0860	0.0755, 0.1654
GOF	1.022	1.040	1.094	1.014

dark purple. The reaction mixture was stirred 12 h at room temperature and then treated with $\{[(-CH_2-)_5]_4$-calix[4]-tetrapyrrole][Li(THF)]$_4$ (9.2 g, 15.0 mmol) in 50 mL of the same solvent. The color instantly changed from dark purple to dark brown, and stirring was continued at room temperature for 6 h. The solvent was evaporated in vacuo and the solid residue redissolved in diethyl ether (100 mL). A small amount of light-colored insoluble material was eliminated by centrifugation, and the dark brown-orange solution was concentrated to small volume. Dark orange prisms of **3** separated upon standing for 2 days at room temperature (2.7 g, 2.6 mmol, 34%). Anal. Calcd (found) for $C_{50}H_{69}N_4O_3ULi$: C, 58.93 (58.87); H, 6.82(6.64); N, 5.50 (5.44). IR (Nujol mull, cm^{-1}): ν 1377 (s), 1365 (s), 1343 (m), 1290 (w), 1263 (m), 1239 (m), 1208 (w), 1179 (w), 1166 (w), 1152 (w), 1123(m), 1095 (m), 1046 (s, br), 990 (m), 981 (m), 959 (s), 893 (s), 873 (s), 831 (m, br), 807 (s), 782 (s), 751 (s), 740 (s), 702 (w), 678 (m), 658 (m), 578 (w). $\mu_{eff} = 2.58$ μ_B.

Preparation of [{[(−CH₂−)₅]₄-calix[4]tetrapyrrole}UK-(DME)₂] (4). A mixture of UI$_3$(DME)$_2$ (1.2 g, 1.4 mmol) and $\{[(-CH_2-)_5]_4$-calix[4]tetrapyrrole$\}$K$_4$(DME)$_2$ (1.6 g, 1.4 mmol) were dissolved in DME (80 mL). The resulting dark green mixture was stirred for 6 h at room temperature. The light-colored insoluble material was separated from the reaction mixture by centrifugation and the resulting solution concentrated to about 30 mL. Dark bluish green crystals separated upon standing for 2 days at −37 °C (1.2 g, 1.15 mmol, 82%). Anal. Calcd (found) for $C_{48}H_{68}N_4O_4UK$: C, 55.32 (55.15); H, 6.58 (6.49); N, 5.38 (5.27). IR (Nujol mull, cm^{-1}): ν 1342 (m), 1294 (w), 1262 (s), 1244 (m), 1191 (m), 1108 (s), 1090 (s), 1069 (s), 1049 (s), 969 (w), 897 (w), 874 (m), 862 (m), 805 (s), 785 (s), 744 (s), 669 (w). $\mu_{eff} = 3.42$ μ_B.

X-ray Crystallography: Structural Determination of 1−4. Suitable crystals were selected, mounted on thin glass fibers using viscous oil, and cooled to the data collection temperature. Despite several attempts at recrystallization, compound **4** consistently yielded small, multiple crystals and the reported structure represents the best effort. Data were collected on a Bruker AX SMART 1K CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[20]

No symmetry higher than triclinic was evident from the diffraction data of **4**. Systematic absences in the diffraction data and unit-cell parameters were consistent for space groups $P4$, $P\bar{4}$, $P4/m$, $P422$, $P4mm$, $P\bar{4}2m$, $P\bar{4}m2$, and $P4/mmm$ for **1** and, uniquely, $P2_1/c$ for **2** and **3**. Solution in the centric space group for **4** yielded chemically reasonable and computationally stable results of refinement. Despite a thorough exploration of the possible space group options, including translation of the atomic coordinates of the stable structure in the various space group options, for **1** only the solution in $P\bar{4}$ yielded

chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2.

The compound molecules of **2** and **1** are located at an inversion center and on a 2-fold axis, respectively. A molecule of THF solvent was found cocrystallized in the asymmetric unit of **1**. To conserve a favorable data/parameter ratio, the carbon atoms were refined isotropically in **4**. Attempts to model three significant peaks in the penultimate difference electron density map of **2**, located away from the compound molecule, as a chemically reasonable solvent molecule failed. These apparent solvent atoms were given arbitrary carbon atom identities at half-occupancy and refined isotropically. All other non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHEXTL 5.10 program library,[21] Crystal data and structure analysis results are given in Table 1.

Results and Discussion

The result of the reaction between UX$_3$(THF)$_4$ (X = Cl, I) and $[\{[(-CH_2-)_5]_4$-calix[4]tetrapyrrole$\}$M(THF)]$_4$ (M = Li, K) was dramatically affected by the nature of both the halogen and the alkali-metal counterion as well as by the stoichiometric ratio. Reaction with the trivalent uranium iodide salt afforded the paramagnetic and dinuclear complex $(\{[(-CH_2-)_5]_4$-calix[4]tetrapyrrole$\}$U-[K(THF)$_3$])$(\mu$-O)·2THF (**1**), which was isolated as paramagnetic orange prisms in moderate yield (Scheme 1).

The molecular connectivity was revealed by an X-ray crystal structure, showing a dimeric complex with two identical $(\{[(-CH_2-)_5]_4$-calix[4]tetrapyrrole$\}$U[K(THF)$_3$]) units bridged by one oxygen atom (U1−O1 = 2.0861(5) Å) and forming a U−O−U linear array (U(1)−O(1)−U(1a) = 171.3(2)°) (Figure 1and Table 2). Within each mononuclear moiety, the ligand adopts the characteristic σ/π bonding mode. Two of the four pyrrole rings are π-bonded to uranium (U1−C11 = 2.743(5) Å, U1−C12 = 2.877(5) Å, U1−C13 = 2.862(5) Å, U1−C14 = 2.749(5) Å, U1−N2 = 2.635(4) Å, U1−C31 = 2.748(5) Å, U1−C32 = 2.823(5) Å, U1−C33 = 2.830(5) Å, U1−C34 = 2.768(4) Å, U1−N4 = 2.668(5) Å) in a slightly bent uranocene type of geometry. The other two rings have the nitrogen atom σ-bonded to the metal

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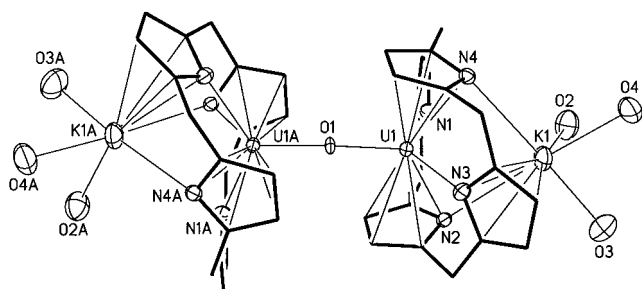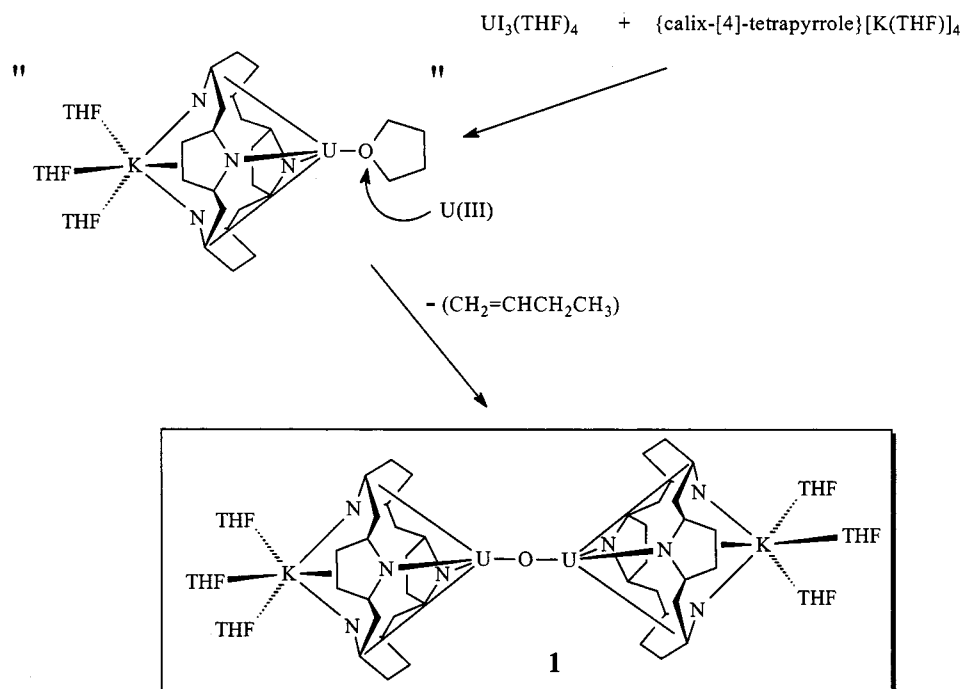(21) Sheldrick, G. M. Bruker AXS: Madison, WI, 1997.

Scheme 1

$$UI_3(THF)_4 \quad + \quad \{calix\text{-}[4]\text{-tetrapyrrole}\}[K(THF)]_4$$

Figure 1. Partial thermal ellipsoid plot of **1**. Thermal ellipsoids are drawn at the 30% probability level. Cyclohexyl rings wearere omitted for clarity.

center (U1−N1 = 2.437(5) Å, U1−N3 = 2.471(4) Å). As a result, the overall geometry around each uranium atom is slightly distorted trigonal bipyramidal. Two centroids of the two π-bonded pyrrolyl rings occupy the axial positions (centroid−U−centroid = 171.2(3)°), while the equatorial plane is defined by two N atoms of the two σ-bonded rings and by the bridging oxygen atom (N1−U1−O1 = 112.5(2)°, N1−U1−N3 = 128.6(2)°). Each ({[(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrole}U) unit is also connected to a K(THF)$_3$ unit by using three of the four pyrrolyl rings. One of these three rings, which is in turn σ-bonded to uranium, is π-bonded to the potassium atom (K1−C21 = 3.349(7) Å, K1−C22 = 3.562(7) Å, K1−C23 = 3.511(6) Å, K1−C24 = 3.265(7) Å, K1−N3 = 3.143(5) Å). Conversely, the two adjacent rings which are π-bonded to uranium have the N-donor atoms oriented toward potassium, forming σ-bonds (K1−N2 = 3.348(5) Å, K1−N4 = 3.275(5) Å). Thus, the coordination geometry around potassium is pseudooctahedral (O4−K1−O3 = 84.4(2)°, O4−K1−N4 = 95.20(17)°, O4−K1−O2 = 81.9-(2)°, O4−K1−centroid = 106.2(2)°), considering one coordination site to be occupied by the centroid of the π-bonded pyrrolide ring (K1-centroid = 3.156(5) Å) and the other five occupied by the three THF oxygen atoms (K1−O2 = 2.839(7) Å, K1−O3 = 2.867(7) Å, K1−O4 =

2.739(7) Å) and two nitrogen atoms of the two σ-bonded pyrrolyl rings (N4−K1−N2 = 86.69(12)°).

Complex **1** contains two tetravalent uranium atoms. Its formation, which implies loss of one electron by each of the two metal centers, is the result of the cooperative attack of two transient trivalent uranium moieties on the oxygen atom of the same THF molecule (Scheme 1). The two-electron degradation of THF results in oxygen atom abstraction and formation of several possible organic residues (1-butene, 2-butene, ethylene, or a combination of them). In the present case, no products other than 1-butene were detected in the GC of the reaction mixture of a dedicated experiment.

A reaction carried out under very similar reaction conditions but using the calix[4]tetrapyrrole tetra*lithium* salt rather than the tetrapotassium derivative only afforded intractable materials. However, upon using excess ligand, a new paramagnetic compound was isolated in crystalline form and acceptable yield (Scheme 2). Formulation of the complex as the dinuclear [{[(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrole}ULi(THF)$_2$]$_2$·hexane (**2**) was elucidated by an X-ray crystal structure.

The complex is a symmetry-generated dimer and is formed by two identical {[(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrole}U}{[Li(THF)$_2$]} units. Within each unit, one of the two β-carbon atoms of one of the four pyrrole rings has been deprotonated and is σ-bonded to the uranium atom of a second identical unit (U1−C2A = 2.436(17) Å) (Figure 2 and Table 2). The macrocycle displays the usual geometry with two of the four pyrrole rings π-bonded to U (U1−C1 = 2.687(15) Å, U1−C2 = 2.826-(16) Å, U1−C3 = 2.830(17) Å, U1−C4 = 2.729(15) Å, U1−N1 = 2.641(13) Å, U1−C21 = 2.717(15) Å, U1−C22 = 2.838(17) Å, U1−C23 = 2.840(16) Å, U1−C24 = 2.735-(17) Å, U1−N3 = 2.651(15) Å, centroid−U−centroid = 176.6(5)°) and the other two forming U−N σ-bonds (U1−N2 = 2.401(13) Å, U1−N4 = 2.409(13) Å). Even in this case, the coordination geometry around uranium can be described as trigonal bipyramidal with the

Table 2. Selected Bond Distances and Angles

Compound 1

U1−O1	2.0861(5)	U1−C13	2.862(5)	U1−C34	2.768(4)	K1−C23	3.511(6)
U1−N1	2.437(5)	U1−C14	2.749(5)	K1−N2	3.348(5)	K1−C24	3.265(7)
U1−N3	2.471(4)	U1−N4	2.668(5)	K1−N4	3.275(5)	K1−O2	2.839(7)
U1−N2	2.635(4)	U1−C31	2.748(5)	K1−N3	3.143(5)	K1−O3	2.867(7)
U1−C11	2.743(5)	U1−C32	2.823(5)	K1−C21	3.349(7)	K1−O4	2.739(7)
U1−C12	2.877(5)	U1−C33	2.830(5)	K1−C22	3.562(7)		
U1−O1−U1A	171.3(2)	N1−U1−N3	128.6(2)	O4−K1−O3	84.4(2)	O4−K1−N4	95.2(2)
N2−U1−N4	118.0(2)	N3−U1−N4	76.4(2)	O4−K1−O2	81.9(2)	N4−K1−N2	86.7(1)
N1−U1−O1	112.5(2)						

Compound 2

U1−C2A	2.44(2)	U1−C1	2.68(2)	U1−N3	2.65(1)	U1−C24	2.73(2)
U1−N2	2.40(1)	U1−C2	2.82(2)	U1−C21	2.71(2)	Li−O1	1.96(3)
U1−N4	2.41(1)	U1−C3	2.83(2)	U1−C22	2.83(2)	Li−O2	1.97(3)
U1−N1	2.64(1)	U1−C4	2.72(2)	U1−C23	2.84(2)	Li−N1	2.05(3)
N2−U1−N4	130.9(4)	N4−U1−N1	73.7(4)	O2−Li−N1	119.4(2)	O2−Li−O1	96.8(2)
N2−U1−C2A	122.9(5)	N1−U1−C2A	117.6(5)	N1−U1−N3	122.3(4)	O1−Li−N1	130.2(2)
N2−U1−N1	82.3(4)	N2−U1−N3	76.1(4)				

Compound 3

U−O1	2.172(6)	U−C2	2.844(9)	U−C22	2.780(9)	Li−O3	1.87(2)
U−N2	2.389(8)	U−C3	2.867(10)	U−C23	2.802(9)	Li−N1	2.037(19)
U−N4	2.430(8)	U−C4	2.775(10)	U−C24	2.721(10)	O1−C41	1.449(12)
U−N1	2.685(8)	U−N3	2.620(8)	Li−O1	2.04(2)	C41−C42	1.505(16)
U−C1	2.689(9)	U−C21	2.727(9)	Li−O2	1.98(2)		
O1−U−N2	106.0(3)	N2−U−N1	80.5(3)	O2−Li−O1	114.9(10)	O3−Li−N1	128.4(11)
O1−U−N4	117.3(3)	N3−U−N1	159.9(3)	O2−Li−N1	104.8(9)	O3−Li−U	117.9(8)
O1−U−N3	121.5(2)	N4−U−N3	79.7(3	O2−Li−U	131.9(9)	Li−N1−U	90.5(6)
O1−U−N1	69.7(2)	N4−U−N1	111.1(3)	O3−Li−O2	109.1(9)	Li−O1−U	106.9(9)
N2−U−N3	80.3(3)	O1−Li−N1	87.1(8)	O3−Li−O1	111.3(9)	O1−C41−C42	110.1(9)
N2−U−N4	136.6(3)	O1−Li−U	37.9(4)				

Compound 4

U−N3	2.526(15)	U−C12	2.867(18)	U−C33	2.874(17)	K−N1	3.370(16)
U−N1	2.525(14)	U−C13	2.944(16)	U−C34	2.808(16)	K−N2	3.188(17)
U−O2	2.627(12)	U−C14	2.829(16)	K−O3	2.724(15)	K−C21	3.150(19)
U−O1	2.688(13)	U−N4	2.733(14)	K−O4	2.713(14)	K−C22	3.209(18)
U−N2	2.736(15)	U−C31	2.818(18)	K−N3	3.062(15)	K−C23	3.157(19)
U−C11	2.805(17)	U−C32	2.876(18)	K−N4	2.961(16)	K−C24	3.067(18)
N3−U−N1	123.2(5)	O1−U−N2	115.1(5)	O4−K−N3	126.4(4)	N4−K−N1	60.7(4)
N3−U−O2	95.5(4)	N3−U−N4	75.0(5)	O3−K−N3	126.6(5)	N3−K−N1	87.2(4)
N1−U−O2	141.3(4)	N1−U−N4	75.4(4)	N4−K−N3	64.3(4)	N2−K−N1	58.0(4)
N3−U−O1	154.9(4)	O2−U−N4	120.1(4)	O3−K−N2	108.0(4)	U−N1−K	71.9(3)
N1−U−O1	81.9(4)	O1−U−N4	116.5(5)	N4−K−N2	96.5(4)	U−N2−K	72.6(3)
O2−U−O1	59.3(4)	N2−U−N4	114.2(5)	N3−K−N2	61.9(4)	U−N3−K	77.6(4)
N3−U−N2	75.3(5)	O4−K−O3	62.6(4)	O4−K−N1	124.8(4)	U−N4−K	76.4(4)
N1−U−N2	74.4(4)	O4−K−N4	93.1(4)	O3−K−N1	134.7(5)	O4−K−N2	169.7(4)
O2−U−N2	120.2(4)	O3−K−N4	155.5(5)				

Scheme 2

UI$_3$(THF)$_4$ +   2 {calix-[4]-tetrapyrrole}[Li(THF)]$_4$

2
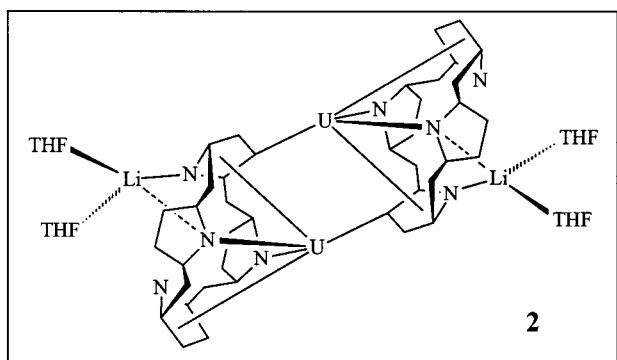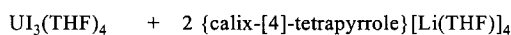
centroids of the two π-bonded rings defining the axis (U1−centroid = 2.056(17) Å and 2.491(17) Å, respectively). The N atom of the two σ-bonded rings and the metalated C atom define the equatorial plane (U1−N2 = 2.401(13) Å, U1−N4 = 2.409(12) Å, N2−U1−N4 = 130.9(4)°, N2−U1−C2A = 122.9(5)°, N4−U1−C2A = 106.2(5)°). Two lithium cations placed at opposite ends of the molecule are each σ-bonded to the N atom of the C-metalated pyrrole ring (Li−N1 = 2.05(3) Å), which is in turn also π-bonded to a second uranium atom. Two molecules of THF complete the coordination geometry of each trigonal-planar lithium (O1−Li−O2 = 96.8(15)°, O1−Li−N1 = 130.2(13)°).

The connectivity of complex **2** as displayed by the crystal structure, and the absence of IR bands attributable to the possible presence of N−H groups arising from pyrrole protonation, clearly attribute the oxidation state +4 to each uranium atom. The formation of the tetravalent **2** (containing a U−C σ-bond) starting from the trivalent UI$_3$(THF)$_4$ is a redox process. The fact that a hydrogen atom was removed from a ring carbon atom indicates that the reaction was initiated by activation of a pyrrole β-(C−H) bond. However, not even traces of hydrogen gas, which should be the partner product of
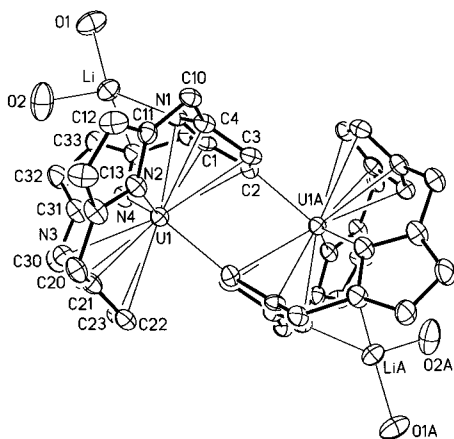
Figure 2. Thermal ellipsoid plot of **2**. Thermal ellipsoids are drawn at the 30% probability level. Bond distances are in angstroms and angles in degrees. Cyclohexyl rings are omitted for clarity.

Figure 3. Thermal ellipsoid plot of **3**. Thermal ellipsoids are drawn at the 30% probability level.

Scheme 3

$$UCl_3(THF)n \quad + \quad 2 \{calix-[4]-tetrapyrrole\}[Li(THF)]_4$$

− ethylene

3

the C−H activation process, could be detected in the reaction mixture. This, in addition to the fact that *excess ligand is necessary* for the formation of **2**, suggests that the deprotonation of the coordinated pyrrolyl ring by a second equivalent of tetralithium salt is a crucial step in the reaction. Accordingly, an IR spectrum of the solid residue obtained from evaporating the reaction mother liquor, which was carefully maintained under an inert atmosphere, clearly showed the presence of a sharp band at 3471 cm^{-1} attributable to N−H stretching. However, the formation of **2** cannot be solely the result of a simple acid−base process, since it requires a one-electron oxidation of each of the two uranium centers. Although the yield of the isolated product is lower than 50%, we have found no evidence for the formation of other uranium complexes in the reaction mixture and the byproducts of the oxidation remain unfortunately undefined.

A possible hint to understand the redox process is offered by the behavior of an identical reaction carried out with trivalent uranium *chloride* rather then the *iodide*. Similar to what is found above, the reaction of in situ generated "UCl$_3$" with 1 equiv of ({[(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrole}[Li(THF)]$_4$ gave only intractable material. Conversely, when the reaction was carried out with excess ligand, the new crystalline material ({[(−CH$_2$−)$_5$]$_4$-calix[4]tetrapyrrole*}ULi(OC$_2$H$_5$)-(THF)$_2$) (**3**; * = isomerized ligand (N-confused)) was isolated in 35% yield (Scheme 3).

The molecular connectivity, as clarified by an X-ray crystal structure, indicated a mononuclear compound where the ligand has undergone ring isomerization by shifting the attachment of the chain of one of the four pyrrole rings from the α- to the β-position (Figure 3 and Table 2). Nevertheless, the ligand adopted the usual conformation with the uranium center. The isomerized pyrrolyl ring, as well as the other ring on the opposite side of the macrocycle, are both π-bonded to the uranium center (U−N1 = 2.685(8) Å, U−C1 = 2.689(9) Å, U−C2 = 2.844(9) Å, U−C3 = 2.876(9) Å, U−C4 = 2.775(9) Å, U−N3 = 2.620(8) Å, U−C21 = 2.727(10) Å, U−C22 = 2.7780(10) Å, U−C23 = 2.802(10) Å, U−C24 = 2.721-(10) Å) with the two centroids forming an almost linear array with the metal center (centroid−U−centroid = 172.7(3)°). The nitrogen atoms of the other two rings

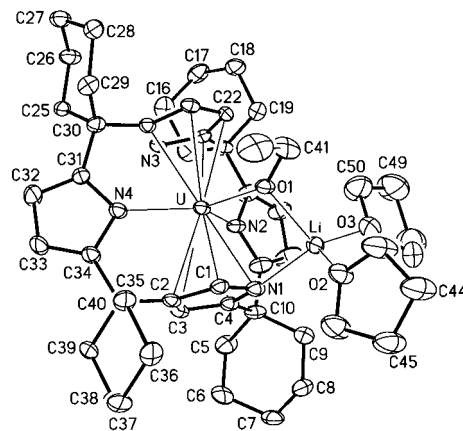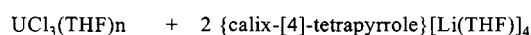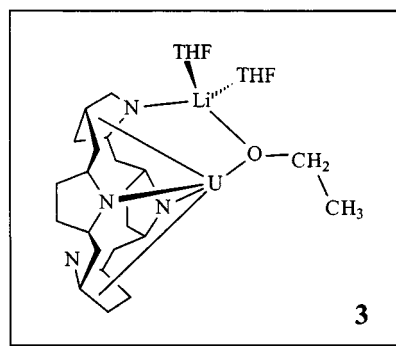are σ-bonded (U−N2 = 2.389(8) Å, U−N4 = 2.430(8) Å) and, together with the oxygen atom of one ethoxide group (U−O1 = 2.172(6) Å, U−O1−C41 = 107.4(2)°), define the equatorial plane of the ideal trigonal bipyramid centered on uranium (O1−U−N4 = 117.3(3)°, N2−U−N4 = 136.6(3)°). One lithium atom, solvated by two molecules of THF, is connected to the ethoxide oxygen atom (Li−O1 = 2.04(2) Å) and to the N atom of the isomerized pyrrolyl ring (Li−N1 = 2.037(19) Å).

The connectivity of **3** clearly indicates that the uranium atom is present in the tetravalent state. The so-called "N-confused"[22] or isomerized calix[4]tetrapyrroles are known in the chemistry of polypyrrole and porphyrins and play an important role in the chemistry and biochemistry of these systems.[23] Also known is the ability of this ligand system to engage into a variety of reorganization.[24] In addition, variable amounts of the N-confused isomers are always present as byproducts of the preparation of calix[4]tetrapyrroles and their

(22) (a) Depraetere, S.; Smet, M.; Dehaen, W. *Angew. Chem., Int. Ed.* **1999**, *38*, 3359 and references therein. (b) Gale, P. A.; Sessler, J. L. *J. Chem. Soc., Chem. Commun.* **1998**, 1 and references therein.

(23) (a) Sessler, J. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1348. (b) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767. (c) Chmielewski, P. J.; Latos-Grazynski, L.; Rachlewicz, K.; Glowiak, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779. (d) Liu, B. Y.; Bruckner, C.; Dolphin, D. *J. J. Chem. Soc., Chem. Commun.* **1996**, 2141.

(24) (a) Campazzi, E.; Solari, E.; Scoppellitti, R.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1999**, 1617. (b) Campazzi, E.; Solari, E.; Scoppellitti, R.; Floriani, C. *Inorg. Chem.* **1999**, *38*, 6240.

Scheme 4
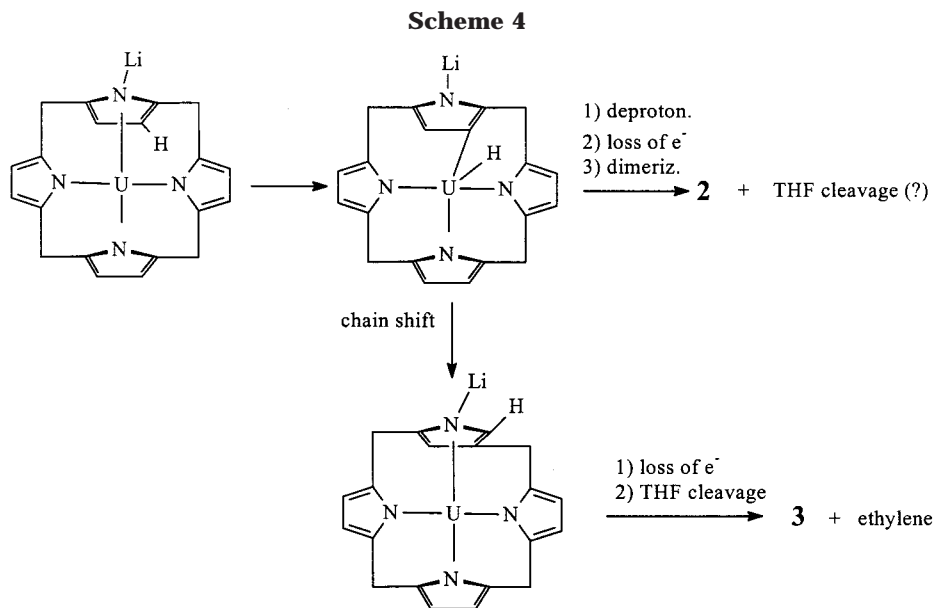
formation was rationalized in a recent publication.[22a] However, in the case of **3**, the ligand used for the preparation was isomer-free and its ^{13}C NMR spectrum did not show the resonance in the region around 112.8 ppm diagnostic of the N-confused ring.[22a] Also the ^{13}C NMR spectrum of the ligand tetralithium salt, whose crystal structure was recently reported,[10a] did not display any anomaly. Thus, there is no doubt that the ligand reorganization forming the N-confused ring was mediated in this particular case by the uranium center.

There are two main issues arising from the formation of **3**: the ring isomerization and the presence of the ethoxide group. The fact that even in this case excess ligand is necessary for the formation of **3** indicates that, in analogy to the case of **2**, at least one critical step of the reaction involves abstraction of one β-hydrogen from one of the coordinated pyrrolyl rings. It should be reiterated, however, that the simple chain shift *does not require electrons to be added or removed*. Thus, if the reaction is initiated by deprotonation followed by chain shift, *a proton should be returned to the ring* in order for the process to be completed. Thus, the primary role of the excess of the tetranion ligand should be that of a Brønsted basic catalyst. Accordingly, the dried residue did not show in this case the absorption due to N–H moieties in the region at 4500–3200 cm^{-1}.

The second point of interest arises from the genesis of the LiOEt fragment. Its formation is clearly the result of another THF fragmentation process. Different from the ligand isomerization, this process requires electrons. THF cleavage is not unusual in the lanthanide and transition-metal chemistry of this particular ligand system, as it is also reiterated by the formation of **1**. The reaction affords a variety of fragments, including oxo, enolate, and ynolate.[25] The formation of an ethoxide group, although precedented,[26] is more unusual. It
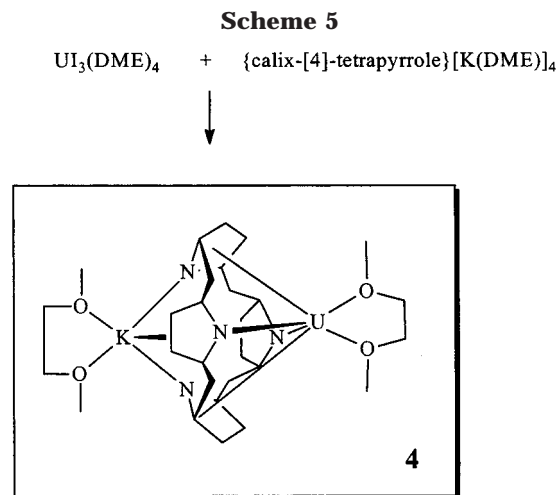
implies the *formal* attack of one hydride (or of one H atom and one electron) upon the β-C atom of THF. While the electron can be provided by the oxidation of the metal center, the H atom was necessarily obtained from another source. The formation of one molecule of ethylene (identified by GC in the case of the formation of **3**) must also accompany this type of fragmentation.

The two-electron deoxygenation of THF, as observed during the formation of **1**, is in striking contrast with the pyrrole ring metalation, as observed in complex **2**, and the ligand isomerization occurring in **3**. The reaction mechanism is obviously complex, given the critical role played by the nature of both the alkali-metal cation and the uranium halide. Nevertheless, the formation of **2** and **3** may be conveniently rationalized in terms of different decomposition pathways of the same intermediate (Scheme 4). The involvement of the ring β-carbon in the formation of both **2** and **3** suggests that an initially formed highly reactive U(III) species performs oxidative attack upon the β-CH bond of one of the two π-bonded pyrrolyl rings. The species generated by this process may form the tetravalent **2** via loss of one proton and of one electron (THF cleavage is a realistic possibility), or alternatively shift the chain and give **3** via reduction of THF and incorporation of the LiOEt fragment. Accordingly, ethylene is the partner product of this process.

The variety of processes leading to the three compounds described so far can be ascribed solely to the different nature of the alkali-metal cation (potassium vs lithium) and of the halogen of the uranium salt starting material. In fact, the reaction conditions and starting materials employed were identical, and reagents were from the same batches of preparation. The ability of the alkali-metal cation to determine the reaction pathway so dramatically seems surprising at first glance. However, it is certainly a main feature of this particular ligand system. In the lanthanide chemistry of the calix[4]tetrapyrrole system, both dinitrogen activation[12] and ethylene coordination[13] are indeed

(25) (a) Aspinall, H. C.; Tillotson, M. R. *Inorg. Chem.* **1996**, *35*, 2163. (b) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291. (c) Jubb, J.; Gambarotta, S. *Inorg. Chem.* **1994**, *33*, 2503. (d) Jubb, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1993**, *115*, 10410. (e) Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **1998**, *17*, 3967. (f) De Angelis, S.; Solari, E.; Floriani, C.; Chiesi-Villa, A. *J. Chem. Soc., Dalton Trans.* **1994**, 2467. (g) Ruppa, K. B.; Gambarotta, S.; Bensimon, C.; Yap, G. P. A. *Inorg. Chim. Acta* **1998**, *280*, 143.

(26) Jubb, J.; Gambarotta, S.; Duchateau, R.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1994**, 2641.

Scheme 5

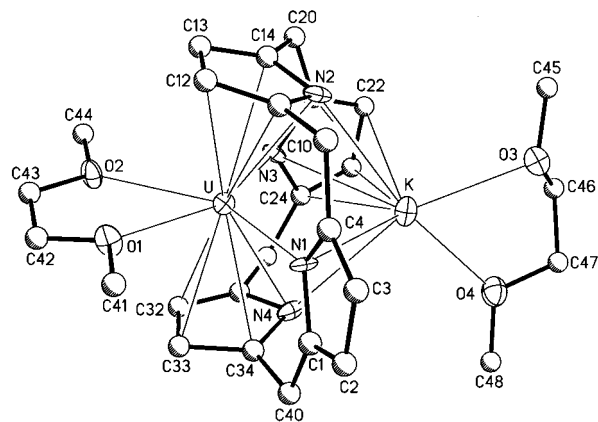$$UI_3(DME)_4 \quad + \quad \{calix\text{-}[4]\text{-}tetrapyrrole\}[K(DME)]_4$$

4

Figure 4. Thermal ellipsoid plot of **4**. Thermal ellipsoids are drawn at the 30% probability level. Cyclohexyl rings are omitted for clarity.

affected by the alkali-metal cation coordinated to the periphery of the macrocycle, by its degree of solvation, and by the particular nature of one counteranion invariably retained in the structure (i.e., chloride vs enolate). On the other hand, the alkali-metal cation is invariably π- or σ-coordinated to the pyrrole rings, which are in turn respectively σ- or π-coordinated to the metal (either U or Ln). Thus, the different nature of the alkali-metal cation and the factors affecting its Lewis acidity may in the end modify the redox potential of the metal as well as determining the type of reactivity and transformation.

The results described so far indicate that U(III) derivatives of the calix[4]tetrapyrrole ligand system are highly reactive species capable of performing molecular activation processes in combination with THF fragmentation. Thus, in an attempt to prevent the complications arising from the involvement of THF in the reactivity of the metal center, we have attempted the same preparation by using a more robust ether, such as dimethoxyethane (DME), as a solvent. The ligand tetrapotassium salt was prepared by an identical procedure in DME and reacted with $UI_3(DME)_2$ starting material (Scheme 5). In this case the reaction under Ar afforded a new dark green crystalline product of the trivalent $[\{[(-CH_2-)_5]_4\text{-}calix[4]tetrapyrrole\}U(DME)]\text{-}[K(DME)]$ (**4**).

Complex **4** is a mononuclear trivalent uranium compound. Its X-ray crystal structure (Figure 4) shows a mononuclear compound with the ligand adopting the usual basket-like conformation. Two pyrrole rings are π-coordinated to the metal (U−C11 = 2.805(17) Å, U−C12 = 2.867(18) Å, U−C13 = 2.944(18) Å, U−C14 = 2.829(16) Å, U−N2 = 2.736(15) Å, U−C31 = 2.818-(18) Å, U−C32 = 2.876(17) Å, U−C33 = 2.874(18) Å, U−C34 = 2.808(18) Å, U−N4 = 2.733(14) Å), and the other two pyrrole rings are σ-bonded (U−N1 = 2.525-(14) Å, U−N3 = 2.526(15) Å). One molecule of DME is also coordinated to uranium (U−O1 = 2.688(12) Å, U−O2 = 2.627(13) Å). The coordination geometry around the metal center can be thus described as pseudooctahedral with the two oxygen atoms of DME

(O1−U−O2 = 59.3(4)°) and the N atoms of the σ-coordinated pyrrole rings defining the equatorial plane (N1−U−N3 = 123.2(5)°, O1−U−N1 = 81.9(4)°). The two centroids of the π-coordinated rings occupy the apical positions, forming a slightly bent uranocene-type structure (centroid−U−centroid = 166.2(5)°). The potassium cation, solvated by one molecule of DME (K−O3 = 2.724(14) Å, K−O4 = 2.713(15) Å), is π-bonded to one of the pyrrole rings (K−C21 = 3.150(18) Å, K−C22 = 3.209(19) Å, K−C23 = 3.157(19) Å, K−C24 = 3.067(18) Å, K−N3 = 3.062(16) Å) and σ-coordinated to the N atoms of the other three rings (K−N1 = 3.370(15) Å, K−N2 = 3.188(15) Å, K−N4 = 2.961(16) Å).

Conclusions

Attempts to prepare trivalent uranium complexes supported by the calix[4]tetrapyrrole ligand system afforded four different products, depending on the reaction conditions, the ligand alkali-metal countercation, the particular uranium halides, and the solvent used for the preparation. At least two compounds, **1** and **3**, clearly arise from different THF cleavage pathways, while it is probable that a similar process occurs even during the formation of **2**. This point is indirectly substantiated by the fact that upon using another solvent (DME) a highly reactive trivalent uranium species (**4**) was isolated with no sign for the formation of other species analogous to **2** or **3**. Despite their very different nature, the formation of **2** and **3** might be the result of different reaction pathways of the same common intermediate.

Supporting Information Available: Tables giving crystallographic data (excluding structure factors) for the structures reported. This material is available free of charge via the Internet at http://pubs.acs.org.