

# A Thermally Robust Di-*n*-Butyl Thorium Complex with an Unstable Dimethyl Analogue

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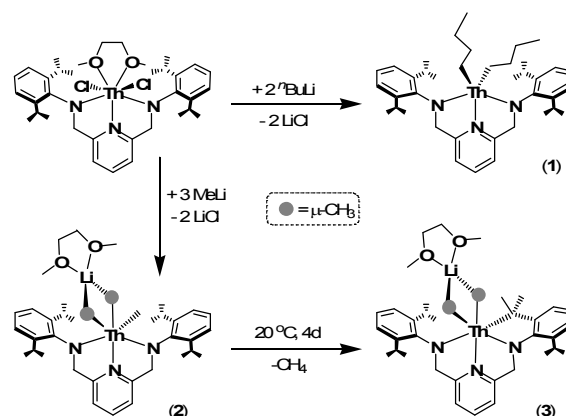
Methyl and *n*-butyl thorium complexes of a rigid 2,6-bis(anilidomethyl)pyridine ligand have been prepared; the *n*-butyl complex is thermally stable, even at 60 °C, while the methyl complexes exhibit a high tendency to eliminate methane via  $\sigma$ -bond metathesis.

Much of organoactinide chemistry has focused on complexes supported by carbocyclic ligands, especially  $C_5R_5^-$  anions,<sup>1</sup> and a broad range of thermally robust  $[Cp^*_2AnR_2]$  and  $[Cp_3AnR]$  (An = Th or U) complexes have been reported. Hydrocarbyl anions in these complexes range from bulky and  $\beta$ -hydrogen-free  $CH_2SiMe_3$  and  $CH_2Ph$  groups, to sterically undemanding methyl groups, to  $\beta$ -hydrogen-containing *n*-butyl,<sup>2</sup> isopropyl, and *tert*-butyl groups.<sup>3,4</sup>

The stability of the  $\beta$ -hydrogen containing derivatives is particularly remarkable and may be attributed, at least in part, to the high strength of An–C bonds, relative to An–H bonds.<sup>5,6</sup> However, the influence of ancillary ligands on An–C bond strengths has been noted,<sup>5</sup> and  $\beta$ -hydrogen elimination was reported as a facile decomposition mechanism in early attempts to prepare polyalkyl derivatives. For example, the reactions of  $UCl_4$  with <sup>n</sup>BuLi or <sup>t</sup>BuLi have been reported as a route to colloidal/pyrophoric uranium metal or soluble uranium(III) hydride species.<sup>7</sup>

A range of non-cyclopentadienyl alkyl complexes have also been prepared. However, most employ bulky (*e.g.*  $CH_2EMe_3$ ; E = Si or C) or potentially polyhapto  $CH_2Ph$  ligands,<sup>4</sup> leaving simple alkyl derivatives less well represented. For example, isolated non-cyclopentadienyl thorium methyl complexes are limited to  $[ThMe\{\mu-Me\}_2Li(tmeda)\}_3]$ ,<sup>8</sup>  $[ThMeR_3(dmpe)_x]$  (R = Me,  $x = 2$ ; R =  $CH_2Ph$ ,  $x = 1$ ),<sup>9</sup>  $[(Me_3Si)_2N\}_3ThMe]$ <sup>10</sup> and  $[(Et_8-calix[4]tetrapyrrole)Th\}_2(\mu-O)(\mu-Me)\{K(dme)\}(\mu-K)-\{K(dme-)_4\}]_n$ ,<sup>11</sup> and well defined non-cyclopentadienyl actinide complexes bearing simple  $\beta$ -hydrogen-containing alkyl groups appear to be absent from the literature.<sup>12</sup> Herein we report the preparation of both methyl and *n*-butyl derivatives of a bulky NNN-donor ligand, BDPP [BDPP = 2,6-bis(2,6-diisopropylanilidomethyl)pyridine].<sup>13</sup>

Reaction of  $[(BDPP)ThCl_2(dme)]^{14}$  with 2 equivalents of <sup>n</sup>BuLi provided highly soluble  $[(BDPP)Th(^nBu)_2]$  (**1**) as an off-white solid in 57 % yield (Scheme 1).§ Complex **1** shows remarkable thermal stability, with no decomposition after days at 60 °C in benzene. The structure of **1** is likely distorted square pyramidal by analogy with  $[(BDPP)Th(CH_2Ph)_2]$ .<sup>15</sup> However, NMR spectra of **1** show one *n*-butyl environment down to –90 °C, with  $ThCH_2$  <sup>1</sup>H and <sup>13</sup>C NMR signals located at 0.35 and 87.7 ppm (<sup>1</sup>*J*<sub>C,H</sub> 118 Hz) at room temperature. By

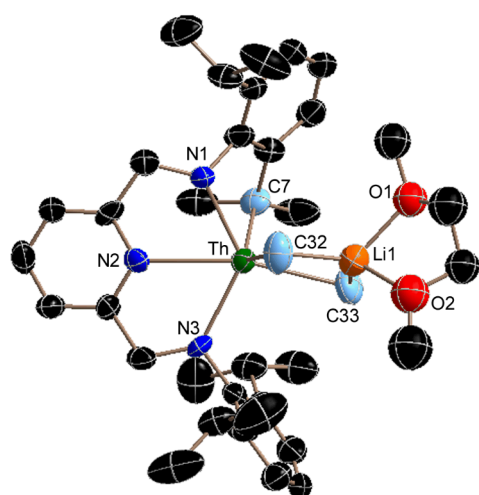


Scheme 1

contrast, two different alkyl group environments were observed in the low temperature NMR spectra of  $[(BDPP)Th(CH_2SiMe_3)_2]$  and  $[(BDPP)Th(CH_2Ph)_2]$ , presumably due to increased steric hindrance relative to **1**, and polyhapto benzyl-coordination in the latter complex.<sup>14,15</sup>

Reaction of  $[(BDPP)ThCl_2(dme)]$  with 3 equivalents of MeLi provided the trimethyl ‘ate’ complex,  $[(BDPP)ThMe_3\{Li(dme)\}]$  (**2**) in 74% isolated yield (Scheme 1).§ At room temperature, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **2** show a single Th–Me peak (<sup>1</sup>H NMR  $\delta$  0.02 ppm; <sup>13</sup>C NMR  $\delta$  55.9 ppm), and only one *CHMe*<sub>2</sub> peak was observed for the BDPP ligand. At –70 °C in *d*<sub>8</sub>-toluene, several BDPP ligand signals began to de-coalesce but were not resolved even at –90 °C. These data require rapid exchange of the in-plane and axial methyl groups in **2**, as well as rapid transfer of the  $Li(dme)^+$  moiety between methyl ligands. The involvement of MeLi dissociation in this process is unlikely given that the thorium-methyl groups in **2** do not undergo exchange with  $LiCD_3/LiI$  in toluene, even after several hours at room temperature. Similar dynamic behaviour was observed for  $[ThMe\{\mu-Me\}_2Li(tmeda)\}_3]$ , in which all thorium methyl groups are equivalent (<sup>1</sup>H NMR  $\delta$  0.02 ppm) on the NMR timescale, even at at –90 °C.<sup>8</sup>

As a solid, compound **2** is stable for extended periods of time at 20 °C. However, in solution, **2** decomposes over several days to form orange-brown  $[(BDPP^*)Th(\mu-Me)_2Li(dme)]$  [**3**; BDPP\* = 2,6-NC<sub>6</sub>H<sub>3</sub>(CH<sub>2</sub>NAr)(CH<sub>2</sub>N{C<sub>6</sub>H<sub>3</sub><sup>Pr</sup>(CMe<sub>2</sub>)-2,6)}; Ar = 2,6-diisopropylphenyl; donor atoms in BDPP\* are underlined]§ as the major product (> 80 % yield by <sup>1</sup>H NMR spectroscopy). Highly soluble **3** was isolated from hexamethyldisiloxane in low yield, and shows no sign of



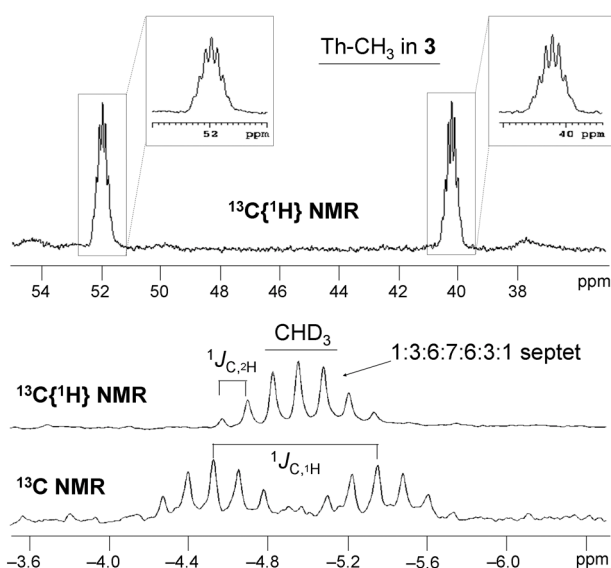
**Fig. 1.** X-Ray Crystal Structure of  $[(\text{BDPP}^*)\text{Th}(\mu\text{-Me})_2\text{Li}(\text{dme})]\cdot\text{hexane}$  (**3-hexane**) with thermal ellipsoids at 50%. Hydrogen atoms and hexane are omitted for clarity. In addition, only one of two orientations of the Li(dme) unit is shown.

decomposition after days in benzene at 80 °C, despite the presence of a  $\beta$ -hydrogen-containing tertiary alkyl group in the BDPP\* ligand. The two methyl groups in **3** are observed at  $-0.09$  and  $-0.32$  ppm in the  $^1\text{H}$  NMR spectrum, and at 53.0 and 41.4 ppm in the  $^{13}\text{C}$  NMR spectrum. The metallated carbon atom ( $\text{ThCMe}_2\text{Ar}$ ) lies at 73.6 ppm in the  $^{13}\text{C}$  NMR spectrum, and the attached methyl groups ( $\text{ThCMe}_2\text{Ar}$ ) give rise to singlets at 2.39 and 1.22 ppm in the  $^1\text{H}$  NMR spectrum.

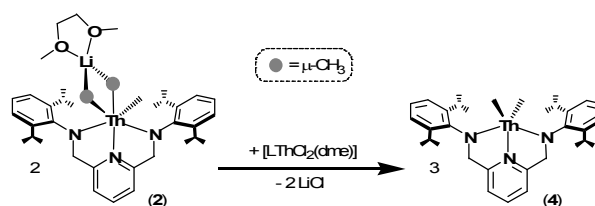
Complex **3** is the product of metallation at the *methyne* carbon in an isopropyl group of the BDPP ligand (Scheme 1). Metallation of *N*-2,6-diisopropylphenyl groups is common in early transition metal and *f*-element chemistry, but typically occurs at a *methyl* group; rare examples of isopropyl methyne metallation have been reported for  $[(\text{BDPP})\text{Lu}(\text{AlMe}_4)]^{16}$  and  $[(\text{nacnac})(\text{X})\text{Ti}=\text{CH}^t\text{Bu}]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{OTf}, \text{BH}_4, \text{CH}_2\text{SiMe}_3$ ).<sup>17</sup>

Crystals of **3-hexane** were obtained from toluene/hexane at  $-30$  °C,<sup>18,19</sup> and reveal distorted octahedral geometry at thorium and approximately tetrahedral geometry at lithium (Fig. 1). Thorium lies in a plane with N(1), N(2), N(3) and C(32), while C(33) and C(7) are located above and below the plane of the BDPP\* ligand backbone. The acute C(32)–Th–C(33) angle  $[80.9(4)^\circ]$  is primarily a consequence of Li(dme)<sup>+</sup> bridging between the two methyl groups, while constraints imposed by the BDPP\* ligand backbone are responsible for the acute N(1)–Th–N(2), N(2)–Th–N(3) and N(1)–Th–C(7) angles of  $63.5(3)^\circ$ ,  $63.9(3)^\circ$  and  $70.7(3)^\circ$ , respectively.

The Th–C(32) and Th–C(33) distances of 2.679(13) and 2.635(12) Å are longer than Th–C(7) [2.566(12) Å], likely due to Li(dme)<sup>+</sup> coordination, but lie at the shorter end of the range of Th–C distances observed for bridging methyl groups in 7-coordinate  $[\text{ThMe}\{\mu\text{-Me}\}_2\text{Li}(\text{tmeda})_3]$  (2.65–2.77 Å).<sup>8</sup> The Th–N(1) distance [2.298(9) Å] in **3** is slightly shorter than Th–N(3) [2.350(9) Å], presumably due to metallation of the aryl substituent on N(1). For comparison, the Th–N<sub>amido</sub> distances in  $[(\text{BDPP})\text{Th}(\text{CH}_2\text{Ph})_2]$  are 2.27 and 2.30 Å. At 2.614(9) Å, the Th–N<sub>py</sub> distance in **3** is longer than that in  $[(\text{BDPP})\text{Th}(\text{CH}_2\text{Ph})_2]$  [2.545(4) Å], but is comparable to Th–N<sub>py</sub> in sterically encumbered  $[\text{Th}(\text{BDPP})_2]$  [2.615(6) Å].<sup>14,15</sup>



**Fig. 2.** Thorium methyl and methane signals in  $^{13}\text{C}$  and/or  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of the reaction to form **3**- $^{13}\text{C}_2\text{d}_6$  from **2**- $^{13}\text{C}_3\text{d}_9$  in  $\text{C}_6\text{D}_6$ .



**Scheme 2**

To probe the mechanism for the formation of complex **3**,  $[(\text{BDPP})\text{Th}(\text{CD}_3)_3\{\text{Li}(\text{dme})\}(\text{LiCl})]$  (**2**- $^{13}\text{C}_3\text{d}_9$ ) was prepared by reaction of  $[(\text{BDPP})\text{ThCl}_2(\text{dme})]$  with  $\text{Li}^{13}\text{CD}_3/\text{LiI}$ . Thermal decomposition of **2**- $^{13}\text{C}_3\text{d}_9$  yielded only  $^{13}\text{CHD}_3$  (not  $^{13}\text{CD}_4$ ) and  $[(\text{BDPP}^*)\text{Th}(\mu\text{-}^{13}\text{CD}_3)_2\text{Li}(\text{dme})]$  (rather than the  $^{13}\text{CD}_3/^{13}\text{CHD}_2$  complex) by  $^{13}\text{C}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopy (Fig. 2). These products are consistent with a simple  $\sigma$ -bond metathesis pathway, rather than a mechanism involving initial  $\alpha$ -deuterium abstraction to release  $\text{CD}_4$ .

Reaction of two equivalents of complex **2** with  $[(\text{BDPP})\text{ThCl}_2]$  provided  $[(\text{BDPP})\text{ThMe}_2]$  (**4**, Scheme 2) in 81 % yield.<sup>§</sup> The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **4** are indicative of a highly symmetric molecule containing a single set of  $\text{CHMe}_2$ ,  $\text{CH}_2$  and  $\text{Th-CH}_3$  environments ( $^1\text{H}$  NMR  $\delta$  0.01 ppm;  $^{13}\text{C}$  NMR  $\delta$  82.5 ppm), even at  $-80$  °C. This behaviour is analogous to that observed for dibutyl complex **1**. However, while organothorium BDPP complexes such as **1**,  $[(\text{BDPP})\text{Th}(\text{CH}_2\text{SiMe}_3)_2]$ ,<sup>14</sup> and  $[(\text{BDPP})\text{Th}(\text{CH}_2\text{Ph})_2]$ <sup>15</sup> rival the thermal stability of their bis-pentamethyl-cyclopentadienyl counterparts,<sup>20</sup> dimethyl complex **4** is entirely decomposed (to yield several unidentified products) after two hours at room temperature.<sup>¶</sup> This behaviour lies in clear contrast to that of  $[\text{Cp}^*_2\text{ThMe}_2]$ , which is *more* stable than the  $\text{CH}_2\text{SiMe}_3$  and  $\text{CH}_2\text{Ph}$  analogues, being only 50 % decomposed after 1 week at 100 °C.<sup>21</sup> The thermal instability of  $\beta$ -hydrogen-free **4** is also unusual in light of the stability of the  $\beta$ -hydrogen-containing *n*-butyl analogue (**1**; *vide supra*).<sup>||</sup> However,

monitoring the decomposition of in-situ generated [(BDPP)Th(<sup>13</sup>CD<sub>3</sub>)<sub>2</sub>] by <sup>13</sup>C and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy again showed the formation of only H<sup>13</sup>CD<sub>3</sub> (rather than <sup>13</sup>CD<sub>4</sub>), consistent with a straightforward σ-bond metathesis mechanism for methane elimination.

In conclusion, a highly soluble 2,6-bis(anilidomethyl)-pyridine di-*n*-butyl thorium complex (**1**) has been prepared, and is resistant to β-hydrogen elimination even at 60 °C. To the best of our knowledge, **1** is the first isolated non-cyclopentadienyl complex bearing simple β-hydrogen-containing alkyl groups. Rare examples of non-cyclopentadienyl thorium methyl complexes (**2-4**) were also prepared, several of which show an unexpectedly high tendency to engage in methane elimination via σ-bond metathesis. Dialkyl complexes such as those reported here are of particular interest as precatalysts for olefin polymerization.<sup>22</sup> This work highlights the extent to which longer chain primary alkyl groups may in some situations provide access to *f*-element dialkyl complexes with greatly enhanced thermal stability and solubility relative to methyl derivatives, and decreased steric hindrance and/or coordinative saturation relative to analogues bearing common CH<sub>2</sub>EMe<sub>3</sub> (E = C or Si) or CH<sub>2</sub>Ph anions.

## Notes and references

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† Electronic Supplementary Information (ESI) available: Crystallographic information, experimental details, and the synthesis and characterisation of all new compounds. See DOI: 10.1039/b000000x/

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§ A qualitative flame test was used to test for lithium in complexes **1-4**. Positive results, indicating the presence of lithium, were obtained for **2** and **3**, but not for **1** and **4**. The presence or absence of lithium in **1-4** was also verified by elemental analysis (for **1-3**), an X-ray crystal structure of **3**, and the incorporation of dme in complexes **2** and **3**, but not **1** and **4**.

¶ Addition of MeLi to the reaction mixture did not result in simplification of the <sup>1</sup>H NMR spectrum.

|| UV-irradiation (medium pressure mercury lamp) of **1** in benzene lead only to extensive decomposition.

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- 18 Structure **3**•hexane: C<sub>43</sub>H<sub>70</sub>LiN<sub>3</sub>O<sub>2</sub>Th, *M* = 900.02, monoclinic, *a* = 34.258(7), *b* = 14.286(3), *c* = 17.419(4) Å, β = 102.922(4), *U* = 8309(3) Å<sup>3</sup>, *T* = 173(2) K, space group *C2/c*, *Z* = 8, 41676 reflections, 7306 unique (*R*<sub>int</sub> = 0.1567), *R*<sub>1</sub> = 0.0645 & *wR*<sub>2</sub> = 0.1268 [*I* > 2σ(*I*)].
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