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Ligand Metallation during the Reduction of a Thorium(IV) Amide Complex

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Summary: The complex $[\{1,3\text{-}[2,6\text{-}(i\text{-}Pr)_2\text{-}C_6H_3N]_2(CH_2)_3\}_2\text{-}ThCl][Li(THF)_4]$ *(**1**), containing two chelating amides, was prepared via straightforward halogen replacement of* $ThCl_4(DME)$ *with dilithium salt of* $1,3\text{-}[2,6\text{-}(i\text{-}Pr)_2\text{-}C_6H_3NH]_2(CH_2)_3$*. Attempts to reduce this species were carried out with K(naphthalenide), affording an intermediate dark colored solution that slowly discolored and yielded colorless crystals of the tetravalent metallacyclic complex* $[\{1,3\text{-}[2,6\text{-}(i\text{-}Pr)_2\text{-}C_6H_3N]_2(CH_2)_3\}\{1,3\text{-}[2\text{-}(i\text{-}Pr)\text{-}6\text{-}(CH_2CHCH_2)C_6H_3N]_2\ (CH_2)_3\}Th][Li(DME)_3]$ *(**2**). In this species, one hydrogen atom of one neighboring ligand methyl group was eliminated to form a metallacyclic structure.*

Introduction

A recent flurry of results, clearly reiterating the very promising potential of trivalent uranium species for molecular activation,[1] has revitalized the interest for the preparation and reactivity of low-valent actinides,[2] or more appropriately, for their low-valent synthetic equivalents (low-valent synthons).[3] In fact, the chemistry of the lower valence state of actinides, which so far has been very rewarding for uranium,[4] poses substantial challenges for thorium given that its chemistry is strictly limited to the tetravalent state[5] with only a very few exceptions. Besides two trivalent Th complexes, both having the COT dianion as a supporting ligand,[6] even the simple ThI_2 is regarded as having the metal resting in a higher oxidation state with the electrons being located in semiconducting bands.[7] Nevertheless, there are some indications that, upon reduction, highly reactive Th species may be generated and uncommon transformations obtained.[8] For example, the reduction of a tetravalent (bis-aryloxide)$_2$Th derivative has provided a unique case of dinitrogen cleavage and hydrogen abstraction with formation of a terminally bonded $-NH_2$ group.[8a] In these transformations, the possibility of forming naphthalenide complexes seems to play an important part. The role of the coordinated naphthalene however is rather ambiguous. While in some cases naphthalene is dissociated in its intact form, thus implying that electrons are used for the reduction of the substrate,[8b] in other cases, it acts as a regular organometallic dianion for example inserting CO_2[9] or metathesizing H atoms from the ligand system.[10] Given that the chelating and bidentate bis-aryloxide ligand has provided so far the most rewarding results in terms of molecular activation,[8] we have now explored a similar reduction of a chelating bis-amide homoleptic Th(IV) derivative to probe how the metal center would respond to the reduction conditions in the presence of a chelating, nitrogen-donor-based ligand system.[11] While the reduction did not allow, in this case, the isolation of a naphthalenide derivative, it afforded the formation of a cyclometalated product via elimination of one hydrogen atom from one of the two methyl groups of the isopropyl substituents.

Experimental Section

All operations were performed under an inert atmosphere by using standard Schlenk techniques or inside a drybox. $ThCl_4(DME)_2$ was prepared from thorium nitrate by boiling with concentrated HCl and then dehydrated with thionyl chloride followed by recrystallization from DME. $1,3\text{-}[2,6\text{-}(i\text{-}Pr)_2\text{-}C_6H_3N]_2(CH_2)_3$ was synthesized according to literature procedures.[11] NMR spectra were recorded on a Bruker Avance 300 spectrometer. 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 Smart CCD area detector.

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Preparation of [{1,3-[2,6-(i-Pr)$_2$-C$_6$H$_3$N]$_2$(CH$_2$)$_3$}$_2$ThCl][Li(THF)$_4$] (1). A solution of methyllithium in ether (0.38 g, 17.7 mmol) was added dropwise at −30 °C to a stirred solution of 1,3-[2,6-(i-Pr)$_2$-C$_6$H$_3$NH]$_2$(CH$_2$)$_3$ (3.39 g, 8.5 mmol) in THF (50 mL). The resulting solution was allowed to reach room temperature before solid ThCl$_4$(DME)$_2$ (2.0 g, 4.3 mmol) was added. Stirring was continued overnight. The resulting solution was filtered and evaporated to dryness. The residual solid was washed with DME and redissolved in THF. Partial evaporation of THF, followed by cooling of the concentrated THF solution to −37 °C, gave colorless crystals of **1** (3.27 g, 56.2% yield). ^{1}H NMR (THF-d_8, 300 MHz, −40 °C): δ 7.12 (t), 6.98 (t), 6.84 (d), 6.75 (d), and 6.58 (t) [C*H* phenyl ring, 12H], 4.39 and 3.83 (septet, C*H* isopropyl, 8H), 3.63 (m, C*H*$_2$, THF, 16H) 3.50 and 3.10 (m, N-C*H*$_2$, 8H], 2.9 (br, N-CH$_2$-C*H*$_2$-CH$_2$, 4H), 1.78 (m, CH$_2$, THF, 16H) 1.52, 1.36, 1.32, 1.25, 1.17, 1.12, 0.87, 0.79 (d, C*H*$_3$ isopropyl, 48H). ^{13}C NMR (THF-d_8, 300 MHz, −40 °C): δ 157.39, 155.11, 146.69, 146.63, 146.31, and 145.36 (quaternary C), 124.63, 124.30, 123.53, 123.36, 123.05, and 121.01 (CH aromatic), 68.23 (CH$_2$ THF) 58.10 [N-*C*H$_2$], and 46.50 [N-CH$_2$-*C*H$_2$-CH$_2$], 26.38 (CH$_2$, THF), 28.72, 28.52, 28.17, and 28.06 [CH isopropyl], 29.26, 27.87, 27.34, 27.0, 26.87, 26.52, 25.90, 24.35 [CH$_3$ isopropyl]. Anal. Calcd (found) for C$_{70}$H$_{112}$ClLiN$_4$O$_4$Th: C, 62.37 (61.98); H, 8.37 (8.21); N, 4.16 (4.05).

Preparation of [{1,3-[2,6-(i-Pr)$_2$-C$_6$H$_3$N]$_2$(CH$_2$)$_3$}{1,3-[2-(i-Pr)-6-(CH$_2$CHCH$_2$)C$_6$H$_3$N]$_2$(CH$_2$)$_3$}Th][Li(DME)$_3$] (2). To a solution of potassium naphthalenide prepared in situ, by stirring potassium (0.08 g, 2.0 mmol) in DME (30 mL) with naphthalene (0.268 g, 2.0 mmol), compound **1** (1.4 g, 1.0 mmol) was added. The solution turned from dark green to dark red within 15 min, and stirring was continued for 12 h, during which time the color vanished. The solution was evaporated to dryness and the solid residue redissolved in ether. The suspension was filtered through Celite to remove a small amount of insoluble material and layered with hexane. Colorless crystals of **2**, contaminated with a dark colored precipitate, were formed after 2 days. X-ray quality crystals and analytically pure samples were obtained after three subsequent recrystallizations by dissolving the crystals in DME and layering with hexane (0.59 g, 44% yield). ^{1}H NMR (THF-d_8, 300 MHz): δ 7.00−6.60 (m, C*H* phenyl ring, 9H), 6.51 (d, C*H* phenyl ring, 2H), 6.21 (t, C*H* phenyl ring, 1H) 4.35 (m, C*H* isopropyl, 1H), 4.05 (m, C*H* isopropyl, 3H), 3.65 (m, C*H* isopropyl, 1H), 3.15 (m, C*H* isopropyl, 1H), 2.53 (m, C*H* isopropyl, 1H), 2.05 (m, C*H* isopropyl, 1H) 3.40 (m, N-C*H*$_2$, 2H), 3.29 (m, N-C*H*$_2$, 4H), 3.18 (m, N-C*H*$_2$, 2H), 3.36 (s, CH$_2$ DME, 12H), 3.15 (s, CH$_3$ DME, 18H), 2.96 (p, N-CH$_2$-C*H*$_2$-CH$_2$, 1H), 2.62 (p, N-CH$_2$-C*H*$_2$-CH$_2$, 1H), 1.50 (p, N-CH$_2$-C*H*$_2$-CH$_2$, 2H), 1.32 (d, isopropyl C*H*$_3$, 3H), 1.16 (m, isopropyl C*H*$_3$, 9H), 1.10 (m, isopropyl C*H*$_3$, 18H), 0.83, 0.80, 0.72, 0.63 (d, isopropyl C*H*$_3$, 12H), 0.55 (d, cyclometalated isopropyl C*H*$_2$, 1H), 0.48 (d, isopropyl C*H*$_3$, 3H), −0.75 (d, cyclometalated isopropyl C*H*$_2$, 1H). ^{13}C NMR (THF-d_8, 300 MHz): δ 157.87, 157.60, 156.69, 155.72, 147.13, 146.31, 145.56, 145.49, 145.42, 139.44 (quaternary aromatic *C*), 123.16, 122.59, 122.39, 121.34, 120.75, 120.66, 120.17, 117.42 (*C*H aromatic), 92.27 (cyclometalated *C*H$_2$), 71.92 (*C*H$_2$, DME), 58.60 (*C*H$_3$, DME) 58.39, 58.11, 55.71, 45.69 [N-*C*H2 (ligand)] 33.55, 32.90 [N-CH$_2$-*C*H$_2$ (ligand)], 35.5 (cyclometalated isopropyl C), 28.68, 27.90, 27.46, 27.37, 25.54 [isopropyl C (ligand)], 28.41, 27.69, 27.64, 27.59, 26.26, 26.08, 25.46, 25.42 [isopropyl methyl C (ligand)]. C$_{66}$H$_{109}$LiN$_4$O$_6$Th: C, 61.28 (61.23); H, 8.49 (8.41); N, 4.33 (4.29).

X-ray Crystallography. The data crystals of **1** and **2** were selected, mounted on thin glass fibers using thick paraffin oil, and cooled to the data collection temperature. Data 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 Edwald sphere. Semiempirical absorption corrections based on equivalent reflections were applied.[12] Systematic absences in the diffraction data sets and unit-cell parameters were consistent with $P\bar{1}$ for **1** and $P2(1)/n$ for **2**, respectively. 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 hydrogens were defined 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 used version being v.6.12 (Sheldrick, G. M. *SHELXTL*; Bruker AXS: Madison, WI, 2001). Crystallographic data and relevant bond distances and angles are reported in Tables 1 and 2, respectively.

Table 1. Crystal Data and Structure Analysis Results

	1	**2**
formula	C$_{70}$H$_{112}$ClLiN$_4$O$_4$Th	C$_{66}$H$_{109}$LiN$_4$O$_6$Th
M_w	1348.07	1293.55
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2(1)/n$
Z	2	4
a (Å)	13.019(2)	12.444(9)
b (Å)	14.487(3)	38.182(3)
c (Å)	19.575(4)	14.2669(10)
α (deg)	78.727(3)	90
β (deg)	78.637(3)	93.7970(10)
γ (deg)	89.989(3)	90
radiation (Mo Kα)	0.71073	0.71073
T (K)	208(2)	208(2)
D_{calcd} (Mg m^{-3})	1.262	1.268
μ_{calcd} (mm^{-3})	2.186	2.253
F_{000}	1404	2688
reflns collcd/unique	30 323/12 022	29 668/9702
R(int)	0.0660	0.1160
params rfnd	730	704
R	0.0584	0.0716
$R_w{}^2$	0.1418	0.1470
GoF	1.052	1.082

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

1		**2**	
Th(1)−N(4)	2.327(6)	Th(1)−N(2)	2.300(10)
Th(1)−N(3)	2.343(7)	Th(1)−N(3)	2.357(14)
Th(1)−N(2)	2.344(7)	Th(1)−N(4)	2.373(11)
Th(1)−N(1)	2.378(7)	Th(1)−N(1)	2.412(10)
Th(1)−Cl(1)	2.750(3)	Th(1)−C(27)	2.528(16)
N(4)−Th(1)−N(3)	89.1(2)	N(2)−Th(1)−N(3)	94.2(4)
N(4)−Th(1)−N(2)	161.0(2)	N(2)−Th(1)−N(4)	147.7(4)
N(3)−Th(1)−N(2))	102.7(2	N(3)−Th(1)−N(4)	84.5(5)
N(4)−Th(1)−N(1)	103.1(2)	N(2)−Th(1)−N(1)	90.0(4)
N(3)−Th(1)−N(1)	105.9(2)	N(3)−Th(1)−N(1)	115.2(4)
N(2)−Th(1)−N(1)	88.1(2)	N(4)−Th(1)−N(1)	119.8(4)
N(4)−Th(1)−Cl(1)	80.62(17)	N(2)−Th(1)−C(27)	72.6(5)
N(3)−Th(1)−Cl(1)	122.63(18)	N(3)−Th(1)−C(27)	134.0(5)
N(2)−Th(1)−Cl(1)	80.48(18)	N(4)−Th(1)−C(27)	85.1(5)
N(1)−Th(1)−Cl(1)	131.42(18)	N(1)−Th(1)−C(27)	108.8(5)

Results and Discussion

The reaction of ThCl$_4$(DME) with 2 equiv of the in situ generated dilithium salt of 1,3-[2,6-(i-Pr)$_2$-C$_6$H$_3$-NH]$_2$(CH$_2$)$_3$ afforded [{1,3-[2,6-(i-Pr)$_2$-C$_6$H$_3$N]$_2$(CH$_2$)$_3$}$_2$-ThCl][Li (THF)$_4$] (**1**) in 56% yield (Scheme 1).

The structure of **1** consists of a pentacoordinated thorium atom bonded to two 1,3-[2,6-(i-Pr)$_2$-C$_6$H$_3$N]$_2$-(CH$_2$)$_3$ units and one chlorine atom (Figure 1). The average Th−N distance [2.348 Å] is in the expected range, while the Th−Cl distance [Th(1)−Cl(1) = 2.750-

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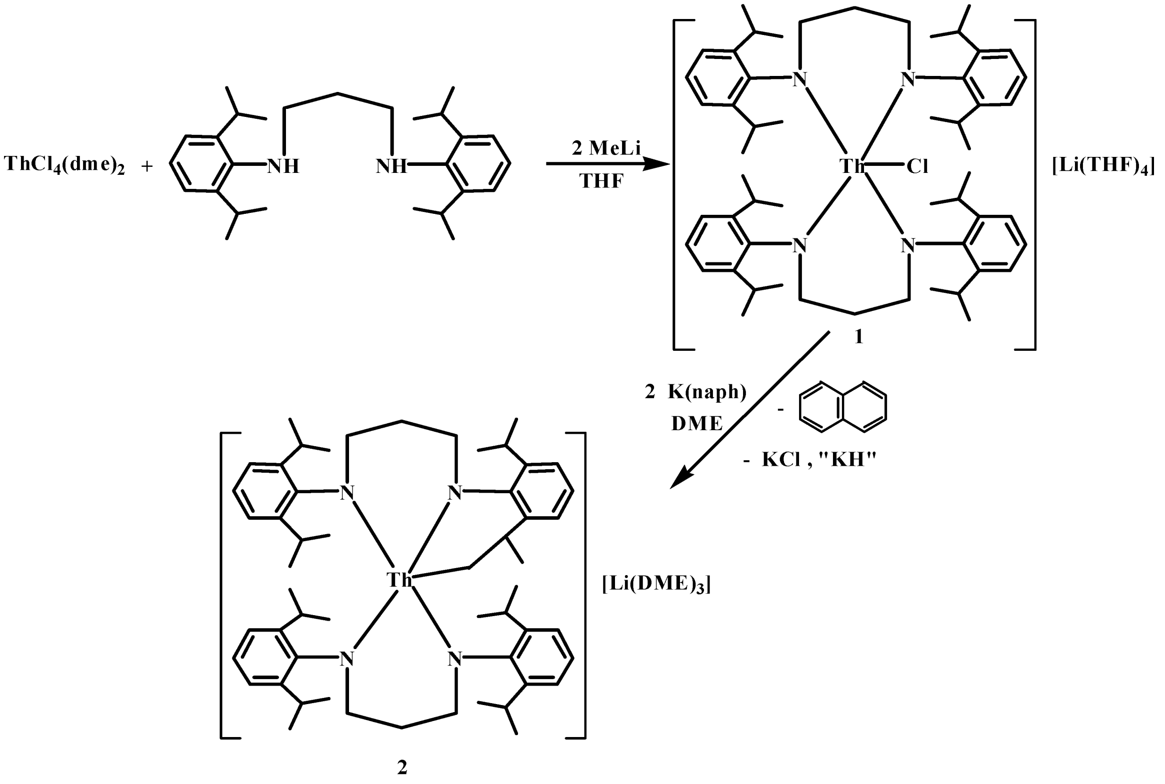
[12] Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

Scheme 1



(3) Å] is slightly longer than usual.[13] The coordination geometry around thorium can be described in terms of a distorted trigonal bipyramid. The chlorine atom and two of the four nitrogen atoms from two different ligands occupy the equatorial positions [N(1)−Th(1)−N(3) = 105.9(2)°, N(3)−Th(1)−Cl(1) = 122.63(18)°, N(1)−Th(1)−Cl(1) = 131.43(18)°], while the other two nitrogens [N(4)−Th(1)−N(2) = 161.0(2)°] are placed on the axial positions. One lithium atom, tetrahedrally solvated by four molecules of THF [average Li−O distance is 1.93 Å], completes the structure.

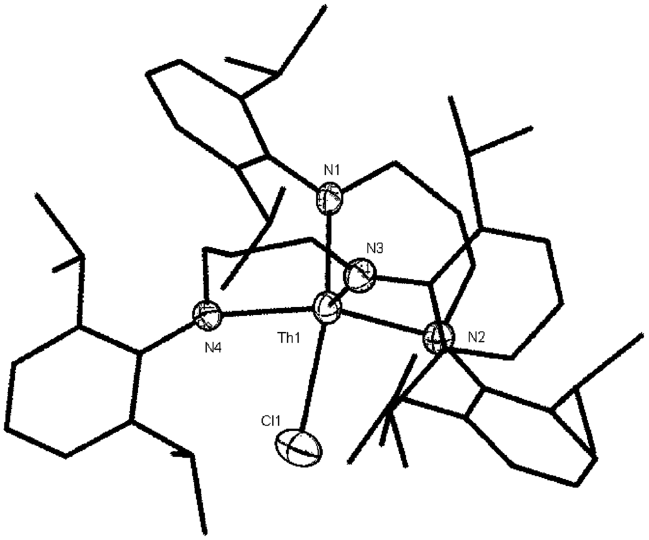


Figure 1. Plot of the anionic unit of **1** showing the thermal ellipsoids drawn at the 30% probability level. Anisotropic ellipsoids are shown only for relevant atoms for clarity reasons.

The room-temperature ^{1}H NMR of **1** was not informative due to broadening of the peaks caused by fluxional behavior in solution. While higher temperature did not improve the spectrum quality, a well-resolved spectrum was obtained at −40 °C. The aromatic region of the spectrum consists of three triplets and one doublet. The isopropyl CH groups appear as two septets at 4.39 and 3.83 ppm. The propyl chain linking the two nitrogen atoms gave two multiplets at 3.50 and 3.10 ppm of equivalent intensity due to the different locations of the contiguous N atom in the Th coordination sphere (axial versus equatorial). The central CH_2 groups appear as a broad singlet at 2.9 ppm. The isopropyl methyl groups attached to the aromatic rings gave eight doublets in the range 1.52 to 0.79 ppm. The ^{13}C NMR also recorded at −40 °C consists of four lines for the isopropyl CH carbon in the region from 28.72 to 28.06 ppm and eight lines for the isopropyl methyl carbon ranging from 29.26 to 24.35 ppm. Two different propyl carbon lines are present at 58.10 ppm, which corresponds to the carbon attached to the axial and equatorial nitrogen, while the line of the central carbon atom is at 46.50 ppm.

Attempts to reduce **1** were carried out by adding a solution of potassium naphthalenide in DME to a solution of **1** also in DME. The reactions gave an instantaneous color change to deep-red, which slowly

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(13) Trnka, T. M.; Bonanno, J. B.; Bridgewater, B. M.; Parkin, G. *Organometallics* **2001**, *20*, 3255.

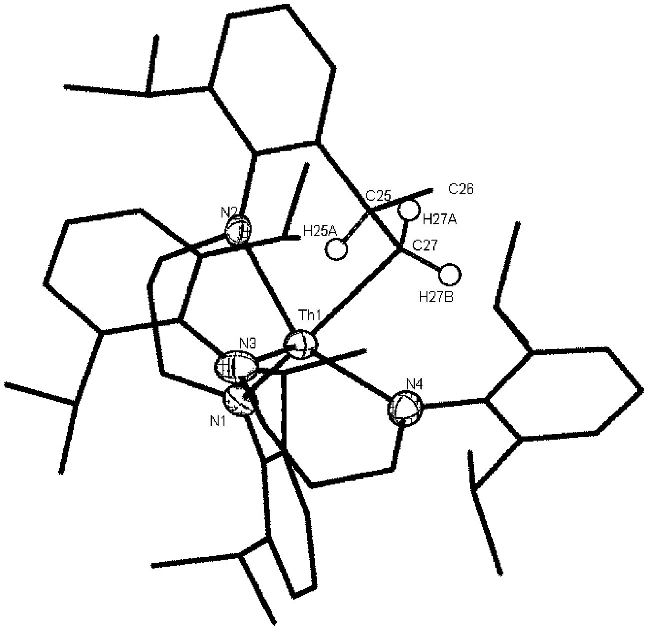

Figure 2. Plot of the anionic unit of **2** showing the thermal ellipsoids drawn at the 30% probability level. Anisotropic ellipsoids are shown only for relevant atoms for clarity reasons.

disappeared at room temperature (12 h). After suitable workup and repeated recrystallization, colorless crystals of $[\{1,3\text{-}[2,6\text{-}(i\text{-}Pr)_2\text{-}C_6H_3N]_2(CH_2)_3\}\{1,3\text{-}[2\text{-}(i\text{-}Pr)\text{-}6\text{-}CH_2\text{-}CHCH_2)C_6H_3N]_2(CH_2)_3\}Th][Li(DME)_3]$ (**2**) were obtained in analytically pure form and moderate yield (Scheme 1).

The structure of **2** consists of a thorium atom surrounded by four nitrogen atoms from two ligands and one carbon from one of the eight isopropyl group carbon atoms (Figure 2), which, by having lost one of the hydrogen atoms, forms a six-membered metallacycle with the thorium center. The Th−C distance [Th(1)−C(27) = 2.528(16) Å] formed with the deprotonated former methyl group is in the expected range for a regular Th−C σ-bond. The average Th−N distance [2.36 Å] compares well with that of complex **1**. As in the case of **1**, the coordination environment around Th may still be described in terms of a trigonal bipyramid despite the severe distortion introduced by the cyclometalation of one propyl group. The metalated carbon atom of the isopropyl group occupies one equatorial position together with the two N atoms, one from each of the two ligands [C(27)−Th(1)−N(3) = 134.0(5)°, C(27)−Th(1)−N(1) = 108.8(5)Å, N(1)−Th(1)−N(3) = 115.2(4)°]. The remaining two nitrogen atoms are located on the axial positions, forming an angle [N(2)−Th(1)−N(4) = 147.7(4)°] that largely deviates from linearity. One lithium atom solvated by three DME molecules and unconnected with the Th moiety completes the ionic structure of the complex

Unlike **1**, the ^{1}H NMR spectrum of **2** at room temperature was well resolved probably due to the fact that the cyclometalation prevented the molecule from being fluxional. The spectrum shows six different isopropyl CH groups. The CH corresponding to the cyclometalated isopropyl group shows a septet at 3.18 ppm, while the corresponding carbon signal appears at 35.5 ppm. The corresponding CH_2 directly bonded to the Th atom appears as two doublets at 0.55 and −0.75 ppm, correlating to the same ^{13}C resonance at 92.27 ppm.

The formation of a metallacycle by deprotonation of a ligand methyl group has a few precedents in the chemistry of thorium.[14] However, in all the reported cases it is a C−H σ-bond metathesis process that is at the origin of the formation of the metallacyclic structure. In the present case, the C−H bond activation leading to the formation of the metallacycle of **2** is occurring *during the reduction* and obviously has to be ascribed to a different pathway. In a first scenario similar to the case of monodentate aryloxide-Th complexes,[10] the naphthalenide anion may act as a base and metathesizes the ligand C−H σ-bond. In this case however, the reaction requires the intervention of two naphthalenide anions, and a mixture of naphthalene and 1,4-dihydronaphthalene should be formed. However, by carrying out reactions in NMR tubes we have exclusively observed formation of free naphthalene with no evidence for the presence of partly or fully hydrogenated forms of naphthalene. In addition, no hydrogen gas evolution could be detected by carrying the reaction in a sealed vessel connected to a Toepler pump. Thus, the only remaining possibility to explain this transformation is to assume that a transient divalent Th, or divalent synthetic equivalent, whose presence is also suggested by the transient dark red color, has performed C−H bond oxidative addition, followed by dissociation of KCl and KH. Although, the formation of KH could not be conclusively proved, nonetheless, the insoluble materials filtered off from the reaction mixture evolved hydrogen gas upon exposure to protic agents. Finally, the fact that a lithium cation instead of potassium is retained in the structure of **2** is likely to be ascribed to solubility or crystal packing reasons.

In summary, we have studied the reduction of a tetravalent thorium amide complex of a chelating amide. Attempts to reduce this species and to form either a naphthalenide complex or a low-valent synthetic equivalent species afforded attack to the ligand and formation of a metallacyclic structure. The reaction proceeds via formation of a dark colored species which slowly disappeared. This, together with the fact that only free naphthalene was observed in the reaction mixture, suggests that an intermediate reduced species may in fact be formed.

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

Supporting Information Available: Listings of atomic coordinates, thermal parameters, and bond distances and angles for the structures reported in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

OM049120W

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[14] See for example: (a) Simpson, S. J.; Turner, H. W.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 2991. (b) Bruno, J. W.; Marks, T. J. *J. Am. Chem. Soc.* **1982**, *104*, 7357. (c) Bruno, J. W.; Smith, G. M.; Marks, T. J.; Fair, C. K.; Schultz, A. J.; Williams, J. M. *J. Am. Chem. Soc.* **1986**, *108*, 40. (d) Bruno, J. W.; Marks, T. J. *J. Organomet. Chem.* **1983**, *250*, 237.