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

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Reaction of the neutral dialkyl complex $[(XA_2)Th(CH_2SiMe_3)_2]$ {1; $XA_2 = 4,5$ -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 $[(XA_2)Th(CH_2SiMe_3)(\eta^6-arene)][B(C_6F_5)_4]$ {arene = C₆H₆ (5) and toluene (5B)}, which were characterized by ¹H, ¹³C, and 2D NMR spectroscopy and by X-ray crystallography (for 5). In close analogy, reaction of $[(XA_2)Th(CH_2Ph)_2]$ (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 $[(XA_2)Th(\eta^2)$ $CH_2Ph(\eta^6-C_6H_5Me)$][B(C₆F₅)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 equiv 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 $[(BDPP)Th(\eta^2-CH_2Ph)(\mu-\eta^1)]$ η^6 -CH₂Ph)Th(η^1 -CH₂Ph)(BDPP)][B(C₆F₅)₄] (7) by X-ray crystallography. Reaction of complex 3 with $B(C_6F_5)_3$ resulted in the formation of $[(XA_2)Th(\eta^1-CH_2Ph)][\eta^6-PhCH_2B(C_6F_5)_3]$ (9), which was characterized in solution by NMR spectroscopy. Complexes 5, 5B, and 6 are rare examples of arene solventseparated 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 π -coordination.

Introduction

The vast majority of catalysts for insertion polymerization of ethylene and/or α -olefins are coordinatively unsaturated cationic metal alkyl complexes,^{1,2} and this field is particularly well developed for the tetravalent group 4 elements zirconium and titanium. Typical catalysts include [Cp*2ZrMe][A], [Cp*(MeInd)TiMe][A] (MeInd = 1-methylindenyl), and $[{SiMe_2(C_5Me_4)(NtBu)}MMe][A] (M = Zr \text{ or } Ti),^1 as well as$ the noncyclopentadienyl complexes [(R₃PN)₂TiMe][A] (Stephan et al.) and [{CH₂(CH₂NAr)₂}TiMe][A] (McConville et al.), where A is a weakly coordinating anion such as $MeB(C_6F_5)_3$ or $B(C_6F_5)_4$ ² 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 noncyclopentadienyl ancillaries.2,3

By contrast, effective actinide olefin polymerization catalysts remain rare, and noncyclopentadienyl 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 $[Cp_{2}ThR][A]$ (R = Me,⁴⁻⁹ CH₂SiMe₃,⁷ CH₂Ph,⁸ allyl,⁴ and H^{7,10}), where A is either a weakly coordinating borate anion or $[M(B_9C_2H_{11})_2]^{x-}$ (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 $[\{Me_2Si(indenyl)_2\}AnMe_2]$ as well as $[Cp_2AnMe_2]$ (An = Th or U) are mentioned in several T. J. Marks patents.¹¹ In addition, The Dow Chemical Co. has patented a variety of pentaalkylcyclopentadienyl actinide polymerization catalysts, including those formed from $[Cp_2AnX_2]$ and $[Cp^*AnX_3]$ (An = Th and U; X = Cl, Me, or CH₂SiMe₃)

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in combination with activators such as MAO.¹² Marks et al. also reported highly active heterogeneous olefin polymerization catalysts, which are similar in nature to $[Cp*_2ThR][A]$, but are formed by reaction of thorium and/or uranium polyalkyl complexes with dehydroxylated γ -alumina or MgCl₂.¹³ 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 $[Cp*_2-ThMe][B(C_6F_5)_4]$ in solution, and the Lewis base-stabilized cations $[Cp*_2ThMe(L)_x][A]$ (L = THF or NR₃; x = 1-3),⁶ $[Cp*_2UMe(THF)][MeBPh_3]$,^{15,16} and $[LU(CH_2Ph)(OEt_2)][BPh_4]$ {L = $Fe(C_3H_4NSi'BuMe_2)_2$ }¹⁷ (Figure 1). Several cationic actinide aryl, alkynyl, and borohydride complexes have also been reported.^{18,19}

As with the lanthanide metals and group 3 metals Y and Lu,^{3,20} many of the challenges in the chemistry of thorium and uranium stem from the large radii and electropositivity of these elements,²¹ which leads to a propensity for donor solvent coordination, dinuclear complex formation, ligand redistribution reactions, and often kinetically facile decomposition.²² However, actinide complexes are unique in their potential for significant

(14) Reaction of $[Cp*_2ThMe][B(C_6F_4Si'BuMe_2)_4]$ or $[Cp*_2ThMe]-[B(C_6F_4Si'Pr_3)_4]$ with $[Cp*_2ThMe_2]$ did not result in the formation of ¹H NMR detectable binuclear species. However, exchange of the methyl group of the cation with those of the neutral dimethyl complex was observed, suggesting that dinuclear cations analogous to $[(Cp*_2ThMe)_2(\mu-Me)][B(C_6F_5)_4]$ are accessible as part of an equilibrium that lies well to the side of the starting materials: ref 4.

(15) Evans, W. J.; Kozimor, S. A.; Ziller, J. W. Organometallics 2005, 24, 3407.

(16) Base-free $[Cp*_2UMe][MeBPh_3]$ has also been detected in solution. However, at temperatures above 238 K, it exists in equilibrium with $[Cp*_2UMe_2]$ and free BPh_3: ref 15.

(17) Monreal, M. J.; Diaconescu, P. L. Organometallics **2008**, 27, 1702. (18) The cationic borohydride complex [(COT)U(BH₄)(THF)₂][BPh₄] was prepared from [(COT)U(BH₄)₂(THF)] by reaction with [NEt₃H][BPh₄], and the adducts [(COT)U(BH₄)L₃][BPh₄] (L = HMPA and OPPh₃) were prepared in situ by reaction with 3 equiv of the appropriate Lewis base. The complex [($\eta^5:\eta^1$ -C₅Me₄-pyridy1-o)₂U(BH₄)][BPh₄] has also been reported: (a) Cendrowski-Guillaume, S. M.; Lance, M.; Nierlich, M.; Ephritikhine, M. Organometallics **2000**, 19, 3257. (b) Moisan, L.; Le Borgne, T.; Villiers, C.; Thuery, P.; Ephritikhine, M. C. R. Chimie **2007**, 10, 883.

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

covalency and f-orbital involvement in bonding,²³ and in actinide organometallic chemistry, unlike lanthanide and group 3 chemistry, the tetravalent state is also dominant.²⁴ These properties not only present challenges for the design of new actinide polymerization catalysts, especially those based on noncyclopentadienyl ligands, but also offer the tantalizing potential for polymerization behavior²⁵ that is significantly different from that of both early transition metal and lanthanide catalysts.

A major focus of our research program is the development of noncyclopentadienyl organoactinide chemistry and, in particular, exploration of ligand features necessary for the synthesis of (a) thermally robust thorium(IV) dialkyl precursors, (b) isolable actinide(IV) alkyl cations, and (c) active ethylene and α -olefin polymerization catalysts. To this end, our research has focused on the tridentate, dianionic supporting ligands 2,6bis(2,6-diisopropylanilidomethyl)pyridine (BDPP)²⁶ and 4,5-

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⁽²⁴⁾ Cerium also has access to the tetravalent oxidation state. However, cerium(IV) alkyl complexes have not yet been prepared, and even $[Ce(\eta^8-C_8R_8)_2]$ and $[Ce(pentalene)_2]$ are best described as complexes of cerium(III), rather than cerium(IV). However, $[Ce\{OCMe_2CH_2(NHC)\}_4]$ (NHC = NCHCHN'PrC) has recently been prepared, and the oxidation state in $[Cp_3CeX]$ and $[Cp_2CeX_2]$ (X = OR or halide) may be closer to cerium(IV) than to cerium(III):(a) Noh, W.; Girolami, G. S. *Polyhedron* **2007**, *26*, 3865. (b) Casely, I. J.; Liddle, S. T.; Blake, A. J.; Wilson, C.; Arnold, P. L. *Chem. Commun.* **2007**, 5037. (c) Evans, W. J.; Deming, T. J.; Ziller, J. W. *Organometallics* **1989**, *8*, 1581. (d) Edelstein, N. M.; Allen, P. G.; Bucher, J. J.; Shuh, D. K.; Sofield, C. D.; Kaltsoyannis, N.; Maunder, G. H.; Russo, M. R.; Sella, A. *J. Am. Chem. Soc.* **1996**, *118*, 13115. (e) Ashley, A.; Balazs, G.; Cowley, A.; Green, J.; Booth, C. H.; O'Hare, D. *Chem. Commun.* **2007**, 1515.



Figure 2. Structures of the BDPP and XA₂ ligands.

bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene (XA₂); Figure 2.^{27,28} Key features of BDPP and XA₂ are a large metal binding pocket, sterically bulky 2,6-diisopropylphenyl rings flanking the metal coordination site, and extremely high rigidity (especially in XA₂). These ligand features are considered important to effectively accommodate large actinide metals, provide sufficient steric and electronic saturation at the metal, and ensure effective positioning of steric bulk. This strategy has allowed the synthesis of the dialkyl complexes [LTh(CH₂SiMe₃)₂] {L = XA₂ (1) and BDPP (2)},²⁷ [(XA₂)-Th(CH₂Ph)₂] (3),²⁹ and [(BDPP)Th(CH₂Ph)₂] (4; this work), which show remarkably high thermal stability. For example, the thermal stability of 2 is even greater than that of [Cp*₂Th(CH₂SiMe₃)₂].³⁰

With robust dialkyl complexes in hand, we turned our attention to the synthesis of thorium(IV) alkyl cations by alkyl abstraction from 1-4. As described above, cationic d⁰ transition metal and f-block complexes of this type are well established as the active species in olefin polymerization catalysis.^{31,32} However, while contact ion pairs (CIPs) such as [Cp*2Zr-Me][MeB(C₆F₅)₃] have been studied in detail, and solventseparated ion pairs (SSIPs) involving strong donor solvents are common (e.g., [Cp*₂ZrMe(THF)][MeB(C₆F₅)₃]),³² SSIPs involving weakly coordinated arene solvents are rare, and their impact on olefin polymerization activity and selectivity is not well understood. McConville et al. invoked species of the form $[{CH_2(CH_2NAr)_2}TiR(\eta^6-toluene)]^+$ {Ar = Xyl or C₆H₃ⁱPr₂-2,6} to explain greatly reduced polymerization activities observed in the presence of small amounts of toluene.³³ In addition, Piers et al. have reported the synthesis of [(nacnac^{Me2})ScMe(η^{6} - C_6R_6][B(C_6F_5)₄] (C_6R_6 = bromobenzene, benzene, toluene, *p*-xylene, or mesitylene), and while $[(nacnac^{Me2})ScMe(\eta^6 C_6H_3Me_3-1,3,5)$ [B(C_6F_5)₄] is an active ethylene polymerization catalyst in bromobenzene, it shows negligible activity in more strongly donating toluene.³⁴ Other d⁰ arene solvent coordinated alkyl complexes are $[Cp''MR_2(\eta^6-toluene)][RB(C_6F_5)_3]$ {M = Zr, R = Me; M = Hf, R = Me or Et; $Cp'' = 1,3-C_5H_3(SiMe_3)_2$ in which the arene is tightly coordinated, ³⁵ [Cp*MMe₂(η^{6} -

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 C_6R_6][MeB(C_6F_5)₃] (M = Ti, C_6R_6 = toluene or mesitylene; M = Zr, C_6R_6 = benzene, toluene, *p*-xylene, *m*-xylene, mesitylene, styrene; M = Hf, C_6R_6 = toluene, *p*-xylene, *m*-xylene, mesitylene, styrene, anisole) in which the arene is particularly labile for M = Ti,³⁶ and [{*t*BuNSiMe₂(η^5 , η^1 - $C_5Me_3CH_2$)}Ti(toluene)][B(C_6F_5)₄] in which the arene is only weakly bound.³⁷

The complexes discussed above highlight a greater tendency toward arene solvent coordination in more sterically open cationic alkyl species, especially monocyclopentadienyl complexes and complexes of certain noncyclopentadienyl ligand systems. It therefore follows that π -arene coordination might be particularly favorable in cationic alkyl complexes of the large f-block metals, and because π -arene coordination can result in diminished or negated olefin polymerization activity (due to limited access of olefin monomer to the metal as a result of π -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 noncyclopentadienyl 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 [CPh₃][B(C₆F₅)₄] and B(C₆F₅)₃ and solution and/or solid-state characterization of the first noncyclopentadienyl thorium alkyl cations: [(XA₂)-Th(CH₂SiMe₃)(η^6 -arene)][B(C₆F₅)₄] [arene = benzene (**5**) or toluene (**5B**)], [(XA₂)Th(η^2 -CH₂Ph)(η^6 -C₆H₅Me)][B(C₆F₅)₄] (**6**), [(BDPP)Th(η^2 -CH₂Ph)(μ - η^1 : η^6 -CH₂Ph)Th(η^1 -CH₂Ph)(BDPP)][B(C₆F₅)₄] (**7**), and [(XA₂)Th(η^1 -CH₂Ph)][η^6 -PhCH₂B(C₆F₅)₃] (**9**).

Results and Discussion

The neutral dialkyl complexes $[LTh(CH_2SiMe_3)_2]$ {L = XA₂ (1) and BDPP (2) 27 and $[(XA_2)Th(CH_2Ph)_2]$ (3) 29 were prepared as previously reported, by reaction of [LThCl₂(dme)] $(L = XA_2 \text{ or BDPP})$ with 2 equiv of LiCH₂SiMe₃ or PhCH₂-MgCl at -78 °C. Dibenzyl complex [(BDPP)Th(η^2 -CH₂Ph)(η^3 -CH₂Ph)] (4) was accessible in a similar fashion using PhCH₂MgCl or KCH₂Ph. 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 η^3 -coordinated in the plane of the ligand $[Th-C32-C33 = 84.6(3)^\circ; Th-C32 = 2.576(6)]$ 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 η^{1} - and η^{2} -coordination [Th-C39-C40 $= 96.7(4)^{\circ}$; Th-C39 = 2.545(6) Å; Th-C40 = 3.087(6) Å]. At -35 °C in d_8 -toluene,³⁸ two distinct benzyl groups are observed by ¹H and ¹³C NMR spectroscopy, consistent with the observation of an axial and an in-plane benzyl group in the solid state. The ${}^{1}J_{C,H}$ coupling constants of 138 and 127 Hz for Th-*CH*₂ are suggestive of bonding approaching either η^2 - or η^3 -coordination, and η^1 -coordination, respectively.^{37,39} Similar ${}^{1}J_{C,H}$ coupling constants were observed in complex 2, and the

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Figure 3. Molecular structure of dibenzyl complex **4** \cdot 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 $\cdot \cdot \cdot C(38)$ 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).

observation of two independent molecules of 2 in the unit cell, each with a different hapticity of the axial benzyl ligand, illustrates the nonstatic nature of polyhapto-benzyl coordination.²⁹

Reaction of a 1.5 mM solution of complex 1 in benzene with 1 equiv of $[CPh_3][B(C_6F_5)_4]$ resulted in the slow (~70% complete after 48 h) formation of "Ph₃CCH₂SiMe₃" and Ph₃CH⁴⁰ (~1 equiv per mole of 1 consumed) and an organometallic product with ¹H and ¹³C NMR spectra consistent with a thorium(IV) alkyl cation (Th-*CH*₂: ¹H NMR δ 0.24 ppm, ¹³C NMR δ 85.5 ppm) exhibiting top-bottom asymmetry (two different *CMe*₂ and *CH*Me₂ environments). The reaction of 1 with 2 equiv of [CPh₃][B(C₆F₅)₄] in C₆D₆ resulted in complete consumption of 1 in just 3 h and formation of the same organometallic product.

Performing the reaction of **1** with $[CPh_3][B(C_6F_5)_4]$ 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, resulted in yellow crystals growing within the oil and protruding into the hexanes solvent.^{41,42} ¹H 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 noncyclopentadienyl 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

(42) Crystals of **5**, **6**, and **7** were always coated with a viscous oil, which prevented investigation by elemental analysis.

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Figure 4. Molecular structure of $[(XA_2)Th(CH_2SiMe_3)(\eta^6-C_6H_6)]$ -[B(C₆F₅)₄] • benzene, (**5**) • benzene, with thermal ellipsoids at the 50% probability level. Hydrogen atoms, isopropyl groups, the borate anion, and noncoordinated 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).

Scheme 1. Synthesis of the Thorium(IV) Alkyl Cations 5 and 6



ion pair, $[(XA_2)Th(CH_2SiMe_3)(\eta^6-C_6H_6)][B(C_6F_5)_4]$ (5), was observed as a result of η^6 -benzene coordination. In addition to being the first structurally characterized noncyclopentadienyl 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.^{33–37}

In the solid-state structure of **5** (Figure 4), the XA₂ 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 CH₂SiMe₃ group is bound in an apical position above the plane of the ligand with a Th–C48–Si angle of 131°, which strongly suggests the presence of an α -agostic C–H–Th interaction (cf., 127° and 128° in complex **1**, in which both alkyl groups engage in temperature-dependent α -agostic C–H–Th interactions).^{27,43} Benzene is approximately η^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**).

While complexes 1-4 do not react with PMe₃, complex **5** reacted rapidly with PMe₃ to precipitate a poorly soluble brown oil, presumably $[(XA_2)Th(CH_2SiMe_3)(PMe_3)_x][B(C_6F_5)_4]$, but attempts to dissolve the oil in d_8 -THF resulted in decomposition

⁽⁴⁰⁾ Reaction of **1** or **2** with [CPh₃][B(C₆F₅)₄] resulted in the formation of several organic byproducts, and comparable spectra were obtained by reaction of [CPh₃][B(C₆F₅)₄] or Ph₃CCl with LiCH₂SiMe₃. Similar observations have been made in the reactions of titanium trimethylsilylmethyl complexes with [CPh₃][B(C₆F₅)₄], and the reaction of Ph₃CCl with LiCH₂SiMe₃ was also reported. The products were identified as two "isomers" of Ph₃CCH₂SiMe₃ (from herein referred to as "Ph₃CCH₂SiMe₃") and ~15% of Ph₃CH [¹H NMR (CD₂Cl₂): δ 5.42 (Ph₃CH), 2.12, 2.06 (CH₂SiMe₃), -0.01, -0.32 (SiMe₃)]: Bolton, P. D.; Clot, E.; Adams, N.; Dubberley, S. R.; Cowley, A. R.; Mountford, P. *Organometallics* **2006**, 25, 2806 In this work, ¹H NMR chemical shifts (confirmed by 2D NMR) for these products were observed at 5.42 (Ph₃CH), 2.12, 2.06 (CH₂SiMe₃), -0.21 (SiMe₃) pm in C₆D₆, and at 5.44 (Ph₃CH), 2.36, 2.06 (CH₂SiMe₃), -0.01, -0.26 (SiMe₃) ppm in C₆D₅Br.

⁽⁴¹⁾ The reaction of $[(BDPP)Th(CH_2SiMe_3)_2]$ (2) with $[CPh_3][B(C_6F_5)_4]$ in benzene or toluene also resulted in precipitation of an insoluble orangebrown oil. However, in this case, the product was insufficiently soluble in benzene or toluene to allow investigation by solution NMR spectroscopy, and crystals of the product could not be obtained.

⁽⁴³⁾ The Th*C*H₂ signal in the ¹³C NMR spectrum of **5** was extremely broad, preventing measurement of a ¹ $J_{C,H}$ coupling constant.



Figure 5. Selected regions of ${}^{1}H{}^{-1}H$ COSY and EXSY (τ_{m} 0.5 s) NMR spectra for **5B** with 6 equiv of toluene in C₆D₅Br at 20 °C (sample generated in situ from the reaction of **1** with 2 equiv of [CPh₃][B(C₆F₅)₄] in toluene, followed by evaporation to dryness in vacuo and redissolution in C₆D₅Br).

to form H₂[XA₂].⁴⁴ Reaction of 5 with pyridine, 4-(dimethylamino)pyridine, Et₃PO, or PhNMe₂ 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 ¹H NMR spectrum of 5 in C₆D₅Br, all benzene signals were obscured by XA₂, "Ph₃CCH₂SiMe₃", Ph₃CH,⁴⁰ and CPh_3^+ signals. However, conducting the reaction of 1 with $[CPh_3][B(C_6F_5)_4]$ (2 equiv) in toluene resulted in the formation of $[(XA_2)Th(CH_2SiMe_3)(\eta^6-toluene)][B(C_6F_5)_4]$ (5B) (complete after 3 h), and subsequent evaporation to dryness and redissolution in C₆D₅Br allowed observation of both free and coordinated toluene in the ¹H NMR spectrum at 20 °C (Figure 5). This confirms that toluene in **5B** is strongly bound in solution⁴⁵ and does not readily exchange with free toluene (6 equiv), or undergo substitution by C₆D₅Br. Similar behavior has been reported for certain d⁰ π -aryl complexes, including [Cp"MMe₂(η^{6} toluene)][MeB(C₆F₅)₃] (M = Ti, Zr, or Hf; Cp'' = 1,3-bis(trimethylsilyl)cyclopentadienyl).35 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 CHMe2 signals), does occur on a longer time scale. A small ${}^{1}J_{C,H}$ coupling constant of 104 Hz for Th CH_{2} is also indicative of the presence of C–H–Th α -agostic interactions in **5B**, an observation consistent with the unusually large Th-C-Si angle in the solid-state structure of 5.

In a reaction analogous to the synthesis of complex **5**, treatment of $[(XA_2)Th(CH_2Ph)_2]$ **3** with 1.0 $[CPh_3][B(C_6F_5)_4]$ in benzene or toluene resulted in the slow formation of 1 equiv of Ph₃CCH₂Ph (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,⁴² 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: $[(XA_2)Th(\eta^2-CH_2Ph)(\eta^6-C_6H_5Me)][B(C_6F_5)_4]$ (**6**; Scheme



Figure 6. Molecular structure of $[(XA_2)Th(\eta^2-CH_2Ph)(\eta^6-C_6H_5-Me)][B(C_6F_5)_4] \cdot 2toluene, (6) \cdot 2toluene, with thermal ellipsoids at the 50% probability level. Hydrogen atoms, isopropyl groups, the borate anion, and noncoordinated toluene solvent are omitted for clarity. Selected bond lengths (Å) and angles (deg): Th–N(1) 2.314(3), Th–N(2) 2.320(3), Th–O 2.455(3), Th–C(48) 2.488(5), Th–C(49) 2.729(4), Th···C(50) 3.293(5), Th···C(54) 3.192(4), Th–C(55) 3.063(5), Th–C(56) 3.092(5), Th–C(57) 3.276(8), Th···C(58) 3.435(6), Th···C(59) 3.367(8), Th–C(60) 3.207(10), Th–C(48)–C(49) 83.2(3).$

1). However, unlike **5**, complex **6** is insoluble in benzene, toluene, OEt_2 , and bromobenzene and polymerizes THF, which precluded direct characterization by NMR spectroscopy.⁴⁶ Further, reaction with PMe₃ did not result in the formation of a more soluble product, and attempted dissolution of the presumed PMe₃-coordinated cation in d_8 -THF resulted in decomposition to release H₂[XA₂].⁴⁴

The solid-state structure of complex **6** shares many similarities with that of **5**. However, in **6**, the arene occupies an apical position, while the anionic R-group (η^2 -CH₂Ph) is bound in the plane of the XA₂ ligand (Figure 6). The arene is also less symmetrically bound to the metal than in **5**, with Th–C distances increasing from 3.06 to 3.44 Å toward the most sterically hindered methyl-substituted position (C58). It is therefore possible that toluene in **6** may be more accurately

⁽⁴⁴⁾ A ¹H NMR spectrum of LiCH₂SiMe₃ was obtained to confirm the absence of water or other protic impurities in the d_8 -THF used.

⁽⁴⁵⁾ Addition of 10 equiv of toluene (C_7H_8) to a solution of 5 in C_6D_6 did not result in the appearance of signals for coordinated toluene in the ¹H NMR spectrum.

⁽⁴⁶⁾ Oils deposited in the reactions of **3** and **4** with $[CPh_3][B(C_6F_5)_4]$ coated the walls of the reaction vessel. This prevented direct NMR spectroscopy of the oils using an NMR insert.



Figure 7. Molecular structure of $[(BDPP)Th(\eta^2-CH_2Ph)(\mu-\eta^{1:}\eta^6-CH_2Ph)Th(\eta^1-CH_2Ph)(BDPP)][B(C_6F_5)_4] \cdot 0.75$ hexane $\cdot 0.55$ benzene, (7) $\cdot 0.75$ hexane $\cdot 0.55$ 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 μ -benzyl group, are omitted. Selected bond lengths (Å) 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) \cdots C(34) 3.317(13), Th(1) \cdots C(38) 3.390(14), Th(1)-C(39) 2.616(11), Th(1) \cdots C(40) 3.442(11), Th(2)-C(77) 2.516(10), Th(2) \cdots C(78) 3.302(9), Th(2) \cdots 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).

described as η^4 - or η^5 -coordinated. However, η^6 -bonding cannot be excluded on the basis of the observed Th–C distances, which lie within the sum of the van der Waals radii for thorium and carbon (~3.60 Å).⁴⁷ In addition, the Th–ring centroid distance of 2.94 Å is almost identical to that observed in complex **5**.

As with complex **5**, a reduction in the Th–N and Th–O bond distances is observed relative to the corresponding neutral precursor (in this case, complex **3**). However, in complex **6**, shortening of the Th–O bond distance relative to that in **3** is particularly pronounced [Th–N = 2.314(3) and 2.320(3) Å versus 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].^{27,48} Comparison of cation **6** with **5** also reveals that the Th–N distances in **6** are significantly longer than those in **5**, while the Th–O distance in **6** is shorter, perhaps as a result of η^2 -benzyl coordination in the plane of the XA₂ ligand, which positions the metal further above the NON-plane and back toward the xanthene backbone of the ligand [displacement from the NON-plane of 0.724 Å in **6**, versus 0.469 Å in **5**].

Other structurally characterized actinide(IV) complexes containing a bound neutral arene are $[\{(\eta^6-C_6Me_6)U^{IV}Cl_2\}_2(\mu-Cl)_3]$ [AlCl₄] 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^{49,50} [cf., 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).⁴⁷ In addition, some indication of the extent to which the increased steric presence and electron density associated with a C₆Me₆ ring, relative to a C₆H₆ 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).⁵¹ Similarly, Sm-C_{mean} distances in $[(\eta^6-C_6R_6)Sm^{III}(AlCl_4)_3]$ vary from 2.91 to 2.89/2.90 to 2.88 Å for C_6R_6 = benzene, *m*-xylene, and mesitylene, respectively.⁵² Based on these data, it appears that much stronger actinide-arene bonding is observed in Cotton's C₆Me₆ complexes.⁴⁹ The long Th-C_{mean} distances in 5 and 6 are likely the result of very significant steric hindrance in the XA₂ and BDPP complexes, perhaps combined with the general trend toward reduced covalency in complexes of thorium, relative to uranium.⁵³ However, it is interesting that, despite long Th- C_{mean} distances in ${\bf 5}$ and ${\bf 6}$ [and presumably **5B** by analogy],⁴⁵ complex **5B** does not undergo rapid exchange of free and bound toluene in C₆D₅Br. 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 noncyclopentadienyl alkyl thorium cations; similar neutral arene coordination has not been reported for [Cp*₂ThMe][BAr₄].⁴⁻⁸

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 equiv 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).⁴²

^{(47) (}a) van der Waals radii: U = 1.86 Å, C = 1.70 Å. Bondi, A. J. *Phys. Chem.* **1964**, 68, 441. The van der Waals radius of Th can be predicted to be approximately 1.91 Å (b) Atomic radii in crystals: Th = 1.80 Å, U = 1.75 Å, C = 0.70 Å. Slater, J. C. J. *Chem. Phys.* **1964**, 41, 3199. (c) Revised effective ionic radii (C.N. 6) of Shannon and Prewitt: Th⁴⁺ 0.94 Å, U⁴⁺ 0.89 Å. Shannon, R. D. *Acta Crystallogr.* **1976**, A32, 751.

⁽⁴⁸⁾ The two sets of Th–N and Th–O bond distances listed for compound 3 correspond to two distinct molecules in the unit cell.

^{(49) (}a) Campbell, G. C.; Cotton, F. A.; Haw, J. F.; Schwotzer, W. Organometallics **1986**, *5*, 274. (b) Cotton, F. A.; Schwotzer, W. Organometallics **1985**, *4*, 942.

⁽⁵⁰⁾ Cotton, F. A.; Schwotzer, W.; Simpson, C. Q. Angew. Chem., Int. Ed. Engl. 1986, 25, 637.

^{(51) (}a) Cotton, F. A.; Schwotzer, W. Organometallics 1987, 6, 1275.
(b) Cesari, M.; Pedretti, U.; Zazzetta, A.; Lugli, G.; Marconi, W. Inorg. Chim. Acta 1971, 5, 439. (c) Garbar, A. V.; Leonov, M. R.; Zakharov, L. N.; Struchkov, Y. T. Russ. Chem. Bull. 1996, 45, 451.

^{(52) (}a) Fan, B.; Shen, Q.; Lin, Y. J. Organomet. Chem. 1989, 376, 61.
(b) Fan, B.; Shen, Q.; Lin, Y. J. Organomet. Chem. 1989, 377, 51. (c) Cotton, F. A.; Schwotzer, W. J. Am. Chem. Soc. 1986, 108, 4657.

⁽⁵³⁾ Manriquez, J. M.; Fagan, P. J.; Marks, T. J. J. Am. Chem. Soc. 1978, 100, 3939.

Complex **7** (Figure 7) is composed of a cationic [(BDPP)-Th(η^1 -CH₂Ph)]⁺ fragment coordinated via an η^6 -interaction to the benzyl group of a molecule of the neutral starting material [(BDPP)Th(CH₂Ph)₂] (**4**). In more detail, the metal center (Th2) in the cationic fragment of **7** is η^1 -coordinated to a benzyl substituent in an axial position, and, in the plane of the ligand, is η^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 η^2 -coordinated to the bridging benzyl group in the plane of the ligand, and η^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 η^2 -benzyl cation **6**; that is, the alkyl group (η^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_{ring} distances in **7** vary from 2.97(1) to 3.35(1) Å, increasing toward the more sterically hindered *ipso*-carbon (C40) of the μ - η^1 : η^6 -benzyl ligand. A similar variation in Th-C_{ring} distances was observed in toluenecoordinated cation **6**. The presence of significant steric hindrance at the arene coordinated cationic thorium center is particularly evident from the degree of twisting of the 2,6-diisopropylphenyl rings of the BDPP ligand on Th2 (Figure 7: view B), resulting in C59····C71 and C62····C74 distances of 4.37 and 8.31 Å, respectively.

Crystallographically characterized complexes containing a μ - η^{1} : η^{n} -benzyl bridging interaction similar to that in 7 have not previously been reported in f-block or early transition metal (groups 3-5) chemistry, and, to the best of our knowledge, no such complexes exist. Observation of this unusual coordination mode in complex 7 further illustrates the propensity of cationic noncyclopentadienyl thorium complexes to engage in π -arene coordination.54 However, it is perhaps unexpected that a π -interaction between the cationic fragment and a molecule of 4 is preferred over an η^6 -interaction with benzene, which was present in vast excess as the solvent. This preference is likely due the more electron-rich nature of metal-benzyl groups, relative to benzene, in part as a result of delocalization of negative charge into the ring. The presence of a more effective interaction between the cationic fragment of 7 and the benzyl group of a molecule of 4, relative to an interaction with a neutral arene, is supported by a Th-ring centroid distance of 2.79 Å, as compared to 2.95 and 2.94 Å in 5 and 6, respectively.

Direct investigation of the organometallic products formed in the reaction of complex 4 with $[CPh_3][B(C_6F_5)_4]$ was prevented by their insolubility in C₆D₆, d₈-toluene, OEt₂, or bromobenzene, and polymerization of d_8 -THF.⁴⁶ However, the reaction of 4 with $[CPh_3][B(C_6F_5)_4]$ could be probed indirectly by monitoring the disappearance of 4 and the formation of Ph₃CCH₂Ph by ¹H NMR spectroscopy in the presence of O(SiMe₃)₂ as an internal standard (Scheme 2). The reaction of 4 with 0.5 equiv of $[CPh_3][B(C_6F_5)_4]$ (no further change after 30 min at 20 °C) resulted in consumption of 0.7 equiv of 4 and release of 0.5 equiv of Ph₃CCH₂Ph, consistent with the formation of a 0.3:0.2:0.3 mixture of unreacted 4, dinuclear 7, and a mononuclear cation (presumably with the composition [(BDPP)-Th(CH₂Ph)(benzene)][B(C₆ F_5)₄] (8) by analogy with cations 5 and 6). This assignment was confirmed by the addition of PMe_3 (10 equiv) to the reaction mixture, which resulted in liberation

Scheme 2. Synthesis of the Thorium(IV) Alkyl Cations 7 and 8^{α}



^{*a*} Product ratios were determined by measurement of the amount of **4** and Ph₃CCH₂Ph in solution by ¹H NMR spectroscopy, both before and after addition of PMe₃ [in the presence of O(SiMe₃)₂ as an internal standard].

of 0.2 equiv of soluble **4** back into solution (addition of toluene (10 equiv) to reaction mixtures containing dinuclear **7** did not release **4**). However, conducting the reaction of **4** with 1.0 equiv of $[CPh_3][B(C_6F_5)_4]$ resulted in an approximately 1:1 ratio of "**4** consumed" to "Ph₃CCH₂Ph produced", consistent with the precipitation of mononuclear **8** as the major product.

In contrast to the reactions of **4** with $[CPh_3][B(C_6F_5)_4]$, monitoring the reaction of $[(XA_2)Th(CH_2Ph)_2]$ (**3**) with 0.5 equiv of $[CPh_3][B(C_6F_5)_4]$ by ¹H NMR spectroscopy (with subsequent addition of PMe₃) did not provide any evidence for the formation of a dinuclear complex analogous to **7**. The greater accessibility of a dinuclear structure with the BDPP ligand, relative to the XA₂ ligand, is likely a consequence of the less sterically bulky and more flexible backbone of the BDPP ligand.

Interestingly, reaction of **4** with 2.0 equiv of $[CPh_3][B(C_6F_5)_4]$ resulted in liberation of 2.0 equiv of Ph₃CCH₂Ph, suggesting the formation of an as-yet unidentified dicationic species. Analogous behavior was observed in the reaction of 2 equiv of $[CPh_3][B(C_6F_5)_4]$ with dibenzyl complex **3**, but not with bistrimethylsilylmethyl complexes **1** and **2**. Both single and double alkyl abstraction was also observed in the reactions of $[(XA_2)Th(CH_2Ph)_2]$ (**3**) with $B(C_6F_5)_3$.^{29,55} However, in this case, the resulting complexes, monocationic $[(XA_2)Th(\eta^1-CH_2Ph)][\eta^6-PhCH_2B(C_6F_5)_3]$ (**9**) and dicationic $[(XA_2)Th[\eta^6-PhCH_2B(C_6F_5)_3]_2$ (**10**), receive additional stabilization as a result of η^6 -benzylborate coordination (Scheme 3).⁵⁶

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 equiv 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 atm (20–100

⁽⁵⁴⁾ The strong tendency to engage in π -arene bonding in this chemistry may also be related to increased covalency in metal-ligand bonding, relative to the trivalent lanthanide metals, and the potential for f-orbital involvement in bonding.

⁽⁵⁵⁾ While the reaction of **3** with 1 equiv of $B(C_6F_5)_3$ resulted in the formation of toluene-soluble **9**, the reactions of **1**, **2**, and **4** with 1 equiv of $B(C_6F_5)_3$ yielded only orange-brown oils, which were not amenable to spectroscopic characterization due to insolubility in solvents with which they did not react. This behavior is similar to that observed in the reactions of **1**–**4** with $[CPh_3][B(C_6F_5)_3]$ in benzene or toluene. However, in the reactions of **1**, **2**, and **4** with $B(C_6F_5)_3$, the products resisted crystallization.

Scheme 3. Synthesis of Complexes 9 and 10⁵⁷



°C), highlighting the significant potential for olefin polymerization activity in more sterically open noncyclopentadienyl thorium alkyl cations to be diminished or negated by arene solvent, neutral dibenzyl precursor, or benzylborate anion coordination. The negative effects of π -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 toward preventing/disfavoring π -arene coordination, as well as the preparation of the analogous uranium complexes, which typically exhibit much greater solubility in low-polarity solvents.⁵³ Polymerization of alternative monomers will also be investigated.

In summary, use of the rigid, dianionic NON- and NNNdonor ligands XA₂ and BDPP has allowed the synthesis and characterization of the first noncyclopentadienyl thorium alkyl cations: $[(XA_2)Th(CH_2SiMe_3)(\eta^6-arene)][B(C_6F_5)_4]$ [arene = benzene (5) or toluene (5B)], $[(XA_2)Th(\eta^2-CH_2Ph)(\eta^6-C_6H_5-$ Me)][B(C₆F₅)₄] (**6**), [(BDPP)Th(η^2 -CH₂Ph)(μ - η^1 : η^6 -CH₂Ph)- $Th(\eta^{1}-CH_{2}Ph)(BDPP)][B(C_{6}F_{5})_{4}](7), and [(XA_{2})Th(\eta^{1}-CH_{2}Ph)][\eta^{6} PhCH_2B(C_6F_5)_3$ (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 6 are rare examples of arene solvent-separated ion pairs, complex 9 exists as a tight contact ion pair, and complex 7 is dinuclear as a result of an unusual μ - η^1 : η^6 -benzyl bridging interaction. The structures of complexes 5, 5B, 6, 7, and 9 highlight the strong preference for π -arene coordination in cationic complexes of the XA₂ and BDPP ligands, and the failure of these complexes to polymerize ethylene highlights the important role that π -arene coordination can play in the reactivity of coordinatively unsaturated f-block alkyl cations.

Experimental Section

General Details. An argon-filled MBraun UNIIab glovebox was employed for the manipulation and storage of all oxygen- and moisture-sensitive compounds, and all compounds were stored in a -30 °C freezer within the glovebox. Commonly utilized specialty glassware includes double manifold high vacuum lines, swivel frit assemblies, J-Young NMR tubes, and thick-walled flasks equipped with Teflon stopcocks (Chemglass and Toonen Glassblowing).⁵⁸ Any residual oxygen and moisture was removed from the argon stream by passage through an Oxisorb-W scrubber from Matheson Gas Products.

Hexanes, toluene, and THF were initially distilled under nitrogen from CaH₂, sodium, and sodium/benzophenone, respectively. They were then stored under vacuum over Na/Ph₂CO (toluene, THF) or Na/Ph₂CO/tetraglyme (hexanes). Benzene, C₆D₆, *d*₈-toluene, THF, *d*₈-THF, OEt₂, *d*₁₀-OEt₂, and O(SiMe₃)₂ were dried directly over Na/Ph₂CO, while C₆D₅Br was dried directly over CaH₂. All solvents were introduced into reactions or storage flasks by vacuum transfer with condensation at -78 °C.

Deuterated solvents were purchased from ACP chemicals. $B(C_6F_5)_3$ was purchased from Boulder Scientific and dried by repeated cycles of stirring in dimethylchlorosilane and sublimation. [CPh₃][B(C₆F₅)₄] was purchased from Strem, and PhCH₂MgCl (1.0 M in OEt₂) was purchased from Aldrich. Ethylene (99.99%) was purchased from Aldrich and used as received. KCH₂Ph,⁵⁹ [(BDPP)ThCl₂(dme)], [(XA₂)Th(CH₂SiMe₃)₂] (1), [(BDPP)Th-(CH₂SiMe₃)₂] (2), and [(XA₂)Th(CH₂Ph)₂] (3)^{27,29} were prepared as previously reported.

Combustion elemental analyses were performed on a Thermo EA1112 CHNS/O analyzer by Dr. Steve Kornic of this department. X-ray crystallographic analyses were performed on suitable crystals coated in Paratone oil and mounted on either (a) a P4 diffractometer with a Bruker Mo rotating-anode generator and a SMART1K CCD area detector or (b) a SMART APEX II diffractometer with a 3 kW sealed tube Mo generator in the McMaster Analytical X-Ray (MAX) Diffraction Facility. The two molecules of noncoordinated toluene in $6 \cdot 2$ toluene and the 0.75 molecules of hexane in $7 \cdot 0.55$ benzene $\cdot 0.75$ hexane were highly disordered and could not be modeled satisfactorily, so were treated using the SQUEEZE routine.⁶⁰

NMR spectroscopy [¹H, ¹³C, ¹³C{¹H}, ¹¹B, ¹⁹F, DEPT-135, COSY, HSQC, HMBC, EXSY (NOESY with τ_m 0.5 s)] was performed on Bruker DRX-500 and AV-600 spectrometers. All ¹H NMR and ¹³C NMR spectra were referenced relative to SiMe₄ through a resonance of the employed deuterated solvent or proteo impurity of the solvent; C₆D₆ (δ 7.15 ppm), C₇D₈ (δ 7.09, 7.00, 6.98, 2.09), C₆D₅Br (δ 7.30, 7.02, 6.94 ppm) for ¹H NMR, and C₆D₆ (δ 128.0 ppm), C₇D₈ (δ 137.86, 129.24, 128.33, 125.49, 20.4), C₆D₅Br (δ 130.9, 129.3, 126.1, 122.3 ppm) for ¹³C NMR. ¹¹B and ¹⁹F NMR spectra were referenced using external standards of BF₃(OEt₂) (0.0 ppm) and CFCl₃ (0.0 ppm), respectively. All NMR spectra were obtained at room temperature unless otherwise specified. Herein, Ar = 2,6-diisopropylphenyl, Bn = CH₂Ph, and the numbering scheme (CH¹, C², CH³, C⁴, C¹⁰, and C¹¹) for the xanthene backbone is shown in Figure 2.

 $[(BDPP)Th(\eta^2-CH_2Ph)(\eta^3-CH_2Ph)]$ (4). A 1.0 M solution of PhCH₂MgCl in OEt₂ (0.41 mL, 0.41 mmol) was added dropwise to a -78 °C solution of [(BDPP)ThCl₂(dme)] (175 mg, 0.21 mmol) in toluene (15 mL), before being warmed to room temperature over 3 h. The mixture was then filtered to remove insoluble salts, and the mother liquors were evaporated to dryness in vacuo. Hexanes (30 mL) were added, followed by sonication and filtration to collect 4 as a yellow solid (120 mg, 0.14 mmol) in 67% yield. X-ray quality crystals of 4.0.5 hexane were obtained by layering a toluene solution of 4 with hexanes at -30 °C. ¹H NMR (C₇D₈, 500 MHz, -35 °C): δ 7.22 (m, 6H, Ar-m, Ar-p, and Bn¹-m), 7.12 (br, s, 2H, Ar-m), 6.96 (br, s, 2H, Bn²-o), 6.80 (app. t, ³J_{H,H} 8 Hz, 2H, Bn²-m), 6.78 (t, ³*J*_{H,H} 8 Hz, 1H, Py-*p*), 6.74 (t, ³*J*_{H,H} 6 Hz, 1H, Bn¹-*p*), 6.32 (d, 2H, ³*J*_{H,H} 8 Hz, Py-*m*), 6.22 (t, 1H, ³*J*_{H,H} 8 Hz, Bn²-*p*), 5.47 (d, 2H, ${}^{3}J_{\rm H,H}$ 8 Hz, Bn¹-o), 5.07, 4.83 (d, 2 × 2H, ${}^{2}J_{\rm H,H}$ 19 Hz, py-CH₂), 3.88, 3.47 (septet, 2 × 2H, ${}^{3}J_{H,H}$ 7 Hz, CHMe₂), 1.49, 1.41, 1.33,

⁽⁵⁶⁾ η^6 -Benzylborate coordination in both **9** and **10** is in keeping with the tendency for π -arene coordination observed in complexes **5**–**7** and solution and solid-state NMR data to suggest π -coordination of the tetraphenylborate anion in [Cp*₂ThMe][BPh₄]: (a) ref 6b; (b) ref 13a.

⁽⁵⁷⁾ Note that in complex 9, the positions (axial or in-plane) of the coordinated benzylborate and alkyl ligand are not known.

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1.07 (d, 4 × 6H, ${}^{3}J_{\text{H,H}}$ 7 Hz, CH*M*e₂), 1.45 (s, 2H, ThC*H*₂Ph¹), 1.15 (s, 2H, ThC*H*₂Ph²). ${}^{13}\text{C}{}^{1}\text{H}$ NMR (C₇D₈, 125 MHz, -35 °C): δ 164.33 (Py-*ortho*), 150 (Bn²-*ipso*), 149.68, 147.74 (Ar-*o*), 145.78 (Bn¹-*ipso*), 141.83 (Ar-*ipso*), 132.43, 126.33 (*p*-Ar and Bn¹-*m*), 124.28 (Bn²-*o*), 124.00, 123.82 (2 × Ar-*m*), 123.51 (Bn¹-*o*), 121.25 (Bn¹-*p*), 118.77 (Bn²-*p*), 117.23 (Py-*m*), 116.29 (Py-*p*), 89.64 (Th-*C*H₂Ph¹), 78.50 (Th-*C*H₂Ph²), 67.45 (py-*C*H₂), 29.95, 28.15 (CHMe₂), 28.03, 27.73, 23.44, 22.78 (CH*M*e₂). Anal. Calcd for C₄₅H₅₅N₃Th: C, 62.13; H, 6.37; N, 4.83. Found: C, 61.91; H, 6.94; N, 4.90.

[(XA₂)Th(CH₂SiMe₃)(η^{6} -C₆H₆)][B(C₆F₅)₄] •C₆H₆, (5) •C₆H₆. Method A. A solution of [Ph₃C][B(C₆F₅)₄] (150 mg, 0.162 mmol) in benzene (10 mL) was added dropwise to a solution of [(XA₂)Th(CH₂SiMe₃)₂] (1; 175 mg, 0.162 mmol) in benzene (10 mL) at room temperature. The mixture was stirred for 15 min and then allowed to settle. The 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 then stored at 20 °C for several days to yield X-ray quality crystals of $5 \cdot C_6H_6$ growing within and at the surface of the oil. Note: Crystals of 5 were always coated with oil, which prevented elemental analysis.

Method B. A solution of [Ph₃C][B(C₆F₅)₄] (17 mg, 0.019 mmol) in C_6D_6 (3 mL) was added dropwise to a solution of [(XA₂)Th(CH₂SiMe₃)₂] (1; 10 mg, 0.009 mmol) in C₆D₆ (3 mL) at room temperature. The solution was stirred for 16 h prior to investigation by ¹H, ¹³C, and 2D NMR spectroscopy. ¹H NMR (C₆D₆, 600 MHz, 20 °C): δ 7.42 (t, ³J_{H,H} 8 Hz, 2H, Ar-*p*), 7.27, 7.25 (app. t, ${}^{3}J_{H,H}$ 7 Hz, 2 × 2H, Ar-*m*), 6.82 (d, ${}^{4}J_{H,H}$ 2 Hz, 2H, CH¹), 5.82 (d, ${}^{4}J_{H,H}$ 2 Hz, 2H, CH³), 3.25, 2.50 (septet, 2 × 2H, ${}^{3}J_{H,H}$ 7 Hz, CHMe₂), 1.61, 1.46 (s, 2 × 3H, CMe₂) 1.28, 1.13, 1.03, 0.86 (d, 4 × 6H, ${}^{3}J_{H,H}$ 7 Hz, CHMe₂), 1.07 (s, 18H, CMe₃), 0.25 (s, 2H, ThCH₂), -0.13 (s, 9H, SiMe₃). ¹³C{¹H} NMR (C₆D₆, 150 MHz, 20 °C): δ 149.97 (C²/Bu), 149.57, 147.53 (Ar-o), 142.40 (C¹¹), 133.07 (Ar-ipso), 131.23 (Ar-p), 129.57 (C¹⁰), 126.56, 126.06 (2 \times Ar-*m*), 113.23 (CH¹), 110.56 (CH³), 85.51 (Th-CH₂), 35.20, 27.16 (CMe₂), 35.03 (CMe₃), 33.91 (CMe₂), 31.25 (CMe₃), 27.62, 25.48 (CHMe₂), 27.90, 25.56, 25.11, 23.72 (CHMe₂), 2.87 (SiMe₃).

 $[(XA_2)Th(CH_2SiMe_3)(\eta^6-toluene)][B(C_6F_5)_4]$ (5B). A solution of [Ph₃C][B(C₆F₅)₄] (17 mg, 0.019 mmol) in toluene (3 mL) was added dropwise to a solution of [(XA₂)Th(CH₂SiMe₃)₂] (1; 10 mg, 0.009 mmol) in toluene (3 mL) at room temperature. The solution was stirred for 3 h and then evaporated to dryness in vacuo. The resulting oil was dissolved in d₅-bromobenzene. ¹H NMR (C₆D₅Br, 600 MHz, 20 °C): δ 7.46 (t, ³J_{H,H} 8 Hz, 2H, Ar-*p*), 7.38, 7.30 (broad d, 2 × 2H, Ar-m), 6.92 (s, 2H, CH¹), 6.92 (m, 1H, p-PhMe^{coord}), 6.67 (d, ³J_{H,H} 7 Hz, 2H, *o-Ph*Me^{coord}), 5.91 (app t, ³J_{H,H} 7 Hz, 2H, *m*-*Ph*Me^{coord}), 5.76 (s, 2H, CH³), 3.24, 2.60 (septet, $2 \times 2H$, ${}^{3}J_{H,H}$ 7 Hz, CHMe₂), 2.02 (s, 3H, PhMe^{coord}), 1.70, 1.67 (s, 2 × 3H, CMe_2), 1.32, 1.18, 1.10, 0.86 (d, 4 × 6H, ${}^{3}J_{H,H}$ 7 Hz, CHMe₂), 1.11 (s, 18H, CMe₃), 0.06 (s, 2H, ThCH₂), -0.16 (s, 9H, SiMe₃). ¹³C{¹H} NMR (C₆D₅Br, 150 MHz, 20 °C): δ 149.53 (C^{2t} Bu), 149.13, 147.53 (Ar-o), 142.06 (C¹¹), 134.95 (o-PhMe^{coord}), 134.49 (m-PhMe^{coord}), 132.86 (Ar-ipso), 130.68 (Ar-p), 129.3 (C¹⁰), 127.70 $(p-PhMe^{coord})$, 126.2, 125.5 (2 × Ar-*m*), 125.38 (*ipso-PhMe*^{coord}), 113.16 (CH¹), 110.20 (CH³), 90.53 (Th-*CH*₂, ¹*J*_{C,H} 104 Hz), 35.15, 27.49 (CMe₂), 34.79 (CMe₃), 34.48 (CMe₂), 31.17 (CMe₃), 29.79, 27.36 (CHMe₂), 27.09, 25.35, 25.28, 23.54 (CHMe₂), 21.44 (Ph Me^{coord}), 2.69 (SiMe₃).

[(XA₂)Th(CH₂Ph)(η^6 -toluene)][B(C₆F₅)₄] • 2toluene, (6) • 2toluene. A solution of [Ph₃C][B(C₆F₅)₄] (150 mg, 0.162 mmol) in toluene (10 mL) was added dropwise to a solution of [(XA₂)Th(CH₂Ph)₂] (**3**; 175 mg, 0.162 mmol) in toluene (10 mL) at room temperature. The mixture was stirred for 15 min 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 $6 \cdot 2C_7H_8$ 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 with which it did not react. This precluded elemental analysis or solution NMR spectroscopy, and, as a result, direct characterization of **6** is limited to single-crystal X-ray crystallography.

 $[(BDPP)Th(\eta^2-CH_2Ph)(\mu-\eta^1:\eta^6-CH_2Ph)Th(\eta^1-CH_2Ph)(BDPP)] [B(C_6F_5)_4] \cdot 0.75$ hexane $\cdot 0.55$ benzene, (7) $\cdot 0.75$ hexane $\cdot 0.55$ benzene. A solution of [Ph₃C][B(C₆F₅)₄] (150 mg, 0.162 mmol) in benzene (10 mL) was added dropwise to a solution of $[(BDPP)Th(CH_2Ph)_2]$ (4; 141 mg, 0.162 mmol) in benzene (10 mL) at room temperature. The mixture was stirred for 15 min and then allowed to settle. The light-orange mother liquors were then decanted to leave an orange-brown oil, which was washed with hexane (10 mL) and then layered with hexanes (10 mL) and stored at 20 °C for several days to yield several X-ray quality crystals of 7.0.75hexane.0.55benzene growing within and at the surface of the oil. These crystals were obtained in low yield (the formation of 7 was presumably due to a slight deficiency in the mount of $[Ph_3C][B(C_6F_5)_4]$ added) and were coated with oil, which precluded elemental analysis. In addition, all products formed in the reactions of 4 with $[Ph_3C][B(C_6F_5)_4]$ are insoluble in solvents with which they do not react, which prevented observation of 7 by solution NMR spectroscopy. As a result, direct characterization of 7 is limited to single-crystal X-ray crystallography.

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Supporting Information Available: X-ray crystallographic data in PDF and CIF format, and selected NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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