Ring Opening and C−O and C−N Bond Cleavage by Transient Reduced Thorium Species

Athimoolam Arunachalampillai, Patrick Crewdson, Ilia Korobkov, and Sandro Gambarotta*

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

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Reduction of the tetravalent complex [{2,5-[$(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]$}$ThCl_2$ (THF)]·THF (**2**) of the tripyrrolide dianion 2,5-[$(C_4H_3N)CPh_2]_2C_4H_2N(Me)$ afforded different products depending on the reaction conditions. In every case, the reaction proceeded via the initial formation of a reduced species, as indicated by the very rapid formation of a dark red color followed by slow and complete discoloration. In the case of the reduction in toluene, the complexes ({2,5-[$(C_4H_3N)CPh_2]_2[C_4H_2N]$}$_2$Th[K(toluene)]$_2$)·1.5(toluene) (**3a**) and {2,5-[$(C_4H_3N)CPh_2]_2[C_4H_2N]$}$_2$Th[K(DME)]$_2$ (**3b**) were obtained, depending on the crystallization solvent (toluene versus DME). In both cases, the products arose from a loss of the methyl group attached to the central pyrrole ring N atom. When the reduction was carried out in DME as a solvent, the complex {[{2,5-[$(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]$}Th$(OMe)_2$(*m*-$OC_2H_4OMe)_2$}· 0.75(hexane) (**5**) was isolated. This species is derived from two different pathways of C−O cleavage of the DME solvent. Reduction of {2,5-[$(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]$}ThCl{$(C_4H_3N)CPh_2[C_4H_3N(Me)]$} (**6**), containing both the monoalkylated tripyrrolide and dipyrrolide ligands, afforded instead pyrrolide ring opening and formation of [({2,5-[$(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]$}Th[$(C_4H_3N)CPh_2$(C═CHCH═CHNMe)])$_2$(*m*-K)]-[$K(DME)_4$]·2(hexane) (**7**).

Introduction

Reduced complexes of f-block elements are typically characterized by very high reactivity.[1] On the wave of the tremendous variety of transformations discovered for divalent samarium,[2] spectacular progress has been achieved in the past few years in expanding the boundary of this chemistry beyond the realm of divalent Eu, Yb, and Sm toward even more reactive and more reducing elements.[3] This is perhaps the key to understanding the recent resurgence of interest in the chemistry of low-valent actinides.[4] Trivalent uranium, which is the most readily accessible low oxidation state, seems to follow a trend of high reactivity similar to that discovered for lanthanides, given that dinitrogen fixation[5] and cleavage,[6] coordination of hydrocarbons,[7] CO oligomerization,[8] and unusual binding of small molecules[9] have been documented. Attempts to prepare complexes of even lower oxidation states, such as U(II), have afforded arene species with the *formal* appearance of a divalent uranium arene.[10] However, DFT calculations have clearly indicated that the metal is in fact in a higher oxidation state, due to a very substantial extent of metal to ligand back-bonding. On the other hand, reactivity studies have clearly pointed out that one of these reduced complexes may act as a two-electron reductant and performs the type of transformations one could expect for a genuine divalent metal.[10] Hence, the terms of *divalent synthon* and *low-valent synthetic equivalents* have been used for this and other reduced actinide complexes, although the metal is most likely higher valent.[10,11]

Reduced species have also been prepared in the case of thorium with the aid of ancillary arene ligands.[12−14] Different

* To whom correspondence should be addressed. E-mail: sgambaro@science.uottawa.ca.

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from the case of uranium, though,[10] the greater extent of backbonding caused a very visible distortion of the arene ligand, thus *doubtlessly assigning a normal tetravalent state to the metal* ion. Similar to the case for the uranium complexes, the very high reactivity of these species is, again, what can be expected for a genuine low-valent species, spanning from solvent cleavage to unusual transformations,[13a] as well as dinitrogen cleavage and its partial hydrogenation.[13b] Although these results do not have a straightforward explanation, they clearly reiterate the potential of reduced actinide species for unusual reactivity. It is worth mentioning that only three thorium compounds are known for the trivalent state[14] and that ThI_2 is the only example of a divalent species, although its actual oxidation state has been argued on the basis of its polymeric solid-state structure.[15]

The choice of the ligand is, of course, vital to the stabilization of reduced species and the occurrence of very high reactivity. As mentioned above, the only examples of reduced actinide species, or low-valent synthetic equivalents, have been obtained so far by using coordinated arenes[10,12,13] or ligand systems with a capability of π-bonding.[10,15] The σ-/π-bonded tetrapyrrolide tetraanion has been versatile from this point of view, since it has assisted dinitrogen cleavage upon reduction of a trivalent uranium complex.[6] The dipyrrolide anions have also been useful for supporting the four-electron reduction of dinitrogen by divalent samarium clusters.[16] With the aim of preparing novel reduced thorium complexes for reactivity studies, we have now designed a new ligand system based on a tripyrrole framework, whose central pyrrole ring has been alkylated at the N atom to ensure π-bonding.[17] Herein, we describe the synthesis of its tetravalent thorium precursors and their reduction, which resulted in a series of uncommon transformations.

Experimental Section

All operations were performed under a purified nitrogen atmosphere by either using standard Schlenk techniques or drybox. Centrifugations and decantations as well as sample preparation were carried out inside the drybox. (*Warning!* Thorium is a highly toxic and weakly radioactive metal. Adequate precautions must be taken to avoid exposure and inhalation.) $Th(NO_3)_4(H_2O)_4$ was used as received (Strem). The N-alkylated tripyrrole 2,5-[(C_4H_3NH)-$CPh_2]_2C_4H_2N(Me)$[17] was synthesized according to literature procedures. NMR spectra were recorded on Bruker Avance 300 and Varian 500 MHz spectrometers. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determinations were obtained with a Bruker diffractometer equipped with a 1k-Smart CCD area detector.

Preparation of $ThCl_4(DME)_2$. A sample of $Th(NO_3)_4(H_2O)_4$ (25 g, 45.3 mmol) was dissolved in concentrated HCl (70 mL). The solution was brought to the boiling point, and stirring was continued at this temperature for 6 h. Rapid evolution of orange-colored gas took place. (*Warning!* Nitrogen oxides are harmful gases. The preparation should be carried out in a well-vented fume hood.) When colored vapors were no longer visible, the volume of the reaction mixture was reduced to 25 mL. The pH of the reaction mixture was adjusted to 6 by slow addition of a concentrated solution of KOH in water. The solution was evaporated in vacuo, and the resulting dry white residue was suspended in thionyl chloride (150 mL). (*Warning!* Sulfur dioxide and hydrogen chloride are harmful and corrosive gases. The preparation should be carried out in a well-vented fume hood.) The reaction mixture was stirred and refluxed by allowing the gases to escape through an oil bubbler. After 12 h no gas evolution could be detected. The white solid was filtered under an inert atmosphere, washed with three portions of toluene (35 mL each), and resuspended in 300 mL of anhydrous DME. The suspension was then refluxed for 12 h. The insoluble microcrystalline solid was filtered and extracted using a Kumagawa extractor. When all the solid was extracted from the filter, the suspension was concentrated to 50 mL and placed in the freezer (−37 °C) for 24 h. White prisms of $ThCl_4(DME)_2$ were separated and dried under vacuum (19.8 g, 5.68 mmol, 79%). Anal. Calcd (found) for $C_8H_{10}O_2ThCl_4$: C, 18.77 (18.62); H, 1.97 (1.88).

Synthesis of 2-(Diphenyl(1*H*-pyrrol-2-yl)methyl)-1-methyl-1*H*-pyrrole (1). A solution of 1-methylpyrrole (9.14 g, 0.11 mol) in THF (100 mL) was placed in a 250 mL Schlenk flask. The solution was then cooled to −78 °C and treated while stirring with a solution of *n*-BuLi in hexane (11.8 mL, 10 M, 0.118 mol). The resulting solution turned slightly brown, and a precipitate formed. The suspension was stirred for 4 h while it was warmed to room temperature, after which time it was slowly added to a cooled solution (−78 °C) of benzophenone (20.59 g, 0.113 mol) in THF. The mixture immediately turned blue-green. The solution was then stirred for 12 h as it was warmed to room temperature. After 12 h the color of the solution was again yellow-brown. The solution was then evaporated under reduced pressure, and 100 mL of hexanes was added along with H_2O (4.068 g, 0.226 mol). The resulting slurry was filtered at the boiling point of hexane and washed with three portions of hot hexane (20 mL). The solution was then allowed to stand at room temperature for 12 h, after which slightly yellow crystals of the carbinol separated. The crystals were filtered and washed twice with cold hexane (10 mL). The crystals were mixed with pyrrole (∼50 mL), and the resulting suspension was gently heated until full dissolution was achieved. The addition of a few drops of methanesulfonic acid turned the color of the solution to red. After the mixture was stirred for 72 h, the gray solid that separated was filtered and washed with four portions of cold MeOH (20 mL), yielding, after drying under vacuum, a white solid of the desired dipyrrole (12.00 g, 34%, 0.04 mol). Anal. Calcd (found) for $C_{22}H_{20}N_2$: C, 84.58 (84.62); H, 6.45 (6.58); N, 8.97 (8.88). ^{1}H NMR ($CDCl_3$): δ 7.74 (1H, br, NH), 7.27 (6H, m, phenyl), 7.13 (4H, m, phenyl), 6.75 (1H, m, NH pyrrole α), 6.65 (1H, m, NMe pyrrole α), 6.18 (1H, m, NMe pyrrole β), 6.14 (1H, m, NMe pyrrole γ), 6.02 (1H, m, NH pyrrole β), 5.62 (1H, m, NH pyrrole γ), 2.94 (3H, s, NCH_3). ^{13}C NMR ($CDCl_3$): δ 145.97 (phenyl, ipso), 136.21 (NMe pyrrole ipso), 134.71 (NH pyrrole ipso), 129.30 (phenyl), 127.64 (phenyl), 126.37 (phenyl), 124.32 (NMe pyrrole α), 117.258 (NH pyrrole α), 111.99 (NMe pyrrole β), 109.04 (NH pyrrole β), 107.72 (NMe pyrrole γ), 105.81 (NH pyrrole γ), 55.44 (quaternary), 35.49 (NCH_3). MS (EI): *m*/*z* calcd (found) 312 (312).

Preparation of [{2,5-[$(C_4H_3N)CPh_2]_2$[$C_4H_2N(Me)$]}K_2(DME)-(THF)]·0.75(hexane) (1). A solution of 2,5-[$(C_4H_3NH)CPh_2]_2C_4H_2N$-(Me) (0.5 g, 0.92 mmol) in THF (20 mL) was treated with KH (0.08 g, 1.84 mmol) and stirred for 3 h. The resulting solution was evaporated to a very small volume, the residue was dissolved in DME, and the resulting solution was layered with hexane. Colorless needles of **1** (0.69 g, 0.88 mmol, 96%) were obtained upon standing for 3 days. Single crystals contained 0.75 molecule of hexane, which was spontaneously lost upon drying the samples. Anal. Calcd. (found) for $C_{47}H_{49}N_3O_3K_2$: C, 72.18 (71.99); H, 6.31 (6.52); N, 5.37 (5.41). ^{1}H NMR (THF-d_8, 500 MHz): δ 7.00−7.20 (m,

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aromatic H, 20H), 6.78 (m, pyrrole H, 2H), 5.98 (m, pyrrole H, 4H), 5.41 (s, pyrrole H, 2H), 3.53 (s, THF, 4H), 3.40 (s, DME, 4H), 3.20 (s, DME, 6H), 2.20 (s, NMe, 3H), 1.73 (s, THF, 4H). ^{13}C NMR (benzene-d_6, 300 MHz): δ 153.42, 145.80, 144.54 (quaternary C), 130.84, 126.20, 128.02 (aromatic C), 116.32, 111.19, 108.11 (pyrrole), 72.06 (DME), 58.80 (DME), 58.21 (bridging C), 32.72 (NMe).

Preparation of [{2,5-[(C$_4$H$_3$N)CPh$_2$]$_2$[C$_4$H$_2$N(Me)]}ThCl$_2$(THF)]·THF (2). A stirred solution of $ThCl_4(DME)_2$ (1.0 g, 2.19 mmol) in DME (25 mL) was slowly combined with a solution of **1** in DME, prepared in situ by reacting **1** (1.19 g, 2.19 mmol) with KH (0.18 g, 4.48 mmol) in DME (25 mL). Stirring was continued for an additional 8 h. A small amount of pale-colored insoluble material was formed, which was removed by filtration. The resulting clear solution was layered with hexane. The colorless crystals, obtained upon standing at room temperature for 3 days, were redissolved in THF and layered with hexane to form X-ray-quality crystals of **2** (1.30 g, 1.30 mmol, 59%). Anal. Calcd (found) for $C_{47}H_{47}Cl_2N_3O_2Th$: C, 57.09 (56.99); H, 4.79 (4.62); N, 4.25 (4.15). ^{1}H NMR (benzene-d_6, 300 MHz): δ 8.17 (d, pyrrole, 2H), 6.98−7.36 (m, aromatic, 20H), 6.56 (d, pyrrole, 2H), 6.52 (s, pyrrole, 2H), 6.41 (t, pyrrole, 2H), 3.53 (s, THF, 8H), 2.40 (s, NMe, 3H), 1.73 (s, THF, 8H). ^{13}C NMR (benzene-d_6, 300 MHz): δ 153.42, 147.03, 145.80, 144.54 (quaternary), 131.80, 128.02, 127.87, 127.06 (aromatic), 128.38, 117.32, 111.19, 108.11 (pyrrole), 72.06 (THF), 58.80 (THF), 58.21 (bridging C), 37.1 2 (NMe).

Preparation of [{2,5-[(C$_4$H$_3$N)CPh$_2$]$_2$[C$_4$H$_2$N]}$_2$Th[K(toluene)]$_2$]·1.5(toluene) (3a). A solution of **2** (0.25 g, 0.55 mmol) in toluene (15 mL) was stirred in the presence of potassium (0.04 g, 1.1 mmol) for 8 h, during which time the solution became dark red and all the potassium was consumed. The solution was centrifuged and decanted to remove the insoluble solid and allowed to slowly evaporate. After 1 week, the color of the solution faded and colorless X-ray-quality crystals of **3a** contaminated with a dark residue were obtained (0.08 g, 0.05 mmol, 10%). The contamination of the product prevented obtaining meaningful spectroscopic and analytical data.

Preparation of {2,5-[(C$_4$H$_3$N)CPh$_2$]$_2$[C$_4$H$_2$N]}$_2$Th[K(DME)]$_2$ (3b). Method A. A colorless suspension of **4** (1.44 g, 1.1 mmol) (see below) in fresh DME (20 mL) was stirred with freshly prepared, finely dispersed potassium (0.09 g, 2.2 mmol). The mixture rapidly turned dark red. After 6 h the dark color of the reaction mixture started showing visible signs of fading and became nearly colorless after 15 h. The solution was centrifuged and decanted, to remove a small amount of insoluble solid, and layered with hexane, affording colorless crystals of **3b** (0.96 g, 0.62 mmol, 54%) upon standing at room temperature for 1 week. Anal. Calcd (found) for $C_{84}H_{76}N_6O_4ThK_2$: C, 65.35 (64.98); H, 4.96 (4.90); N, 5.44 (5.38). ^{1}H NMR (THF-d_8, 300 MHz): δ 7.00−7.19 (m, aromatic, 40H), 6.63 (d, pyrrole, 2H), 6.62 (d, pyrrole 2H), 5.86 (t, pyrrole 4H), 5.62 (d, pyrrole, 2H), 5.61 (d, pyrrole, 2H), 5.55 (s, central pyrrole, 4H), 3.38 (s, DME, 8H), 3.20 (s, DME, 12H). ^{13}C NMR (THF-d_8, 300 MHz): δ 145.12, 134.81, 133.64 (quaternary), 128.02, 125.60, 124.51 (aromatic), 115.79, 107.84, 106.90, 104.88 (pyrrole), 70.31 (DME), 56.46 (DME), 54.39 (bridging quaternary).

Method B. The crude crystalline mass of **3a**, as obtained by evaporation to dryness of the reaction mixture, was redissolved in DME, and this solution was layered with hexane. Complex **3b** formed in analytically pure form upon standing at room temperature for 7 days (0.32 g, 0.20 mmol, 40% based on **4**).

Preparation of {2,5-[(C$_4$H$_3$N)CPh$_2$]$_2$[C$_4$H$_2$N(Me)]}$_2$Th (4). A stirred solution of $ThCl_4(DME)_2$ (0.5 g, 1.1 mmol) in DME (10 mL) was treated with a suspension of **1** also in DME prepared in situ by reacting 2,5-[(C$_4$H$_3$NH)CPh$_2$]$_2$C$_4$H$_2$N(Me) (1.19 g, 2.19 mmol) with KH (0.18 g, 4.48 mmol) in DME (25 mL) for 2 h. The mixture was stirred overnight. Colorless and insoluble **4** separated as a colorless solid (1.14 g, 0.87 mmol, 79%), which was filtered and washed with DME (5 mL). The lack of solubility in the most common organic solvents prevented recording NMR spectra. Anal. Calcd. (found) for $C_{78}H_{62}N_6Th$: C, 71.22 (70.88); H, 4.75 (4.42); N, 6.39 (6.12).

Preparation of {[{2,5-[(C$_4$H$_3$N)CPh$_2$]$_2$[C$_4$H$_2$N(Me)]}Th(OMe)]$_2$-(μ-OC$_2$H$_4$OMe)$_2$}·0.75(hexane) (5). A solution of **2** (0.25 g, 0.55 mmol) in DME (15 mL) was stirred in the presence of potassium (0.04 g, 1.1 mmol). The finely dispersed potassium was rapidly consumed to afford a dark red solution whose color started fading after a few hours. Complete discoloration was achieved within 15 h. The solution was centrifuged to remove a small amount of insoluble solid and layered with hexane. Colorless crystals of **5** were obtained after 15 days (0.18 g. 0.20 mmol, 18%). Similar to the case of **4**, the very poor solubility prevented recording NMR spectra. Satisfactory analytical data have been obtained only upon crushing the crystalline mass in a mortar and exposing the sample to vacuum for 2 h. Anal. Calcd (found) for $C_{43}H_{41}N_3O_3Th$: C, 58.70 (58.61); H, 4.70 (4.52); N, 4.78 (4.62).

Preparation of {2,5-[(C$_4$H$_3$N)CPh$_2$]$_2$[C$_4$H$_2$N(Me)]}ThCl-{(C$_4$H$_3$N)CPh$_2$[C$_4$H$_3$N(Me)]} (6). A stirred solution of **2** (0.5 g, 0.51 mmol) in DME (15 mL) was slowly combined with a solution of [C$_4$H$_3$NK]CPh$_2$[C$_4$H$_3$N(Me)] prepared in situ by reacting [C$_4$H$_3$N-(H)]CPh$_2$[C$_4$H$_3$N(Me)] (0.18 g, 0.55 mmol) with KH (0.03 g, 0.55 mmol) in DME (15 mL). The resulting mixture was stirred for 6 h at room temperature, centrifuged to remove a small amount of insoluble solid, and then layered with hexane. Colorless crystals of **6** were obtained after 12 h of standing (0.5 g, 0.44 mmol, 80%). Anal. Calcd (found) for $C_{61}H_{50}ClN_5Th$: C, 65.38 (65.27); H, 4.50 (4.46); N, 6.25 (6.18). ^{1}H NMR (THF-d_8, 300 MHz): δ 7.10−7.30 (m, aromatic, 30H), 6.77 (d, dipyrrole, 2H), 6.65 (d, tripyrrole, 2H), 6.06−5.97 (m, pyrrole H, 6H), 5.98 (m, dipyrrole, 2H), 5.50 (s, tripyrrole, 2H), 2.9 (s, NMe dipyrrole, 3H), 2.40 (s, NMe tripyrrole, 3H). ^{13}C NMR (THF-d_8, 300 MHz): δ 147.16, 146.85 (quaternary), 139.09, 136.78, 134.84, 134.41 (aromatic), 130.05, 129.94, 129.14, 128.38, 127.18, 127.59, 126.76, 125.52, 124.20 (pyrrole), 56.45, 55.96 (bridging C,), 35.23 (NMe, tripyrrole), 32.00 (NMe, dipyrrole).

Preparation of [({2,5-[(C$_4$H$_3$N)CPh$_2$]$_2$[C$_4$H$_2$N(Me)]}Th-[(C$_4$H$_3$N)CPh$_2$(C=CHCH=CHNMe)])$_2$(μ-K)][K(DME)$_4$]·2-(hexane) (7). A stirred solution of **6** (0.5 g, 0.44 mmol) in DME (10 mL) was combined with a solution of potassium naphthalenide in DME (prepared from potassium (0.04 g, 0.90 mmol) and naphthalene (0.12, 0.90 mmol) in DME (20 mL)). The color became dark red upon mixing, and the mixture was stirred overnight. The solution was then centrifuged to remove a small amount of insoluble residue and layered with hexane. Colorless plates of **7**, mixed together with a dark red oily residue, were obtained after 1 week. The solid mass was recrystallized by dissolving it in DME and layering the resulting solution with hexane, affording crystalline, analytically pure, colorless **7** (0.38 g, 0.26 mmol, 58% per Th). Satisfactory analytical data have been obtained only upon crushing the crystalline mass in a mortar and exposing the sample to vacuum for 2 h. Anal. Calcd. (found) for $C_{69}H_{70}N_5O_4KTh$: C, 63.53 (63.28); H, 5.41 (5.39); N, 5.37 (5.33). ^{1}H NMR (THF-d_8, 300 MHz): δ 7.08−7.28 (m, aromatic, 30H), 6.80 (t, pyrrole, 2H), 6.75 (t, pyrrole, 1H), 6.70 (m, vinylic, 1H), 6.62 (t, vinylic proton, 1H), 5.98 (m, pyrrole, 4H), 5.92 (m, pyrrole, 2H), 5.55 (dd, vinylic, 1H), 5.45 (s, central pyrrole, 2H), 3.38 (s, DME, 8H), 3.20 (s, DME, 12H), 2.32 (s, NMe, 3H), 2.25 (s, NMe, 3H). ^{13}C NMR (THF-d_8, 300 MHz): δ 146.81, 139.02, 129.9, 129.08, 125.45 (quaternary), 130.01, 128.32, 125.45 (aromatic), 117.71, 110.22−109.35 (eight overlapping resonances), 107.12 (pyrrole and vinylic), 72.17 (DME), 58.32 (DME), 56.39 (bridging C), 35.12 (NMe), 34.05 (NMe).

X-ray Crystallography. Appropriate single crystals of the reported compounds were selected, mounted on glass fibers using paraffin oil, and cooled to the data collection temperature. Data

Table 1. Crystal Data and Structure Analysis Results

	1	2	3a	3b	5	6	7
formula	$C_{47}H_{49}N_3O_3K_2$·0.75(hexane)	$C_{43}H_{39}Cl_2N_3$-OTh·THF	$C_{90}H_{72}N_6K_2Th$·1.5(toluene)	$C_{84}H_{76}N_6$-O_4KTh	$C_{43}H_{41}N_3O_3Th$·0.75(hexane)	$C_{61}H_{50}Cl$-N_5Th	$C_{69}H_{70}KN_5O_4Th$·2(hexane)
mol wt	850.20	988.82	1685.98	1543.75	944.46	1120.55	1559.56
cryst syst	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group, Z	$P2_1/c$, 4	$P2_1/n$, 4	$C2/c$, 4	$P\bar{1}$, 2	$C2/c$	$C2$	$C2/c$
a (Å)	11.912(2)	18.207(6)	33.390(7)	11.975(6)	22.762(16)	38.78(3)	17.67(7)
b (Å)	16.888(3	11.789(4)	12.531(3)	13.569(7)	15.890(9)	10.427(7)	29.83(14)
c (Å)	22.019(4)	20.908(7)	20.740(5)	25.327(12)	23.217(12)	12.221(8)	25.61(15)
α (deg)				93.768(7)			
β (deg)	92.454(4)	113.429(6)	97.642(4)	92.503(7)	94.75(4)	104.467(10	96.4(3)
γ (deg)				113.128(7)			
V (Å^3)	4425.5(13)	4118(2)	8602(3)	3766(3)	8368(9)	4785(6)	13417(11)
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	208(2)	209(2)	226(2)	207(2)	209(2)	208(2)	208(2)
D_{calcd} (g cm^{-3})	1.222	1.595	1.302	1.362	1.499	1.555	1.444
μ_{calcd} (cm^{-1})	0.258	0.3793	0.1880	0.2144	0.3607	0.3219	0.2343
F_{000}	1731	1960	3428	1564	3772	2232	5965
R, R_w[a]	0.0737, 0.1366	0.0607, 0.1066	0.0393, 0.0800	0.0376, 0.0890	0.0649, 0.1245	0.0487, 0.1335	0.0768, 0.1495
GOF	1.015	1.085	1.052	1.046	1.036	1.026	1.032

[a] $R = \Sigma||F_o - F_c||/\Sigma|F_o|$; $R_w = [\Sigma(F_o - F_c)^2/\Sigma wF_o^2\ ]^{1/2}$.

were collected on a Bruker AXS SMART 1k CCD diffractometer using 0.3° ω-scans at 0, 90, and 180° in ϕ. Initial 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.[18]

The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELTX program library with the latest version used being v.6.12 (G. M. Sheldrick, SHELXTL; Bruker AXS, Madison, WI, 2001). Crystallographic data and relevant bond distances and angles are reported in Tables 1 and 2.

Partially occupied molecules of hexane were found in the lattice in the case of **1** and **5**. Partially occupied toluene was also present in the lattice of **3a**, and one molecule of THF with full occupancy was found in the lattice of **2**. In the case of **7** the DME coordinated to potassium as well as the lattice hexane molecule were heavily disordered. The data were therefore processed with the Squeeze routine of PLATON[19] and successfully refined.

(a) Compound 1. The structure of **1** consists of an infinite polymer composed by identical tetrameric units. Each tetrameric unit is symmetry-generated with four potassium atoms surrounded by two tripyrrolide dianions (Figure 1). The ligand adopts the expected bonding mode with one of the two nonequivalent K atoms σ-bonded to the two lateral pyrrolide rings through the two deprotonated nitrogens (K(1)−N(1) = 2.870(4) Å, K(1)−N(3) = 2.781(4) Å) and orthogonally oriented with respect to the central ring, which appears to be π-bonded (K(1)−centroid(2) = 2.909(12) Å). A second potassium atom, solvated by one THF and one DME molecule (K(2)−O(1) = 2.692(5) Å, K(2)−O(3) = 2.770(4) Å, K(2)−O(2) = 2.795(4) Å), resides at the exterior of the cavity defined by the ligand and is connected via π-bonding to one of the two deprotonated pyrrolide rings (K(2)−centroid(3) = 2.848(4) Å). The tetramer is formed by the π-interaction of the first potassium atom with the second deprotonated pyrrolide ring of a second identical unit (K(1)−centroid(1) = 3.018(5) Å). The polymeric arrangement of the tetrameric units is provided by the π-interaction of the potassium atom located at the exterior of the ligand with the pyrrolyl ring of another identical tetrameric unit. Each potassium atom shows also an additional weak interaction with one of the phenyl substituents. Labile and partially occupied hexane (0.75 mol for the formula unit) was also present in the unit cell.

(b) Compound 2. The structure of **2** consists of a hexacoordinated thorium (Figure 2) σ-bonded to two nitrogens of the two coplanar deprotonated pyrrole rings (Th(1)−N(1) = 2.408(7) Å, Th(1)−N(3) = 2.399(7) Å) and to two chlorine atoms (Th(1)−Cl(1) = 2.650(2) Å, Th(1)−Cl(2) = 2.681(2) Å). The oxygen atom of a coordinated THF molecule (Th(1)−O(1) = 2.512(5) Å) and the centroid of the π-bonded central pyrrole ring (Th−centroid = 2.638(8) Å) complete the pseudo-octahedral coordination geometry of the metal center (N(3)−Th(1)−Cl(1) = 90.77(2)°, N(3)−Th(1)−O(1) = 174.6(2)°, N(1)−Th(1)−centroid = 84.058(2)°, Cl(1)−Th(1)−Cl(2) = 87.48(9)°, N(1)−Th(1)−centroid = 84.058(2)°, Cl(2)−Th(1)−centroid = 100.752(6)°). One molecule of THF was also found in the lattice.

(c) Compound 3a. The structure consists of a pseudo-octahedral thorium atom surrounded by two tripyrrolide ligands which, by having lost the methyl groups attached to the N atoms, have become trianionic. Two potassium ions complete the structure (Figure 3). The two pyrrole rings at the side of the tripyrrole of each ligand adopted the usual σ-bonding mode (the average Th−N distance is 2.529(8) Å), while the central pyrrole ring, although demethylated, is still π-bonded to the thorium center (Th−centroid = 2.651(4) Å). Therefore, the overall severely distorted pseudo-octahedral coordination geometry of the thorium ion is defined by the coordination of four σ-bonded nitrogen atoms and the centroid of the two π-bonded rings (N(3)−Th(1)−N(3′) = 166.794(22)°, N(1)−Th(1)−N(1′) = 75.734(22)°, N(1)−Th(1)−centroid = 91.966(17)°, centroid−Th(1)−centroid = 120.584(9)°). Two identical potassium atoms counterbalance the two negative charges of the Th-containing unit. Each potassium is π-coordinated to two pyrrolide rings, one from each ligand, which in turn are σ-bonded to thorium. The coordination sphere is completed by the η^6-coordination of one molecule of toluene (K(1)−centroid = 2.606(20) Å) and the σ-coordination of the N atom of the demethylated pyrrole ring (K(1)−N(2) = 2.810(6) Å).

(d) Compound 3b. The structure of **3b** is nearly identical with that of **3a** (Figure 4) with very similar bond distances (Th(1)−N(1) = 2.573(4) Å, Th(1)−N(3) = 2.499(4) Å, Th(1)−N(4) = 2.531(4) Å, Th(1)−N(6) = 2.510(4) Å, K(1)−N(2) = 2.861(4) Å) and angles (N(1)−Th(1)−N(3) = 85.45(13)°, N(1)−Th(1)−N(6) = 101.45(14)°, N(1)−Th(1)−N(4) = 171.84(13)°, N(4)−Th(1)−N(3) = 100.66(13)°, N(6)−Th(1)−N(3) = 76.76(14)°). The only difference arises from the solvation of the two potassium atoms

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

Compound **1**[a]

K(1)−N(1)	2.870(4)	K(1)−centroid 1′	3.018(5)	K(2)−centroid 3	2.848(4)	K(2)−O(3)	2.770(4)
K(1)−N(3)	2.781(4)	K(1)−centroid 2	2.909(4)	K(2)−O(1)	2.692(5)	K(2)−O(2)	2.795(4)

N(1)−K(1)−N(3)	106.996(12)	N(1)−K(1)−centroid 1′	107.588(8)	centroid 3−K(2)−O(3)	94.581(10)
N(3)−K(1)−centroid 2	75.291(8)	N(3)−K(1)−centroid 1′	143.060(8)	O(1)−K(2)−O(2)	89.387(15)
N(1)−K(1)−centroid 2	74.065(8)	centroid 3−K(2)−O(1)	162.561(11)	O(1)−K(2)−O(3)	87.475(15)
centroid 2−K(1)−centroid 1′	127.016(4)	centroid 3−K(2)−O(2)	106.719(10)	O(2)−K(2)−O(3)	60.550(11)

Compound **2**[b]

Th(1)−N(3)	2.399(7)	Th(1)−O(1)	2.512(5)	Th(1)−Cl(2)	2.681(2)	Th(1)−centroid	2.638(8)
Th(1)−N(1)	2.408(7)	Th(1)−Cl(1)	2.650(2)				

N(3)−Th(1)−N(1)	99.2(2)	N(1)−Th(1)−O(1)	85.0(2)	O(1)−Th(1)−Cl(1)	85.70(2)
N(3)−Th(1)−Cl(2)	97.93(2)	N(1)−Th(1)−Cl(1)	89.55(2)	O(1)−Th(1)−centroid	100.979(2)
N(3)−Th(1)−Cl(1)	90.77(2)	N(1)−Th(1)−Cl(2)	162.68(2)	Cl(1)−Th(1)−Cl(2)	87.48(9)
N(3)−Th(1)−O(1)	174.6(2)	N(1)−Th(1)−centroid	84.058(2)	Cl(1)−Th(1)−centroid	170.297(6)
N(3)−Th(1)−centroid	83.078(2)	O(1)−Th(1)−Cl(2)	77.80(2)	Cl(2)−Th(1)−centroid	100.752(6)

Compound **3a**[c]

Th(1)−N(1)	2.518(8)	Th(1)−centroid 2	2.651(4)	K(1)−centroid 1	2.795(4)	K(1)−centroid 4	2.977(6)
Th(1)−N(3)	2.539(8)	K(1)−N(2)	2.814(8)	K(1)−centroid 3	2.797(5)		

N(1)−Th(1)−N(1′)	75.734(22)	N(3)−Th(1)−centroid 2	81.473(16)	centroid 4−K(1)−centroid 1	126.140(12)
N(1)−Th(1)−N(3)	85.990(22)	N(1)−Th(1)−centroid 2′	91.966(17	centroid 4−K(1)−N(2)	133.131(18)
N(1)−Th(1)−N(3′)	104.566(22)	N(3)−Th(1)−N(3′)	166.794(22)	centroid 1−K(1)−centroid 3	111.756(11)
N(1)−Th(1)−centroid 2	82.238(17)	centroid 2−Th(1)−centroid 2′	120.584(9)	centroid 3−K(1)−N(2)	76.071(16)
N(1)−Th(1)−centroid 2′	156.565(18)	centroid 4−K(1)−centroid 3	118.108(11)	centroid 1−K(1)−N(2)	76.754(16)

Compound **3b**[d]

Th(1)−N(3)	2.500(4)	Th(1)−centroid 2	2.604(10)	K(1)−N(2)	2.861(5)	K(2)−O(3)	2.744(12)
Th(1)−N(6)	2.511(5)	Th(1)−centroid 5	2.6113(13)	K(1)−centroid 1	2.8128(21)	K(2)−N(5)	2.883(5)
Th(1)−N(4)	2.533(5)	K(1)−O(2)	2.730(6)	K(1)−centroid 3	2.820(17)	K(2)−centroid 4	2.851(16)
Th(1)−N(1)	2.571(5)	K(1)−O(1)	2.793(7)	K(2)−O(4)	2.74(2)	K(2)−centroid 6	2.854(18)

N(1)−Th(1)−N(4)	171.956(15)	N(4)−Th(1)−centroid 5	81.663(12)	centroid 1−K(1)−centroid 3	113.049(5)
N(1)−Th(1)−N(3)	85.438(16)	N(4)−Th(1)−N(6)	85.232(16)	O(3)−K(2)−N(5)	119.7(3)
N(1)−Th(1)−N(6)	101.466(16)	N(6)−Th(1)−centroid 5	82.723(12)	O(4)−K(2)−N(5)	169.1(4)
N(1)−Th(1)−centroid 2	171.956(15)	O(2)−K(1)−O(1)	60.7(2)	centroid 6−K(2)−N(5)	74.558(10)
N(1)−Th(1)−centroid 5	94.671(12)	O(2)−K(1)−N(2)	120.89(16)	O(3)−K(2)−O(4)	60.9(4)
N(3)−Th(1)−centroid 2	82.630(12)	O(1)−K(1)−N(2)	171.0(2)	O(3)−K(2)−centroid 4	104.179(3)
N(4)−Th(1)−centroid 2	93.262(12)	O(2)−K(1)−centroid 1	139.284(15)	O(4)−K(2)−centroid 4	95.292(4)
N(6)−Th(1)−centroid 2	158.605(12)	O(1)−K(1)−centroid 1	123.5(2)	N(5)−K(2)−centroid 4	73.947(9)
centroid 5−Th(1)−centroid 2	118.236	N(2)−K(1)−centroid 1	109.382(19)	centroid 4−K(2)−centroid 6	109.587(5)
N(3)−Th(1)−centroid 5	158.998(12)	O(2)−K(1)−centroid 3	107.405(12)	O(3)−K(2)−centroid 6	146.011(3)
N(3)−Th(1)−N(4)	100.563(16)	O(1)−K(1)−centroid 3	96.117(17)	O(4)−K(2)−centroid 6	111.246(5)
N(3)−Th(1)−N(6)	76.700(17)	N(2)−K(1)−centroid 3	74.882(10)		

Compound **4**[e]

Th(1)−O(3)	2.103(6)	Th(1)−O(2′)	2.465(6)	Th(1)−N(3)	2.511(8)	Th(1)−centroid 1	2.751(13)
Th(1)−O(2)	2.400(5)	Th(1)−N(1)	2.502(7)	Th(1)−O(1)	2.683(6)		

O(3)−Th(1)−O(2)	105.9(2)	O(2)−Th(1)−N(3)	127.9(2)	N(3)−Th(1)−O(1)	71.6(2)
O(3)−Th(1)−O(2′)	85.1(2)	O(2′)−Th(1)−N(3)	167.2(2)	O(3)−Th(1)−centroid	159.860(14)
O(2)−Th(1)−O(2′)	63.8(2)	N(1)−Th(1)−N(3)	92.3(2)	O(2)−Th(1)−centroid	107.165(13)
O(3)−Th(1)−N(1)	89.5(2)	O(3)−Th(1)−O(1)	76.0(2)	O(2′)−Th(1)−centroid	93.994(12)
O(2′)−Th(1)−N(1)	137.0(2)	O(2)−Th(1)−O(1)	63.22(19)	N(1)−Th(1)−centroid	77.908(2)
O(2)−Th(1)−N(1)	78.2(2)	O(2′)−Th(1)−O(1)	115.1(2)	N(3)−Th(1)−centroid	78.835(2)
O(3)−Th(1)−N(3)	86.1(2)	N(1)−Th(1)−O(1)	158.8(2)	O(1)−Th(1)−centroid	111.172(14)

Compound **5**[f]

Th(1)−N(1)	2.446(6)	Th(1)−N(3)	2.473(4)	Th(1)−Cl(1)	2.683(5)	Th(1)−centroid 2	2.807(13)
Th(1)−centroid 1	2.686(6)	Th(1)−N(4)	2.458(4)				

N(1)−Th(1)−centroid 1	80.756(2)	N(3)−Th(1)−centroid 1	81.716(12)	N(4)−Th(1)−centroid 1	100.998(10)
N(1)−Th(1)−N(3)	98.6(3)	N(3)−Th(1)−centroid 2	96.724(12)	N(4)−Th(1)−centroid 2	78.883(9)
N(1)−Th(1)−N(4)	91.8(3)	N(3)−Th(1)−centroid 2	96.724(12)	Cl(1)−Th(1)−centroid 1	87.539(11)
N(1)−Th(1)−Cl(1)	168.08(2)	N(3)−Th(1)−N(4)	169.57(2)	Cl(1)−Th(1)−centroid 2	82.740(11)
N(1)−Th(1)−centroid 2	108.962(2)	N(4)−Th(1)−Cl(1)	88.20(2)	centroid 1−Th(1)−centroid 2	170.278(3)
N(3)−Th(1)−Cl(1)	81.83(2)				

Compound **6**[g]

Th(1)−C(41)	2.808(16)	Th(1)−C(44)	2.381(16)	Th(1)−N(3)	2.466(13)	K(1)−C(15)	3.17(2)
Th(1)−C(43)	2.866(17)	Th(1)−N(1)	2.494(14)	Th(1)−N(4)	2.381(14)	K(1)−C(14)	3.22(2)
Th(1)−C(42)	2.880(15)	Th(1)−centroid 1	2.874(13)	Th(1)−N(5)	2.487(15)	K(1)−centroid 2	3.032(10)

Table 2 (Continued)

Compound **6**

N(4)−Th(1)−C(44)	78.9(5)	N(3)−Th(1)−N(1)	123.9(3)	C(15′)−K(1)−centroid 2	126.9(4)
N(4)−Th(1)−N(3)	99.8(5)	N(5)−Th(1)−N(1)	81.0(4)	C(14′)−K(1)−centroid 2	105.7(4)
C(44)−Th(1)−N(3)	113.3(5)	N(4)−Th(1)−centroid 1	89.820(3)	C(15′)−K(1)−centroid 2′	56.4(4)
N(4)−Th(1)−N(5)	134.8(5)	C(44)−Th(1)−centroid 1	164.364(4)	C(14′)−K(1)−centroid 2′	78.7(4)
C(44)−Th(1)−N(5)	63.1(5)	N(3)−Th(1)−centroid 1	79.138(3)	C(15′)−K(1)−C(15)	173.471(4)
N(3)−Th(1)−N(5)	75.8(5)	N(5)−Th(1)−centroid 1	131.447(3)	C(15′)−K(1)−C(14)	154.025(4)
N(4)−Th(1)−N(1)	131.3(4)	N(1)−Th(1)−centroid 1	79.138(3)	C(14′)−K(1)−C(14)	169.851(4)
C(44)−Th(1)−N(1)	99.7(5)	centroid 2−K(1)−centroid 2′	115.527(12)		

[a] Definitions: centroid 1, plane of [C(1), C(2), C(3), C(4), N(1)]; centroid 1′, plane of [C(1′), C(2′), C(3′), C(4′), N(1′)]; centroid 2, plane of [C(6), C(7), C(8), C(9), N(2)]; centroid 3, C(12), C(13), C(14), C(15), N(3). [b] Definition: centroid, plane of [C(7), C(8), C(9), C(10), N(11)]. [c] Definitions: centroid 1, plane of [C(1),C(2), C(3), C(4), N(1)]; centroid 2, plane of [C(18), C(19), C(20), C(21), N(2)]; centroid 3, plane of [C(35), C(36), C(37), C(38), N(3)]; centroid 2′, plane of [C(18′), C(19′), C(20′), C(21′), N(2′)]. [d] Definitions: centroid 1, plane of [C(1), C(2), C(3), C(4), N(1)]; centroid 2, plane of [C(6), C(7), C(8), C(9), N(2)]; centroid 3, plane of [C(11), C(12), C(13), C(14), N(3)]; centroid 4, plane of [C(1), C(2), C(3), C(4), N(1)]; centroid 5 = plane of [C(6), C(7), C(8), C(9), N(2)]; centroid 6, plane of [C(11), C(12), C(13), C(14), N(3)]. [e] Definitions: centroid 1, plane of [C(1), C(2), C(3), C(4), N(1)]; centroid 2, plane of [C(6), C(7), C(8), C(9), N(2)]; centroid 3, plane of [C(11), C(12), C(13), C(14), N(3)]; centroid 4, plane of [C(39), C(40), C(41), C(42), N(4)]; centroid 5, plane of [C(44), C(45), C(46), C(47), N(5)]; centroid 6, plane of [C(49), C(50), C(51), C(52), N(6)]. [f] Definitions: centroid 1, plane of [C(18), C(19), C(20), C(21), N(2)]; centroid 2, plane of [C(57), C(58), C(59), C(60), N(5)]. [g] Definitions: centroid 1, plane of [C(6), C(7), C(8), C(9), N(2)]; centroid 2, plane of [C(46), C(47), C(48), C(49), N(5)]; centroid 2′, plane of [C(46′), C(47′), C(48′), C(49′), N(5′)].

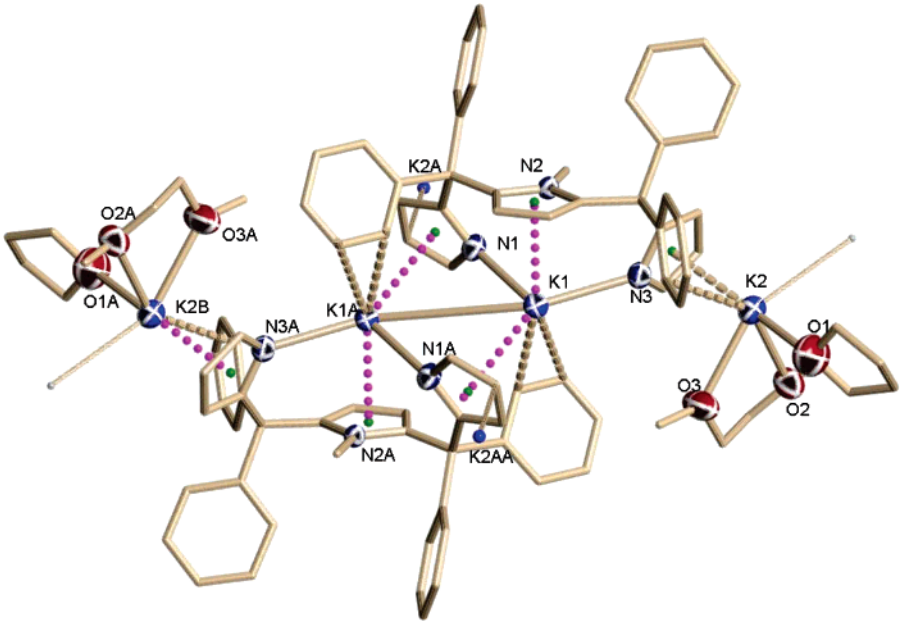


Figure 1. Simplified drawing of **1** with thermal ellipsoids drawn at the 30% probability level.

(K(1)−N(2) = 2.861(4) Å), which are each surrounded by one molecule of coordinated DME (K(1)−O(1) = 2.791(6) Å, K(1)−O(2) = 2.728(5) Å).

(e) Compound 5. The structure (Figure 5) consists of a symmetry-generated dimer where each of the two identical hepta-coordinate thorium atoms is surrounded by one tripyrrolide dianion, one methoxy group (Th(1)−O(3) = 2.103(6) Å), and one methoxyethoxide anion (Th(1)−O(2) = 2.400(5) Å) arising from the demethylation of DME (Th(1)−O(1) = 2.683(6) Å). The sharing of the anionic oxygen atom of this residue provides the bridging interaction which enforces the dinuclear structure (Th(1)−O(1) = 2.682(6) Å, Th(1)−O(2) = 2.433(6) Å). Each thorium atom is σ-bonded to two nitrogen atoms of the terminal pyrrole rings of the tripyrrolide (Th(1)−N(1) = 2.502(7) Å, Th(1)−N(3) = 2.511-(8) Å). The central alkylated pyrrole ring of the tripyrrolide dianion is also π-bonded to the metal (Th(1)−centroid = 2.751(7) Å). The overall geometry around thorium can be best described as a highly distorted pseudo pentagonal bipyramid with the axial positions occupied by the centroid of the π-coordinated central pyrrole of the tripyrrolide dianion and the oxygen atom of the methoxy group (centroid−Th(1)−O(3) = 159.86(14)°). The equatorial plane is defined by two σ-bonded nitrogen atoms of the terminal pyrrole rings of the tripyrrolide dianion, the two oxygen atoms of one methoxyethoxide, and the bridging oxygen atom of the methoxyethoxide group of the second identical unit (O(2)−Th(1)−O(2′) = 63.8(2)°, O(2′)−Th(1)−N(1) = 78.2(2)°, N(3)−Th(1)−O(1) = 71.6(2)°, N(1)−Th(1)−N(3) = 92.3(2)°, O(2)−Th(1)−N(1) = 78.2-(2)°).

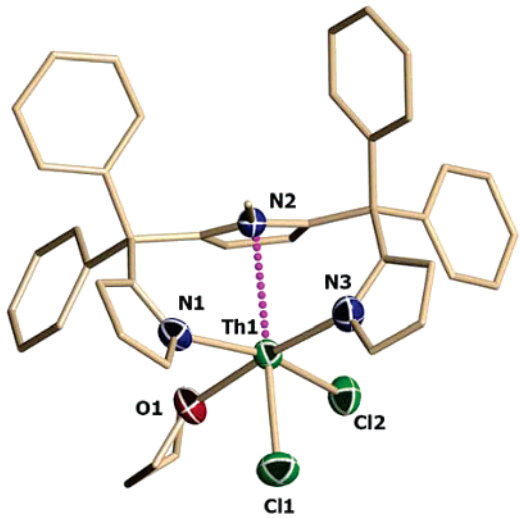


Figure 2. Simplified drawing of **2** with thermal ellipsoids drawn at the 30% probability level.

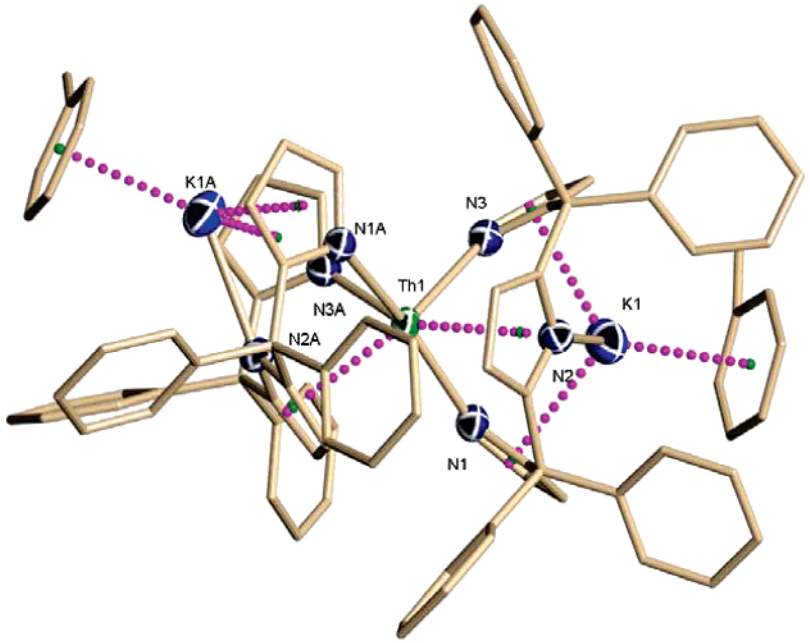


Figure 3. Simplified drawing of **3a** with thermal ellipsoids drawn at the 30% probability level.

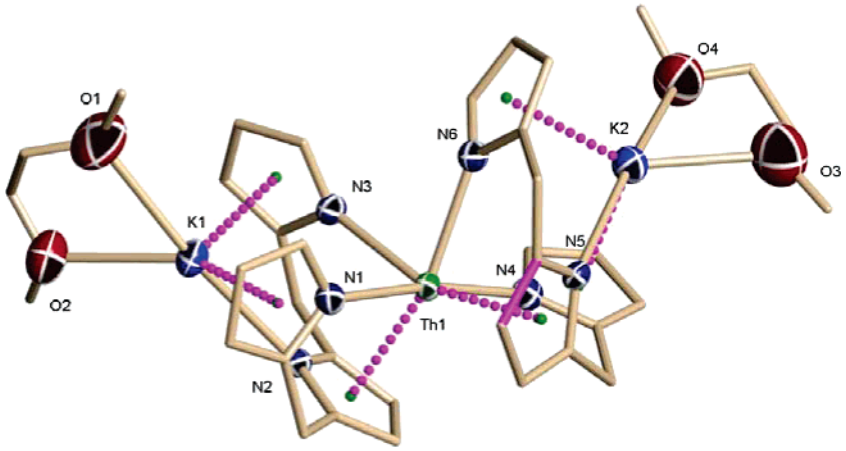


Figure 4. Simplified drawing of **3b** with thermal ellipsoids drawn at the 30% probability level. Aromatic rings have been omitted for clarity.

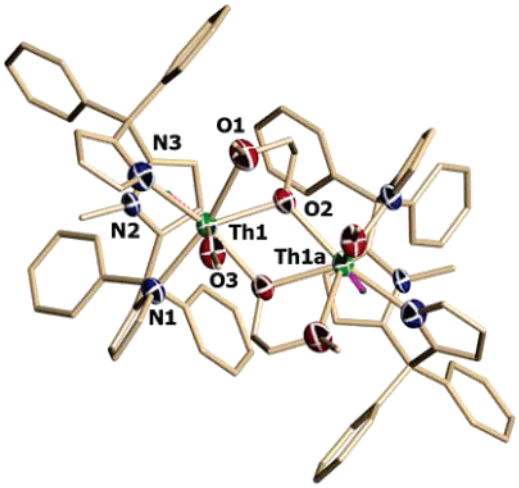


Figure 5. Simplified drawing of **5** with thermal ellipsoids drawn at the 30% probability level.

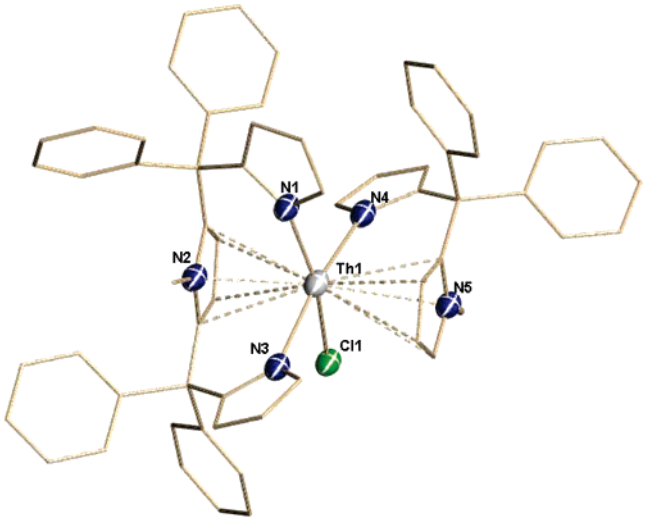


Figure 6. Simplified drawing of **6** with thermal ellipsoids drawn at the 30% probability level.

(f) Compound 6. The structure of **6** consists of a thorium atom surrounded by one tripyrrolide dianion, one dipyrrolide anion, and a chlorine atom (Th(1)−Cl = 2.683(5) Å) (Figure 6). The tripyrrolide dianion adopted the usual bonding mode with the two lateral rings σ-bonded at the N atoms (Th(1)−N(1) = 2.446(6) Å,

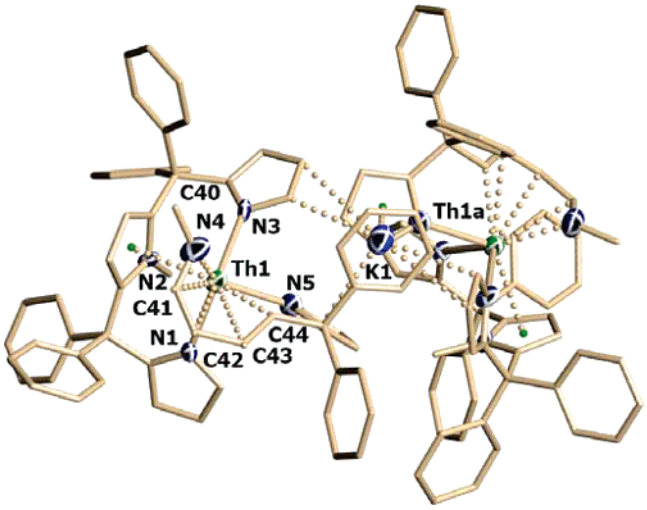


Figure 7. Thermal ellipsoid plot of the anionic part of **7**. Hydrogen atoms are omitted for clarity.

Th(1)−N(3) = 2.473(4) Å) and the central ring π-bonded to the metal (Th(1)−centroid = 2.753(8) Å). The dipyrrolide ligand also adopted the expected bonding mode with the deprotonated anionic ring σ-bonded to the metal (Th(1)−N(4) = 2.458(4) Å) and the alkylated ring π-bonded (Th(1)−centroid = 2.997(9) Å). Thus, the presence of two π-bonded rings from the two ligands confers a metallocene type of structure to the thorium atom sandwiched between two N-methylated pyrrole rings (centroid−Th(1)−centroid = 170.278(3)°). The chlorine and the other σ-bonded N atoms define the distorted equatorial plane of the overall pseudo-octahedral geometry (N(1)−Th(1)−N(3) = 98.6(3)°, N(1)−Th(1)−N(4) = 91.8(3)°, N(3)−Th(1)−Cl(1) = 81.83(17)°, N(4)−Th(1)−Cl(1) = 88.20(17)°).

(g) Compound 7. The structure of **7** consists of a hexacoordinated thorium atom surrounded by an intact tripyrrolide dianion and by a residue which appears to be the result of the opening of the alkylated ring of the dipyrrolide ligand (Figure 7). The tripyrrolide dianion adopted the usual geometry with the central ring π-bonded, although with a considerable ring slippage (Th(1)−N(2) = 2.938(15) Å, Th(1)−C(6) = 3.037(17) Å, Th(1)−C(9) = 3.118(18) Å). The two lateral rings are, as usual, σ-bonded through the N atoms (Th(1)−N(1) = 2.494(14) Å, Th(1)−N(3) = 2.466(13) Å). The former dipyrrolide ligand appears to have undergone a major transformation as a result of the reduction. The nonalkylated ring remained unmodified and σ-bonded to the metal center (Th(1)−N(5) = 2.487(15) Å). The N-alkylated ring has been opened via oxidative addition at the C−N bond, forming a pentadienyl−amido residue. This unit is σ-bonded to the N(Me) atom (Th(1)−N(4) = 2.381(14) Å), which appears to be sp^2 hybridized (C(41)−N(4)−Th(1) = 94.1(9)°, C(40)−N(4)−Th(1) = 139.2(9)°, C(41)−N(4)−C(40) = 115.7(13)°). The plane of the π-system of the pentadienyl−amide moiety is orthogonally oriented with respect to the metal center and with which is π-bonded (Th(1)−C(41) = 2.808(16) Å, Th(1)−C(42) = 2.880(15) Å, Th(1)−C(43) = 2.866(17) Å, Th(1)−C(44) = 2.381(16) Å). The resulting Th−C distances, although slightly longer, are still comparable to those of the Th−arene complexes.[6,12−14] Two nonequivalent potassium atoms (one per thorium) are also part of the dimeric unit. One of the two potassium atoms holds together two identical Th-containing units by π-coordinating one pyrrolide ring of the tripyrrole and the intact pyrrolide of the pentadienyl−amide of each thorium-containing unit. The second potassium is solvated by four molecules of DME and has no bonding contact with the dithorium−potassium anionic unit. Regrettably, the coordinated molecules of DME appeared to be heavily disordered over four positions and attempts at satisfactorily modeling the disorder failed. A satisfactory refinement with acceptable convergence factors was obtained by excluding the disordered molecules of DME by using the SQUEEZE routine of the PLATON program.[20]

Results and Discussion

The deprotonation of the tripyrrole ligand 2,5-[$(C_4H_3NH)CPh_2]_2C_4H_2N(Me)$ to give the corresponding dipotassium salt {2,5-[$(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]K$}[$K(DME)(THF)]_2$ (**1**) was conveniently carried out via standard treatment with a slight excess of KH in THF through a vigorous hydrogen-evolving reaction. (*Warning!* Hydrogen gas is a highly flammable and explosive gas, and proper care should be taken in venting.) Crystalline samples of **1** were obtained upon evaporation of the reaction mixture, followed by crystallization from DME. The ^{1}H NMR spectrum of **1** showed the two expected multiplets and a singlet, respectively, at 6.78, 5.98, and 5.41 ppm for the three pyrrole rings, while the *N*-methyl protons gave a sharp resonance at 2.20 ppm.

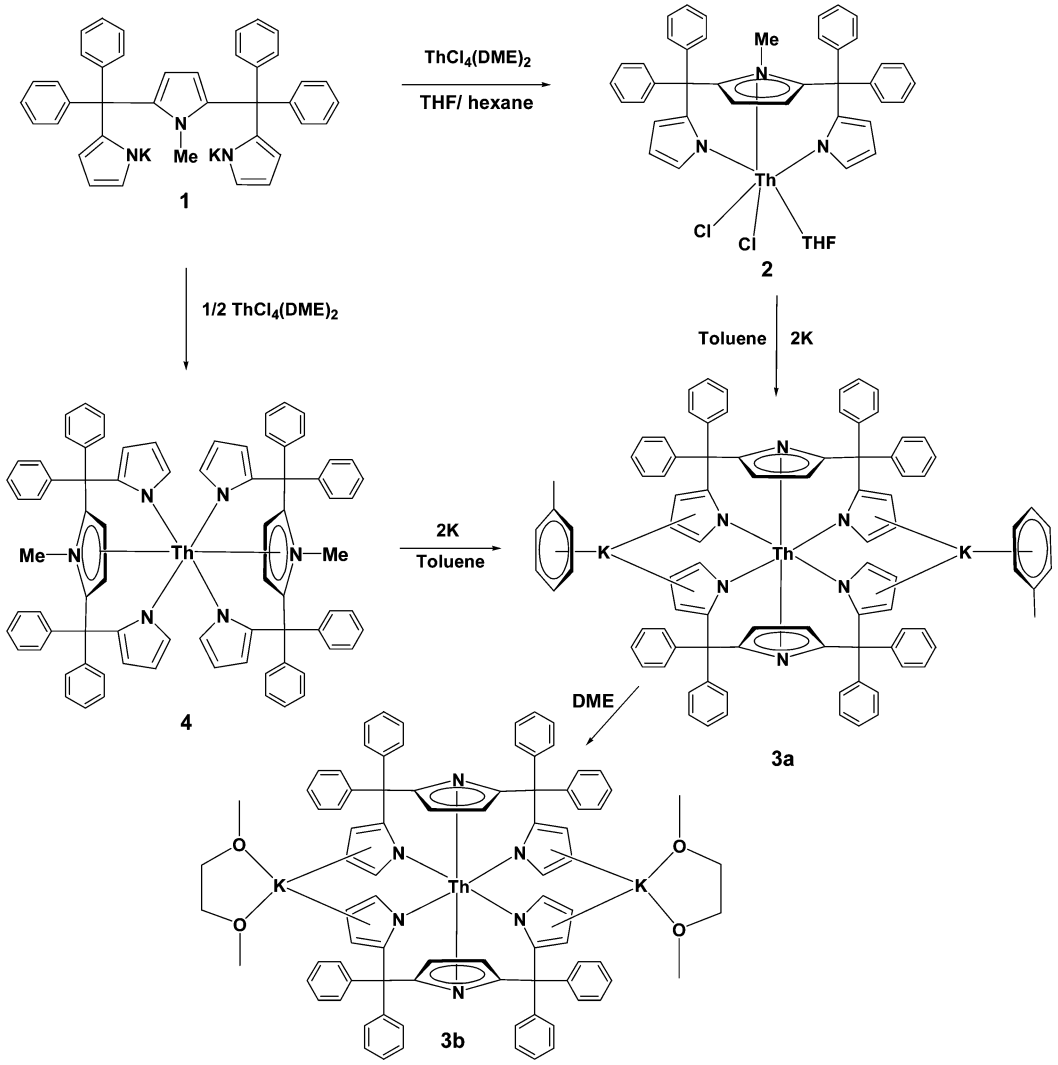
The complexation of **1** with $ThCl_4(DME)_2$ was carried out at room temperature in DME, affording the corresponding {2,5-[$(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]$}$ThCl_2(DME)$ (**2**) in 59% yield (Scheme 1). The yield of the reaction and the purity of the compounds were not significantly affected if **1** was generated in situ. The anionic pyrrole protons of **2** are present as two doublets at 8.17 and 6.56 ppm and as a triplet at 6.41 ppm in the ^{1}H NMR spectrum. The central pyrrole gives a sharp singlet at 6.52 ppm. The *N*-methyl protons form a sharp singlet at 2.40 ppm, corresponding to the ^{13}C NMR resonance at 37.12 ppm. The bridging quaternary carbon signal resonates at 58.21 ppm.

The π-interaction of the alkylated pyrrole ring in combination with the σ-bonding of the lateral rings makes the arrangement of the ligand reminiscent of that of the calix-tetrapyrrole ligands which were employed in lanthanide and actinide chemistry for a range of transformations.[2q−t,6,12] In the case of thorium, the use of porphyrinogen allowed for the isolation of a reduced Th complex of high reactivity.[12] Reduction of **2** was attempted with 2 equiv of metallic potassium in either toluene or DME at room temperature. In both cases, a dark red color developed rapidly upon stirring, followed by a slow discoloration over a few days of standing inside a drybox in a sealed vessel. In the case of the reduction in toluene, a rather substantial amount of colorless crystals was obtained by slow evaporation of the solvent. Unfortunately, any attempt to obtain analytically pure material of sufficient purity for a meaningful NMR characterization failed, due to the presence of an oily residue which could not be separated. Therefore, the formulation of the colorless crystals as {$[(C_4H_3N)CPh_2]_2[C_4H_2N]\}_2Th[K(toluene)]_2$ (**3a**) exclusively relied on its crystal structure determination. However, analytically pure, colorless crystals of the DME-solvated analogue {$[(C_4H_3N)CPh_2]_2[C_4H_2N]\}_2ThK_2(DME)_3$ (**3b**) were obtained in significant yield upon recrystallization from DME of the semicrystalline mass obtained upon evaporation of the reaction mixture of **3a**. The ^{1}H NMR spectrum confirmed the absence of *N*-methyl protons. The pyrrolide protons appear as two sets of two doublets at 6.63 and 6.62 ppm and at 5.62 and 5.61 ppm, and a triplet at 5.86 ppm appears for the protons of the terminal pyrrole rings. A singlet at 5.55 ppm is assigned to the protons of the central pyrrole ring.

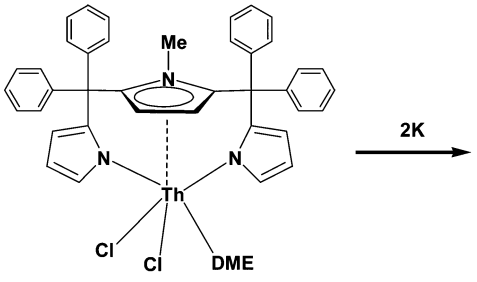
There are two main points of interest in the formation of **3a**,**b**. First, the structure of the complexes implies a major reorganization during the formation of the dark red intermediate or its subsequent decomposition. The fact that in complexes **3** each

(20) Berube, C. D.; Gambarotta, S.; Yap, G. P. A. *Organometallics* **2003**, *22*, 3742.

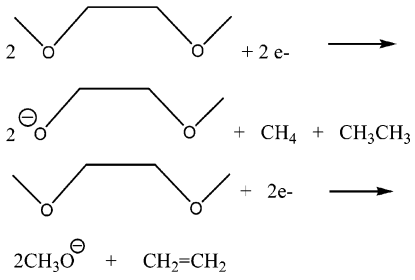
Scheme 1

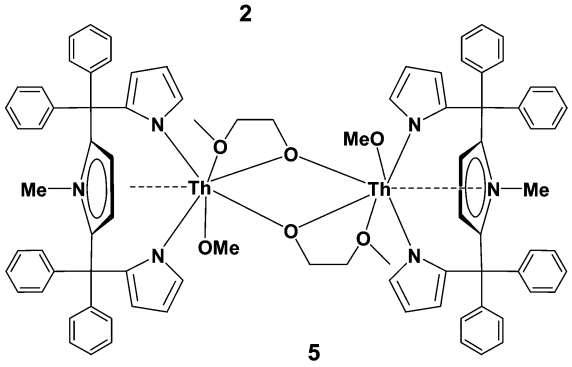


Scheme 2



Scheme 3

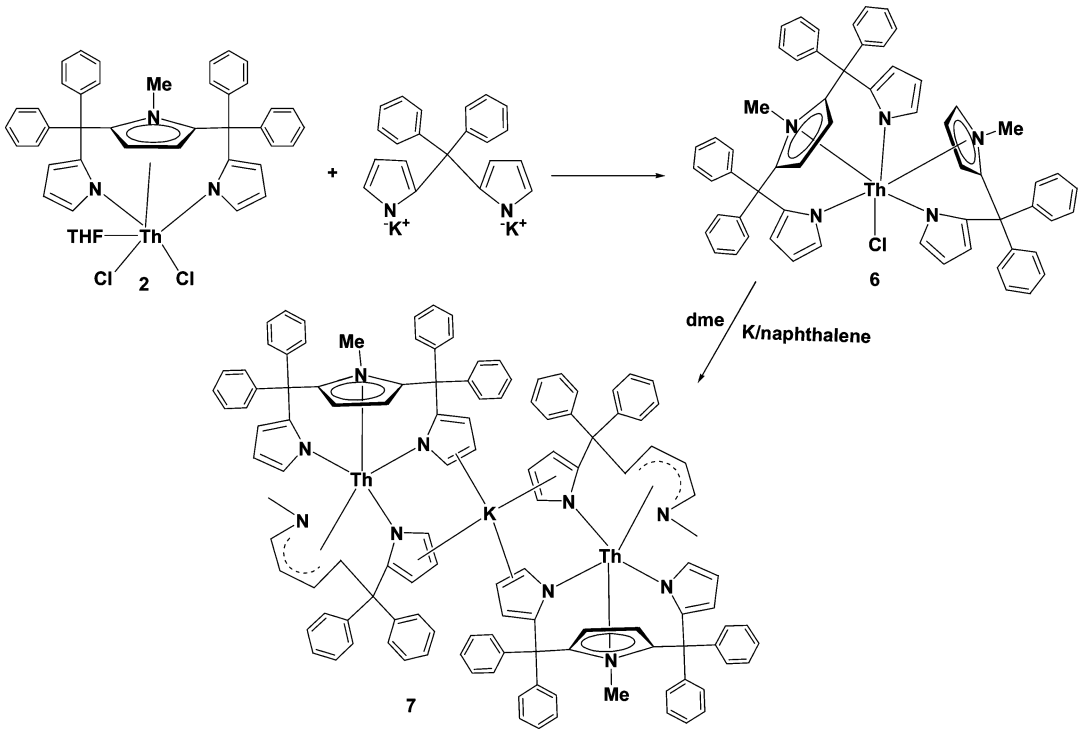




thorium atom is surrounded by two ligands implies that one metal has lost the ligand system. For this reason, reductions were also attempted under identical reaction conditions on the complex $\{2,5\text{-}[(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]\}_2Th$ (**4**), which already has *two* ligands surrounding the thorium atom. Complex **4** was readily obtained upon reaction of $ThCl_4(DME)_2$ with *2* equiv of **1**. Different from the case for **2**, **4** was completely insoluble in all common organic solvents, thus regrettably preventing its crystallization and spectroscopic characterization. However, combustion analysis data in agreement with the proposed formulation were obtained. As anticipated, reduction of **4** afforded a substantially higher yield of **3b** (56% isolated crystalline mass).

Second, the methyl group bonded to the N atom of the central ring has been eliminated, transforming the *di*anionic ligand into a rare tripyrrolide *tri*anion.[20] Given the structure of complexes **3**, it seems reasonable to propose that the C−N bond cleavage

Scheme 4



is most probably the result of a *one*-electron attack on the ligand system by a transient reduced species. Accordingly, the presence of both methane and ethane was clearly visible in the GC of the reaction mixtures. The reaction can be rationalized by assuming that the dark red intermediate, most probably a two-electron-reduced species according to the stoichiometry of the reduction, performed a one-electron attack at each N−Me bond of the two ligands present in **4**. In the case of the reduction of **2**, the transformation required the acquisition by the metal of the second ligand system; therefore, that reduction of **4** to **3** proceeds with substantially higher yield (56% isolated crystalline material) was just as expected.

When the reduction of **2** was carried out in DME instead of toluene, the reaction followed a very different pathway, leading to DME fragmentation resulting in the formation of a new complex, $[\{[(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]\}Th(OMe)(OC_2H_4OMe)]_2$ (**5**) (Scheme 2). Even in this case, the reaction proceeded through the transient formation of a dark red color, which slowly vanished, affording a colorless solution. Colorless crystals of **5** were obtained upon removal of the insoluble residue and layering of the filtrate with hexane for 15 days. The NMR spectra showed the expected resonances in the normal range and were in good agreement with the structural data.

Ether cleavage is not an infrequent event in the case of reduced f-block elements.[21] Although DME is normally regarded as the most resilient to attack, its deoxygenation and fragmentation have been already observed in the case of reduced thorium species.[12,13] Overall, the formation of **5** is the result of two different types of solvent cleavage performed by two metal centers on *three* molecules of DME. The presence of two methoxyethoxide anions, $MeOCH_2CH_2O^-$, in complex **5** implies that, from the formal point of view, *each of the two molecules of DME solvent has undergone a one-electron attack at one of the two Me−O bonds*. The result of each one-electron attack is the formation of one methyl radical and one methoxyethoxide anion. Accordingly, both CH_4 and ethane were present in the reaction mixture. On the other hand, the formation of the two methoxide anions may be the result of one-electron attack at each of the two $MeO-CH_2$ bonds of the *same* molecule of DME. In this event, one molecule of ethylene (also present in the reaction mixture) should be formed (Scheme 3). In the end, complex **5** may be formally regarded as the result of ligand scrambling between (ligand)$Th(OCH_2CH_2OMe)_2$ and (ligand)-$Th(OMe)_2$ complexes, each resulting from an overall two-electron attack by two reduced thorium species to, respectively, two or one DME molecule.

The formations of **3** and **5**, respectively, involving ligand C−N or solvent C−O bond cleavage, are both the result of overall *two*-electron redox processes per thorium atom. However, the type of attack and nature of the products seem to indicate that each bond cleavage is the result of separate *one*-electron attacks. This enhanced radical behavior by a reduced species with availability of more than one electron is also in line with the partial cleavage and hydrogenation of dinitrogen, as observed in the case of a reduced thorium complex.[13] Thus, in view of attempting further reduction reactions aimed at isolating the red intermediate, we have explored the possibility of adding one additional pyrrolide anion to **2** by replacing one of the two chlorine atoms with the *N*-Me dipyrrolide monoanion $\{[C_4H_3Nh]CPh_2[C_4H_3N(Me)]\}^-$. This ligand was regarded as especially promising because of the possibility of introducing additional π-coordination through its alkylated ring, which might provide even more electronic flexibility and delocalization.

The reaction of **2** with the potassium salt of the dipyrrole $[C_4H_3Nh]CPh_2[C_4H_3N(Me)]$ in DME and at room temperature afforded the corresponding $\{[(C_4H_3N)CPh_2]_2[C_4H_2N(Me)]\}$-

(21) See for example: (a) Evans, W. J.; Grate, J. W.; Hughes, L. A.; Zhang, H.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 3728. (b) Shumann, H. *Angew. Chem., Int. Ed. Engl*. **1984**, *23*, 474. (c) Dubé, T.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **1999**, *38*, 1432. (d) Korobkov, I.; Gambarotta, S.; Yap, G. P. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 814. (e) Schumann, H.; Palamidis, E.; Loebel, J. *J. Organomet. Chem.* **1990**, *384*, C49. (f) Pasynkiewicz, S.; Buchowicz, W.; Pietrzykowski, A. *J. Organomet. Chem.* **1997**, *531*, 121. (g) Ekkehard, B. *J. Organomet. Chem.* **1985**, *284*, 149. (h) Evans, W. J.; Allen, N. T.; Ziller, J. W. *J. Am. Chem. Soc*. **2001**, *123*, 7927.

ThCl{(C_4H_3N)CPh_2[C_4H_3N(Me)]} (**6**) in very good yield (81%) (Scheme 4). Its ^{1}H NMR spectrum showed the resonances for the pyrrolide rings as a series of multiples or doublets in the expected range and with the appropriate intensity ratio. The protons of the central pyrrole of the tripyrrole ligand N afforded a singlet at 5.50 ppm. The *N*-methyl protons of both dipyrrole and tripyrrole ligands appeared as two sharp resonances at 2.90 and 2.40 ppm corresponding to the ^{13}C signals at 35.23 and 32.00 ppm, respectively.

The reduction of **6** was carried out by adding 2 equiv of a solution of potassium naphthalenide in DME to a solution of **6** also in DME. The reactions proceeded via an instantaneous color change to deep red. The color of the solution slowly faded upon standing at room temperature, affording a colorless solution from which colorless plates of [{[(C_4H_3N)CPh_2]$_2$[C_4H_2N(Me)]}Th-{(C_4H_3N)CPh_2(C═CHCH═CHNMe)]}$_2$(*m*-K)][K(dme)$_4$] (**7**) were obtained after centrifugation and decantation of the reaction mixture followed by 1 week of slow diffusion of hexane (Scheme 4).

The formation of **7** is clearly the result of a straightforward two-electron oxidative addition of a reduced metal species to the ring C−N bond of the alkylated pyrrole of the dipyrrolide ligand. It is worth observing that a blank reaction of the dipyrrole ligand potassium salt carried out with potassium in the absence of Th did not afford ring opening. The presence of one potassium atom per thorium (one as part of the dinuclear array and the other in the lattice) clearly indicates that the amido−pentadiene moiety, generated by the ring opening, is dianionic. The ^{1}H NMR of **7** in THF-d_8 at room temperature was rather informative, showing a doublet of doublets at 5.55 ppm and a triplet at 6.80 ppm corresponding to the protons of the ring-opened pyrrolic moiety. The corresponding ^{13}C signals appear at 109.35 and 124.14 ppm. The resonance of the third vinylic proton is hidden under the multiplet of other pyrrolic protons in the range 5.97−6.06 ppm. A singlet at 5.50 ppm is assigned to the protons of the central pyrrole of the tripyrrolide dianion corresponding to the ^{13}C NMR resonance at 110.22 ppm. The signal for the *N*-methyl protons of the ring-opened pyrrole resonates at 2.90 ppm, whereas that of the tripyrrolide dianion appears at 2.40 ppm. These two resonances correlate with the corresponding ^{13}C NMR signals at 34.04 and 31.95 ppm, respectively.

In conclusion, attempts to isolate reduced thorium derivatives of the tripyrrolide dianion did not afford a clearly characterized reduced complex. Nonetheless, highly reactive intermediates, with lifetimes sufficiently long to enable an interesting variety of uncommon transformations, have been formed during the reduction. Each of the reactions reported above implies an overall two-electron attack by an intermediate two-electron-reduced thorium complex. However, it is rather interesting that, with the exception of the ring opening, the transformations are the result of two separate one-electron attacks at either C−O or C−N bonds. In turn, this suggests that reduced thorium species may provide radical types of reactivity. Should this behavior be confirmed and generalized, it will open interesting perspectives for a variety of molecular activation purposes. We are currently examining this possibility.

Acknowledgment. This work was supported by the Natural Science and Engineering Council of Canada (NSERC).

Supporting Information Available: Complete crystallographic data (CIF files) for all of the complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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