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Cyclometalation and Solvent Deoxygenation during Reduction of a Homoleptic Th(OAr)$_4$ Complex: Serendipitous Formation of a Terminally Bonded Th−OH Function[†]

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Reduction of the homopletic (ArO)$_4$Th (**1**;Ar = 2,6-Ph$_2$Ph) afforded different products, depending on the reaction conditions used in carrying out the reduction. Reduction with K(naphthalene) in DME afforded the doubly ortho-metalated product [(μ-OAr)K$_2$][(μ-2-Ph,6-C$_6$H$_4$)$_2$Th(OAr)](μ-OAr)[K(DME)$_2$] (**2**), while treatment with finely dispersed K in toluene and in the presence of a stoichiometric amount of DME afforded, after treatment with a solution of 18-crown-6 in THF, {[Th(OAr)$_4$(OH)THF][K(18-crown-6)(THF)$_2$]}·C$_7$H$_8$ (**3**). The presence of a terminally bonded OH group in **3** is probably the result of solvent cleavage.

Introduction

The redox chemistry of thorium is almost nonexistent, given that its complexes are exclusively limited to the tetravalent oxidation state,[1] the only exceptions being provided by three trivalent derivatives[2] and ThI$_2$.[3] An intrinsic instability of the low-valent state is most likely at the basis of this paucity of the literature. For example, it is believed that even in ThI$_2$ the actual oxidation state of the metal may be higher than +2. This is most unfortunate, because of the great potential for reactivity studies which can be envisioned in light of the remarkable reactivity of trivalent uranium[4] and other low-valent f-block elements.[5]

An ingenious strategy which has been successfully developed to bypass the synthetic and stability problems encountered with the preparation of low-valent actinides consists of the use of low-valent synthetic equivalents (or low-valent synthons).[6] These are species which, although they contain the metal in higher oxidation states, display reducing behavior, as could be expected for a low-valent compound. By using this approach, a Th(naphthalenide) derivative was recently obtained by reducing a tetravalent calyx[4]tetrapyrrolide complex with K(naphthalene).[7] In this species, the ring coordinated to the Th atom bears a substantial distortion which doubtlessly assigns the tetravalent state to the metal atom. Nevertheless, its reactivity is characterized by the release of the intact arene followed by transformations, including DME solvent fragmentation, as expected for a genuine two-electron reductant.[7] On the other hand, the complex may also perform straight insertion reactions into the Th−C$_{\mathrm{naphth}}$ bond, as would a normal tetravalent organometallic species.[8] On a similar line, reduction of a tetravalent Th complex of the *bidentate* bis(aryloxide) ligand [(2-t-Bu-4-Me-C$_6$H$_2$O)$_2$-CH$_2$]$^{2-}$, also with K(naphthalenide),[9] afforded a complex redox transformation, probably triggered by a bis(naphthalenide) low-valent synthetic equivalent, which resulted in dinitrogen cleavage and partial hydrogenation.

In an attempt to clarify this unusual behavior, we have now attempted reduction of another thorium complex supported by the sterically demanding *monodentate* aryloxide ligand successfully used by Rothwell in Ta chemistry.[10] It was hoped that, by using another aryloxide-based ligand system with larger steric hindrance and lower denticity, the reactivity toward dinitrogen would remain unchanged. On the other hand, the different nature of the ligand might perhaps give possibilities for isolating other species capable of shining light on the complex dinitrogen cleavage/protonation. The reaction, however, took a different pathway and did

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[†] Dedicated to the memory of Prof. Ian P. Rothwell.

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not allow the isolation of a reduced species, nor could reactivity with dinitrogen be obtained. However, the reaction afforded transformations (C−H bond intramolecular activation and solvent deoxygenation) which are clearly the result of the attack on either the ligand system or the solvent.

Experimental Section

All operations were performed under an inert atmosphere by using standard Schlenk type techniques or with the use of a drybox. 2,6-Ph_2PhOH and KH were purchased (Aldrich) and used as received. $ThCl_4(DME)_2$ was prepared according to a modification of the literature procedure.[11] Elemental analyses were obtained with a Perkin-Elmer 2400 CHN analyzer. Data for the X-ray crystal structure determinations were obtained with a Bruker diffractometer equipped with a Smart CCD area detector. NMR spectra were recorded on a Bruker AMX-500 spectrometer.

Preparation of $[2,6\text{-}Ph_2PhO]_4Th$ (1). Solid diphenylphenol (1.010 g, 4.10 mmol) was dissolved in DME (5 mL) and treated with KH (0.164 g, 4.10 mmol). After the gas evolution ceased, the resulting solution was mixed with a suspension of $ThCl_4(DME)_2$ (0.568 g, 1.03 mmol) in DME (7 mL). The reaction mixture was stirred at room temperature for an additional 3 h. The insoluble materials were separated via centrifugation, and the volume of the solution was reduced to about 4 mL by evaporation. The solution was allowed to stand at −37 °C for 3 days, upon which colorless prisms of **1** were formed (1.130 g, 0.93 mmol, 90.3%). Anal. Calcd (found) for $Th(C_{72}H_{52}O_4)$: C, 71.28 (71.05); H, 4.32 (4.27). ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.28, 7.26, 7.25, 7.24 (three overlapping doublets), 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.02, 7.009 (overlapping triplets and doublets). $^{13}C\{^1H\}$ NMR (C_6D_6, 123.72 MHz, 25 °C): δ 119.35 (C−H_{meta} phenoxide), 126.78 ppm (C−H_{para} phenoxide), 128.45, 128.94, and 129.70 (C−H phenyl groups), 159.35, 140.80, and 131.19 (quaternary C).

Preparation of $[(\mu\text{-}OAr)K_2][(\mu\text{-}2\text{-}Ph,6\text{-}C_6H_4)_2Th(OAr)](\mu\text{-}OAr)[K(DME)_2]$ (2). A solution of K(naphthalene) prepared from K (0.042 g, 1.05 mmol) and naphthalene (0.132 g, 1.03 mmol) in DME (5 mL) was combined with a solution of **1** (0.625 g, 0.52 mmol) in the same solvent (4 mL). The color of the solution instantly changed to dark red upon mixing. The reaction mixture was stirred for 6 h at room temperature, during which time full discoloration of the mixture occurred. The insoluble materials were separated by centrifugation, and the resulting colorless solution was concentrated to about one-third of the initial volume. After standing for 3 days at −37 °C colorless prisms of **2** separated (0.408 g, 0.25 mmol, 71.4%). Anal. Calcd (found) for $C_{94}H_{73}O_7ThK_3$: C, 67.85 (67.81); H, 4.42 (4.39). ^1H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 7.49 (ddd, 2H, metalated ring), 7.24 (br d, 16H, phenyl group), 7.22 (ddd, 2H, metalated ring), 7.19 (br s., 4H, metalated ring), 7.12 (d, 10H, H_{meta} phenoxy ring), 6.94 (t, 16H, phenyl ring), 6.87 (t, 5H, H_{ortho} phenoxy ring), 6.84 (tt, 8H, phenyl groups), 3.36 (s, 8H, CH_2 DME), 3.15 (s, 12H, CH_3 DME). $^{13}C\{^1H\}$ NMR (C_6D_6, 123.72 MHz, 25 °C): δ 120.77, 127.65, 128.03, 128.70 (metalated ring), 129.97, 119.68 (phenoxy rings), 128.76, 129.19, 126.96 (phenyl groups), 159.80, 141.19, 138.04, 131.64 (quaternary C), 71.95 (CH_2, DME), 58.40 (CH_3, DME).

Preparation of $\{[Th(OAr)_4(OH)THF][K(18\text{-}crown\text{-}6)(THF)_2]\}\cdot C_7H_8$ (3). Complex **1** (0.635 g, 0.52 mmol) was dissolved in toluene (10 mL) and stirred with finely dispersed K (0.041 g, 1.05 mmol). To start the reaction, 2 drops of DME (~0.04 mL) were added to the reaction mixture. The solution was stirred for 12 h at room temperature. During this period the reaction mixture slowly changed from colorless to bright yellow. When all the potassium disappeared, toluene was evaporated in vacuo and a solution of 18-crown-6 (0.277 g, 1.05 mmol) in THF (5 mL) was added to the dry residue. The resulting bright yellow solution was layered with 10 mL of *n*-heptane. The bright yellow microcrystalline powder which separated after 3 days was filtered, dried, and then recrystallized from hot toluene (3.5 mL), affording bright yellow crystals of **3** (0.834 g, 0.45 mmol, 86.5%). Anal. Calcd (found) for $ThK(C_{103}H_{109}O_{14})$: C, 67.16 (67.05); H, 5.96 (5.89). ^1H NMR (d_8-THF, 500 MHz, 25 °C): δ 7.28 (dd, 16 H, H_{ortho} phenyl groups), 7.17 (dt, 8H, H_{para} phenyl groups), 7.12 (dd, 8H, H_{meta} phenyl groups), 6.99 (8H, H_{meta} phenyl groups), 6.89 (d, 8H, H_{meta} phenoxy groups), 6.49 (t, 4H, H_{para} phenoxy groups), 3.61 (s, 24H, 18-crown-6), 3.67 (m, 12H, THF), 3.11 (1H, OH group), 1.78 (m, 12H, THF). $^{13}C\{^1H\}$ NMR (d_8-THF, 123.72 MHz, 25 °C): δ 131.83 (broad, C_{ortho} phenyl groups), 130.62 (C_{meta} phenoxy groups), 129.93 (C_{meta} phenyl groups), 127.93 (C_{para} phenyl groups), 115.2 (C_{para} phenoxy groups), 164.58, 143.51, 127.65 (quaternary C).

X-ray Crystallography. Compounds **1**−**3** consistently yielded crystals that diffracted weakly, and the results presented are the best of several trials. The crystals were mounted on thin glass fibers using paraffin oil and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1k CCD diffractometer. Data for the compounds **1** and **3** were collected with a sequence of 0.3° ω scans at 0, 120, and 240° in φ. To obtain acceptable redundancy data for compound **2**, the sequence of 0.3° ω scans at 0, 90, 180, and 270° in φ was used. Initial unit cell parameters were determined from 50 data frames collected at the different sections of the Ewald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[12] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with hexagonal $P6_5$ for **1**, triclinic $P\bar{1}$ for **2**, and orthorhombic *Pcca* for **3**. Solutions in the noncentrosymmetric space group for **1** and centrosymmetric space groups for **2** and **3** yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on F^2. The compound molecule was not located on symmetry operators in **1** and **2**. Vice versa, in the structure of **3** a molecule of the Th complex was located on a 2-fold axis and a molecule of the K countercation was located in the inversion center. One molecule of toluene with a half-occupancy located on the 2-fold axes was found in the lattice of **3**. All non-hydrogen atoms, except those of the DME solvent molecules in **2** and toluene solvent molecule in **3**, were refined with anisotropic displacement coefficients. DME solvent molecule carbon atoms in **2** and toluene solvent molecule carbon atoms in **3** were refined isotropically. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12 (G. M. Sheldrick, Bruker AXS, Madison, WI, 2001). The crystal of **1** diffracted particularly poorly, and thus, due to the low data-to-parameter ratio, "rigid bonds" and "similar anisotropic displacement coefficients" restraints were applied to all carbon atoms in order to allow full anisotropic refinement of the structure. Crystallographic data and relevant bond distances and angles are reported in Tables 1 and 2.

Results and Discussion

The preparation of the homoleptic tetrakis(aryloxide) $(ArO)_4Th$ (**1**; Ar = 2,6-Ph_2PhO) was carried out according to a modification of the original literature procedure[13] via the straightforward reaction of $ThCl_4(dme)_2$

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Table 1. Crystal Data and Structure Analysis Results

	1	**2**	**3**
formula	$C_{72}H_{52}O_4Th$	$C_{94}H_{73}K_3O_7Th$	$C_{99.50}H_{105}KO_{14}Th$
M_w	1213.18	1663.86	1795.97
cryst syst	hexagonal	triclinic	orthorhombic
space group, Z	$P6_5$, 6	$P\bar{1}$, 2	$Pcca$, 4
a (Å)	12.9421(11)	13.2109(15)	25.5160(30)
b (Å)	12.9421(11)	16.1868(18)	14.5265(18)
c (Å)	56.420(9)	20.9980(20)	24.4060(30)
α (deg)	90	94.686(2)	90
β (deg)	90	91.598(2)	90
γ (deg)	120	101.466(2)	90
V (Å^3)	8184.1(16)	4381.5(9)	9046.3(19)
λ(Mo Kα)	0.71073	0.71073	0.71073
T (K)	203(2)	213(2)	206(2)
D_{calcd} (g cm^{-3})	1.477	1.261	1.319
μ_{calcd} (mm^{-1})	2.785	1.895	1.756
F_{000}	3636	1680	3692
R1, wR2[a]	0.0738, 0. 1504	0.0727, 0.1808	0.0676, 0.1353
GOF	1.234	1.048	1.062

[a] $R1 = \sum F_o - F_c/\sum F_o$; $wR2 = [(\sum(F_o - F_c)^2/\sum wF_o^2)]^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg)

	Compound **1**		
Th−O(1)	2.177(7)	Th−O(2)	2.189(8)
Th−O(4)	2.187(10)	Th−O(3)	2.211(9)
O(1)−Th−O(4)	104.5(3)	O(1)−Th−O(3)	115.8(4)
O(1)−Th−O(2)	119.9(3)	O(4)−Th−O(3)	110.9(3)
O(4)−Th−O(2)	112.8(4)	O(2)−Th−O(3)	92.9(3)
	Compound **2**		
Th(1)−O(1)	2.276(8)	Th(1)−O(3)	2.400(7)
Th(1)−O(2)	2.281(8)	Th(1)−C(47)	2.589(11)
Th(1)−O(4)	2.338(7)	Th(1)−C(61)	2.599(12)
O(1)−Th(1)−O(2)	97.5(3)	C(61)−Th(1)−K(2)	102.4(2)
O(1)−Th(1)−O(4)	172.8(3)	O(1)−Th(1)−K(1)	132.2(2)
O(2)−Th(1)−O(4)	85.2(3)	O(2)−Th(1)−K(1)	117.6(2)
O(1)−Th(1)−O(3)	104.3(3)	O(4)−Th(1)−K(1)	41.55(19)
O(2)−Th(1)−O(3)	158.2(3)	O(3)−Th(1)−K(1)	45.60(17)
O(4)−Th(1)−O(3)	73.3(2)	Th(1)−O(3)−K(1)	98.7(2)
C(47)−Th(1)−C(61)	152.1(4)	Th(1)−O(3)−K(2)	97.1(3)
O(1)−Th(1)−K(2)	139.5(2)	Th(1)−O(4)−K(1)	104.7(3)
O(2)−Th(1)−K(2)	114.0(2)	Th(1)−O(4)−K(2)	102.5(2)
O(4)−Th(1)−K(2)	43.12(18)	Th(1)−C(47)−K(2)	87.6(3)
O(3)−Th(1)−K(2)	46.78(19)	Th(1)−C(61)−K(1)	90.5(3)
C(47)−Th(1)−K(2)	52.6(3)		
	Compound **3**		
Th(1)−O(1)	2.105(13)	K(1)−O(7)	2.690(15)
Th(1)−O(2)	2.290(8)	K(1)−O(6)A	2.782(12)
Th(1)−O(2)A	2.290(8)	K(1)−O(6)	2.782(12)
Th(1)−O(3)	2.303(7)	K(1)−O(5)	2.79(3)
Th(1)−O(3)A	2.303(7)	K(1)−O(5)A	2.79(3)
Th(1)−O(4)	2.552(12)	K(1)−O(8)A	2.909(15)
K(1)−O(7)A	2.690(15)	K(1)−O(8)	2.909(15)
O(1)−Th(1)−O(2)	96.8(2)	O(3)−Th(1)−O(4)	87.1(2)
O(2)−Th(1)−O(2)A	166.4(4)	O(7)A−K(1)−O(5)	88.5(7)
O(1)−Th(1)−O(3)	92.9(2)	O(7)−K(1)−O(5)	91.5(7)
O(2)−Th(1)−O(3)	89.2(3)	O(6)A−K(1)−O(5)	86.1(6)
O(2)A−Th(1)−O(3)	90.1(3)	O(6)−K(1)−O(5)	93.9(6)
O(3)−Th(1)−O(3)A	174.1(5)	O(5)−K(1)−O(5)A	180
O(1)−Th(1)−O(4)	180	Th(1)−O(1)	2.105(13)
O(2)−Th(1)−O(4)	83.2(2)		

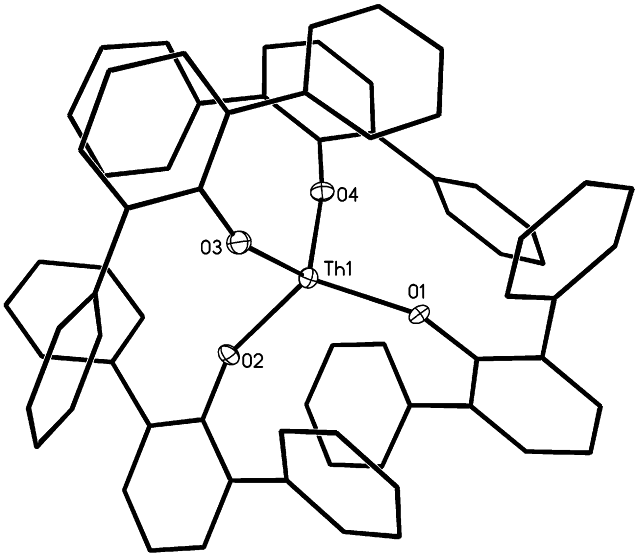
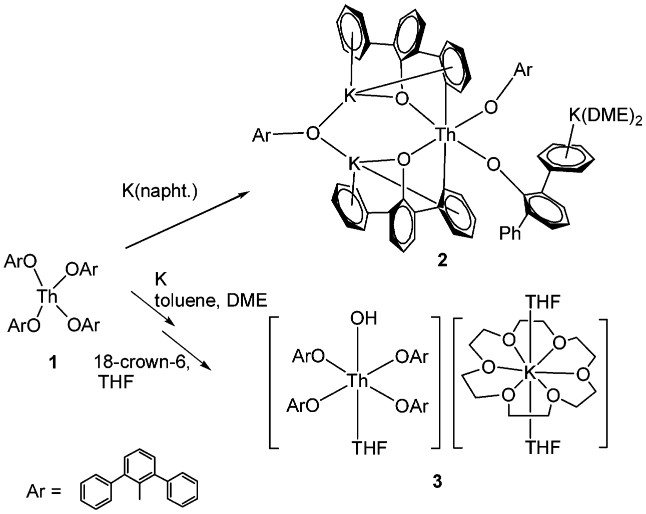


Figure 1. Plot of the anionic unit of **1** showing the thermal ellipsoids drawn at the 30% probability level. Anisotropic ellipsoids are shown only for relevant atoms for clarity reasons.

Scheme 1



with 4 equiv of ArOK. The reaction occurred rapidly at room temperature and in DME to afford **1** in good yield. The connectivity, which was confirmed by an X-ray crystal structure (Figure 1), did not show any significant features other than the distorted-tetrahedral arrangement of the four oxygen atoms around the Th atom (O(1)−Th(1)−O(2) = 119.9(3)°, O(1)−Th(1)−O(3) = 115.8(4) Å, O(1)−Th(1)−O(4) = 104.5(3)°, O(2)−Th(1)−O(3) = 92.9(3)°), which form Th−O distances in the expected range (Th(1)−O(1) = 2.177(7) Å, Th(1)−O(2) = 2.189(8) Å, Th(1)−O(3) = 2.211(9) Å, Th−O(4) = 2.187(10) Å). The structural parameters compared well with those of Th(O-2,6-t-Bu-C_6H_3)$_4$.[14]

The ^1H NMR spectrum did not show any particularly informative features, displaying only two set of multiplets centered at 7.26 and 7.06 ppm.

Attempts to reduce **1** were carried out with either K(naphthalene) in DME or with finely dispersed metallic K in toluene. The two reactions gave completely different results (Scheme 1). The reduction with K(naphthalene) afforded, upon mixing, the same deep red color as observed in the two previously reported cases of Th(naphthalenide) complexes.[7,9] Furthermore, following the same trend of the reaction reducing N_2,[9] the color of the reaction mixture slowly started to fade at room

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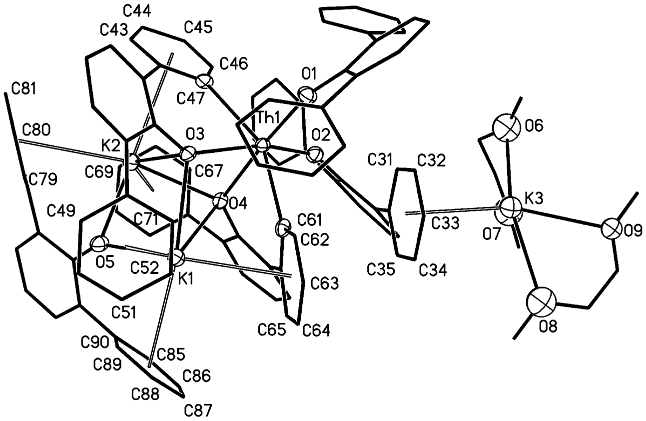

Figure 2. Plot of the anionic unit of **2** showing the thermal ellipsoids drawn at the 30% probability level. For clarity, anisotropic ellipsoids are shown only for relevant atoms.

temperature. Complete discoloration of the reaction mixture occurred within 6 h, and colorless crystals of the new compound ([2,6-Ph_2PhO][K(DME)$_2$(2-Ph-μ,6-Ph)PhO][(μ-2,6-Ph_2PhO)K_2{(2-Ph-μ,6-C_6H_4)PhO}$_2$])Th (**2**) were isolated in over 70% yield. The complex connectivity of this species in the solid state was clarified by an X-ray crystal structure (Figure 2). The molecule consists of five aryloxide anions, one thorium atom, and three potassium atoms linked by a network of bridging phenyl rings and oxygen atoms. Of the five aryloxide units, one has the oxygen atom bridging two potassium atoms (K(1)−O(5) = 2.531(8) Å, K(2)−O(5) = 2.657(9) Å) and is unconnected with thorium. Of the remaining four, two have one of the two phenyl substituents ortho-metalated to the thorium atom, each having lost one hydrogen atom at the ortho position of one of the two phenyl substituents. The resulting Th−C σ-bonds (Th(1)−C(47) = 2.589(11) Å, Th(1)−C(61) = 2.599(12) Å) are rather normal, with distances falling in the range of those for other organothorium derivatives.[1] Each oxygen atom of each of these two aryloxide ligands is bridging the two potassium atoms (O(3)−K(1) = 2.940(8) Å, O(3)−K(2) = 2.967(8) Å, O(4)−K(1) = 2.789(8) Å, O(4)−K(2) = 2.828(7) Å) and thorium (Th(1)−O(3) = 2.400(7) Å, Th(1)−O(4) = 2.38(7) Å). The last two aryloxide rings are terminally bonded to the Th atom (Th(1)−O(1) = 2.276(8) Å, Th(1)−O(2) = 2.281(8) Å). In summary, the coordination geometry around thorium is distorted octahedral (O(1)−Th−O(2) = 97.5(3)°, O(1)−Th(1)−O(3) = 104.3(3)°, O(1)−Th(1)−O(4) = 172.8(3)°, O(1)−Th(1)−C(47) = 94.3(3)°, O(1)−Th(1)−C(61) = 101.3(3)°, O(2)−Th(1)−O(3) = 158.2(3)°, C(47)−Th(1)−C(61) = 152.1(4)°), the coordination environment being defined by the four oxygen atoms of two terminally bonded and two bridging aryloxides and two carbon atoms of two metalated phenyl rings. The two C atoms are located in trans positions. Of the three potassium atoms, the third is located at the periphery and is connected to the rest of the molecule via para coordination of one of the two phenyl rings of one aryloxide bonded to thorium (K(3)−C(31) = 3.401(14) Å, K(3)−C(32) = 3.281(15) Å, K(3)−C(33) = 3.265(18) Å, K(3)−C(34) = 3.371(19) Å, K(3)−C(35) = 3.498(16) Å, K(3)−C(36) = 3.515(13) Å). Two molecules of DME complete its coordination sphere. The other two potassium atoms, which are bridged by one oxygen atom of one aryloxide group not connected to thorium, have their coordination sphere completed by two centroids of two para-coordinated phenyl rings of the two ortho-metalated aryloxides.

In contrast to the complexity of the solid-state structure, the solution NMR spectra of **2** are remarkably simple, indicating that the molecule is possibly fluxional in solution. However, no line broadening could be observed upon lowering the temperature. The aromatic region of the ^{1}H NMR spectrum consists of three multiplets and two doublets for the three intact aryloxides. The other two aryloxides gave one doublet and one triplet for the phenoxide rings, whereas the intact phenyl substituents gave one triple triplet, one double triplet, and one broad doublet, all with satisfactory integration. The ortho-metalated rings gave two complex signals, roughly appearing as multiple doublets, and one broad feature, probably a poorly resolved double triplet.

Complex **2** obviously is the result of a multiple transformation, given that during the reduction one ArOK unit has been acquired. In addition, the transient appearance of a deep red color suggests that, similar to the case of the dinitrogen-cleaving system,[9] an intermediate naphthalenide derivative might also be involved in this transformation. The formation of a similar bis(naphthalenide) complex would imply four-electron reduction and dissociation of at least two ArOK units. The intramolecular C−H bond activation of an aromatic ring resulting in ortho metalation is a rather well-known phenomenon in transition-metal chemistry, and it is often observed as a result of C−H σ-bond metathesis reactions.[15] However, it can also be the result of oxidative addition to the C−H bond by highly reactive low-valent intermediates. For example, Rothwell has observed that, during the reduction of a pentavalent Ta complex of the same 2,6-Ph_2PhO anion, a similar ortho-metalated derivative was obtained.[16] In that particular case, the C−H bond activation and consequent formation of the metallacycle was probably achieved by reoxidation of a transient, highly reactive trivalent tantalum species, as suggested by the release of H_2. In our case, no evolution of hydrogen gas was observed. Formation of 1,4-dihydronaphthalene instead was clearly observed during NMR-tube experiments and in the GC-MS of the reaction mixtures. This result confirms that, as in the previous case of the bis(aryloxide) derivative, a naphthalenide species may indeed be formed, as also indicated by the transient color. However, an intramolecular C−H σ-bond metathetic reaction occurred between the coordinated naphthalenide dianion and the ortho C−H bonds of the aryloxide phenyl groups to afford **2** and 1,4-dihydronaphthalene.

This behavior prompted a second attempt to reduce **1** in the absence of naphthalene. The reduction performed with finely dispersed metallic K only gave intractable materials, as a result of the formation of complicated mixtures, as suggested by the NMR spectra. However, if a small amount of DME was present during

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(15) See for example: (a) Steffey, B. D.; Chamberlain, L. R.; Chesnut, R. W.; Chebi, D. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1989**, *8*, 1419. (b) Chesnut, R. W.; Yu, J. S.; Fanwick, P. E.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1990**, *9*, 1051. (c) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1989**, *8*, 1431. (d) Chesnut, R. W.; Gayatry, G. J.; Yu, J. S.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1991**, *10*, 321.

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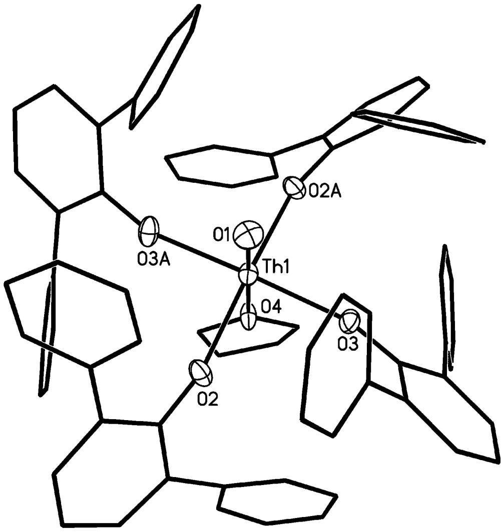

Figure 3. ORTEP plot of the anionic unit of **3** showing the thermal ellipsoids drawn at the 30% probability level.

the reduction, the reaction became remarkably clean and, after treatment with a THF solution of 18-crown-6, afforded a high yield of a new species formulated as $\{[Th(OAr)_4(OH)THF][K(18\text{-crown-}6)(THF)_2]\}\cdot C_7H_8$ (**3**) on the basis of its X-ray crystal structure.

The structure revealed an octahedrally arranged Th atom connected to four terminally bonded aryloxide groups (Th(1)−O(2) = 2.290(8) Å, Th(1)−O(3) = 2.303(7) Å), one molecule of THF (Th(1)−O(4) = 2.552(12) Å), and one terminally bonded hydroxyl group (Th(1)−O(1) = 2.105(13) Å). One potassium cation, surrounded by one crown ether and two molecules of THF in axial positions and unconnected with the Th-containing anion, completes the structure of **3**. Overall, the coordination sphere of the Th atom is octahedral (O(1)−Th(1)−O(2) = 96.8(2)°, O(1)−Th(1)−O(3) = 92.9(2)°, O(1)−Th(1)−O(4) = 180°, O(3)−Th(1)−O(3a) = 174.1(5)°, O(2)−Th(1)−O(2a) = 166.4(4)°) (Figure 3). The four intact aryloxide groups occupy the equatorial plane, while one molecule of THF and one terminally bonded OH group occupy the two axial positions.

The NMR spectra of **3** are rather simple, showing the aryloxide ring resonances present as a triplet and a doublet. The phenyl substituents give a sharp doublet for the ortho H atom, while the meta H atoms gave a more complex pattern. The OH group gave one sharp resonance at 3.17 ppm whose identity was confirmed by the lack of correlation in the HMQC spectrum. Lack of correlation with ^{14}N and the absence of an N resonance in the ^{14}N NMR spectrum, as well as the absence of nitrogen in the combustion analysis data, conclusively ruled out the possibility that the OH group could in reality be the same NH_2 function as observed in the case of $[(\text{bis(aryloxide)})_2Th(NH_2)]^-$.[9] In further agreement, the bond distance formed by Th with the terminal −OH group (Th(1)−O(1) = 2.105(13) Å) shows the expected shortening with respect to Th−NH_2 (Th−N = 2.2431(6) Å).[9]

The reaction affording **3** in very high yield is a reproducible phenomenon. The formation of the terminal OH group under rigorously anhydrous conditions with or without using silylated glassware can be explained only by assuming that a highly reactive species, generated during the reduction, attacked the ethereal solvent. The process implies both O−C bond cleavage of the ethereal solvent and hydrogen abstraction. The deoxygenation or fragmentation of an ether promoted by an f-block element in a strongly reducing environment, although not common, is documented in the literature.[17] Interestingly, the naphthalenide complex of Th supported by a calyx[4]tetrapyrrolide ligand quantitatively reacts with DME at 50 °C to form a dinuclear oxo/methyl derivative.[7,8b] The abstraction of hydrogen to form a hydroxyl group of **3** is somewhat reminiscent of the formation of a tetranuclear Sm hydroxyl derivative,[18] obtained during the reaction of a divalent Sm complex of a tetradentate Schiff base with anhydrous oxygen. It is also more closely related to the partial hydrogenation of the N atom during the N_2 cleavage obtained with the reduction of the $(\text{bis(aryloxide)})_2Th$ species.[9] Finally, complex **3** is the first example of a thorium compound containing a terminally bonded OH group. Interestingly, the Th−OH bonding distance (2.105 Å) is only slightly shorter than those of the three other existing examples of terminally bonded U−OH derivatives (ranging from 2.117(9) to 2.146(1) Å).[19] Differently from the hydroxo-bridged $(Cp')_4U_2(\mu\text{-}OH)_2$ (Cp′ = CpR, where R = Me_3C, Me_3Si), which gave an oxidative elimination of hydrogen upon heating to form an oxo-bridged species,[20] complex **3** is thermally robust.

In summary, we have attempted the reduction of a homoleptic Th complex of a monodentate aryloxide under two different reaction conditions. Reduction with K(naphthalene) gave ligand ortho metalation as a probable result of the C−H σ-bond metathetic process between the aryloxide ligand of the naphthalenide of an intermediate complex. The reduction with metallic K afforded ligand scrambling and attack on the solvent with formation of an OH group. The lack of dinitrogen cleavage in this reaction, while compared to the reduction of a chelating bis(aryloxide),[9] can be only ascribed to both the different denticity and nature of substituents of the aryloxide ligand. This difference of behavior is striking and will stimulate further work in an attempt to elucidate the remarkable behavior of reduced thorium compounds.

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Supporting Information Available: Tables giving complete crystallographic data for all the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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