

# Mono(pentamethylcyclopentadienyl)thorium Chemistry: Synthesis, Structural Characterization, and Reactivity of Aryloxy and Alkyl Derivatives

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Reaction of  $\text{ThBr}_4(\text{THF})_4$  with 1 equiv of  $\text{Cp}^*\text{MgBr}(\text{THF})$  ( $\text{Cp}^* = \eta\text{-C}_5\text{Me}_5$ ) produces the mono(pentamethylcyclopentadienyl) complex  $\text{Cp}^*\text{ThBr}_3(\text{THF})_3$  (**1**). Treatment of **1** with 1 or 2 equiv of  $\text{KOAr}$  ( $\text{Ar} = 2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3$ ) yields the mono- and bis(aryloxy) species  $\text{Cp}^*\text{ThBr}_2(\text{OAr})(\text{THF})$  (**2**) and  $\text{Cp}^*\text{ThBr}(\text{OAr})_2$  (**3**), respectively. Alkylation of **2** with 2 equiv of  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  leads to isolation of the bis(alkyl) complex  $\text{Cp}^*\text{Th}(\text{OAr})(\text{CH}_2\text{SiMe}_3)_2$  (**4**), while **3** reacts with 1 equiv of  $\text{MeMgBr}$  to form the mono(alkyl) derivative  $\text{Cp}^*\text{ThMe}(\text{OAr})_2$  (**5**). **4** reacts with dihydrogen to produce the trimeric thorium dihydride  $[\text{Cp}^*\text{ThH}_2(\text{OAr})]_3$  (**6**), while thermolysis of **4** in the presence of triphenylphosphine oxide leads to the isolation of the metallacyclic species  $\text{Cp}^*\text{Th}(\text{OC}_6\text{H}_3\text{-}t\text{-BuCMe}_2\text{CH}_2)(\text{OAr})(\text{O}=\text{PPh}_3)$  (**7**). In the presence of 1 equiv of  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ , **4** is found to catalyze the hydrogenation of 1-hexene and also the polymerization of ethylene. Compounds **1–7** have been characterized by  $^1\text{H}$  NMR and IR spectroscopy, by microanalysis, and, in the case of **3**, **4**, and **7**, by single-crystal X-ray diffraction studies.  $\text{Cp}^*\text{ThBr}(\text{OAr})_2$  (**3**) exhibits a somewhat distorted three-legged piano-stool geometry with  $\text{Th}-\text{Cp}^*_{\text{centroid}}$ ,  $\text{Th}-\text{O}$ , and  $\text{Th}-\text{Br}$  distances of 2.57(1), 2.16(1) (av), and 2.821(2) Å, respectively.  $\text{Cp}^*\text{Th}(\text{OAr})(\text{CH}_2\text{SiMe}_3)_2$  (**4**) also displays a three-legged piano-stool geometry with  $\text{Th}-\text{C}$  distances to the alkyl groups of 2.460(9) and 2.488(12) Å.  $\text{Th}-\text{Cp}^*_{\text{centroid}}$  and  $\text{Th}-\text{O}$  distances are very similar to those found in **3**, at 2.53(1) and 2.186(6) Å, respectively.  $\text{Cp}^*\text{Th}(\text{OC}_6\text{H}_3\text{-}t\text{-BuCMe}_2\text{CH}_2)(\text{OAr})(\text{O}=\text{PPh}_3)$  (**7**) features a distorted trigonal bipyramidal geometry about the metal center, with the  $\text{Cp}^*$  ligand and the oxygen atom of the cyclometalated aryloxy ligand occupying axial sites ( $\text{Cp}^*_{\text{centroid}}-\text{Th}-\text{O} = 168.3(3)^\circ$ ). The  $\text{Th}-\text{C}$  distance to the *tert*-butyl methylene group is 2.521(12) Å, while  $\text{Th}-\text{O}$  distances to the aryloxy and triphenylphosphine oxide ligands are 2.199(7) (av) and 2.445(7) Å, respectively.

## Introduction

The ubiquitous cyclopentadienyl and pentamethylcyclopentadienyl ligands have proven to be invaluable in facilitating the development of organometallic chemistry of the early actinide elements over the last two decades, due to their ability to provide steric saturation of these large metal centers.<sup>2</sup> This field of chemistry has thus been dominated by complexes based upon the  $\text{Cp}^*_2\text{An}$  or  $\text{Cp}_3\text{An}$  frameworks ( $\text{Cp}^* = \eta\text{-C}_5\text{Me}_5$ ,  $\text{Cp} = \eta\text{-C}_5\text{H}_5$ ,  $\text{An} = \text{Th}, \text{U}$ ), with reports of actinide compounds containing mono(cyclopentadienyl)<sup>3</sup> or mono(pentamethylcyclopentadienyl)<sup>4</sup> ancillary ligand sets being considerably less common. However, it would appear that the relative steric and electronic unsaturation of the mono(cyclopentadienyl)actinide framework would make this class of complexes an attractive synthetic goal, with the possibility of enhanced reactivity being provided by the

relatively open coordination sphere of the metal center in these systems.

(3) See for example: (a) Cramer, R. E.; Bruck, M. A.; Gilje, J. W. *Organometallics* **1988**, *7*, 1465. (b) Eigenbrot, C. W.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653. (c) Ernst, R. D.; Kenelly, W. J.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2656. (d) Bagnall, K. W.; Benetollo, F.; Bombieri, G.; de Paoli, G. *J. Chem. Soc., Dalton Trans.* **1984**, 67. (e) Bagnall, K. W.; Beheshti, A.; Heatley, F. *J. Less-Common Met.* **1978**, *61*, 63. (f) Delavaux-Nicot, B.; Ephritikhine, M. *J. Organomet. Chem.* **1990**, *399*, 77. (g) Baudry, D.; Dorion, P.; Ephritikhine, M. *J. Organomet. Chem.* **1988**, *356*, 165. (h) Baudry, D.; Ephritikhine, M. *J. Organomet. Chem.* **1988**, *349*, 123. (i) Domingos, A.; Marques, N.; Pires de Matos, A. *Polyhedron* **1990**, *9*, 69. (j) Bagnall, K. W.; Edwards, J.; Tempest, A. C. *J. Chem. Soc., Dalton Trans.* **1978**, 295. (k) Bagnall, K. W.; Beheshti, A.; Edwards, J.; Heatley, F.; Tempest, A. C. *J. Chem. Soc., Dalton Trans.* **1979**, 1241. (l) Baudin, C.; Ephritikhine, M. *J. Organomet. Chem.* **1989**, *364*, C1. (m) Edelman, M. A.; Lappert, M. F.; Atwood, J. L.; Zhang, H. *Inorg. Chim. Acta* **1987**, *139*, 185. (n) Bombieri, G.; de Paoli, G.; Del Pra, A.; Bagnall, K. W. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 359. (o) Cramer, R. E.; Mori, A. L.; Maynard, R. B.; Gilje, J. W.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1984**, *106*, 5920. (p) Brianese, N.; Casellato, U.; Ossola, F.; Porchia, M.; Rossetto, G.; Zanella, P.; Graziani, R. *J. Organomet. Chem.* **1989**, *365*, 223. (q) Rebizant, J.; Spirlet, M. R.; Apostolidis, A.; Kanellakopoulos, B. *Acta Crystallogr.* **1992**, *48C*, 452.

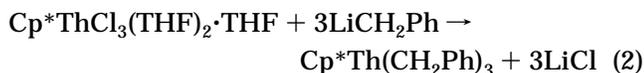
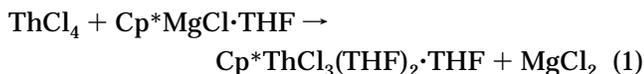
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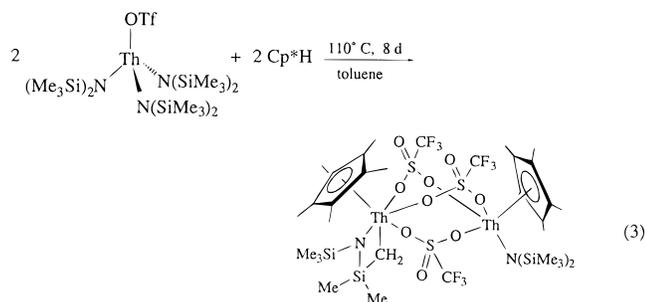
(2) (a) Marks, T. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 3, pp 211–223. (b) Ephritikhine, M. *New J. Chem.* **1992**, *16*, 451. (c) Clark, D. L.; Sattelberger, A. P. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: New York, 1994; Vol. 1, pp 19–34.

In the case of thorium, the range of mono(pentamethylcyclopentadienyl) complexes described in the literature is extremely limited. Marks and co-workers have reported the preparation of the trichloride derivative  $\text{Cp}^*\text{ThCl}_3(\text{THF})_2\cdot\text{THF}$  (eq 1) and the subsequent



reaction of this complex with 3 equiv of benzyl lithium to form the tris(benzyl) complex  $\text{Cp}^*\text{Th}(\text{CH}_2\text{C}_6\text{H}_5)_3$  (eq 2).<sup>4a</sup> More recently, Sattelberger *et al.* have described the isolation of the mixed-ring complex  $(\eta\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{Me}_5)\text{ThCl}(\text{THF})_x$  from the reaction of  $(\eta\text{-C}_8\text{H}_8)\text{ThCl}_2(\text{THF})_2$  with a pentamethylcyclopentadienyl Grignard reagent and its subsequent derivatization to produce  $(\eta\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{Me}_5)\text{Th}[\text{CH}(\text{SiMe}_3)_2]$ ,  $[(\eta\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{Me}_5)\text{ThH}]_x$  and  $(\eta\text{-C}_8\text{H}_8)(\eta\text{-C}_5\text{Me}_5)\text{Th}(\mu\text{-Cl})_2\text{Mg}(\text{CH}_2\text{-}t\text{Bu})(\text{THF})$ .<sup>4b</sup>

We recently reported the isolation of a mono(pentamethylcyclopentadienyl)thorium derivative which was prepared by utilizing an alternative synthetic route to the more common halide metathesis methods. Thermolysis of the thorium amido complex  $\text{Th}(\text{OSO}_2\text{CF}_3)[\text{N}(\text{SiMe}_3)_2]_3$  with 1 equiv of pentamethylcyclopentadiene was found to produce the dinuclear triflate-bridged species  $\text{Cp}^*[(\text{Me}_3\text{Si})_2\text{N}]\text{Th}(\mu_2\text{-OSO}_2\text{CF}_3)_3\text{Th}[\text{N}(\text{SiMe}_3)(\text{SiMe}_2\text{CH}_2)]\text{Cp}^*$ , as indicated in eq 3.<sup>5</sup>

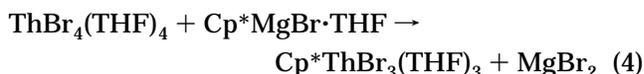


In an elegant series of studies, Marks and co-workers have shown that bis(pentamethylcyclopentadienyl) derivatives of thorium possess extremely high catalytic activity in reactions such as  $\alpha$ -olefin polymerization and hydrogenation and arene hydrogenation.<sup>6</sup> By comparison, only limited studies have been carried out to determine the catalytic properties of the corresponding mono(pentamethylcyclopentadienyl) derivatives.<sup>6d,7,8</sup> As part of our ongoing studies of the inorganic and organometallic chemistry of the early actinide elements,<sup>9</sup> we were interested in further exploring the structural, reactivity, and catalytic properties of mono(pentamethylcyclopentadienyl)thorium species containing a variety of supporting ligands and determining whether the

somewhat less sterically hindered coordination sphere of the mono-ring complexes would lead to enhanced reactivity.

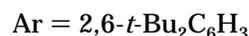
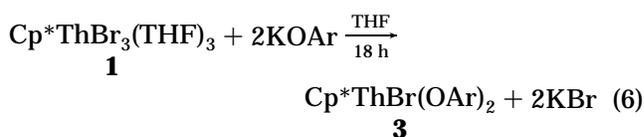
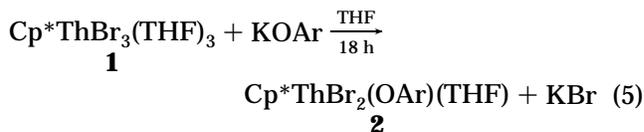
## Results and Discussion

**Synthesis and Reactivity.** The reaction of anhydrous  $\text{ThCl}_4$  with 1 equiv of  $\text{Cp}^*\text{MgCl}\cdot\text{THF}$  has previously been reported to produce the mono(pentamethylcyclopentadienyl) species  $\text{Cp}^*\text{ThCl}_3(\text{THF})_2\cdot\text{THF}$  (eq 1).<sup>4a</sup> A directly analogous reaction in which a THF solution of  $\text{ThBr}_4(\text{THF})_4$ <sup>9c</sup> is treated with 1 equiv of  $\text{Cp}^*\text{MgBr}\cdot\text{THF}$ , followed by addition of dioxane to precipitate magnesium halide, was found to lead to the formation of the analogous tribromide complex  $\text{Cp}^*\text{ThBr}_3(\text{THF})_3$  (**1**) in moderate yield (eq 4). **1** is soluble in THF and



may be recrystallized from this solvent at low temperature. Crystalline samples of **1** are observed to powder upon standing in the drybox atmosphere, presumably due to partial loss of THF from the complex.

**1** was found to react smoothly with 1 equiv of KOAr (Ar = 2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) to yield the mono(aryloxi) complex  $\text{Cp}^*\text{ThBr}_2(\text{OAr})(\text{THF})$  (**2**) in 65% yield following crystallization from toluene (eq 5). In a directly analo-



gous reaction, **1** also reacts with 2 equiv of KOAr to produce the bis(aryloxi) species  $\text{Cp}^*\text{ThBr}(\text{OAr})_2$  (**3**), which may be isolated in 73% yield after crystallization from hexane (eq 6). The colorless crystalline complexes were characterized by NMR and IR spectroscopy and elemental analysis.

The thorium halide derivatives **2** and **3** may be readily alkylated with Grignard reagents in the presence of dioxane to give thorium alkyl species. Thus the addition of 2 equiv of  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  to a toluene solution of  $\text{Cp}^*\text{ThBr}_2(\text{OAr})(\text{THF})$  (**2**), followed by addition of dioxane and crystallization from toluene, leads

(5) Butcher, R. J.; Clark, D. L.; Grumbine, S. K.; Watkin, J. G. *Organometallics* **1995**, *14*, 2799.

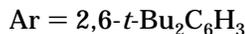
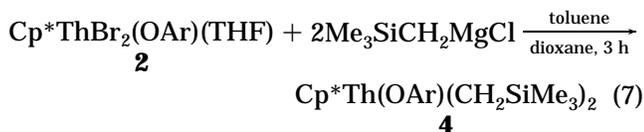
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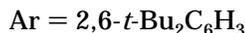
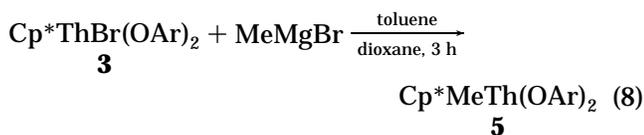
(8) Finch, W. C.; Gillespie, R. D.; Hedden, D.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 6221.

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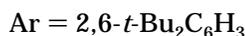
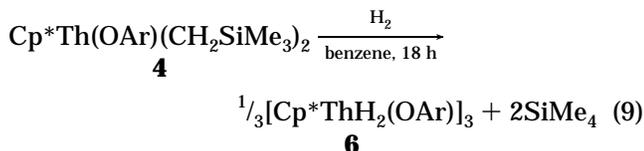
to the isolation of the bis(alkyl) complex  $\text{Cp}^*\text{Th}(\text{OAr})-(\text{CH}_2\text{SiMe}_3)_2$  (**4**) as colorless crystals in 54% yield (eq 7).



In a similar manner,  $\text{Cp}^*\text{ThBr}(\text{OAr})_2$  (**3**) is found to react smoothly with 1 equiv of  $\text{MeMgBr}$  to yield the thorium alkyl complex  $\text{Cp}^*\text{ThMe}(\text{OAr})_2$  (**5**), which may be isolated by low-temperature crystallization from hexane solution as colorless crystals in 74% yield (eq 8).



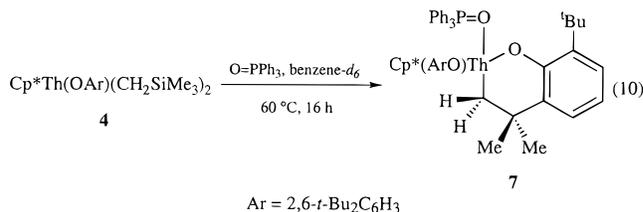
A benzene solution of the bis(alkyl) complex  $\text{Cp}^*\text{Th}(\text{OAr})(\text{CH}_2\text{SiMe}_3)_2$  (**4**) is found to react with 1 atmosphere of dihydrogen over a period of 18 h at room temperature to produce a crystalline solid (**6**) with the empirical formula  $\text{Cp}^*\text{ThH}_2(\text{OAr})$  (eq 9). A solution



molecular weight determination of the crystalline material (isopiestic method, benzene solution) supported the formulation of this material as a trimer (calcd for  $[\text{Cp}^*\text{ThH}_2(\text{OAr})]_3 = 1724$ , found = 1780), which is also consistent with the nuclearity of the closely-related thorium dihydride species  $\text{Th}_3(\mu_3\text{-H})_2(\mu_2\text{-H})_4(\text{O}-2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)_6$  which has recently been isolated.<sup>10</sup> **6** is found to be soluble in toluene and sparingly soluble in hexane.

Thermolysis of benzene- $d_6$  solutions of **4** (60 °C, 12 h) resulted in the liberation of  $\text{SiMe}_4$ , but no tractable products could be isolated from the reaction mixture. However, in the presence of 1.1 equiv of triphenylphosphine oxide the thermolysis of **4** (benzene- $d_6$ , 16 h, 60 °C) yielded a crystalline product which <sup>1</sup>H NMR spectroscopy revealed to contain a cyclometalated aryloxy ligand. A single-crystal X-ray diffraction study (*vide infra*) confirmed the identity of this ligand redistribution

complex as  $\text{Cp}^*\text{Th}(\text{OC}_6\text{H}_3\text{-}t\text{-BuCMe}_2\text{CH}_2)(\text{OAr})(\text{O}=\text{PPh}_3)$  (**7**) (eq 10). Although freshly-prepared single crystals of **7** are found to contain a molecule of toluene solvent within the lattice (*vide infra*), <sup>1</sup>H NMR data show that this lattice solvent is lost quite rapidly upon exposure to vacuum and thoroughly-dried crystalline samples of



**7** give microanalytical data consistent with the solvent-free formulation.

**Spectroscopic Studies.** Interpretation of the room-temperature <sup>1</sup>H NMR spectra of  $\text{Cp}^*\text{ThBr}_3(\text{THF})_3$  (**1**),  $\text{Cp}^*\text{ThBr}_2(\text{OAr})(\text{THF})$  (**2**), and  $\text{Cp}^*\text{ThBr}(\text{OAr})_2$  (**3**) was straightforward. In each case the spectra revealed the presence of  $\text{Cp}^*$ , aryloxy, and/or THF ligands in the expected ratio. The <sup>1</sup>H NMR spectrum of the bis(alkyl) complex  $\text{Cp}^*\text{Th}(\text{OAr})(\text{CH}_2\text{SiMe}_3)_2$  (**4**) contains resonances assigned to  $\text{Cp}^*$  and aryloxy ligands in a 1:1 ratio, in addition to two (trimethylsilyl)methyl groups possessing diastereotopic methylene protons which are observed as doublets ( $J_{\text{HH}} = 12$  Hz) at  $\delta -0.08$  and  $0.17$  ppm. In the proton-coupled <sup>13</sup>C NMR spectrum of **4**, the methylene carbon resonance appears at  $\delta 91.23$  as a slightly broadened triplet which exhibits a coupling constant ( $J_{\text{CH}} = 100$  Hz) significantly smaller than that expected for an  $\text{sp}^3$ -hybridized carbon atom. A similarly reduced  $J_{\text{CH}}$  coupling constant ( $J_{\text{CH}} = 99$  Hz) has been observed previously in the bis(cyclopentadienyl)thorium complex  $[\text{Me}_2\text{Si}(\eta\text{-C}_5\text{Me}_4)_2]\text{Th}(\text{CH}_2\text{SiMe}_3)_2$ , in which  $\alpha$ -agostic interactions of the methylene groups with the metal center were believed to be responsible for the reduced coupling.<sup>11b</sup> Additional evidence for a possible  $\alpha$ -agostic interaction has also been observed in the solid-state structure of **4** (*vide infra*).

<sup>1</sup>H NMR spectra of  $\text{Cp}^*\text{ThMe}(\text{OAr})_2$  (**5**) indicate the presence of  $\text{Cp}^*$  and aryloxy ligands in a 1:2 ratio, in addition to a distinctive resonance at  $\delta 0.88$  assigned to the thorium-bound methyl group. Ambient-temperature <sup>1</sup>H NMR spectra of the trimeric species  $[\text{Cp}^*\text{ThH}_2(\text{OAr})]_3$  (**6**) show a singlet resonance at  $\delta 18.54$  (relative integral 2) which is indicative of thorium-bound hydride ligands,<sup>11,12</sup> and the appearance of this resonance remains unchanged down to  $-80$  °C in toluene- $d_6$  solution. In addition to the hydride resonance in the ambient temperature spectrum, there are three aryloxy *tert*-butyl resonances which each integrate for 18 protons and two  $\text{Cp}^*$  resonances with relative integrals of 30 and 15 protons. The aromatic portion of the spectrum contains two triplet *para*-proton resonances in a 2:1 ratio, in addition to two resonances assigned to *meta*-protons in a 4:2 ratio.

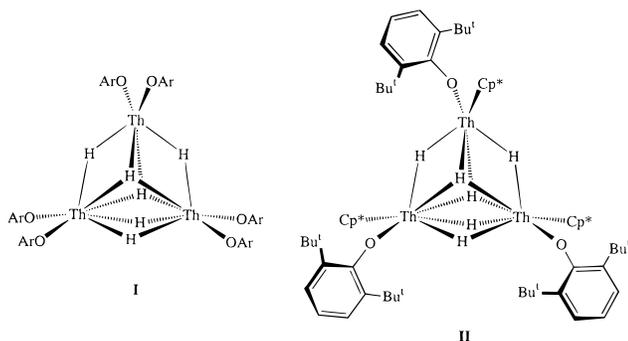
Since a limiting <sup>1</sup>H NMR spectrum of the hydride region of **6** could not be obtained even at  $-80$  °C, the arrangement of hydride ligands about the trimetallic core cannot be determined with any certainty. However, in proposing a tentative structure for **6**, we draw precedence from the structurally characterized bis(aryloxy) complex  $\text{Th}_3(\mu_3\text{-H})_2(\mu_2\text{-H})_4(\text{O}-2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)_6$ <sup>10</sup> in which a triangular arrangement of three thorium

(11) (a) Fendrick, C. M.; Mintz, E. A.; Schertz, L. D.; Marks, T. J.; Day, V. W. *Organometallics* **1984**, *3*, 819. (b) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828.

(12) (a) Fagan, P. J.; Manriquez, J. M.; Maatta, E. A.; Seyam, A. M.; Marks, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 6650. (b) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051. (c) Turner, H. W.; Simpson, S. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 2782.

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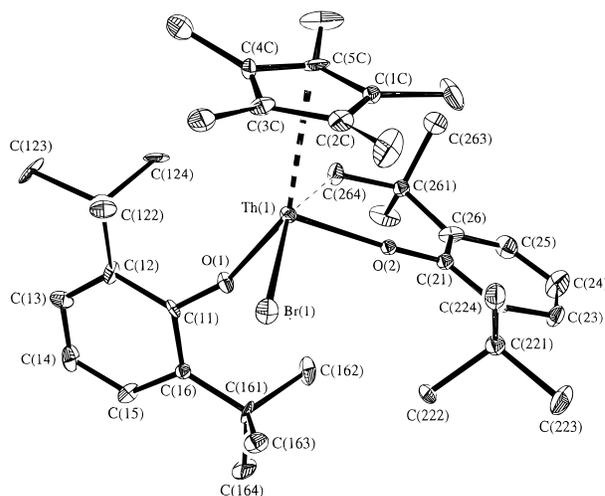
metal centers, each bearing two terminal aryloxide ligands, is capped by two  $\mu_3$ -hydride ligands. Two sides of the trimetallic core are bridged by single  $\mu_2$ -hydride ligands, while the third side is bridged by two  $\mu_2$ -hydride ligands, as shown schematically in **I**. Other possible



hydride configurations in **6** would have all  $\mu_2$ -hydride ligands or a combination of  $\mu_2$ - and terminal hydrides, since both arrangements have precedence in the literature with the structures of  $\{[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2]\text{Th}(\mu_2\text{-H})_2\}_2$  and  $[\text{Cp}^*_2\text{Th}(\mu_2\text{-H})\text{H}]_2$ .<sup>11,12</sup> The observation of two Cp\* resonances in a 2:1 ratio in the <sup>1</sup>H NMR spectrum of **6** is consistent with the presence of two Cp\* ligands below the plane of the three thorium metal centers and one above (as shown schematically in **II**). If rotation about the Th–O–C bonds of the aryloxide ligands was restricted by the presence of the bulky Cp\* moieties, then the *tert*-butyl groups on the lower two aryloxides in **II** would be rendered inequivalent. The upper aryloxide resonance would be unaffected by the hindered rotation since the aryloxide ligand lies on a mirror plane, and thus we would expect to observe three *tert*-butyl resonances in a 1:1:1 ratio, which is consistent with the NMR data for **6**. In the aromatic region of the spectrum, we would expect structure **II** to exhibit two *para*-proton resonances in a 2:1 ratio and three *meta*-resonances in a 2:2:2 ratio. NMR spectra of **6** are consistent with this expectation, given the fact that two of the meta-proton resonances appear as an overlapping multiplet. Attempts to collect single-crystal X-ray data for **6** were thwarted by extremely rapid powdering of the crystals as soon as mother liquor was removed.

<sup>1</sup>H NMR spectra of Cp\*Th(OC<sub>6</sub>H<sub>3</sub>-*t*-BuCMe<sub>2</sub>CH<sub>2</sub>)(OAr)(O=PPh<sub>3</sub>) (**7**) may be readily explained by reference to the solid state structure (*vide infra*). Although the aromatic portion of the spectrum is complicated by overlapping resonances from the triphenylphosphine oxide ligand, the remaining portion of the spectrum clearly establishes the presence of a cyclometalated aryloxide ligand, and the presence of inequivalent substituents on the second aryloxide moiety due to hindered rotation. Thus three *tert*-butyl resonances are observed in a 1:1:1 ratio (relative integral of each resonance is 9 protons), together with two separate methyl group resonances and two doublet resonances at  $\delta$  1.27 and 1.18 ( $J_{\text{HH}} = 11$  Hz, relative integral 1 proton) for the diastereotopic methylene group bound to the thorium metal center.

**Solid-State and Molecular Structures.** Cp\*ThBr(O-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> (**3**). Crystals of **3** suitable for an X-ray diffraction study were grown by cooling a concentrated toluene solution to  $-40$  °C. A summary of data collection and crystallographic parameters is given in



**Figure 1.** ORTEP representation (40% probability ellipsoids) of the molecular structure of Cp\*ThBr(O-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> (**3**) giving the atom-numbering scheme used in the tables.

**Table 1.** Summary of Crystallographic Data

	compound <sup>a</sup>		
	<b>3</b>	<b>4</b>	<b>7</b>
empirical formula	C <sub>38</sub> H <sub>57</sub> BrO <sub>2</sub> Th	C <sub>32</sub> H <sub>58</sub> OSi <sub>2</sub> Th	C <sub>63</sub> H <sub>78</sub> O <sub>3</sub> PTh
space group	<i>P</i> <sub>2</sub> / <i>1</i> / <i>c</i>	<i>P</i> <sub>2</sub> / <i>1</i> / <i>c</i>	<i>P</i> <sub>2</sub> / <i>1</i> / <i>c</i>
cell dimens			
<i>a</i> , Å	18.556(4)	9.652(2)	12.802(2)
<i>b</i> , Å	9.871(2)	23.314(5)	18.441(2)
<i>c</i> , Å	21.104(4)	15.592(3)	23.552(4)
$\beta$ , deg	110.69(3)	92.35(3)	92.02(2)
<i>V</i> , Å <sup>3</sup>	3622.4	3505.5	5556.7
<i>Z</i> (molecules/cell)	4	4	4
<i>fw</i>	858	747.0	1117.1
<i>D</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.573	1.415	1.335
abs coeff, cm <sup>-1</sup>	52.5	43.43	27.54
$\lambda$ (Mo K $\alpha$ )	0.710 69	0.710 69	0.710 69
temp, °C	-70	-70	-100
$2\theta$ range, deg	2.0–55.0	3.0–45.0	3.0–45.0
measd rflns	9005	5006	10 186
unique intensities	8272	4535	7267
obsd rflns	4578	3128	4730
	( <i>F</i> > 3.0 $\sigma$ ( <i>F</i> ))	( <i>F</i> > 4.0 $\sigma$ ( <i>F</i> ))	( <i>F</i> > 4.0 $\sigma$ ( <i>F</i> ))
<i>R</i> ( <i>F</i> ) <sup>b</sup>	0.0644	0.0337	0.0521
<i>R</i> <sub>w</sub> ( <i>F</i> ) <sup>c</sup>	0.0700	0.0410	0.0558
goodness-of-Fit	1.37	1.05	1.15

<sup>a</sup> **3** = Cp\*ThBr(OAr)<sub>2</sub>; **4** = Cp\*Th(OAr)(CH<sub>2</sub>SiMe<sub>2</sub>)<sub>2</sub>; **7** = Cp\*Th(OC<sub>6</sub>H<sub>3</sub>-*t*-BuCMe<sub>2</sub>CH<sub>2</sub>)(OAr)(O=PPh<sub>3</sub>). <sup>b</sup> *R*(*F*) =  $\sum ||F_o| - F_c| / \sum |F_o|$ . <sup>c</sup> *R*<sub>w</sub>(*F*) =  $[\sum w(|F_o| - F_c)|^2 / \sum w|F_o|^2]^{1/2}$ .

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for Cp\*ThBr(O-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> (**3**)

Th(1)–O(1)	2.18(1)	Th(1)–O(2)	2.139(8)
Th(1)–Br(1)	2.821(2)	Th(1)–C(264)	3.19(1)
Th(1)–Cp*(cent)	2.57(1)	Th(1)–Cp*(av)	2.84(3)
Cp*(cent)–Th(1)–O(1)	151.0(3)	Cp*(cent)–Th(1)–O(2)	107.6(3)
Cp*(cent)–Th(1)–Br(1)	100.7(3)	O(1)–Th(1)–O(2)	96.7(4)
Br(1)–Th(1)–O(1)	89.3(3)	Br(1)–Th(1)–O(2)	101.9(3)
Th(1)–O(1)–C(1)	161.6(9)	Th(1)–O(2)–C(21)	169.8(9)

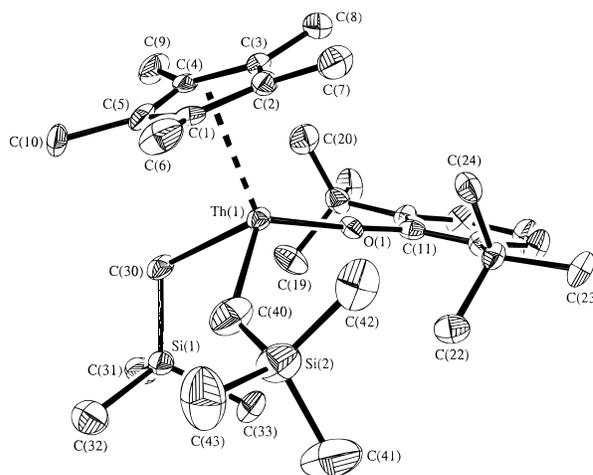
Table 1, while selected bond lengths and angles are presented in Table 2. An ORTEP drawing giving the atom-numbering scheme used in the tables is shown in Figure 1. The overall molecular structure of **3** consists of a distorted three-legged piano-stool geometry about the thorium metal center, with the Cp\*<sub>centroid</sub>–Th(1)–O(1) angle of 151.0(3)° being considerably larger than the Cp\*<sub>centroid</sub>–Th(1)–O(2) or Cp\*<sub>centroid</sub>–Th(1)–Br angles, which are close to tetrahedral values. The average Th–C distance to the Cp\* ligand of 2.84(3) Å is directly

**Table 3.** Selected Bond Distances (Å) and Angles (deg) for  $\text{Cp}^*(\text{O}-2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)\text{Th}(\text{CH}_2\text{SiMe}_3)_2\cdot\text{C}_7\text{H}_8$  (**4**)

Th(1)–C(30)	2.460(9)	Th(1)–C(40)	2.488(2)
Th(1)–O(1)	2.186(6)	Th(1)–Cp*(cent)	2.53(1)
Th(1)–Cp*(av)	2.81(1)		
O(1)–Th(1)–C(30)	100.8(3)	O(1)–Th(1)–C(40)	122.9(3)
Cp*(cent)–Th(1)–C(30)	105.6(5)	Cp*(cent)–Th(1)–C(40)	105.3(5)
Cp*(cent)–Th(1)–O(1)	123.5(4)	C(30)–Th(1)–C(40)	91.8(4)
Th(1)–C(30)–Si(1)	120.0(4)	Th(1)–C(40)–Si(2)	139.8(6)
Th(1)–O(1)–C(11)	171.4(5)		

comparable to the distances observed in a number of other structurally characterized (pentamethylcyclopentadienyl)thorium complexes,<sup>13</sup> while the Th–O bond lengths of the aryloxy ligands (2.18(1) and 2.139(8) Å) are similar to those found in  $\text{Th}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)_4$  (2.189(6) Å),<sup>9d</sup>  $\text{Th}(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)_4(\text{py})_2$  (2.198(6) Å),<sup>9d</sup> and  $\text{Th}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)_2(\text{CH}_2\text{-py-6-Me})_2$  (2.190(9) Å).<sup>14</sup> The Th–Br distance of 2.821(2) Å is very similar to the distances of 2.859(3) and 2.85(2) Å found in  $\text{ThBr}_4\text{-(THF)}_4^{9c}$  and  $\beta\text{-ThBr}_4$ ,<sup>15</sup> respectively. One of the *tert*-butyl methyl groups is observed to make a relatively short nonbonding contact with the metal center ( $\text{Th}(1)\text{-C}(264) = 3.19(1)$  Å), presumably due to the relative steric unsaturation of the metal center. This Th–Me distance may be compared with the U–Me distance of 3.09(2) Å found in the uranium(III) alkyl  $\text{U}[\text{CH}(\text{SiMe}_3)_2]_3$ <sup>16</sup> and Th–Me distances of 3.073(10) and 3.064(10) Å in the thorium amido complex  $\text{Th}[\text{N}(\text{SiMe}_3)_2]_2(\text{NMePh})_2$ .<sup>9i</sup> In both of these cases, agostic interactions between a methyl group and the metal center were proposed. The large Th–O–C angles within the aryloxy ligands (161.6(9) and 169.8(9)°) are typical of those seen in many other f-element alkoxide and aryloxy complexes.<sup>17</sup>

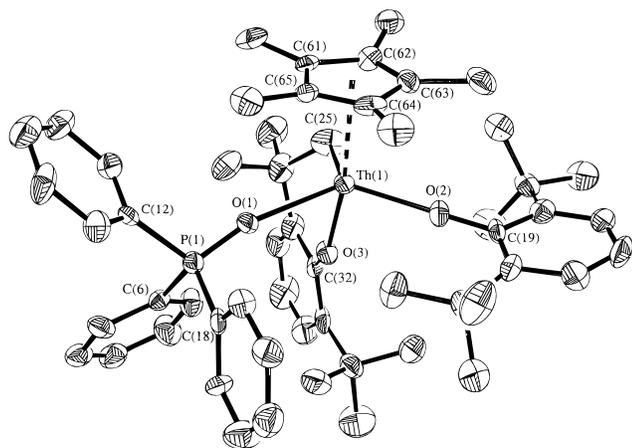
**$\text{Cp}^*\text{Th}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{SiMe}_3)_2$  (**4**).** Crystals of **4** suitable for an X-ray diffraction study were grown by cooling a concentrated toluene solution to  $-40$  °C. A summary of data collection and crystallographic parameters is given in Table 1, while selected bond lengths and angles are presented in Table 3. An ORTEP drawing giving the atom-numbering scheme used in the tables is shown in Figure 2. The four ligands bound to the metal center in **4** define a slightly distorted three-legged piano stool, with the  $\text{Cp}^*\text{centroid}\text{-Th}(1)\text{-O}(1)$  angle having the largest deviation from a tetrahedral value (123.5(4)°). The average Th–C distance to the Cp\*

**Figure 2.** ORTEP representation (40% probability ellipsoids) of the molecular structure of  $\text{Cp}^*\text{Th}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)(\text{CH}_2\text{SiMe}_3)_2$  (**4**) giving the atom-numbering scheme used in the tables.

ligand (2.81(1) Å) and the Th–O distance to the aryloxy ligand (2.186(6) Å) are both directly comparable with the values observed in **3** (*vide supra*). The Th–C distances to the (trimethylsilyl)methyl ligands of 2.460(9) and 2.488(12) Å are slightly shorter than the average Th–C distances of 2.55(1), 2.55(2), 2.51(2), and 2.58(1) Å observed in the thorium alkyl complexes  $\text{Th}(\text{O}-2,6\text{-}t\text{-Bu}_2\text{C}_6\text{H}_3)_2(\text{CH}_2\text{-py-6-Me})_2$ ,<sup>14</sup>  $\text{Th}(\text{CH}_2\text{C}_6\text{H}_5)_4(\text{Me}_2\text{PCH}_2\text{-CH}_2\text{PMe}_2)$ ,<sup>18</sup>  $[\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)_2]\text{Th}(\text{CH}_2\text{SiMe}_3)_2$ ,<sup>11a</sup> and  $\text{Cp}^*\text{Th}(\text{CH}_2\text{C}_6\text{H}_5)_3$ ,<sup>4a</sup> although they are comparable to the Th–C distances found in the metallacyclic species  $\text{Cp}^*_2\text{Th}[(\text{CH}_2)_2\text{SiMe}_2]$  (2.463(13) and 2.485(14) Å).<sup>19</sup> Th–C–Si angles within the alkyl ligands are considerably larger than the tetrahedral values expected for  $\text{sp}^3$ -hybridized carbon atoms, with the  $\text{Th}(1)\text{-C}(30)\text{-Si}(1)$  and  $\text{Th}(1)\text{-C}(40)\text{-Si}(2)$  angles having values of 120.0(4) and 139.8(6)°, respectively. Similar values for Th–C–Si angles have previously been observed in the complexes  $\text{Cp}^*_2\text{Th}(\text{CH}_2\text{SiMe}_3)_2$ <sup>20</sup> (Th–C = 2.51(1) and 2.46(1) Å, Th–C–Si = 132.0(6) and 148.0(7)°, respectively) and  $\text{Me}_2\text{Si}(\eta\text{-C}_5\text{Me}_4)_2\text{Th}(\text{CH}_2\text{SiMe}_3)_2$ <sup>11</sup> (Th–C = 2.54(2) and 2.48(2) Å, Th–C–Si = 123.7(14) and 149.5(12)°, respectively). These unusually large Th–C–Si angles may provide additional evidence, together with the significantly reduced  $J_{\text{CH}}$  coupling constant noted above, for some degree of  $\alpha$ -agostic interaction between the methylene groups and the metal center. Theoretical studies<sup>21</sup> of the large Th–C $_{\alpha}$ –C $_{\beta}$  angles in the related bis(neopentyl) derivative  $\text{Cp}^*_2\text{Th}(\text{CH}_2\text{-}t\text{-Bu})_2$ <sup>13g</sup> have also concluded that  $\alpha$ -agostic interactions play a role in stabilizing these distortions.

**$\text{Cp}^*\text{Th}(\text{OC}_6\text{H}_3\text{-}t\text{-BuCMe}_2\text{CH}_2)(\text{OAr})(\text{O}=\text{PPh}_3)$  (**7**).** Crystals of **7** suitable for an X-ray diffraction study were grown by cooling a concentrated toluene solution to  $-40$  °C. Data collection and crystallographic parameters are given in Table 1, while selected bond lengths and angles are presented in Table 4. An ORTEP drawing giving

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**Figure 3.** ORTEP representation (40% probability ellipsoids) of the molecular structure of  $\text{Cp}^*\text{Th}(\text{OC}_6\text{H}_3\text{-}t\text{-BuCMe}_2\text{CH}_2)(\text{OAr})(\text{O}=\text{PPh}_3)$  (**7**) giving the atom-numbering scheme used in the tables.

**Table 4. Selected Bond Distances (Å) and Angles (deg) for**

<b><math>\text{Cp}^*\text{Th}(\text{OC}_6\text{H}_3\text{-}t\text{-BuCMe}_2\text{CH}_2)(\text{OAr})(\text{O}=\text{PPh}_3)</math> (<b>7</b>)</b>			
Th(1)–C(25)	2.521(12)	Th(1)–O(1)	2.445(7)
Th(1)–O(2)	2.205(7)	Th(1)–O(3)	2.192(6)
Th(1)–Cp*(cent)	2.62(1)	Th(1)–Cp*(av)	2.88(4)
Cp*(cent)–Th(1)–O(3)	168.3(3)	Cp*(cent)–Th(1)–C(25)	99.2(3)
Cp*(cent)–Th(1)–O(2)	101.4(3)	Cp*(cent)–Th(1)–O(1)	98.7(3)
O(3)–Th(1)–C(25)	70.6(3)	O(3)–Th(1)–O(2)	86.9(3)
O(3)–Th(1)–O(1)	80.5(2)	O(1)–Th(1)–C(25)	111.6(3)
O(2)–Th(1)–C(25)	104.4(3)	O(1)–Th(1)–O(2)	134.9(3)
Th(1)–C(25)–C(26)	116.8(8)	Th(1)–O(1)–P(1)	166.6(4)
Th(1)–O(2)–C(19)	162.6(6)	Th(1)–O(3)–C(32)	148.4(6)

the atom-numbering scheme used in the tables is shown in Figure 3. **7** comprises a thorium metal center bearing a pentamethylcyclopentadienyl ligand, a 2,6-di-*tert*-butylphenoxide moiety, and a second aryloxy ligand which has undergone a cyclometalation reaction involving one of the *tert*-butyl methyl groups. A triphenylphosphine oxide ligand completes the coordination sphere. If the  $\text{Cp}^*$  ligand in **7** is considered to occupy a single coordination site, then the geometry about the metal center may best be described as distorted trigonal bipyramidal with the  $\text{Cp}^*$  centroid and O(3) occupying axial sites ( $\text{Cp}^*_{\text{centroid}}\text{-Th(1)-O(3)} = 168.3(3)^\circ$ ). The angles between the three ligands in the equatorial plane sum to  $350.9^\circ$ , indicating near-planarity of this ligand set. Th–C distances to the  $\text{Cp}^*$  ligand and Th–O distances to the aryloxy ligands are again comparable to those observed in the structures of **3** and **4** (Th–Cp\* = 2.88(4) Å (av) and Th–O = 2.199(7) Å (av)). The Th–C distance to the cyclometalated alkyl ligand is 2.521(12) Å, which is within the range observed for other thorium alkyl bond distances as described above. The Th–O–C angle for the cyclometalated aryloxy ligand (Th(1)–O(3)–C(32) =  $148.4(6)^\circ$ ) is, as expected, somewhat smaller than that of the monodentate aryloxy ligand (Th(1)–O(2)–C(19) =  $162.6(6)^\circ$ ), due to geometric constraints within the six-membered metallacyclic ring. While cyclometalated aryloxy ligands have been observed in a number of crystallographically characterized transition metal complexes, especially of group 5,<sup>22</sup> we believe **7** to be the first example of a structurally characterized cyclometalated aryloxy ligand in f-element chemistry. The Th–O distance to the triph-

enylphosphine oxide ligand is 2.445(7) Å, which is comparable to the distances of 2.376(10) (av), 2.35(2) (av), and 2.36(1) Å found for the triphenylphosphine oxide ligands in  $\text{ThCl}_4(\text{O}=\text{PPh}_3)_3$ ,<sup>23</sup>  $\text{Th}(\text{NO}_3)_4(\text{O}=\text{PPh}_3)_2$ ,<sup>24</sup> and  $\text{Th}(\text{NO}_3)_2(\text{C}_{17}\text{H}_{13}\text{N}_2\text{O}_2)_2(\text{O}=\text{PPh}_3)_2$ .<sup>25</sup>

**Catalytic Studies.** Marks and co-workers have reported the extremely high catalytic activities of cationic thorium species such as  $[\text{Cp}^*_2\text{ThMe}][\text{X}]$  (X =  $\text{BPh}_4$ ,<sup>26</sup>  $\text{B}(\text{C}_6\text{F}_5)_4$ ,<sup>27</sup>  $t\text{-BuCH}_2\text{CH}[\text{B}(\text{C}_6\text{F}_5)_2]_2\text{H}^{6a}$ ), and the hydride complexes  $[\text{Cp}^*_2\text{Th}(\mu\text{-H})\text{H}]_2$ <sup>12a</sup> and  $[\text{Me}_2\text{Si}(\eta\text{-C}_5\text{-Me}_4)_2\text{Th}(\mu\text{-H})_2]_2$ ,<sup>11</sup> in reactions such as ethylene polymerization and olefin hydrogenation. It was of interest to compare the catalytic activities of the bis(alkyl) complex  $\text{Cp}^*\text{Th}(\text{OAr})(\text{CH}_2\text{SiMe}_3)_2$  (**4**) and the dihydride species  $[\text{Cp}^*\text{ThH}_2(\text{OAr})]_3$  (**6**) with the related bis(pentamethylcyclopentadienyl) complexes listed above. It was hoped that such a comparison of catalytic activities would provide information concerning the effects upon reactivity of replacing one pentamethylcyclopentadienyl ligand with an aryloxy moiety, both in terms of steric and electronic factors.

In the case of the alkyl derivative  $\text{Cp}^*\text{Th}(\text{OAr})(\text{CH}_2\text{-SiMe}_3)_2$  (**4**), the ammonium salt  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  was employed as a proton source to remove one alkyl ligand and form a cationic thorium complex with the noncoordinating tetrakis(perfluorophenyl)borate anion. It was found that the addition of 1 equiv of **4** to a toluene suspension of  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  resulted in the formation of a slightly cloudy solution and the subsequent separation of an oily material. A  $^1\text{H}$  NMR spectrum of this material showed the presence of  $\text{SiMe}_4$ , consistent with the protonation of a  $\text{ThCH}_2\text{SiMe}_3$  group, but attempts to fully characterize the presumed ionic species  $[\text{Cp}^*\text{Th}(\text{OAr})(\text{CH}_2\text{SiMe}_3)][\text{B}(\text{C}_6\text{F}_5)_4]$  were unsuccessful. Thus for the catalytic studies described in this section, a mixture of **4** and  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  was used *in situ* as the active catalyst. The addition of an equimolar quantity of **4** to a toluene suspension of  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  under 1 atm of ethylene led to formation of a white precipitate of polyethylene over a period of 130 s. GPC analysis (polystyrene standards) indicated a moderate molecular weight polymer ( $M_n = 1.8 \times 10^4$ ,  $M_w = 3.1 \times 10^4$ ), while the catalyst activity was calculated to be  $34\,600\text{ g h}^{-1}\text{ atm}^{-1}$  (mol catalyst)<sup>-1</sup> ( $N_t = 0.35\text{ s}^{-1}$ ). The catalytic activity of this system toward ethylene polymerization is thus somewhat greater than the cationic bis(pentamethylcyclopentadienyl) complex  $[\text{Cp}^*_2\text{ThMe}][\text{BPh}_4]$  ( $1100\text{ g h}^{-1}\text{ atm}^{-1}$  (mol catalyst)<sup>-1</sup>,  $N_t = 0.01\text{ s}^{-1}$ ),<sup>6a</sup> which contains the relatively coordinating tetraphenylborate anion. However, a more direct comparison is provided by the analogous cationic species containing noncoordinating anions.

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Indeed it has been reported that the complexes  $[\text{Cp}^*_2\text{ThMe}][\text{B}(\text{C}_6\text{F}_5)_4]$  ( $3.6 \times 10^6 \text{ g h}^{-1} \text{ atm}^{-1} (\text{mol catalyst})^{-1}$ ,  $N_t = 36 \text{ s}^{-1}$ )<sup>27</sup> and  $[\text{Cp}^*_2\text{ThMe}]\{t\text{-BuCH}_2\text{CH}[\text{B}(\text{C}_6\text{F}_5)_2]_2\text{H}\}$  ( $5.8 \times 10^6 \text{ g h}^{-1} \text{ atm}^{-1} (\text{mol catalyst})^{-1}$ ,  $N_t = 58 \text{ s}^{-1}$ )<sup>27</sup> show catalytic activity approximately 100 times greater than  $4/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ .<sup>6a</sup>

The activity of the  $4/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  system toward the catalytic hydrogenation of 1-hexene was also studied. The addition of 1-hexene to an equimolar toluene solution of **4** and  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ , followed by admission of 1 atm of dihydrogen, led to the catalytic hydrogenation of the olefin. Analysis of the volatiles from the reaction mixture by GC-MS, and quantification of the hexane present, allowed calculation of the turnover rate of  $3 \text{ h}^{-1}$ . The activity is thus substantially lower than that of the cationic methyl derivative  $[\text{Cp}^*_2\text{ThMe}][\text{B}(\text{C}_6\text{F}_5)_4]$ , for which a turnover rate of  $16\,450 \text{ h}^{-1}$  has been reported.<sup>27</sup> The dihydride species  $[\text{Cp}^*\text{ThH}_2(\text{OAr})_3]$  (**6**) was also found to be a single-component catalyst for the hydrogenation of olefins. Thus a toluene solution of **6** was found to catalyze the hydrogenation of 1-hexene under 1 atm of dihydrogen at a modest turnover rate of  $10 \text{ h}^{-1}$ . The activity of **6** is thus somewhat greater than the bis(pentamethylcyclopentadienyl) analog  $[\text{Cp}^*_2\text{Th}(\mu\text{-H})\text{H}]_2$  ( $0.5 \text{ h}^{-1}$ )<sup>12a</sup> but considerably lower than that of the "tied-back" derivative  $[\text{Me}_2\text{Si}(\eta\text{-C}_5\text{Me}_4)_2\text{Th}(\mu\text{-H})_2]$  ( $610 \text{ h}^{-1}$ ).<sup>11b</sup>

The relatively modest activity of  $4/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  and **6** in catalytic reactions, in comparison with similar bis(pentamethylcyclopentadienyl) systems, may be rationalized by the presence of the aryloxy ligand, which is capable of substantial  $\pi$ -donation to the metal center. It has been reported previously that the presence of alkoxide ligands in  $\text{Cp}^*_2\text{Th}(\text{X})(\text{Y})$  systems can significantly lower the rate of alkyl ligand hydrolysis by decreasing the electrophilicity of the metal center.<sup>28</sup> The presence of alkoxide ligands can also result in an increase in Th-R bond disruption enthalpies by 2–4 kcal mol<sup>-1</sup>.<sup>28</sup> Thus it would appear that the deleterious electronic effects of the aryloxy ligand significantly outweigh the somewhat less sterically hindered coordination sphere of the mono(pentamethylcyclopentadienyl)thorium species.

**Concluding Remarks.** We have shown that the tribromide complex  $\text{Cp}^*\text{ThBr}_3(\text{THF})_3$  (**1**) provides a convenient entry into the chemistry of mono(pentamethylcyclopentadienyl) derivatives of thorium. Aryloxy and alkyl derivatives may readily be prepared by treatment of **1** with potassium aryloxy or alkyl Grignard reagents, respectively. In the presence of the ammonium salt  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$ , the bis(alkyl) complex  $\text{Cp}^*\text{Th}(\text{OAr})(\text{CH}_2\text{SiMe}_3)_2$  (**4**) has been shown to exhibit moderate catalytic activity in ethylene polymerization and 1-hexene hydrogenation experiments. The trimeric hydride derivative  $[\text{Cp}^*\text{ThH}_2(\text{OAr})_3]$  (**6**) has also been shown to be a single-component catalyst for the hydrogenation of 1-hexene and exhibits an activity of 10 turnovers  $\text{h}^{-1}$ . The catalytic activity for hydrogenation of  $4/[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  is substantially lower than the related bis(pentamethylcyclopentadienyl) complex  $[\text{Cp}^*_2\text{ThMe}][\text{B}(\text{C}_6\text{F}_5)_4]$ , possibly as a result of  $\pi$ -donation from the aryloxy ligand reducing the

electrophilicity of the thorium metal center. The activity of **6** toward 1-hexene hydrogenation is found to be somewhat greater than that of dimeric  $[\text{Cp}^*_2\text{Th}(\mu\text{-H})\text{H}]_2$ , but lower than that of the "tied-back" analog  $[\text{Me}_2\text{Si}(\eta\text{-C}_5\text{Me}_4)_2\text{Th}(\mu\text{-H})_2]$ .

## Experimental Section

**General Procedures and Techniques.** All manipulations were carried out under an inert atmosphere of oxygen-free UHP grade argon using standard Schlenk techniques or under oxygen-free helium in a Vacuum Atmospheres glovebox.  $\text{ThBr}_4(\text{THF})_4$  was prepared as described previously.<sup>9c</sup>  $\text{MeMgBr}$  (3.0 M in THF) and  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  (1.0 M in  $\text{Et}_2\text{O}$ ) solutions were purchased from Aldrich and used as received. KO-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub> was prepared from the reaction of 2,6-di-*tert*-butylphenol with potassium hydride in THF.  $[\text{HNMe}_2\text{Ph}][\text{B}(\text{C}_6\text{F}_5)_4]$  was obtained from Quantum Design and used as received.  $\text{Cp}^*\text{MgBr}$  was prepared from *i*-PrMgBr and  $\text{Cp}^*\text{H}$  using the method of Marks *et al.*<sup>12a</sup> Solvents were degassed and distilled from Na or Na/benzophenone ketyl under nitrogen. Benzene-*d*<sub>6</sub> was dried with Na/benzophenone ketyl and then trap-to-trap distilled before use.

NMR spectra were recorded at 22 °C on a Bruker WM 300 spectrometer in benzene-*d*<sub>6</sub>. All <sup>1</sup>H NMR chemical shifts are reported in ppm relative to the <sup>1</sup>H impurity in benzene-*d*<sub>6</sub> at  $\delta$  7.15. Infrared spectra were recorded on a BioRad FTS-40 spectrophotometer as Nujol mulls between KBr salt plates. GPC measurements were carried out by Polytech in trichlorobenzene solvent, using polystyrene standards. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Elemental analysis samples were prepared and sealed in tin capsules in the glovebox prior to combustion.

**$\text{Cp}^*\text{ThBr}_3(\text{THF})_3$  (**1**).** THF (120 mL) was added to a flask containing  $\text{ThBr}_4(\text{THF})_4$  (15.0 g, 17.9 mmol) and  $\text{Cp}^*\text{MgBr}(\text{THF})$  (5.55 g, 17.9 mmol), and the resulting solution was stirred for 20 h at room temperature. All volatiles were removed under vacuum, and the residue was extracted with a 12:1  $\text{CH}_2\text{Cl}_2/\text{dioxane}$  solution (130 mL) and filtered. This solution was pumped dry, extracted with THF ( $3 \times 100 \text{ mL}$ ), and concentrated to 50 mL. Cooling of the solution to  $-40 \text{ }^\circ\text{C}$  resulted in the formation of colorless crystals which were collected by filtration. Yield: 5.3 g, 36%. <sup>1</sup>H NMR (300 MHz, benzene-*d*<sub>6</sub>):  $\delta$  4.18 (br s, 4 H,  $\alpha$ -THF), 3.72 (br s, 8 H,  $\alpha$ -THF), 2.42 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 1.28 (br s, 12 H,  $\beta$ -THF). Anal. Calcd for  $\text{C}_{22}\text{H}_{39}\text{Br}_3\text{O}_3\text{Th}$ : C, 32.10; H, 4.77. Found: C, 31.90; H, 4.78.

**$\text{Cp}^*\text{ThBr}_2(\text{O-2,6-}t\text{-Bu}_2\text{C}_6\text{H}_3)(\text{THF})$  (**2**).** THF (25 mL) was added to a flask containing  $\text{Cp}^*\text{ThBr}_3(\text{THF})_3$  (4.00 g, 5.49 mmol) and KO-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (1.40 g, 5.74 mmol) and the resulting mixture stirred for 18 h at room temperature, resulting in much precipitate. All volatiles were removed under vacuum from the mixture, and the solid was extracted with toluene ( $2 \times 10 \text{ mL}$ ) and filtered through Celite. Cooling to  $-40 \text{ }^\circ\text{C}$  led to the formation of crystals which were isolated by filtration (1.30 g). A second crop was collected upon concentration and recooling of the mother liquor giving a total yield of 1.84 g (65%). <sup>1</sup>H NMR (300 MHz, benzene-*d*<sub>6</sub>):  $\delta$  7.19 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2 H, *meta* OAr), 6.79 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 1 H, *para* OAr), 3.11 (m, 4 H,  $\alpha$ -THF), 2.33 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 1.53 (s, 18 H, *t*-Bu), 1.11 (m, 4 H,  $\beta$ -THF). IR (cm<sup>-1</sup>): 1410 (m), 1307 (w), 1259 (w), 1223 (s), 1201 (s), 1124 (m), 1095 (w), 1039 (w), 1024 (w sh), 1013 (m), 923 (w), 868 (s), 822 (m), 796 (m), 750 (s), 723 (m), 666 (s), 596 (w), 556 (w). Anal. Calcd for  $\text{C}_{38}\text{H}_{57}\text{Br}_2\text{O}_2\text{Th}$ : C, 42.65; H, 5.62. Found: C, 42.31; H, 5.58.

**$\text{Cp}^*\text{ThBr}(\text{O-2,6-}t\text{-Bu}_2\text{C}_6\text{H}_3)_2$  (**3**).** THF (25 mL) was added to a solid mixture of  $\text{Cp}^*\text{ThBr}_3(\text{THF})_3$  (1.50 g, 2.00 mmol) and KO-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (0.97 g, 4.0 mmol) and stirred at room temperature for 18 h with much precipitate being formed. The mixture was filtered through Celite, and all volatiles were removed *in vacuo*. The resulting solid was dissolved in hexane (10 mL) and concentrated under reduced pressure to 2 mL,

(28)  $\text{Cp}^*_2\text{ThMe}_2$  is found to undergo hydrogenolysis  $4 \times 10^3$  times faster than  $\text{Cp}^*_2\text{Th}(\text{OR})(\text{R})$ : Lin, Z.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7979.

resulting in deposition of colorless crystals which were isolated and washed with hexane (2 mL). Yield: 1.25 g (73%) with a trace of HO-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub> visible by <sup>1</sup>H NMR. <sup>1</sup>H NMR (300 MHz, benzene-*d*<sub>6</sub>): δ 7.19 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2 H, *para* OAr), 6.79 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 4 H, *meta* OAr), 2.18 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 1.54 (s, 36 H, *t*-Bu). IR (cm<sup>-1</sup>): 1583 (w), 1407 (s), 1318 (w), 1264 (m), 1218 (s), 1197 (s), 1122 (m), 1097 (m), 1020 (w), 862 (s), 819 (m), 794 (w), 750 (s), 723 (m), 657 (s), 593 (w), 549 (m), 453 (m), 417 (w). Anal. Calcd for C<sub>38</sub>H<sub>57</sub>BrO<sub>2</sub>Th: C, 53.21; H, 6.70. Found: C, 53.52; H, 6.63.

**Cp\*Th(O-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (4).** A diethyl ether solution of Me<sub>3</sub>SiCH<sub>2</sub>MgCl (1 M, 3.1 mL, 3.1 mmol) was added to a toluene (20 mL) solution of Cp\*ThBr<sub>2</sub>(O-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(THF) (1.30 g, 1.65 mmol) and stirred for 5 min at room temperature. Dioxane (1 mL) was then added, causing much precipitation, and the mixture was stirred for 3 h before all volatiles were removed under vacuum. The solid residue was extracted with toluene (2 × 15 mL), filtered through Celite, and then cooled to -40 °C resulting in colorless crystals. Yield: 0.65 g (54%). <sup>1</sup>H NMR (300 MHz, benzene-*d*<sub>6</sub>): δ 7.23 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2 H, *meta* OAr), 6.82 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 1 H, *para* OAr), 2.00 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 1.50 (s, 18 H, *t*-Bu), 0.34 (s, 18 H, SiMe<sub>3</sub>), 0.17 (d, <sup>3</sup>J<sub>HH</sub> = 12 Hz, 2 H, ThCH<sub>2</sub>), -0.08 (d, <sup>3</sup>J<sub>HH</sub> = 12 Hz, 2 H, ThCH<sub>2</sub>). IR (cm<sup>-1</sup>): 1584 (w), 1474 (m), 1409 (s), 1388 (m), 1359 (w sh), 1353 (w), 1265 (w sh), 1254 (w), 1241 (s), 1226 (s), 1197 (m), 1125 (m), 1102 (w), 1060 (w), 1021 (w), 886 (m), 867 (s), 848 (s), 822 (s), 747 (s), 730 (w), 709 (m), 675 (w), 659 (m), 551 (w), 454 (w). Anal. Calcd for C<sub>32</sub>H<sub>58</sub>OSi<sub>2</sub>Th: C, 51.45; H, 7.83. Found: C, 50.83; H, 8.02.

**Cp\*ThMe(O-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> (5).** In the drybox, a 3.0 M THF solution of MeMgBr (0.44 mL, 1.4 mmol) was added to a cold (-40 °C) mixture of Cp\*ThBr(O-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> (1.00 g, 1.17 mmol), hexane (20 mL), THF (15 mL), and dioxane (2 mL), resulting in an immediate white precipitate. After the mixture was stirred for 3 h, all volatiles were removed under vacuum, and the solid was extracted with hexane (2 × 20 mL) and filtered through Celite. The filtrate was concentrated to 10 mL and cooled to -40 °C resulting in the formation of colorless crystals which were isolated by filtration. Yield: 0.68 g (74%) <sup>1</sup>H NMR (300 MHz, benzene-*d*<sub>6</sub>): δ 7.21 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 1 H, *para* OAr), 6.78 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2 H, *meta* OAr), 2.07 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 1.48 (s, 36 H, *t*-Bu), 0.88 (s, 3 H, ThMe). IR (hexane, cm<sup>-1</sup>): 1582 (w), 1406 (m), 1300 (w br), 1262 (m), 1220 (s), 1188 (s), 1121 (m), 1101 (w), 1020 (w), 973 (w), 884 (w), 867 (s), 855 (s), 819 (s), 893 (m), 748 (s), 740 (s), 654 (s), 544 (w). Anal. Calcd for C<sub>39</sub>H<sub>60</sub>O<sub>2</sub>Th: C, 59.07; H, 7.63. Found: C, 58.48; H, 7.61.

**[Cp\*ThH<sub>2</sub>(O-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (6).** A benzene solution (3 mL) of **4** (0.250 g, 0.335 mmol) contained in a Schlenk vessel was pressurized with 1.5 atm of dihydrogen, and the resulting solution was stirred for 18 h at room temperature. All volatiles were removed under vacuum, and the product was crystallized from a 1:10 toluene/hexane (1 mL) solution at -40 °C. Yield: 0.078 g (41%). <sup>1</sup>H NMR (300 MHz, benzene-*d*<sub>6</sub>): δ 18.54 (s, 6 H, ThH), 7.36 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2 H, *meta* OAr), 7.27 (m, 4 H, *meta* OAr), 6.89 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 1 H, *para* OAr), 6.82 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 2 H, *para* OAr), 2.32 (s, 30 H, C<sub>5</sub>Me<sub>5</sub>), 2.25 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 1.82 (s, 18 H, *t*-Bu), 1.71 (s, 18 H, *t*-Bu), 1.67 (s, 18 H, *t*-Bu). IR (cm<sup>-1</sup>): 1583 (w), 1477 (m), 1407 (s), 1389 (m), 1359 (w sh), 1353 (w), 1322 (m br), 1265 (m), 1216 (s br), 1197 (s), 1120 (m), 1098 (w), 1021 (w), 950 (m br), 859 (s), 820 (s), 793 (w), 747 (s), 727 (w sh), 656 (s), 548 (w), 454 (w). Anal. Calcd for C<sub>24</sub>H<sub>38</sub>OTh: C, 50.17; H, 6.67. Found: C, 52.35; H, 7.11. Ebullioscopic molecular weight determination in benzene solution gave *M* = 1780, calculated for [Cp\*ThH<sub>2</sub>(OAr)]<sub>3</sub> = 1724.

**Cp\*Th(OC<sub>6</sub>H<sub>3</sub>-*t*-BuCMe<sub>2</sub>CH<sub>2</sub>)(OAr)(O=PPh<sub>3</sub>) (7).** Cp\*Th(OAr)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (**4**) (0.050 g, 0.067 mmol) and triphenylphosphine oxide (0.019 g, 1.1 equiv) were dissolved in benzene-*d*<sub>6</sub> and heated to 60 °C in an oil bath. After 16 h the reaction showed two main products by <sup>1</sup>H NMR spectroscopy.

Solvent was removed by slow evaporation resulting in an oil which formed crystals upon addition of toluene (0.5 mL) and hexane (0.2 mL). The colorless needles were isolated by decantation and washing with a small amount of cold (-40 °C) hexane. Yield: 0.028 g (40%). <sup>1</sup>H NMR (300 MHz, benzene-*d*<sub>6</sub>): δ 7.57 (m, 6 H, O=PPh<sub>3</sub>), 7.38 (d, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 1 H, *meta* OAr), 7.27 (m, 3 H, OAr), 6.98 (m, 6 H, O=PPh<sub>3</sub>), 6.87 (m, 5 H, O=PPh<sub>3</sub>, OAr), 6.79 (t, <sup>3</sup>J<sub>HH</sub> = 8 Hz, 1 H, *para* OAr), 2.15 (s, 15 H, C<sub>5</sub>Me<sub>5</sub>), 1.76 (s, 3 H, ThCH<sub>2</sub>CMe<sub>2</sub>), 1.64 (s, 3 H, ThCH<sub>2</sub>CMe<sub>2</sub>), 1.55 (s, 9 H, *t*-Bu), 1.44 (s, 9 H, *t*-Bu), 1.36 (s, 9 H, *t*-Bu), 1.27 (d, <sup>3</sup>J<sub>HH</sub> = 11 Hz, 1 H, ThCH<sub>2</sub>CMe<sub>2</sub>), 1.18 (d, <sup>3</sup>J<sub>HH</sub> = 11 Hz, 1 H, ThCH<sub>2</sub>CMe<sub>2</sub>). IR (cm<sup>-1</sup>): 1585 (w), 1407 (s), 1312 (w), 1269 (m), 1257 (m), 1239 (s), 1188 (w), 1121 (s), 1068 (s), 1026 (w), 998 (w), 871 (m sh), 863 (s), 819 (m), 795 (w), 746 (s), 723 (s), 693 (s), 656 (m), 540 (s). Anal. Calcd for C<sub>56</sub>H<sub>71</sub>O<sub>3</sub>PTh: C, 63.74; H, 6.78. Found: C, 63.59; H, 7.02.

**Hydrogenation of 1-Hexene by 4.** Toluene (5.6 mL) was added to a mixture of **4** (0.017 g, 0.023 mmol) and [HNMe<sub>2</sub>-Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.019 g, 0.023 mmol), and the resulting solution was stirred for 3 min. Hexene (0.62 g, 7.2 mmol) was syringed into the flask, and after 5 min a dihydrogen atmosphere was introduced over the solution. The reaction was stirred for 3 h and then quenched with 1-propanol. All volatiles were vacuum transferred to a second flask and analyzed by GC-mass spectroscopy. Hexane found: 0.20 mmol, 3 turnover h<sup>-1</sup>.

**Hydrogenation of 1-Hexene by 6.** Toluene (5.6 mL) was added to [Cp\*ThH<sub>2</sub>(OAr)]<sub>3</sub> (**6**) (0.013 g, 0.0075 mmol), and a dihydrogen atmosphere was introduced over the solution. After 5 min of rapid stirring, hexene (0.62 g, 7.2 mmol) was syringed into the flask and the solution was stirred for 1 h before 1-propanol was added to quench the reaction. All volatiles were vacuum transferred to a second flask and analyzed by GC-mass spectroscopy. Hexane found: 0.22 mmol, 10 turnover h<sup>-1</sup> (Th atom)<sup>-1</sup>.

**Polymerization of Ethylene by 4.** An ethylene atmosphere was introduced over a toluene (40.0 mL) solution of [HNMe<sub>2</sub>Ph][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.016 g, 0.020 mmol) and rapidly stirred for 5 min. A toluene solution (0.40 mL) of **4** (0.015 g, 0.020 mmol) was syringed into the rapidly stirring ethylene solution, and after 15 s the solution became cloudy with formation of a precipitate. The reaction was quenched with 1 mL of methanol after 130 s and the polymer was collected by filtration and dried to yield 0.025 g of polyethylene (*M*<sub>n</sub> = 1.8 × 10<sup>4</sup>, *M*<sub>w</sub> = 3.1 × 10<sup>4</sup>).

**Crystallographic Studies.** Cp\*ThBr(O-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)<sub>2</sub> (**3**). The clear, well-formed crystals were examined in mineral oil under an argon stream. The chosen crystal was affixed to the goniometer head of a CAD4 diffractometer (employing graphite-monochromated Mo Kα radiation) using Apiezon grease and cooled to -70 °C in a cold nitrogen stream. Unit cell parameters were determined from the least-squares refinement of ((sin θ)/λ)<sup>2</sup> values for 25 accurately centered reflections with a 2θ range between 16 and 32°. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time.

The data were reduced using the Structure Determination Package provided by Enraf-Nonius and corrected for absorption empirically using high-χ ψ-scans. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to "ride" upon the appropriate carbon atoms, final refinement using 4578 unique observed [*F* > 3σ(*F*)] reflections converged at *R* = 0.064 and *R*<sub>w</sub> = 0.070 {where *w* = [σ<sup>2</sup>(*F*) + 0.0002(*F*)<sup>2</sup>]<sup>-1</sup>}. A final difference Fourier contained some residual electron density around the thorium, the largest peak being 2.63 e/Å<sup>3</sup>. All data refinement calculations were performed using the Siemens SHELXTL PLUS computing package.<sup>29</sup>

(29) Siemens Analytical X-ray Instruments, Inc., 6300 Enterprise Lane, Madison, WI 53719.

**Cp\*Th(O-2,6-*t*-Bu<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>·C<sub>7</sub>H<sub>8</sub> (4).** The clear, well-formed crystals were examined in mineral oil under an argon stream. The chosen platelike crystal measuring 0.25 × 0.23 × 0.13 mm was affixed to the goniometer head of a CAD4 diffractometer (employing graphite-monochromated Mo K $\alpha$  radiation) using Apiezon grease and cooled to -70 °C in a cold nitrogen stream. Unit cell parameters were determined from the least-squares refinement of ((sin  $\theta$ )/ $\lambda$ )<sup>2</sup> values for 25 accurately centered reflections with a 2 $\theta$  range between 16 and 32°. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time.

The data were reduced using the Structure Determination Package provided by Enraf-Nonius and corrected for absorption empirically using high- $\chi$   $\psi$ -scans. The thorium atom was located by direct methods, and the remaining non-hydrogen atoms were located in subsequent difference Fourier maps, the refinement being by full-matrix least squares. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to "ride" upon the appropriate carbon atoms, final refinement using 3128 unique observed [ $F > 4\sigma(F)$ ] reflections converged at  $R = 0.034$  and  $R_w = 0.041$  {where  $w = [\sigma^2(F) + 0.0007(F)^2]^{-1}$ }. A final difference Fourier contained some residual electron density around the thorium, the largest peak being 1.65 e/Å<sup>3</sup>. All data refinement calculations were performed using the Siemens SHELXTL PLUS computing package.<sup>29</sup>

**Cp\*Th(OC<sub>6</sub>H<sub>3</sub>-*t*-BuCMe<sub>2</sub>CH<sub>2</sub>)(OAr)(O=PPh<sub>3</sub>)·C<sub>7</sub>H<sub>8</sub> (7).** A colorless needle-shaped crystal measuring 0.17 × 0.21 × 0.42 mm was coated with mineral oil and epoxy and mounted on a thin glass fiber under an argon stream. The crystal was then immediately placed under a cold nitrogen stream (-100 °C) on a Siemens P4/PC diffractometer (Mo K $\alpha$ ,  $\lambda = 0.71069$  Å). The lattice parameters were optimized from a least-squares calculation on 32 carefully centered reflections of high Bragg angle. Three check reflections monitored every 97 reflections showed a constant decrease in data intensity corresponding to 15% over the course of the data collection. Lattice determination and data collection were carried out using XSCANS Version 2.10b software. All data reduction, including Lorentz and polarization corrections, structure solution, and graphics, was performed using SHELXTL PC Version 3.2/360 software.<sup>29</sup> All data were corrected for absorption using the ellipsoid

routine in the XEMP facility of SHELXTL PC, and the refinement was carried out using SHELXTL PLUS (VMS) due to the large number of least-squares parameters.

The structure was solved in the space group  $P2_1/c$  using direct methods and Fourier techniques and refined by full-matrix least squares. The phenyl groups were refined as fixed hexagons using the AFIX facility in SHELXTL PLUS. Non-hydrogen atoms were treated anisotropically except for a toluene molecule in the lattice. The refinement of the toluene molecule was problematical, with large isotropic temperature factors hampering final convergence. The large temperature factors were taken to be an artifact of disorder, and attempts to refine the toluene molecule anisotropically failed. In the final refinement a damping factor was used, but two of the toluene carbon atom temperature factors still had  $\Delta/\sigma$  values of approximately 0.04. Convergence was assumed since all other parameters in the structure had reasonable  $\Delta/\sigma$  values. All hydrogen atoms were fixed in positions corresponding to a C-H distance of 0.96 Å using the HFIX facility in SHELXTL PLUS. Hydrogen atoms had their isotropic temperature factors fixed at 0.08 Å<sup>2</sup>. The final refinement using 4730 unique observed [ $F > 4\sigma(F)$ ] reflections converged at  $R = 0.052$  and  $R_w = 0.056$  {where  $w = [\sigma^2(F) + 0.0007(F)^2]^{-1}$ }.<sup>29</sup>

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**Supporting Information Available:** Tables of fractional atomic coordinates, bond lengths and angles, isotropic and anisotropic thermal parameters, and hydrogen atom coordinates for complexes **3**, **4**, and **7** and a fully labeled ORTEP plot of **7** (21 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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