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5 Cationic Thorium Alkyl Complexes of Rigid NON-  
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10 and NNN-Donor Ligands:  $\pi$ -Arene Coordination as a  
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14 Persistent Structural Motif  
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**Abstract**

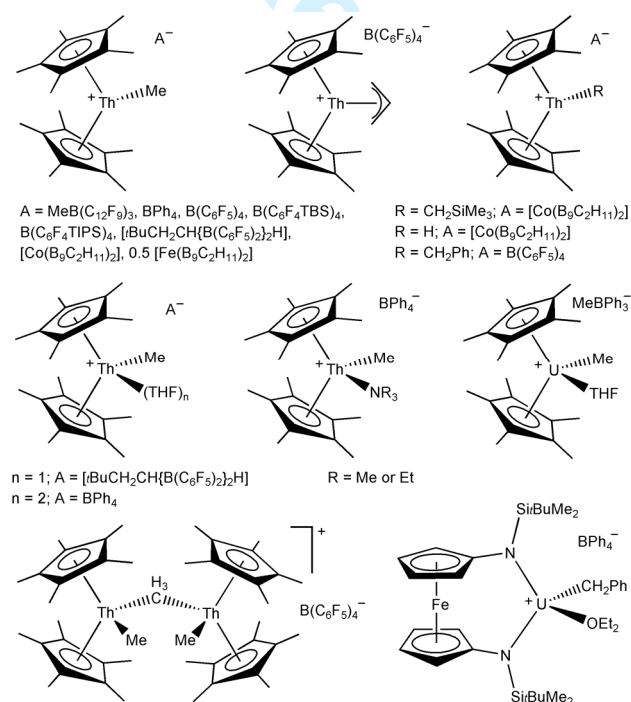
Reaction of the neutral dialkyl complex  $[(X_{A_2})Th(CH_2SiMe_3)_2]$  (**1**;  $X_{A_2}$  = 4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene) with  $[CPh_3][B(C_6F_5)_4]$  in benzene or toluene at room temperature resulted in the formation of  $[(X_{A_2})Th(CH_2SiMe_3)(\eta^6\text{-arene})][B(C_6F_5)_4]$  {arene =  $C_6H_6$  (**5**) and toluene (**5B**)}, which were characterized by  $^1H$ ,  $^{13}C$  and 2D NMR spectroscopy and by X-ray crystallography (for **5**). In close analogy, reaction of  $[(X_{A_2})Th(CH_2Ph)_2]$  (**3**) with  $[CPh_3][B(C_6F_5)_4]$  in toluene at room temperature resulted in the formation of 1 equiv of  $Ph_3CCH_2R$  ( $R = Ph$ ) and precipitation of an insoluble orange-brown oil, which upon layering with hexanes yielded crystals of  $[(X_{A_2})Th(\eta^2\text{-}CH_2Ph)(\eta^6\text{-}C_6H_5Me)][B(C_6F_5)_4]$  (**6**). NMR investigation of the reactions of **1** and **3** with substoichiometric amounts of  $[CPh_3][B(C_6F_5)_4]$  provided no evidence for dinuclear monocation formation. By contrast, reaction of  $[(BDPP)Th(CH_2Ph)_2]$  (**4**; BDPP = 2,6-bis(2,6-diisopropylanilidomethyl)pyridine) with 0.5 equivalents of  $[CPh_3][B(C_6F_5)_4]$  resulted in the precipitation of an insoluble oil containing a mixture of a mononuclear and a dinuclear cation; the dinuclear cation was identified as  $[(BDPP)Th(\eta^2\text{-}CH_2Ph)(\mu\text{-}\eta^1:\eta^6\text{-}CH_2Ph)Th(\eta^1\text{-}CH_2Ph)(BDPP)][B(C_6F_5)_4]$  (**7**) by X-ray crystallography. Reaction of complex **3** with  $B(C_6F_5)_3$  resulted in the formation of  $[(X_{A_2})Th(\eta^1\text{-}CH_2Ph)][\eta^6\text{-}PhCH_2B(C_6F_5)_3]$  (**9**) which was characterized in solution by NMR spectroscopy. Complexes **5**, **5B** and **6** are rare examples of arene solvent-separated ion pairs, complex **9** exists as a tight contact ion pair, and dinuclear **7** exhibits a unique benzyl ligand bridging mode. The structures of cations **5-7** and **9** highlight a pronounced tendency for these systems to engage in arene  $\pi$ -coordination.

## Introduction

The vast majority of catalysts for insertion polymerization of ethylene and/or  $\alpha$ -olefins are coordinatively unsaturated cationic metal alkyl complexes,<sup>1,2</sup> and this field is particularly well developed for the tetravalent group 4 elements zirconium and titanium. Typical catalysts include  $[\text{Cp}^*_2\text{ZrMe}][\text{A}]$ ,  $[\text{Cp}^*(\text{MeInd})\text{TiMe}][\text{A}]$  (MeInd = 1-methylindenyl) and  $[\{\text{SiMe}_2(\text{C}_5\text{Me}_4)(\text{N}t\text{Bu})\}\text{MMe}][\text{A}]$  (M = Zr or Ti),<sup>1</sup> as well as the non-cyclopentadienyl complexes  $[(\text{R}_3\text{PN})_2\text{TiMe}][\text{A}]$  (Stephan et al.) and  $[\{\text{CH}_2(\text{CH}_2\text{NAr})_2\}\text{TiMe}][\text{A}]$  (McConville et al.) where A is a weakly coordinating anion such as  $\text{MeB}(\text{C}_6\text{F}_5)_3$  or  $\text{B}(\text{C}_6\text{F}_5)_4$ .<sup>2</sup> Polymerization catalysts of the predominantly trivalent group 3 and lanthanide metals have also been a subject of intense recent investigation, and high activities have now been achieved for neutral, monocationic and dicationic complexes bearing either cyclopentadienyl or non-cyclopentadienyl ancillaries.<sup>2,3</sup>

By contrast, effective actinide olefin polymerization catalysts remain rare, and non-cyclopentadienyl systems have yet to be developed. In fact, the only isolated base-free mononuclear actinide alkyl cations (Figure 1) have been reported by the Marks group, and are of the form  $[\text{Cp}^*_2\text{ThR}][\text{A}]$  (R = Me,<sup>4-9</sup>  $\text{CH}_2\text{SiMe}_3$ ,<sup>7</sup>  $\text{CH}_2\text{Ph}$ ,<sup>8</sup> allyl<sup>4</sup> and  $\text{H}^{7,10}$ ) where A is either a weakly-coordinating borate anion or  $[\text{M}(\text{B}_9\text{C}_2\text{H}_{11})_2]^{x-}$  (M = Co,  $x = 1$ ; M = Fe,  $x = 2$ ). In these publications, activity for ethylene polymerization was reported only for methyl complexes paired with borate anions. However, olefin polymerization catalysts prepared from  $[\{\text{Me}_2\text{Si}(\text{indenyl})_2\}\text{AnMe}_2]$  as well as  $[\text{Cp}^*_2\text{AnMe}_2]$  (An = Th or U) are mentioned in several T. J. Marks patents.<sup>11</sup> In addition, The Dow Chemical Company has patented a variety of pentaalkylcyclopentadienyl actinide polymerization catalysts, including those formed from  $[\text{Cp}^*_2\text{AnX}_2]$  and  $[\text{Cp}^*\text{AnX}_3]$  (An = Th and U; X = Cl, Me or  $\text{CH}_2\text{SiMe}_3$ ) in combination with activators such as MAO.<sup>12</sup> Marks *et al.* also reported highly active heterogeneous olefin polymerization catalysts, which are similar in nature to  $[\text{Cp}^*_2\text{ThR}][\text{A}]$ , but are formed by reaction of thorium and/or uranium polyalkyl complexes with dehydroxylated  $\gamma$ -alumina or  $\text{MgCl}_2$ .<sup>13</sup> Other actinide alkyl cations are

$[(Cp^*_2ThMe)_2(\mu-Me)][B(C_6F_5)_4]^{4,8,14}$  which exists in equilibrium with  $[Cp^*_2ThMe_2]$  and  $[Cp^*_2ThMe][B(C_6F_5)_4]$  in solution, and the Lewis base stabilized cations  $[Cp^*_2ThMe(L)_x][A]$  ( $L = THF$  or  $NR_3$ ;  $x = 1-3$ ),<sup>6</sup>  $[Cp^*_2UMe(THF)][MeBPh_3]^{15,16}$  and  $[LU(CH_2Ph)(OEt_2)][BPh_4]$  ( $L = Fe(C_5H_4NSiBuMe_2)_2$ )<sup>17</sup> (Figure 1). Several cationic actinide aryl, alkynyl and borohydride complexes have also been reported.<sup>18,19</sup>

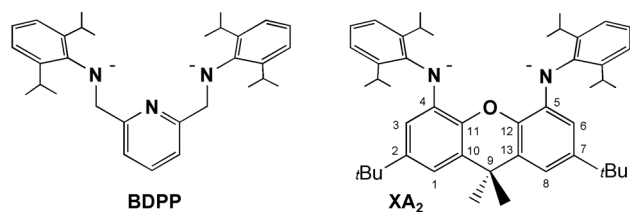


**Figure 1.** Literature examples of cationic thorium and uranium alkyl complexes.

As with the lanthanide metals and group 3 metals Y and Lu,<sup>3,20</sup> many of the challenges in the chemistry of thorium and uranium stem from the large radii and electropositivity of these elements,<sup>21</sup> which leads to a propensity for donor solvent coordination, dinuclear complex formation, ligand redistribution reactions, and often kinetically facile decomposition.<sup>22</sup> However, actinide complexes are unique in their potential for significant covalency and *f*-orbital involvement in bonding,<sup>23</sup> and in actinide organometallic chemistry, unlike lanthanide and group 3 chemistry, the tetravalent state is also dominant.<sup>24</sup>

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2 These properties not only present challenges for the design of new actinide polymerization catalysts,  
3 especially those based on non-cyclopentadienyl ligands, but also offer the tantalizing potential for  
4 polymerization behaviour<sup>25</sup> that is significantly different from that of both early transition metal and  
5 lanthanide catalysts.  
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11 A major focus of our research program is the development of non-cyclopentadienyl organoactinide  
12 chemistry, and in particular, exploration of ligand features necessary for the synthesis of: (a) thermally  
13 robust thorium(IV) dialkyl precursors, (b) isolable actinide(IV) alkyl cations, and (c) active ethylene and  
14  $\alpha$ -olefin polymerization catalysts. To this end, our research has focused on the tridentate, dianionic  
15 supporting ligands 2,6-bis(2,6-diisopropylanilidomethyl)pyridine (BDPP)<sup>26</sup> and 4,5-bis(2,6-  
16 diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene (XA<sub>2</sub>); Figure 2.<sup>27,28</sup> Key features of BDPP and  
17 XA<sub>2</sub> are a large metal binding pocket, sterically bulky 2,6-diisopropylphenyl rings flanking the metal  
18 coordination site, and extremely high rigidity (especially in XA<sub>2</sub>). These ligand features are considered  
19 important in order to effectively accommodate large actinide metals, provide sufficient steric and  
20 electronic saturation at the metal, and ensure effective positioning of steric bulk. This strategy has allowed  
21 the synthesis of the dialkyl complexes [LTh(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] {L = XA<sub>2</sub> (**1**) and BDPP (**2**)},<sup>27</sup>  
22 [(XA<sub>2</sub>)Th(CH<sub>2</sub>Ph)<sub>2</sub>] (**3**)<sup>29</sup> and [(BDPP)Th(CH<sub>2</sub>Ph)<sub>2</sub>] (**4**; this work)}, which show remarkably high thermal  
23 stability. For example, the thermal stability of **2** is even greater than that of [Cp\*<sub>2</sub>Th(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>].<sup>30</sup>  
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52 **Figure 2.** Structures of the BDPP and XA<sub>2</sub> Ligands.  
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2 With robust dialkyl complexes in hand, we turned our attention to the synthesis of thorium(IV)  
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4 alkyl cations by alkyl abstraction from **1-4**. As described above, cationic  $d^0$  transition metal and  $f$ -block  
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6 complexes of this type are well established as the active species in olefin polymerization catalysis.<sup>31,32</sup>  
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8 However, while contact ion pairs (CIPs) such as  $[\text{Cp}^*\text{ZrMe}][\text{MeB}(\text{C}_6\text{F}_5)_3]$  have been studied in detail,  
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10 and solvent-separated ion pairs (SSIPs) involving strong donor solvents are common (e.g.  
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12  $[\text{Cp}^*\text{ZrMe}(\text{THF})][\text{MeB}(\text{C}_6\text{F}_5)_3]$ ),<sup>32</sup> SSIPs involving weakly coordinated arene solvents are rare, and  
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14 their impact on olefin polymerization activity and selectivity is not well understood. McConville *et al.*  
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16 invoked species of the form  $[\{\text{CH}_2(\text{CH}_2\text{NAr})_2\}\text{TiR}(\eta^6\text{-toluene})]^+$  {Ar = Xyl or  $\text{C}_6\text{H}_3i\text{Pr}_{2-2,6}$ } to explain  
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18 greatly reduced polymerization activities observed in the presence of small amounts of toluene.<sup>33</sup> In  
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20 addition, Piers *et al.* have reported the synthesis of  $[(\text{nacnac}^{\text{Me}_2})\text{ScMe}(\eta^6\text{-C}_6\text{R}_6)][\text{B}(\text{C}_6\text{F}_5)_4]$  ( $\text{C}_6\text{R}_6$  =  
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22 bromobenzene, benzene, toluene, *p*-xylene or mesitylene), and while  $[(\text{nacnac}^{\text{Me}_2})\text{ScMe}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3\text{-}$   
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24  $1,3,5)][\text{B}(\text{C}_6\text{F}_5)_4]$  is an active ethylene polymerization catalyst in bromobenzene, it shows negligible  
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26 activity in more strongly donating toluene.<sup>34</sup> Other  $d^0$  arene solvent coordinated alkyl complexes are:  
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28  $[\text{Cp}''\text{MR}_2(\eta^6\text{-toluene})][\text{RB}(\text{C}_6\text{F}_5)_3]$  {M = Zr, R = Me; M = Hf, R = Me or Et; Cp'' = 1,3- $\text{C}_5\text{H}_3(\text{SiMe}_3)_2$ }  
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30 in which the arene is tightly coordinated,<sup>35</sup>  $[\text{Cp}^*\text{MMe}_2(\eta^6\text{-C}_6\text{R}_6)][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (M = Ti,  $\text{C}_6\text{R}_6$  = toluene  
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32 or mesitylene; M = Zr,  $\text{C}_6\text{R}_6$  = benzene, toluene, *p*-xylene, *m*-xylene, mesitylene, styrene; M = Hf,  $\text{C}_6\text{R}_6$   
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34 = toluene, *p*-xylene, *m*-xylene, mesitylene, styrene, anisole) in which the arene is particularly labile for  
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36 M = Ti,<sup>36</sup> and  $[\{t\text{BuNSiMe}_2(\eta^5, \eta^1\text{-C}_5\text{Me}_3\text{CH}_2)\}\text{Ti}(\text{toluene})][\text{B}(\text{C}_6\text{F}_5)_4]$  in which the arene is only weakly  
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38 bound.<sup>37</sup>

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48 The complexes discussed above highlight a greater tendency towards arene solvent coordination  
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50 in more sterically open cationic alkyl species, especially mono-cyclopentadienyl complexes and  
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52 complexes of certain non-cyclopentadienyl ligand systems. It therefore follows that  $\pi$ -arene coordination  
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54 might be particularly favorable in cationic alkyl complexes of the large  $f$ -block metals, and since  $\pi$ -arene  
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56 coordination can result in diminished or negated olefin polymerization activity (due to limited access of  
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olefin monomer to the metal as a result of  $\pi$ -arene coordination, or the much lower solubility of many SSIPs relative to CIPs), insight into the favorability and nature of metal-arene interactions has implications for both the design of new non-cyclopentadienyl supporting ligands for use in *f*-block olefin polymerization catalysis, and the choice of olefin polymerization conditions.

Herein we report the reactions of **1-4** with  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  and  $\text{B}(\text{C}_6\text{F}_5)_3$ , and solution and/or solid-state characterization of the first non-cyclopentadienyl thorium alkyl cations:

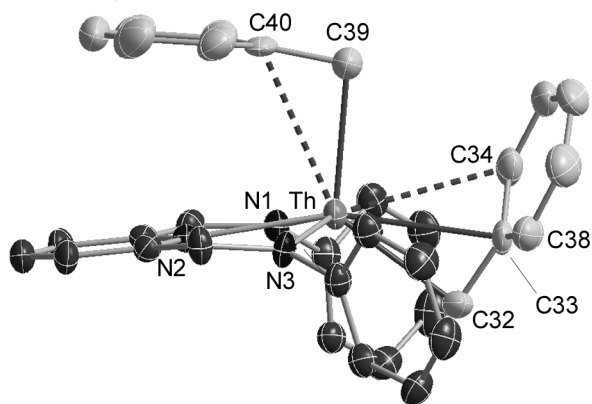
$[(\text{XA}_2)\text{Th}(\text{CH}_2\text{SiMe}_3)(\eta^6\text{-arene})][\text{B}(\text{C}_6\text{F}_5)_4]$  [arene = benzene (**5**) or toluene (**5B**)],  
 $[(\text{XA}_2)\text{Th}(\eta^2\text{-CH}_2\text{Ph})(\eta^6\text{-C}_6\text{H}_5\text{Me})][\text{B}(\text{C}_6\text{F}_5)_4]$  (**6**),  $[(\text{BDPP})\text{Th}(\eta^2\text{-CH}_2\text{Ph})(\mu\text{-}\eta^1\text{:}\eta^6\text{-CH}_2\text{Ph})\text{Th}(\eta^1\text{-CH}_2\text{Ph})(\text{BDPP})][\text{B}(\text{C}_6\text{F}_5)_4]$  (**7**) and  $[(\text{XA}_2)\text{Th}(\eta^1\text{-CH}_2\text{Ph})][\eta^6\text{-PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]$  (**9**).

## Results and Discussion

The neutral dialkyl complexes  $[\text{LTh}(\text{CH}_2\text{SiMe}_3)_2]$  {L =  $\text{XA}_2$  (**1**) and BDPP (**2**)<sup>27</sup> and  $[(\text{XA}_2)\text{Th}(\text{CH}_2\text{Ph})_2]$  (**3**)<sup>29</sup> were prepared as previously reported; by reaction of  $[\text{LThCl}_2(\text{dme})]$  (L =  $\text{XA}_2$  or BDPP) with two equivalents of  $\text{LiCH}_2\text{SiMe}_3$  or  $\text{PhCH}_2\text{MgCl}$  at  $-78$  °C. Dibenzyl complex  $[(\text{BDPP})\text{Th}(\eta^2\text{-CH}_2\text{Ph})(\eta^3\text{-CH}_2\text{Ph})]$  (**4**) was accessible in a similar fashion using  $\text{PhCH}_2\text{MgCl}$  or  $\text{KCH}_2\text{Ph}$ . X-ray quality crystals of **4**·0.5hexane were grown from toluene/hexanes at  $-30$  °C (Figure 3), and in the solid state, one benzyl group is  $\eta^3$ -coordinated in the plane of the ligand [Th–C32–C33 =  $84.6(3)$  °; Th–C32 =  $2.576(6)$  Å; Th–C33 =  $2.836(5)$  Å; Th1–C34 =  $3.095(6)$  Å] while the other occupies an apical site and adopts a coordination mode intermediate between  $\eta^1$ - and  $\eta^2$ -coordination [Th–C39–C40 =  $96.7(4)$  °; Th–C39 =  $2.545(6)$  Å; Th–C40 =  $3.087(6)$  Å]. At  $-35$  °C in  $d_8$ -toluene,<sup>38</sup> two distinct benzyl groups are observed, consistent with the observation of an axial and an in-plane benzyl group in the solid state. The  $^1J_{\text{C,H}}$  coupling constants of 138 and 127 Hz for Th– $\text{CH}_2$  are suggestive of bonding approaching either  $\eta^2$ - or  $\eta^3$ -coordination, and  $\eta^1$ -coordination, respectively.<sup>37,39</sup> Similar  $^1J_{\text{C,H}}$  coupling constants were observed in complex **2**, and the observation of two independent molecules of **2** in the unit



cell, each with a different hapticity of the axial benzyl ligand illustrates the non-static nature of polyhapto-benzyl coordination.<sup>29</sup>



**Figure 3.** Molecular structure of dibenzyl complex **4**·0.5hexane with thermal ellipsoids at the 50% probability level. Hydrogen atoms, isopropyl groups and hexane solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Th–N(1) 2.300(5), Th–N(2) 2.545(4), Th–N(3) 2.273(5), Th–C(32) 2.576(6), Th–C(33) 2.836(5), Th–C(34) 3.095(6), Th···C(38) 3.554(8), Th–C(39) 2.545(6), Th–C(40) 3.087(6), Th–C(32)–C(33) 84.6(3), Th–C(39)–C(40) 96.7(4).

Reaction of a 1.5 mM solution of complex **1** in benzene with one equivalent of  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  resulted in the slow (~ 70 % complete after 48 hours) formation of ‘ $\text{Ph}_3\text{CCH}_2\text{SiMe}_3$ ’ and  $\text{Ph}_3\text{CH}^{40}$  (~ 1 equivalent per mole of **1** consumed) and an organometallic product with  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra consistent with a thorium(IV) alkyl cation ( $\text{Th}-\text{CH}_2$ :  $^1\text{H}$  NMR  $\delta$  0.24 ppm,  $^{13}\text{C}$  NMR  $\delta$  85.5 ppm) exhibiting top-bottom asymmetry (two different  $\text{CMe}_2$  and  $\text{CHMe}_2$  environments). The reaction of **1** with two equivalents of  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  in  $\text{C}_6\text{D}_6$  resulted in complete consumption of **1** in just 3 hours and formation of the same organometallic product.

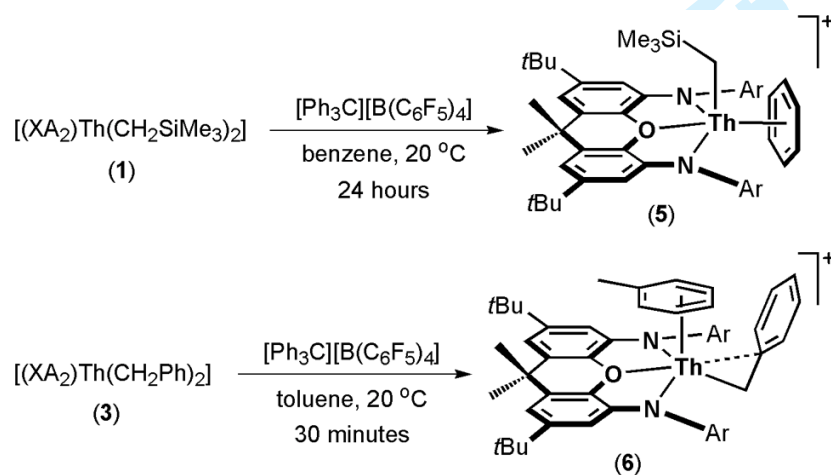
Performing the reaction of **1** with  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  at higher concentrations (*e.g.* 15 mM in benzene) resulted in precipitation of an orange-brown oil, which upon layering with hexanes at 20 °C,

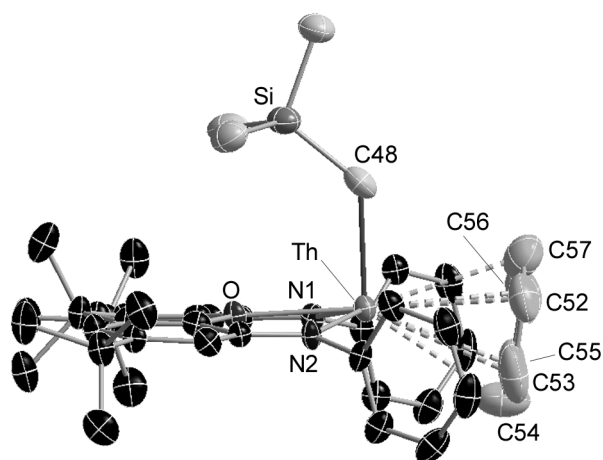


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resulted in yellow crystals growing within the oil and protruding into the hexanes solvent.<sup>41,42</sup>  $^1\text{H}$  NMR spectroscopy showed that this product is identical to that observed under more dilute conditions, and an X-ray crystal structure revealed that abstraction of a trimethylsilylmethyl group had indeed occurred to form a non-cyclopentadienyl thorium alkyl cation (Scheme 1; Figure 4). However, rather than formation of a coordinatively unsaturated species stabilized through weak interactions with the tetrakis(pentafluorophenyl)borate anion, a solvent-separated ion pair,  $[(\text{XA}_2)\text{Th}(\text{CH}_2\text{SiMe}_3)(\eta^6\text{-C}_6\text{H}_6)][\text{B}(\text{C}_6\text{F}_5)_4]$  (**5**), was observed as a result of  $\eta^6$ -benzene coordination. In addition to being the first structurally characterized non-cyclopentadienyl thorium alkyl cation, complex **5** is a rare example of an arene solvent-coordinated alkyl cation, and is to the best of our knowledge, the first example of this type of complex for an *f*-block metal.<sup>33-37</sup>

**Scheme 1.** Synthesis of the thorium(IV) alkyl cations **5** and **6**.



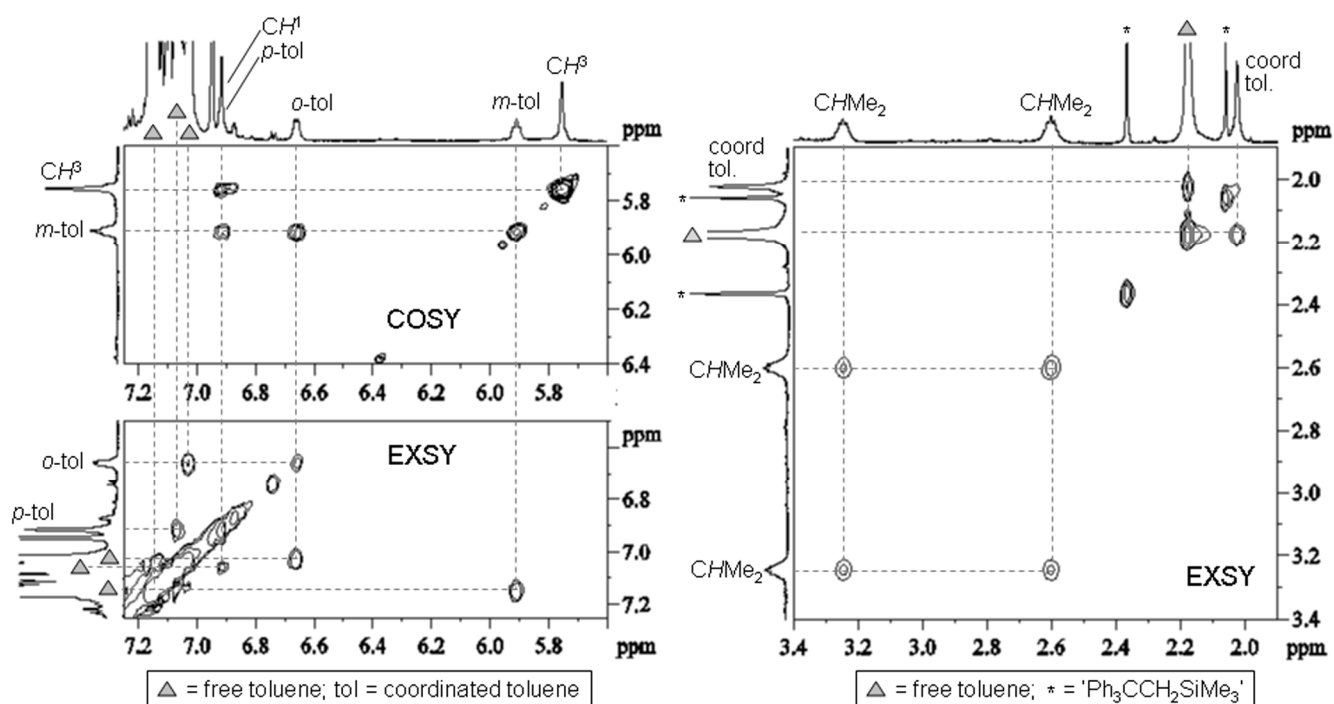


**Figure 4.** Molecular structure of  $[(XA_2)Th(CH_2SiMe_3)(\eta^6-C_6H_6)][B(C_6F_5)_4]\cdot benzene$ , (**5**)·benzene with thermal ellipsoids at the 50% probability level. Hydrogen atoms, isopropyl groups, the borate anion, and non-coordinated benzene solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Th–N(1) 2.278(3), Th–N(2) 2.288(3), Th–O 2.496(5), Th–C(48) 2.434(5), Th–C(52) 3.285(7), Th–C(53) 3.310(7), Th–C(54) 3.179(8), Th–C(55) 3.294(5), Th–C(56) 3.299(7), Th–C(57) 3.209(7), Th–C(48)–Si 131.0(2).

In the solid state structure of **5** (Figure 4), the  $XA_2$  ligand is bound to thorium via somewhat shorter Th–N and Th–O bonds than in neutral complex **1** [Th–N = 2.278(3) and 2.288(3) Å versus 2.292(4) and 2.312(4) Å, and Th–O = 2.496(5) versus 2.534(3) Å], and the  $CH_2SiMe_3$  group is bound in an apical position above the plane of the ligand with a Th–C48–Si angle of  $131^\circ$ , which strongly suggests the presence of an  $\alpha$ -agostic C–H–Th interaction (c.f.  $127^\circ$  and  $128^\circ$  in complex **1**, in which both alkyl groups engage in temperature dependant  $\alpha$ -agostic C–H–Th interactions).<sup>27,43</sup> Benzene is approximately  $\eta^6$ -coordinated in the plane of the ligand with Th–C bond lengths in the range 3.18–3.31 Å, and a distance of 2.95 Å from thorium to the centroid of the ring (see below for further discussion of thorium-arene coordination in **5**).

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2 While complexes **1-4** do not react with  $\text{PMe}_3$ , complex **5** reacted rapidly with  $\text{PMe}_3$  to precipitate a  
3 poorly soluble brown oil; presumably  $[(\text{XA}_2)\text{Th}(\text{CH}_2\text{SiMe}_3)(\text{PMe}_3)_x][\text{B}(\text{C}_6\text{F}_5)_4]$ , but attempts to dissolve  
4 the oil in  $d_8$ -THF resulted in decomposition to form  $\text{H}_2[\text{XA}_2]$ .<sup>44</sup> Reaction of **5** with pyridine,  
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While complexes **1-4** do not react with  $\text{PMe}_3$ , complex **5** reacted rapidly with  $\text{PMe}_3$  to precipitate a poorly soluble brown oil; presumably  $[(\text{XA}_2)\text{Th}(\text{CH}_2\text{SiMe}_3)(\text{PMe}_3)_x][\text{B}(\text{C}_6\text{F}_5)_4]$ , but attempts to dissolve the oil in  $d_8$ -THF resulted in decomposition to form  $\text{H}_2[\text{XA}_2]$ .<sup>44</sup> Reaction of **5** with pyridine, 4-(dimethylamino)pyridine,  $\text{Et}_3\text{PO}$  or  $\text{PhNMe}_2$  also resulted in decomposition, and addition of THF to base-free **5** resulted in THF polymerization. However, complex **5** is stable under vacuum and may be redissolved without decomposition in bromobenzene. In the  $^1\text{H}$  NMR spectrum of **5** in  $\text{C}_6\text{D}_5\text{Br}$ , all benzene signals were obscured by  $\text{XA}_2$ , ' $\text{Ph}_3\text{CCH}_2\text{SiMe}_3$ ',  $\text{Ph}_3\text{CH}$ <sup>40</sup> and  $\text{CPh}_3^+$  signals. However, conducting the reaction of **1** with  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  (2 equiv) in toluene resulted in the formation of  $[(\text{XA}_2)\text{Th}(\text{CH}_2\text{SiMe}_3)(\eta^6\text{-toluene})][\text{B}(\text{C}_6\text{F}_5)_4]$  (**5B**) (complete after 3 hours), and subsequent evaporation to dryness and re-dissolution in  $\text{C}_6\text{D}_5\text{Br}$  allowed observation of both free and coordinated toluene in the  $^1\text{H}$  NMR spectrum at 20 °C (Figure 5). This confirms that toluene in **5B** is strongly bound in solution,<sup>45</sup> and does not readily exchange with free toluene (6 equiv), or undergo substitution by  $\text{C}_6\text{D}_5\text{Br}$ . Similar behavior has been reported for certain  $d^0$   $\pi$ -aryl complexes, including  $[\text{Cp}''\text{MMe}_2(\eta^6\text{-toluene})][\text{MeB}(\text{C}_6\text{F}_5)_3]$  ( $\text{M} = \text{Ti}, \text{Zr}$  or  $\text{Hf}$ ;  $\text{Cp}'' = 1,3\text{-bis}(\text{trimethylsilyl})\text{cyclopentadienyl}$ ).<sup>35</sup> However, an EXSY NMR spectrum of **5B** (Figure 5) revealed that exchange of free and coordinated toluene, and loss of top-bottom asymmetry (cross peaks between  $\text{CHMe}_2$  signals), does occur on a longer time scale. A small  $^1J_{\text{C,H}}$  coupling constant of 104 Hz for  $\text{ThCH}_2$  is also indicative of the presence of C-H-Th  $\alpha$ -agostic interactions in **5B**; an observation consistent with the unusually large Th-C-Si angle in the solid state structure of **5**.



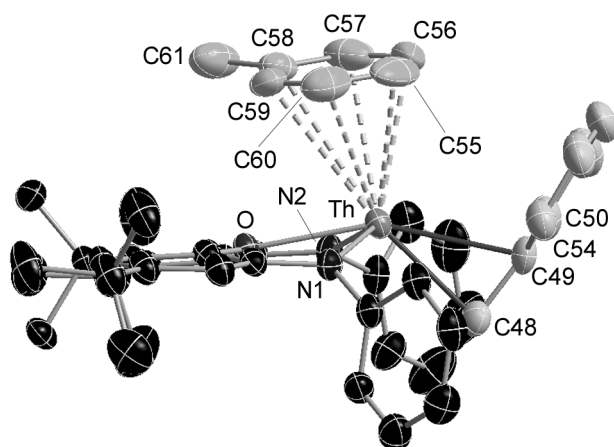
**Figure 5.** Selected regions of  $^1\text{H}$ - $^1\text{H}$  COSY and EXSY ( $\tau_m$  0.5s) NMR spectra for **5B** with six equivalents of toluene in  $\text{C}_6\text{D}_5\text{Br}$  at 20 °C (sample generated in situ from the reaction of **1** with 2 equiv of  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  in toluene, followed by evaporation to dryness in vacuo and redissolution in  $\text{C}_6\text{D}_5\text{Br}$ ).

In a reaction analogous to the synthesis of complex **5**, treatment of  $[(\text{XA}_2)\text{Th}(\text{CH}_2\text{Ph})_2]$  **3** with 1.0  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  in benzene or toluene resulted in the slow formation of 1 equivalent of  $\text{Ph}_3\text{CCH}_2\text{Ph}$  (per equiv. of **3** consumed), and precipitation of an orange-brown oil. For the oil deposited from toluene, layering with hexanes provided yellow crystals growing within the oil and protruding out into the solvent,<sup>42</sup> and X-ray diffraction of the crystals revealed the formation of a second example of an organothorium cation existing as an arene solvent separated ion pair:  $[(\text{XA}_2)\text{Th}(\eta^2\text{-CH}_2\text{Ph})(\eta^6\text{-C}_6\text{H}_5\text{Me})][\text{B}(\text{C}_6\text{F}_5)_4]$  (**6**; Scheme 1). However, unlike **5**, complex **6** is insoluble in benzene, toluene,  $\text{OEt}_2$  and bromobenzene, and polymerizes THF, which precluded direct characterization by NMR spectroscopy.<sup>46</sup> Further, reaction with  $\text{PMe}_3$  did not result in the formation of a more soluble product, and

1 attempted dissolution of the presumed  $\text{PMe}_3$ -coordinated cation in  $d_8$ -THF resulted in decomposition to  
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4 release  $\text{H}_2[\text{XA}_2]$ .<sup>44</sup>  
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6 The solid state structure of complex **6** shares many similarities with that of **5**. However, in **6**, the  
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8 arene occupies an apical position, while the anionic R-group ( $\eta^2$ - $\text{CH}_2\text{Ph}$ ) is bound in the plane of the  
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10  $\text{XA}_2$  ligand (Figure 6). The arene is also less symmetrically bound to the metal than in **5**, with Th–C  
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12 distances increasing from 3.06–3.44 Å towards the most sterically hindered methyl-substituted position  
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14 (C58). It is therefore possible that toluene in **6** may be more accurately described as  $\eta^4$  or  $\eta^5$ -  
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16 coordinated. However,  $\eta^6$ -bonding cannot be excluded on the basis of the observed Th–C distances,  
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18 which lie within the sum of the van der Waals radii for thorium and carbon ( $\sim 3.60$  Å).<sup>47</sup> In addition, the  
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20 Th–ring centroid distance of 2.94 Å is almost identical to that observed in complex **5**.  
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26 As with complex **5**, a reduction in the Th–N and Th–O bond distances is observed relative to the  
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28 corresponding neutral precursor (in this case complex **3**). However, in complex **6**, shortening of the Th–  
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30 O bond distance relative to that in **3** is particularly pronounced [Th–N = 2.314(3) and 2.320(3) Å versus  
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32 2.318(2), 2.331(2) and 2.332(2), 2.339(3) Å, and Th–O = 2.455(3) versus 2.526(2), 2.519(2) Å].<sup>27,48</sup>  
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34 Comparison of cation **6** with **5** also reveals that the Th–N distances in **6** are significantly longer than  
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36 those in **5**, while the Th–O distance in **6** is shorter, perhaps as a result of  $\eta^2$ -benzyl coordination in the  
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38 plane of the  $\text{XA}_2$  ligand, which positions the metal further above the NON-plane and back towards  
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40 the xanthene backbone of the ligand [displacement from the NON-plane of 0.724 Å in **6**, versus  
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42 0.469 Å in **5**].  
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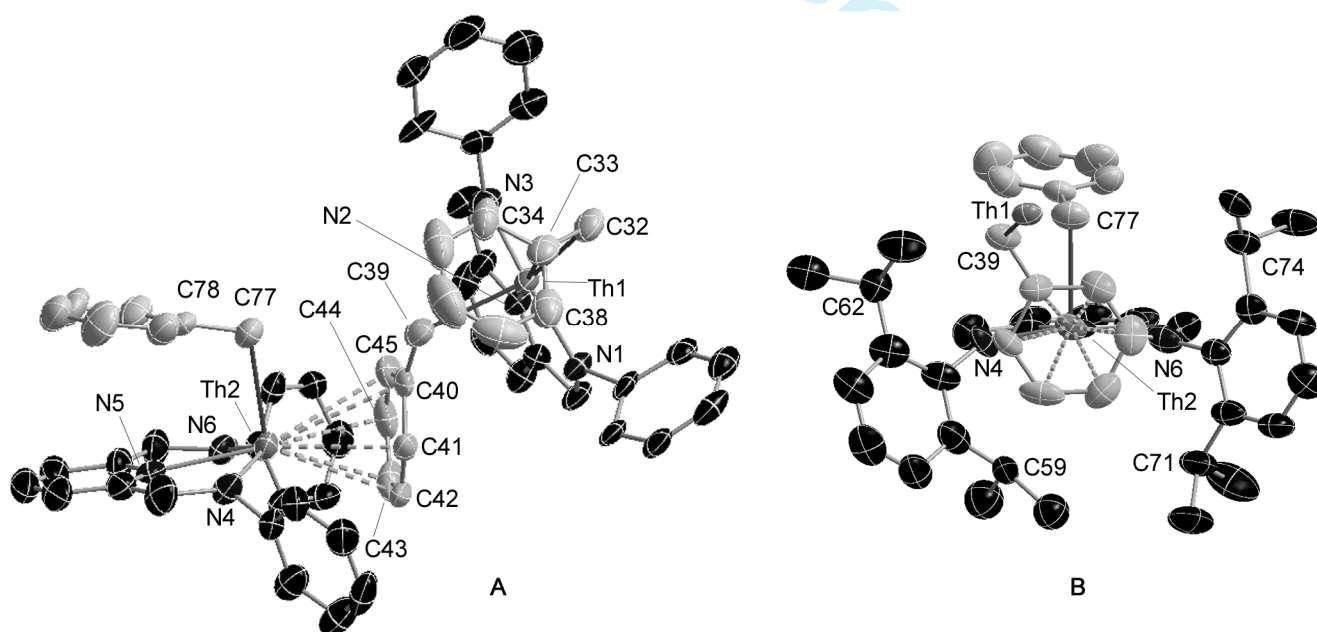


**Figure 6.** Molecular structure of  $[(XA_2)Th(\eta^2-CH_2Ph)(\eta^6-C_6H_5Me)][B(C_6F_5)_4] \cdot 2toluene$ , (**6**)·2toluene with thermal ellipsoids at the 50% probability level. Hydrogen atoms, isopropyl groups, the borate anion and non-coordinated toluene solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Th–N(1) 2.314(3), Th–N(2) 2.320(3), Th–O 2.455(3), Th–C(48) 2.488(5), Th–C(49) 2.729(4), Th···C(50) 3.293(5), Th···C(54) 3.192(4), Th–C(55) 3.063(5), Th–C(56) 3.092(5), Th–C(57) 3.276(8), Th···C(58) 3.435(6), Th···C(59) 3.367(8), Th–C(60) 3.207(10), Th–C(48)–C(49) 83.2(3).

Other structurally characterized actinide(IV) complexes containing a bound neutral arene are  $[\{(\eta^6-C_6Me_6)U^{IV}Cl_2\}_2(\mu-Cl)_3][AlCl_4]$  and  $[\{(\eta^6-C_6Me_6)U^{IV}Cl_2(\mu-Cl)_3\}_2UCl_2]$  reported by Cotton *et al.*, with  $U-C_{mean}$  bond distances of 2.92 and 2.94 Å respectively<sup>49,50</sup> [c.f. 3.26 Å in **5** and 3.24 Å in **6**]. To allow meaningful comparison with complex **5**, the  $M-C_{mean}$  distances can be adjusted to take into account the larger ionic radius of thorium(IV) (0.94 Å), relative to uranium(IV) (0.89 Å).<sup>47</sup> In addition, some indication of the extent to which the increased steric presence and electron density associated with a  $C_6Me_6$  ring, relative to a  $C_6H_6$  ring, affects  $M-C_{mean}$  bond distances can be assessed with reference to  $[(\eta^6-C_6R_6)U^{III}(AlCl_4)_3]$ ; only small variations in  $U-C_{mean}$  are observed for  $C_6R_6 =$  benzene, toluene and mesitylene (2.92, 2.94 and 2.93 Å, respectively).<sup>51</sup> Similarly,  $Sm-C_{mean}$  distances in  $[(\eta^6-C_6R_6)Sm^{III}(AlCl_4)_3]$  vary from 2.91 Å to 2.89/2.90 to 2.88 Å for  $C_6R_6 =$  benzene, *m*-xylene and

mesitylene, respectively.<sup>52</sup> Based on these data, it appears that much stronger actinide-arene bonding is observed in Cotton's  $C_6Me_6$  complexes.<sup>49</sup> The long Th- $C_{mean}$  distances in **5** and **6** are likely the result of very significant steric hindrance in the  $XA_2$  and BDPP complexes, perhaps combined with the general trend towards reduced covalency in complexes of thorium, relative to uranium.<sup>53</sup> However, it is interesting that despite long Th- $C_{mean}$  distances in **5** and **6** [and presumably **5B** by analogy],<sup>45</sup> complex **5B** does not undergo rapid exchange of free and bound toluene in  $C_6D_5Br$ . The current observations of arene solvent coordination, even in the presence of a polyhapto-coordinating benzyl ligand (in **6**), further highlight the extent to which metal-arene interactions become favorable in the chemistry of more sterically open non-cyclopentadienyl alkyl thorium cations; similar neutral arene coordination has not been reported for  $[Cp^*_2ThMe][BAR_4]$ .<sup>4-8</sup>

In contrast to the reactions of **1** and **3** with  $[CPh_3][B(C_6F_5)_4]$ , which formed only mononuclear products, addition of between 0.5 and 1.0 equivalents of  $[CPh_3][B(C_6F_5)_4]$  to solutions of **4** in benzene resulted in precipitation of orange-brown oils, which upon layering with hexanes at 20 °C yielded crystals of dinuclear  $[(BDPP)Th(\eta^2-CH_2Ph)(\mu-\eta^1:\eta^6-CH_2Ph)Th(\eta^1-CH_2Ph)(BDPP)][B(C_6F_5)_4]$  (**7**).<sup>42</sup>





**Figure 7.** Molecular structure of  $[(\text{BDPP})\text{Th}(\eta^2\text{-CH}_2\text{Ph})(\mu\text{-}\eta^1\text{:}\eta^6\text{-CH}_2\text{Ph})\text{Th}(\eta^1\text{-CH}_2\text{Ph})(\text{BDPP})][\text{B}(\text{C}_6\text{F}_5)_4]\cdot 0.75\text{hexane}\cdot 0.55\text{benzene}$ , (**7**) $\cdot 0.75\text{hexane}\cdot 0.55\text{benzene}$  with thermal ellipsoids at the 50% probability level. The borate anion, hydrogen atoms and solvent are omitted for clarity. In view A, isopropyl groups are also omitted, while in view B, all ligands on Th1, other than the  $\mu$ -benzyl group are omitted. Selected bond lengths ( $\text{\AA}$ ) and angles (deg): Th(1)–N(1) 2.274(7), Th(1)–N(2) 2.548(8), Th(1)–N(3) 2.283(9), Th(2)–N(4) 2.269(8), Th(2)–N(5) 2.527(9), Th(2)–N(6) 2.299(9), Th(1)–C(32) 2.563(11), Th(1)–C(33) 2.813(11), Th(1)···C(34) 3.317(13), Th(1)···C(38) 3.390(14), Th(1)–C(39) 2.616(11), Th(1)···C(40) 3.442(11), Th(2)–C(77) 2.516(10), Th(2)···C(78) 3.302(9), Th(2)···C(40) 3.349(10), Th(2)–C(41) 3.211(10), Th(2)–C(42) 3.069(9), Th(2)–C(43) 2.973(11), Th(2)–C(44) 3.017(11), Th(2)–C(45) 3.133(12), Th(1)–C(32)–C(33) 84.8(7), Th(1)–C(39)–C(40) 112.3(7), Th(2)–C(77)–C(78) 108.4(7).

Complex **7** (Figure 7) is composed of a cationic  $[(\text{BDPP})\text{Th}(\eta^1\text{-CH}_2\text{Ph})]^+$  fragment coordinated via an  $\eta^6$ -interaction to the benzyl group of a molecule of the neutral starting material  $[(\text{BDPP})\text{Th}(\text{CH}_2\text{Ph})_2]$  (**4**). In more detail; the metal center (Th2) in the cationic fragment of **7** is  $\eta^1$ -coordinated to a benzyl substituent in an axial position, and in the plane of the ligand, is  $\eta^6$ -coordinated to the benzyl group of a molecule of the neutral starting material (**4**). By contrast, the metal center (Th1) in the coordinated molecule of **4** is  $\eta^2$ -coordinated to a benzyl group in the plane of the ligand, and  $\eta^1$ -coordinated to the bridging benzyl ligand, which occupies an axial position.

The arrangement of the ligands in the cationic portion of **7** is more similar to that observed in the trimethylsilylmethyl cation, **5**, than  $\eta^2$ -benzyl cation **6** – i.e. the alkyl group ( $\eta^1$ -benzyl in **7**) does not lie in the plane of the ligand, but rather occupies an apical site. However, while benzene is bound quite symmetrically in complex **5**, the Th–C<sub>ring</sub> distances in **7** vary from 2.97(1) to 3.35(1)  $\text{\AA}$ , increasing

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2 towards the more sterically hindered *ipso*-carbon (C40) of the  $\mu\text{-}\eta^1\text{:}\eta^6$ -benzyl ligand. A similar variation  
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4 in Th-C<sub>ring</sub> distances was observed in toluene-coordinated cation **6**. The presence of significant steric  
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6 hindrance at the arene coordinated cationic thorium center is particularly evident from the degree of  
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8 twisting of the 2,6-diisopropylphenyl rings of the BDPP ligand on Th2 (Figure 7: View B), resulting in  
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10 C59...C71 and C62...C74 distances of 4.37 and 8.31 Å, respectively.  
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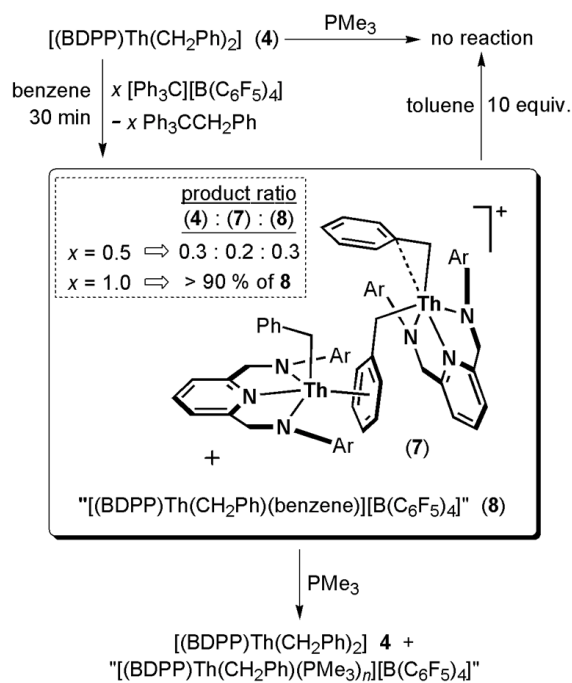
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14 Crystallographically characterized complexes containing a  $\mu\text{-}\eta^1\text{:}\eta^n$ -benzyl bridging interaction  
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16 similar to that in **7** have not previously been reported in *f*-block or early transition metal (group 3-5)  
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18 chemistry, and to the best of our knowledge, no such complexes exist. Observation of this unusual  
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20 coordination mode in complex **7** further illustrates the propensity of cationic non-cyclopentadienyl  
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22 thorium complexes to engage in  $\pi$ -arene coordination.<sup>54</sup> However, it is perhaps unexpected that a  $\pi$ -  
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24 interaction between the cationic fragment and a molecule of **4** is preferred over an  $\eta^6$ -interaction with  
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26 benzene, which was present in vast excess as the solvent. This preference is likely due the more electron  
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28 rich nature of metal-benzyl groups, relative to benzene, in part as a result of delocalization of negative  
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30 charge into the ring. The presence of a more effective interaction between the cationic fragment of **7** and  
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32 the benzyl group of a molecule of **4**, relative to an interaction with a neutral arene, is supported by a Th-  
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34 ring centroid distance of 2.79 Å, compared with 2.95 and 2.94 Å in **5** and **6**, respectively.  
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41 Direct investigation of the organometallic products formed in the reaction of complex **4** with  
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43 [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was prevented by their insolubility in C<sub>6</sub>D<sub>6</sub>, d<sub>8</sub>-toluene, OEt<sub>2</sub> or bromobenzene, and  
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45 polymerization of d<sup>8</sup>-THF.<sup>46</sup> However, the reaction of **4** with [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] could be probed  
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47 indirectly by monitoring the disappearance of **4** and the formation of Ph<sub>3</sub>CCH<sub>2</sub>Ph by <sup>1</sup>H NMR  
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49 spectroscopy in the presence of O(SiMe<sub>3</sub>)<sub>2</sub> as an internal standard (Scheme 2). The reaction of **4** with 0.5  
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51 equivalents of [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (no change after 30 minutes at 20 °C) resulted in consumption of 0.7  
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53 equivalents of **4** and release of 0.5 equivalents of Ph<sub>3</sub>CCH<sub>2</sub>Ph, consistent with the formation of a  
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55 0.3:0.2:0.3 mixture of unreacted **4**, dinuclear **7**, and a mononuclear cation (presumably with the  
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1 composition [(BDPP)Th(CH<sub>2</sub>Ph)(benzene)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (**8**) by analogy with cations **5** and **6**. This  
2 assignment was confirmed by the addition of PMe<sub>3</sub> (10 equiv) to the reaction mixture, which resulted in  
3 liberation of 0.2 equivalents of soluble **4** back into solution (addition of toluene (10 equiv) to reaction  
4 mixtures containing dinuclear **7** did not release **4**). However, conducting the reaction of **4** with 1.0  
5 equivalent of [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] resulted in an approximately 1:1 ratio of '4 consumed' to  
6 'Ph<sub>3</sub>CCH<sub>2</sub>Ph produced', consistent with the precipitation of mononuclear **8** as the major product.  
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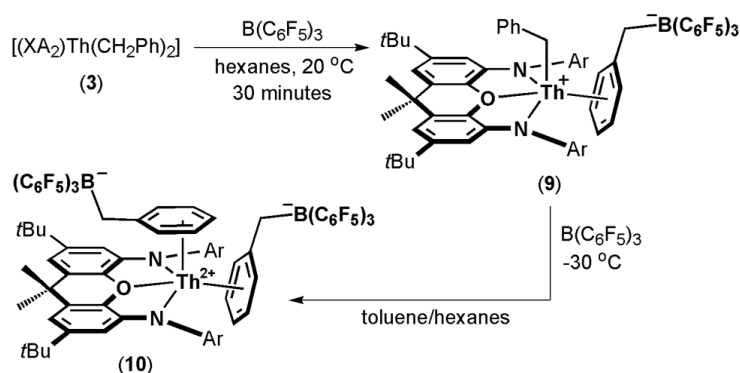
9 In contrast to the reactions of **4** with [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], monitoring the reaction of  
10 [(XA<sub>2</sub>)Th(CH<sub>2</sub>Ph)<sub>2</sub>] (**3**) with 0.5 equivalents of [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] by <sup>1</sup>H NMR spectroscopy (with  
11 subsequent addition of PMe<sub>3</sub>) did not provide any evidence for the formation of a dinuclear complex  
12 analogous to **7**. The greater accessibility of a dinuclear structure with the BDPP ligand, relative to the  
13 XA<sub>2</sub> ligand, is likely a consequence of the less sterically bulky and more flexible backbone of the BDPP  
14 ligand.  
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33 **Scheme 2.** Synthesis of the thorium(IV) alkyl cations **7** and **8**. Product ratios were determined by  
34 measurement of the amount of **4** and Ph<sub>3</sub>CCH<sub>2</sub>Ph in solution by <sup>1</sup>H NMR spectroscopy, both before and  
35 after addition of PMe<sub>3</sub> [in the presence of O(SiMe<sub>3</sub>)<sub>2</sub> as an internal standard].  
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Interestingly, reaction of **4** with 2.0 equivalents of [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] resulted in liberation of 2.0 equivalents of Ph<sub>3</sub>CCH<sub>2</sub>Ph, suggesting the formation of an as-yet unidentified dicationic species. Analogous behavior was observed in the reaction of two equivalents of [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] with dibenzyl complex **3**, but not with bis-trimethylsilylmethyl complexes **1** and **2**. Both single and double alkyl abstraction was also observed in the reactions of [(XA<sub>2</sub>)Th(CH<sub>2</sub>Ph)<sub>2</sub>] (**3**) with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>29,55</sup> However, in this case, the resulting complexes, monocationic [(XA<sub>2</sub>)Th(η<sup>1</sup>-CH<sub>2</sub>Ph)][η<sup>6</sup>-PhCH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (**9**) and dicationic [(XA<sub>2</sub>)Th][η<sup>6</sup>-PhCH<sub>2</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>]<sub>2</sub> (**10**), receive additional stabilization as a result of η<sup>6</sup>-benzylborate coordination (Scheme 3).<sup>56</sup>

**Scheme 3.** Synthesis of complexes **9** and **10**.<sup>57</sup>



Solutions of complex **5** or **9** in benzene or toluene, or complexes **5-8** generated as oils by the addition of 1.0 or 0.5 equivalents of  $[CPh_3][B(C_6F_5)_4]$  to **1**, **3** or **4** in benzene or toluene as described above, do not polymerize ethylene at 1 atmosphere (20-100 °C), highlighting the significant potential for olefin polymerization activity in more sterically open non-cyclopentadienyl thorium alkyl cations to be diminished or negated by arene solvent, neutral dibenzyl precursor or benzylborate anion coordination. The negative effects of  $\pi$ -arene coordination can be explained on the basis of hindered access of olefin monomers to the metal center, and/or the greatly reduced solubility of many solvent-separated ion pairs, relative to contact ion pairs. Future work will focus on ligand modifications directed towards preventing/disfavoring  $\pi$ -arene coordination, as well as the preparation of the analogous uranium complexes, which typically exhibit much greater solubility in low-polarity solvents.<sup>53</sup> Polymerization of alternative monomers will also be investigated.

In summary, use of the rigid, dianionic NON- and NNN-donor ligands  $XA_2$  and BDPP has allowed the synthesis and characterization of the first non-cyclopentadienyl thorium alkyl cations:  $[(XA_2)Th(CH_2SiMe_3)(\eta^6\text{-arene})][B(C_6F_5)_4]$  [arene = benzene (**5**) or toluene (**5B**)],  $[(XA_2)Th(\eta^2\text{-CH}_2\text{Ph})(\eta^6\text{-C}_6\text{H}_5\text{Me})][B(C_6F_5)_4]$  (**6**),  $[(BDPP)Th(\eta^2\text{-CH}_2\text{Ph})(\mu\text{-}\eta^1\text{:}\eta^6\text{-CH}_2\text{Ph})Th(\eta^1\text{-CH}_2\text{Ph})(BDPP)][B(C_6F_5)_4]$  (**7**) and  $[(XA_2)Th(\eta^1\text{-CH}_2\text{Ph})][\eta^6\text{-PhCH}_2B(C_6F_5)_3]$  (**9**). All complexes were prepared by alkyl abstraction from the appropriate dialkyl precursor (**1-4**), and were investigated in solution by NMR spectroscopy and/or in the solid state by X-ray crystallography. Complexes **5**, **5B** and

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2 **6** are rare examples of arene solvent separated ion pairs, complex **9** exists as a tight contact ion pair, and  
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4 complex **7** is dinuclear as a result of an unusual  $\mu\text{-}\eta^1\text{:}\eta^6\text{-benzyl}$  bridging interaction. The structures of  
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6 complexes **5**, **5B**, **6**, **7** and **9** highlight the strong preference for  $\pi$ -arene coordination in cationic  
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8 complexes of the  $\text{XA}_2$  and BDPP ligands, and the failure of these complexes to polymerize ethylene  
9  
10 highlights the important role that  $\pi$ -arene coordination can play in the reactivity of coordinatively  
11  
12 unsaturated *f*-block alkyl cations.  
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## 19 Experimental Section

20  
21 **General Details.** An argon-filled MBraun UNIlab glove box was employed for the manipulation and  
22  
23 storage of all oxygen and moisture sensitive compounds, and all compounds were stored in a  $-30\text{ }^\circ\text{C}$   
24  
25 freezer within the glove box. Commonly utilized specialty glassware includes double manifold high  
26  
27 vacuum lines, swivel frit assemblies, J-Young NMR tubes, and thick walled flasks equipped with Teflon  
28  
29 stopcocks (Chemglass and Toonen Glassblowing).<sup>58</sup> Any residual oxygen and moisture was removed  
30  
31 from the argon stream by passage through an Oxisorb-W scrubber from Matheson Gas Products.  
32  
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34

35 Hexanes, toluene and THF were initially distilled under nitrogen from  $\text{CaH}_2$ , sodium, and  
36  
37 sodium/benzophenone respectively. They were then stored under vacuum over  $\text{Na/Ph}_2\text{CO}$  (toluene,  
38  
39 THF) or  $\text{Na/Ph}_2\text{CO/tetraglyme}$  (hexanes). Benzene,  $\text{C}_6\text{D}_6$ , *d*<sub>8</sub>-toluene, THF, *d*<sub>8</sub>-THF,  $\text{OEt}_2$ , *d*<sub>10</sub>- $\text{OEt}_2$  and  
40  
41  $\text{O}(\text{SiMe}_3)_2$  were dried directly over  $\text{Na/Ph}_2\text{CO}$ , while  $\text{C}_6\text{D}_5\text{Br}$  was dried directly over  $\text{CaH}_2$ . All solvents  
42  
43 were introduced into reactions or storage flasks by vacuum transfer with condensation at  $-78\text{ }^\circ\text{C}$ .  
44  
45  
46

47 Deuterated solvents were purchased from ACP chemicals.  $\text{B}(\text{C}_6\text{F}_5)_3$  was purchased from Boulder  
48  
49 Scientific and dried by repeated cycles of stirring in dimethylchlorosilane and sublimation.  
50  
51  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  was purchased from Strem, and  $\text{PhCH}_2\text{MgCl}$  (1.0 M in  $\text{OEt}_2$ ) was purchased from  
52  
53 Aldrich. Ethylene (99.99%) was purchased from Aldrich and used as received.  $\text{KCH}_2\text{Ph}$ ,<sup>59</sup>  
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1  
2 [(BDPP)ThCl<sub>2</sub>(dme)], [(XA<sub>2</sub>)Th(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] (**1**), [(BDPP)Th(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] (**2**) and [(XA<sub>2</sub>)Th(CH<sub>2</sub>Ph)<sub>2</sub>]  
3  
4 (**3**)<sup>27,29</sup> were prepared as previously reported.

5  
6 Combustion elemental analyses were performed on a Thermo EA1112 CHNS/O analyzer by  
7  
8 Dr. Steve Kornic of this department. X-ray crystallographic analyses were performed on suitable crystals  
9  
10 coated in Paratone oil and mounted on either: (a) a P4 diffractometer with a Bruker Mo rotating-anode  
11  
12 generator and a SMART1K CCD area detector, or (b) a SMART APEX II diffractometer with a 3 kW  
13  
14 Sealed tube Mo generator in the McMaster Analytical X-Ray (MAX) Diffraction Facility. The two  
15  
16 molecules of non-coordinated toluene in **6**·2toluene and the 0.75 molecules of hexane in  
17  
18 **7**·0.55benzene·0.75hexane were highly disordered, and could not be modeled satisfactorily, so were  
19  
20 treated using the SQUEEZE routine.<sup>60</sup>

21  
22 NMR spectroscopy [<sup>1</sup>H, <sup>13</sup>C, <sup>13</sup>C{<sup>1</sup>H}, <sup>11</sup>B, <sup>19</sup>F, DEPT-135, COSY, HSQC, HMBC, EXSY  
23  
24 (NOESY with τ<sub>m</sub> 0.5s)] was performed on Bruker DRX-500 and AV-600 spectrometers. All <sup>1</sup>H NMR  
25  
26 and <sup>13</sup>C NMR spectra were referenced relative to SiMe<sub>4</sub> through a resonance of the employed deuterated  
27  
28 solvent or proteo impurity of the solvent; C<sub>6</sub>D<sub>6</sub> (δ 7.15 ppm), C<sub>7</sub>D<sub>8</sub> (δ 7.09, 7.00, 6.98, 2.09), C<sub>6</sub>D<sub>5</sub>Br  
29  
30 (δ 7.30, 7.02, 6.94 ppm) for <sup>1</sup>H NMR, and C<sub>6</sub>D<sub>6</sub> (δ 128.0 ppm), C<sub>7</sub>D<sub>8</sub> (δ 137.86, 129.24, 128.33, 125.49,  
31  
32 20.4), C<sub>6</sub>D<sub>5</sub>Br (δ 130.9, 129.3, 126.1, 122.3 ppm) for <sup>13</sup>C NMR. <sup>11</sup>B and <sup>19</sup>F NMR spectra were  
33  
34 referenced using external standards of BF<sub>3</sub>(OEt<sub>2</sub>) (0.0 ppm) and CFCl<sub>3</sub> (0.0 ppm) respectively. All NMR  
35  
36 spectra were obtained at room temperature unless otherwise specified. Herein, Ar = 2,6-  
37  
38 diisopropylphenyl, Bn = CH<sub>2</sub>Ph, and the numbering scheme (CH<sup>1</sup>, C<sup>2</sup>, CH<sup>3</sup>, C<sup>4</sup>, C<sup>10</sup> and C<sup>11</sup>) for the  
39  
40 xanthene backbone is shown in Figure 2.

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49 [(BDPP)Th(η<sup>2</sup>-CH<sub>2</sub>Ph)(η<sup>3</sup>-CH<sub>2</sub>Ph)] (**4**). A 1.0 M solution of PhCH<sub>2</sub>MgCl in OEt<sub>2</sub> (0.41 mL, 0.41  
50  
51 mmol) was added dropwise to a -78 °C solution of [(BDPP)ThCl<sub>2</sub>(dme)] (175 mg, 0.21 mmol) in toluene  
52  
53 (15 mL), before warming to room temperature over 3 hours. The mixture was then filtered to remove  
54  
55 insoluble salts and the mother liquors were evaporated to dryness *in vacuo*. Hexanes (30 mL) were  
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58  
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1 added, followed by sonication and filtration to collect **4** as a yellow solid (120 mg, 0.14 mmol) in 67%  
2 yield. X-Ray quality crystals of **4**·0.5hexane were obtained by layering a toluene solution of **4** with  
3 hexanes at -30 °C. <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>, 500 MHz, -35 °C): δ 7.22 (m, 6H, *Ar-m*, *Ar-p* & *Bn*<sup>1</sup>-*m*), 7.12 (br, s,  
4 2H, *Ar-m*), 6.96 (br, s, 2H, *Bn*<sup>2</sup>-*o*), 6.80 (app. t, <sup>3</sup>J<sub>H,H</sub> 8 Hz, 2H, *Bn*<sup>2</sup>-*m*), 6.78 (t, <sup>3</sup>J<sub>H,H</sub> 8 Hz, 1H, *py-p*),  
5 6.74 (t, <sup>3</sup>J<sub>H,H</sub> 6 Hz, 1H, *Bn*<sup>1</sup>-*p*), 6.32 (d, 2H, <sup>3</sup>J<sub>H,H</sub> 8 Hz, *Py-m*), 6.22 (t, 1H, <sup>3</sup>J<sub>H,H</sub> 8 Hz, *Bn*<sup>2</sup>-*p*), 5.47 (d,  
6 2H, <sup>3</sup>J<sub>H,H</sub> 8 Hz, *Bn*<sup>1</sup>-*o*), 5.07, 4.83 (d, 2 x 2H, <sup>2</sup>J<sub>H,H</sub> 19 Hz, *py-CH*<sub>2</sub>), 3.88, 3.47 (septet, 2 x 2H, <sup>3</sup>J<sub>H,H</sub> 7  
7 Hz, *CHMe*<sub>2</sub>), 1.49, 1.41, 1.33, 1.07 (d, 4 x 6H, <sup>3</sup>J<sub>H,H</sub> 7 Hz, *CHMe*<sub>2</sub>), 1.45 (s, 2H, *ThCH*<sub>2</sub>*Ph*<sup>1</sup>), 1.15 (s, 2H,  
8 *ThCH*<sub>2</sub>*Ph*<sup>2</sup>). <sup>13</sup>C {<sup>1</sup>H} NMR (C<sub>7</sub>D<sub>8</sub>, 125 MHz, -35 °C): δ 164.33 (*py-ortho*), 150 (*Bn*<sup>2</sup>-*ipso*), 149.68,  
9 147.74 (*Ar-o*), 145.78 (*Bn*<sup>1</sup>-*ipso*), 141.83 (*Ar-ipso*), 132.43, 126.33 (*p-Ar* & *Bn*<sup>1</sup>-*m*), 124.28 (*Bn*<sup>2</sup>-*o*),  
10 124.00, 123.82 (2 x *Ar-m*), 123.51 (*Bn*<sup>1</sup>-*o*), 121.25 (*Bn*<sup>1</sup>-*p*), 118.77 (*Bn*<sup>2</sup>-*p*), 117.23 (*Py-m*), 116.29 (*Py-*  
11 *p*), 89.64 (*Th-CH*<sub>2</sub>*Ph*<sup>1</sup>), 78.50 (*Th-CH*<sub>2</sub>*Ph*<sup>2</sup>), 67.45 (*py-CH*<sub>2</sub>), 29.95, 28.15 (*CHMe*<sub>2</sub>), 28.03, 27.73,  
12 23.44, 22.78 (*CHMe*<sub>2</sub>). Anal. Calcd. for C<sub>45</sub>H<sub>55</sub>N<sub>3</sub>Th: C, 62.13; H, 6.37; N, 4.83. Found: C, 61.91; H,  
13 6.94; N, 4.90 %.

14 [(X<sub>A</sub>)<sub>2</sub>Th(CH<sub>2</sub>SiMe<sub>3</sub>)(η<sup>6</sup>-C<sub>6</sub>H<sub>6</sub>)] [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]-C<sub>6</sub>H<sub>6</sub>, (**5**)·C<sub>6</sub>H<sub>6</sub>. *Method A*: A solution of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]  
15 (150 mg, 0.162 mmol) in benzene (10 mL) was added dropwise to a solution of [(X<sub>A</sub>)<sub>2</sub>Th(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>]  
16 (**1**; 175 mg, 0.162 mmol) in benzene (10 mL) at room temperature. The mixture was stirred for 15  
17 minutes, and then allowed to settle. The orange mother liquors were then decanted to leave an orange-  
18 brown oil, which was washed with hexanes (10 mL), layered with hexanes (10 mL), and then stored at  
19 20 °C for several days to yield X-ray quality crystals of **5**·C<sub>6</sub>H<sub>6</sub> growing within and at the surface of the  
20 oil. Note: Crystals of **5** were always coated with oil, which prevented elemental analysis. *Method B*: A  
21 solution of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (17 mg, 0.019 mmol) in C<sub>6</sub>D<sub>6</sub> (3 mL) was added dropwise to a solution of  
22 [(X<sub>A</sub>)<sub>2</sub>Th(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] (**1**; 10 mg, 0.009 mmol) in C<sub>6</sub>D<sub>6</sub> (3 mL) at room temperature. The solution was  
23 stirred for 16 hours prior to investigation by <sup>1</sup>H, <sup>13</sup>C and 2D NMR spectroscopy. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 600  
24 MHz, 20 °C): δ 7.42 (t, <sup>3</sup>J<sub>H,H</sub> 8 Hz, 2H, *Ar-p*), 7.27, 7.25 (app. t, <sup>3</sup>J<sub>H,H</sub> 7 Hz, 2 x 2H, *Ar-m*), 6.82 (d, <sup>4</sup>J<sub>H,H</sub>  
25 2 Hz, 2H, *CH*<sup>1</sup>), 5.82 (d, <sup>4</sup>J<sub>H,H</sub> 2 Hz, 2H, *CH*<sup>3</sup>), 3.25, 2.50 (septet, 2 x 2H, <sup>3</sup>J<sub>H,H</sub> 7 Hz, *CHMe*<sub>2</sub>), 1.61, 1.46  
26 23.44, 22.78 (*CHMe*<sub>2</sub>).

(s, 2 x 3H,  $CMe_2$ ) 1.28, 1.13, 1.03, 0.86 (d, 4 x 6H,  $^3J_{H,H}$  7 Hz,  $CHMe_2$ ), 1.07 (s, 18H,  $CMe_3$ ), 0.25 (s, 2H,  $ThCH_2$ ), -0.13 (s, 9H,  $SiMe_3$ ).  $^{13}C$  { $^1H$ } NMR ( $C_6D_6$ , 150 MHz, 20 °C):  $\delta$  149.97 ( $C^2_tBu$ ), 149.57, 147.53 (Ar-*o*), 142.40 ( $C^{11}$ ), 133.07 (Ar-*ipso*), 131.23 (Ar-*p*), 129.57 ( $C^{10}$ ), 126.56, 126.06 (2 x Ar-*m*), 113.23 ( $CH^1$ ), 110.56 ( $CH^3$ ), 85.51 (Th- $CH_2$ ), 35.20, 27.16 ( $CMe_2$ ), 35.03 ( $CMe_3$ ), 33.91 ( $CMe_2$ ), 31.25 ( $CMe_3$ ), 27.62, 25.48 ( $CHMe_2$ ), 27.90, 25.56, 25.11, 23.72 ( $CHMe_2$ ), 2.87 ( $SiMe_3$ ).

**[( $XA_2$ )Th( $CH_2SiMe_3$ )( $\eta^6$ -toluene)][B( $C_6F_5$ ) $_4$ ] (5B).** A solution of [ $Ph_3C$ ][B( $C_6F_5$ ) $_4$ ] (17 mg, 0.019 mmol) in toluene (3 mL) was added dropwise to a solution of [( $XA_2$ )Th( $CH_2SiMe_3$ ) $_2$ ] (**1**; 10 mg, 0.009 mmol) in toluene (3 mL) at room temperature. The solution was stirred for 3 hours and then evaporated to dryness in vacuo. The resulting oil was dissolved in  $d_5$ -bromobenzene.  $^1H$  NMR ( $C_6D_5Br$ , 600 MHz, 20 °C):  $\delta$  7.46 (t,  $^3J_{H,H}$  8 Hz, 2H, Ar-*p*), 7.38, 7.30 (broad d, 2 x 2H, Ar-*m*), 6.92 (s, 2H,  $CH^1$ ), 6.92 (m, 1H, *p*- $PhMe^{coord}$ ), 6.67 (d,  $^3J_{H,H}$  7 Hz, 2H, *o*- $PhMe^{coord}$ ), 5.91 (app t,  $^3J_{H,H}$  7 Hz, 2H, *m*- $PhMe^{coord}$ ), 5.76 (s, 2H,  $CH^3$ ), 3.24, 2.60 (septet, 2 x 2H,  $^3J_{H,H}$  7 Hz,  $CHMe_2$ ), 2.02 (s, 3H,  $PhMe^{coord}$ ), 1.70, 1.67 (s, 2 x 3H,  $CMe_2$ ), 1.32, 1.18, 1.10, 0.86 (d, 4 x 6H,  $^3J_{H,H}$  7 Hz,  $CHMe_2$ ), 1.11 (s, 18H,  $CMe_3$ ), 0.06 (s, 2H,  $ThCH_2$ ), -0.16 (s, 9H,  $SiMe_3$ ).  $^{13}C$  { $^1H$ } NMR ( $C_6D_5Br$ , 150 MHz, 20 °C):  $\delta$  149.53 ( $C^2_tBu$ ), 149.13, 147.53 (Ar-*o*), 142.06 ( $C^{11}$ ), 134.95 (*o*- $PhMe^{coord}$ ), 134.49 (*m*- $PhMe^{coord}$ ), 132.86 (Ar-*ipso*), 130.68 (Ar-*p*), 129.3 ( $C^{10}$ ), 127.70 (*p*- $PhMe^{coord}$ ), 126.2, 125.5 (2 x Ar-*m*), 125.38 (*ipso*- $PhMe^{coord}$ ), 113.16 ( $CH^1$ ), 110.20 ( $CH^3$ ), 90.53 (Th- $CH_2$ ,  $^1J_{C,H}$  104 Hz), 35.15, 27.49 ( $CMe_2$ ), 34.79 ( $CMe_3$ ), 34.48 ( $CMe_2$ ), 31.17 ( $CMe_3$ ), 29.79, 27.36 ( $CHMe_2$ ), 27.09, 25.35, 25.28, 23.54 ( $CHMe_2$ ), 21.44 ( $PhMe^{coord}$ ) 2.69 ( $SiMe_3$ ).

**[( $XA_2$ )Th( $CH_2Ph$ )( $\eta^6$ -toluene)][B( $C_6F_5$ ) $_4$ ] $\cdot$ 2toluene, (**6**) $\cdot$ 2toluene.** A solution of [ $Ph_3C$ ][B( $C_6F_5$ ) $_4$ ] (150 mg, 0.162 mmol) in toluene (10 mL) was added dropwise to a solution of [( $XA_2$ )Th( $CH_2Ph$ ) $_2$ ] (**3**; 175 mg, 0.162 mmol) in toluene (10 mL) at room temperature. The mixture was stirred for 15 minutes, and then allowed to settle. The light orange mother liquors were then decanted to leave an orange-brown oil, which was washed with hexanes (10 mL), layered with hexanes (10 mL) and stored at 20 °C for several days to yield X-ray quality crystals of **6** $\cdot$ 2C $_7$ H $_8$  growing within and at the surface of the oil. Extremely air-sensitive **6** was always obtained as an oil, or as crystals coated with oil, and was insoluble in solvents

1 with which it did not react. This precluded elemental analysis or solution NMR spectroscopy, and as a  
2  
3  
4 result, direct characterization of **6** is limited to single crystal X-ray crystallography.

5  
6 **[(BDPP)Th( $\eta^2$ -CH<sub>2</sub>Ph)( $\mu$ - $\eta^1$ : $\eta^6$ -CH<sub>2</sub>Ph)Th( $\eta^1$ -CH<sub>2</sub>Ph)(BDPP)][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]**·0.75hexane·0.55benzene,**  
7  
8 **(7)**·0.75hexane·0.55benzene.******

9 A solution of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (150 mg, 0.162 mmol) in benzene (10 mL)  
10  
11 was added dropwise to a solution of [(BDPP)Th(CH<sub>2</sub>Ph)<sub>2</sub>] (**4**; 141 mg, 0.162 mmol) in benzene (10 mL)  
12  
13 at room temperature. The mixture was stirred for 15 minutes, and then allowed to settle. The light  
14  
15 orange mother liquors were then decanted to leave an orange-brown oil, which was washed with hexane  
16  
17 (10 mL) and then layered with hexanes (10 mL) and stored at 20 °C for several days to yield several  
18  
19 X-ray quality crystals of **7·0.75hexane·0.55benzene** growing within and at the surface of the oil. These  
20  
21 crystals were obtained in low yield (the formation of **7** was presumably due to a slight deficiency in the  
22  
23 amount of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] added), and were coated with oil, which precluded elemental analysis. In  
24  
25 addition, all products formed in the reactions of **4** with [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] are insoluble in solvents with  
26  
27 which they do not react, which prevented observation of **7** by solution NMR spectroscopy. As a result,  
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29 direct characterization of **7** is limited to single crystal X-ray crystallography.  
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51 **Supporting Information Available:** X-ray crystallographic data in PDF and CIF format, and selected  
52  
53 NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.  
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14 and comparable spectra were obtained by reaction of [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] or Ph<sub>3</sub>CCl with  
15 LiCH<sub>2</sub>SiMe<sub>3</sub>. Similar observations have been made in the reactions of titanium  
16 trimethylsilylmethyl complexes with [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], and the reaction of Ph<sub>3</sub>CCl with  
17 LiCH<sub>2</sub>SiMe<sub>3</sub> was also reported. The products were identified as two 'isomers' of Ph<sub>3</sub>CCH<sub>2</sub>SiMe<sub>3</sub>  
18 (from herein referred to as 'Ph<sub>3</sub>CCH<sub>2</sub>SiMe<sub>3</sub>') and ~15% of Ph<sub>3</sub>CH [<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 5.42  
19 (Ph<sub>3</sub>CH), 2.12, 2.06 (CH<sub>2</sub>SiMe<sub>3</sub>), -0.01, -0.32 (SiMe<sub>3</sub>): Bolton, P. D.; Clot, E.; Adams, N.;  
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22 (Ph<sub>3</sub>CH), 2.12, 2.06 (CH<sub>2</sub>SiMe<sub>3</sub>), 0.12, -0.21 (SiMe<sub>3</sub>) ppm in C<sub>6</sub>D<sub>6</sub>, and at 5.44 (Ph<sub>3</sub>CH), 2.36,  
23 2.06 (CH<sub>2</sub>SiMe<sub>3</sub>), -0.01, -0.26 (SiMe<sub>3</sub>) ppm in C<sub>6</sub>D<sub>5</sub>Br.
- 24 (41) The reaction of [(BDPP)Th(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>] (**2**) with [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] in benzene or toluene also  
25 resulted in precipitation of an insoluble orange-brown oil. However, in this case, the product was  
26 insufficiently soluble in benzene or toluene to allow investigation by solution NMR  
27 spectroscopy, and crystals of the product could not be obtained.
- 28 (42) Crystals of **5**, **6** and **7** were always coated with a viscous oil, which prevented investigation by  
29 elemental analysis.
- 30 (43) The ThCH<sub>2</sub> signal in the <sup>13</sup>C NMR spectrum of **5** was extremely broad, preventing measurement  
31 of a <sup>1</sup>J<sub>C,H</sub> coupling constant.
- 32 (44) A <sup>1</sup>H NMR spectrum of LiCH<sub>2</sub>SiMe<sub>3</sub> was obtained to confirm the absence of water or other  
33 protic impurities in the *d*<sub>8</sub>-THF used.
- 34 (45) Addition of 10 equivalents of toluene (C<sub>7</sub>H<sub>8</sub>) to a solution of **5** in C<sub>6</sub>D<sub>6</sub> did not result in the  
35 appearance of signals for coordinated toluene in the <sup>1</sup>H NMR spectrum.
- 36 (46) Oils deposited in the reactions of **3** and **4** with [CPh<sub>3</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] coated the walls of the reaction  
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6 (54) The strong tendency to engage in  $\pi$ -arene bonding in this chemistry may also be related to  
7 increased covalency in metal-ligand bonding, relative to the trivalent lanthanide metals, and the  
8 potential for  $f$ -orbital involvement in bonding.  
9 (55) While the reaction of **3** with 1 equivalent of  $B(C_6F_5)_3$  resulted in the formation of toluene-soluble  
10 **9**, the reactions of **1**, **2** and **4** with 1 equivalent of  $B(C_6F_5)_3$  yielded only orange-brown oils which  
11 were not amenable to spectroscopic characterization due to insolubility in solvents with which  
12 they did not react. This behavior is similar to that observed in the reactions of **1-4** with  
13  $[CPh_3][B(C_6F_5)_4]$  in benzene or toluene. However, in the reactions of **1**, **2** and **4** with  $B(C_6F_5)_3$ ,  
14 the products resisted crystallization.  
15 (56)  $\eta^6$ -Benzylborate coordination in both **9** and **10** is in keeping with the tendency for  $\pi$ -arene  
16 coordination observed in complexes **5-7**, and solution and solid-state NMR data to suggest  $\pi$ -  
17 coordination of the tetraphenylborate anion in  $[Cp^*_2ThMe][BPh_4]$ : (a) reference 6b. (b) reference  
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## For Table of Contents Use Only

Cationic Thorium Alkyl Complexes of Rigid NON- and NNN-Donor Ligands:  $\pi$ -Arene Coordination as a Persistent Structural Motif

Carlos A. Cruz, David J. H. Emslie,\* Craig M. Robertson, Laura E. Harrington, Hilary A. Jenkins and James F. Britten

### TOC Text

The reactions of neutral NON- and NNN-donor ligated thorium(IV) dialkyl complexes with  $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$  and  $\text{B}(\text{C}_6\text{F}_5)_3$  in benzene and toluene provided the first examples of non-cyclopentadienyl thorium alkyl cations. The structures of the observed thorium alkyl cations vary from arene solvent-separated ion pairs, to a binuclear complex with a  $\mu:\eta^1, \eta^6$ -benzyl ligand, to a contact ion pair with the  $\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3$  anion. However, a feature common to all of the solid state structures is  $\pi$ -arene coordination.

### TOC Graphic

