Sterically Demanding Aryloxides as Supporting Ligands in Organoactinide Chemistry. Synthesis, Structural Characterization, and Reactivity of Th(O-2,6-*t*-Bu₂C₆H₃)₂(CH₂SiMe₃)₂ and Formation of the Trimeric Thorium Hydride Th₃H₆(O-2,6-*t*-Bu₂C₆H₃)₆

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Reaction of ThBr₄(THF)₄ with 2 equiv of KOAr (Ar = 2,6-*t*-Bu₂C₆H₃) produces the bis-(aryloxide) complex ThBr₂(OAr)₂(THF)₂ (**1**) in 67% yield. Alkylation of **1** with 2 equiv of Me₃SiCH₂MgCl allows the isolation of Th(OAr)₂(CH₂SiMe₃)₂ (**2**) in 61% yield. Thermolysis of **2** (benzene, 60 °C, 36 h) in the presence of NEt₃ results in the formation of the cyclometalated ligand redistribution product Th(OC₆H₃-*t*-BuCMe₂CH₂)(OAr)₂ (**3**). Reaction of **2** with 1 equiv of 2,6-dimethylphenyl isocyanate leads to insertion into the Th−C bond to yield (ArO)₂Th[OC(=NR)CH₂SiMe₃](CH₂SiMe₃) (**4**; R = 2,6-Me₂C₆H₃). Aminolysis of **2** with 2 equiv of 2,6-diisopropylaniline allows the isolation of the bis(amido) species Th(OAr)₂(NH-2,6-*i*-Pr₂C₆H₃)₂ (**5**) in 92% yield. **2** reacts with dihydrogen (1.5 atm) over a period of 7 days to form the trimeric dihydride complex Th₃(μ₃-H)₂(μ₂-H)₄(OAr)₆ (**6**). In the presence of 1 equiv of [HNMe₂Ph][B(C₆F₅)₄], **2** catalyzes the hydrogenation of 1-hexene (N_t = 1 h⁻¹), while **6** is found to be a single-component catalyst for the analogous process (N_t = 3 h⁻¹). Complexes **1**−**6** have been characterized by ¹H NMR and IR spectroscopy, microanalysis, and, in the case of **2** and **6**, by single-crystal X-ray diffraction studies. **2** comprises a pseudotetrahedral thorium metal center bearing two aryloxide and two alkyl ligands. The O−Th−O angle between the aryloxide ligands (119.2(4)°) is significantly larger than the C−Th−C angle (101.4(6)°). Th−O and Th−C distances average 2.137(11) and 2.462(18) Å, respectively, while Th−C−Si angles are 125.9(8) and 122.8(8)°. The alkyl groups of **2** also display a reduced C−H coupling constant (J_{CH} = 98 Hz), suggestive of α-agostic interaction between the methylene group and the Th metal center. **6** exhibits a triangular arrangement of three thorium metal centers, each bearing two terminal aryloxide ligands. Two sides of the trimetallic core (Th−Th distances 3.781(1) and 3.818(1) Å) are bridged by single μ₂-hydride ligands, while the third side is bridged by two μ₂-hydride ligands (Th−Th distance 3.588(1) Å). Each face of the trimer is capped by a μ₃-hydride ligand to produce a structurally unique M₃(μ₃-X)₂(μ₂-X)₄X₆ geometry. Th−(μ₂-H) and Th−(μ₃-H) distances lie in the ranges 2.0(1)−2.3(1) and 2.3(1)−2.6(1) Å, respectively, while Th−O distances range from 2.126(7) to 2.164(7) Å.

Introduction

The synthesis of σ-alkyl derivatives of the early actinide elements has long represented a synthetic challenge,[2] due to the fact that the large size of the actinide metal center often imparts a degree of steric unsaturation to the isolated complex and can provide facile decomposition pathways, such as β-elimination, for alkyl-containing complexes. Therefore, it is not surprising that the earliest attempts to prepare homoleptic actinide alkyl complexes often led to the isolation of mixtures of thermally unstable products which proved difficult to characterize.[3,4] Numerous methodologies have subsequently been employed to overcome the problem of stabilizing homoleptic actinide σ-alkyl derivatives, including the preparation of anionic alkyl complexes which possess high coordination numbers at the metal center,[5] the use of phosphine ligands to prepare base-stabilized alkyl complexes ThR₄(Me₂PCH₂-

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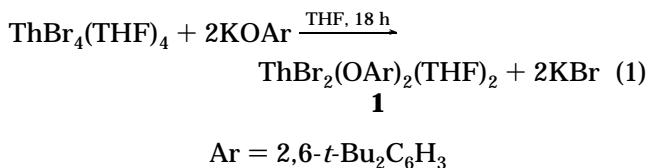
CH_2PMe_2) (R = Me, CH_2Ph),[6] and the use of the sterically demanding bis(trimethylsilyl)methyl ligand to prepare the homoleptic uranium(III) alkyl derivative $U[CH(SiMe_3)_2]_3$.[7] Many alkyl derivatives of the actinide elements have also been isolated by using carbocyclic supporting ligands such as cyclopentadienyl[8] and cyclooctatetraenyl[9] to produce steric saturation at the metal center and thus inhibit potential decomposition reactions. As an alternative to the ubiquitous cyclopentadienyl moiety, other workers have successfully employed sterically encumbered pyrazolylborate,[10] bis-(trimethylsilyl)amide,[11] and bis(trimethylsilyl)benzamidinato[12] ligands for the stabilization of actinide alkyl complexes.

The pioneering investigations of Marks and co-workers into the use of the pentamethylcyclopentadienyl moiety as a sterically demanding supporting ligand in organoactinide chemistry have led to a recent resurgence of interest in actinide σ-alkyl derivatives, following the discovery of extremely high catalytic activity of many of these species in hydrogenation and polymerization processes.[13] Our interest in the alkoxide and aryloxide chemistry of the f-elements has recently been directed toward investigation of the sterically encumbered 2,6-di-*tert*-butylphenoxide ligand as a surrogate for the pentamethylcyclopentadienyl moiety, and we have recently reported the synthesis of the mono-(pentamethylcyclopentadienyl) complex (η-C_5Me_5)Th-(OAr)(CH_2SiMe_3)$_2$ (Ar = 2,6-*t*-$Bu_2C_6H_3$) and compared its catalytic activity with that of analogous bis(pentamethylcyclopentadienyl) alkyl species.[14] Having noted the extensive series of investigations by Rothwell and co-workers in which aryloxide-supported alkyl complexes of groups 4 and 5 have been found to mediate a number of catalytic and stoichiometric reactions,[15] we wished to investigate whether thorium complexes of the type Th(OAr)$_2R_2$ (Ar = 2,6-*t*-$Bu_2C_6H_3$) would exhibit similar reactivity. There have been a limited number of reports in the literature of alkoxide and aryloxide moieties being

utilized as supporting ligands for actinide σ-alkyl complexes,[16] but reactivity studies of these species have not been undertaken. This paper describes the synthesis and structural characterization of the bis(alkyl) complex Th(OAr)$_2$(CH_2SiMe_3)$_2$ (Ar = 2,6-*t*-$Bu_2C_6H_3$) and compares its reactivity with that of both cyclopentadienyl-supported actinide alkyls as well as alkyl–aryloxide derivatives of the group 4 transition metals. A portion of this work has been the subject of a previous communication.[17]

Results and Discussion

Synthesis and Reactivity. Addition of 2 equiv of KOAr (Ar = 2,6-*t*-$Bu_2C_6H_3$) to a THF solution of $ThBr_4$-(THF)$_4$,[18] followed by crystallization from toluene, leads to isolation of the bis(aryloxide) complex $ThBr_2(OAr)_2$-(THF)$_2$ (**1**) as colorless crystals in 67% yield (eq 1).

$$ThBr_4(THF)_4 + 2KOAr \xrightarrow{\text{THF, 18 h}}$$
$$ThBr_2(OAr)_2(THF)_2 + 2KBr \quad (1)$$
$$\mathbf{1}$$

$$Ar = 2,6\text{-}t\text{-}Bu_2C_6H_3$$

Microanalytical and ^{1}H NMR spectral data for **1** support the proposed formulation. We note the isolation by Burns *et al.* of the related uranium aryloxide derivative $UI_2(OAr)_2(THF)\cdot THF$,[19] in which one THF ligand is bound to the metal center while a second THF molecule is contained within the lattice. We formulate **1** as $ThBr_2(OAr)_2(THF)_2$ rather than $ThBr_2(OAr)_2(THF)$·THF, since the slightly larger ionic radius of thorium compared to uranium and the smaller steric requirement of bromide compared to iodide ligands would appear to facilitate the coordination of a second molecule of THF at the metal center. In addition, analysis samples of **1** were recrystallized from toluene solution, which would mitigate against the inclusion of THF into their lattice structures. ^{1}H NMR spectra of the crude reaction mixture from eq 1 contained minor resonances which may tentatively be assigned to the mono- and tris-(aryloxide) complexes $ThBr_x(OAr)_{4-x}$ (x = 1, 3).

Compound **1** may be smoothly alkylated with 2 equiv of a diethyl ether solution of Me_3SiCH_2MgCl, followed by addition of dioxane. Subsequent crystallization from

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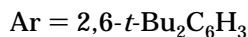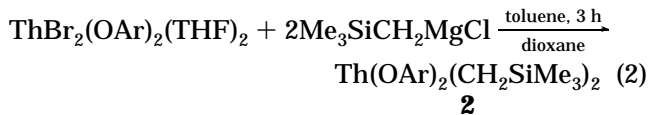
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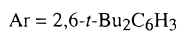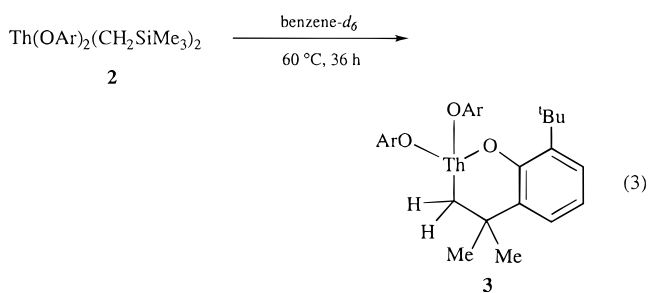
Scheme 1
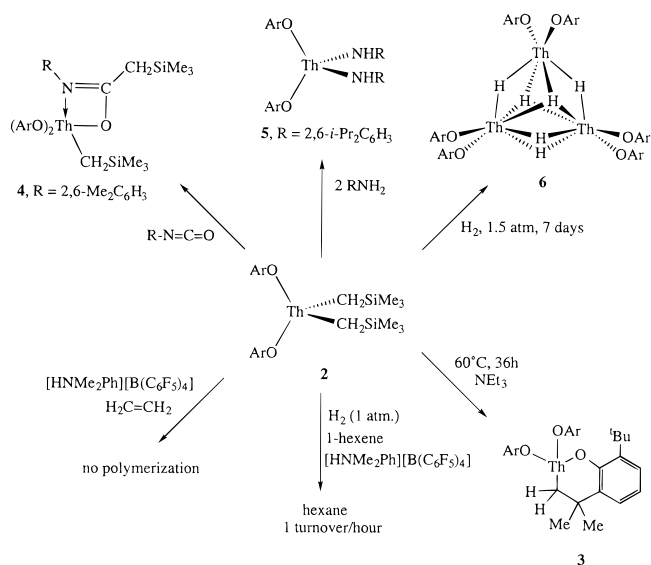
toluene allows the isolation of the bis(alkyl) complex Th-$(OAr)_2(CH_2SiMe_3)_2$ (**2**) as colorless crystals in 61% yield (eq 2).

$$ThBr_2(OAr)_2(THF)_2 + 2Me_3SiCH_2MgCl \xrightarrow[\text{dioxane}]{\text{toluene, 3 h}}$$

$$Th(OAr)_2(CH_2SiMe_3)_2 \quad (2)$$
$$\mathbf{2}$$

$$Ar = 2,6\text{-}t\text{-}Bu_2C_6H_3$$

The reactivity of complex **2** has been investigated, and a summary of its behavior is presented in Scheme 1. Thermolysis of **2** (benzene-d_6, 60 °C, 36 h) in the presence of NEt_3 (to capture any potential $Th(OAr)_2$-(=CHR) species) leads to the formation of a complex which is formulated on the basis of ^{1}H NMR and microanalytical data as the cyclometalated species Th-$(OC_6H_3\text{-}t\text{-}BuCMe_2CH_2)(OAr)_2$ (**3**) (eq 3). ^{1}H NMR stud-

$$Th(OAr)_2(CH_2SiMe_3)_2 \xrightarrow[\text{60 °C, 36 h}]{\text{benzene-}d_6}$$
$$\mathbf{2}$$
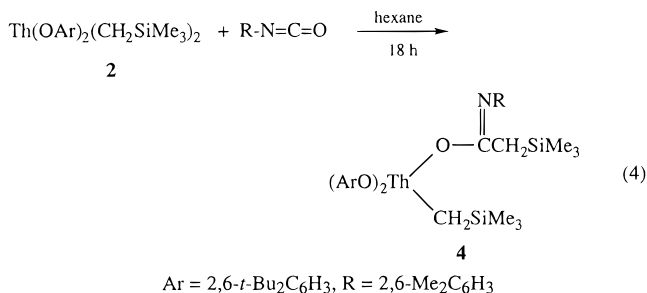

$$(3)$$

$$Ar = 2,6\text{-}t\text{-}Bu_2C_6H_3$$

ies showed the formation of $SiMe_4$ as the reaction progressed, but no other thorium-containing species could be conclusively identified in the reaction mixture. Compound **3** may be isolated in 24% yield following crystallization from hexane. The cyclometalation[20] and aryloxide ligand redistribution[15i,19] reactions necessary for the formation of **3** both have precedent in the literature, and we also note that the overall reactivity depicted in eq 3 closely parallels that observed upon thermolysis of the related complex $Cp^*Th(OAr)(CH_2SiMe_3)_2$

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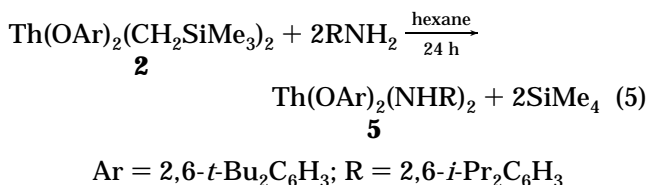
in the presence of $O=PPh_3$, which results in isolation of the cyclometalated ligand redistribution product $Cp^*Th(OC_6H_3\text{-}t\text{-}BuCMe_2CH_2)(OAr)(O=PPh_3)$.[14] The titanium and zirconium analogs of **3** have been described previously, following reaction of the metallacyclic species $M(OC_6H_3\text{-}t\text{-}BuCMe_2CH_2)(OAr)(CH_2Ph)$ (M = Ti, Zr) with a further 1 equiv of 2,6-di-*tert*-butylphenol.[15i]

Complex **2** reacts with 1 equiv of 2,6-dimethylphenyl isocyanate in hexane at room temperature to form the monoinsertion product $(ArO)_2Th[OC(=NR)CH_2SiMe_3]$-$(CH_2SiMe_3)$ (**4**; R = 2,6-$Me_2C_6H_3$) in 67% isolated yield (eq 4). **4** does not react with a second equivalent of isocyanate over a period of 18 h at room temperature in benzene-d_6.
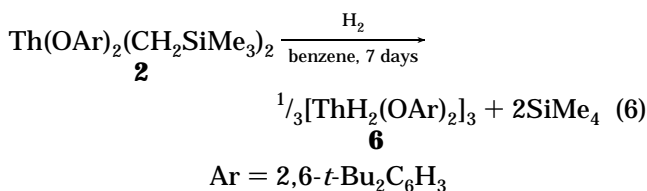
$$Th(OAr)_2(CH_2SiMe_3)_2 + R\text{-}N=C=O \xrightarrow[\text{18 h}]{\text{hexane}}$$
$$\mathbf{2}$$

$$(4)$$

$$Ar = 2,6\text{-}t\text{-}Bu_2C_6H_3, R = 2,6\text{-}Me_2C_6H_3$$

The alkyl groups in **2** are susceptible to protonation by amines, as demonstrated by the reaction of **2** with 1 equiv of $H_2N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3$ in cold (−78 °C) hexane. A ^{1}H NMR spectrum of the crude reaction mixture showed resonances due to unreacted **2** in addition to signals consistent with the presence of the mono- and bis(amide) species $Th(OAr)_2(NHR)(CH_2SiMe_3)$ and $Th(OAr)_2(NHR)_2$ (R = 2,6-i-$Pr_2C_6H_3$). Addition of a second equivalent of amine to the crude reaction mixture, followed by stirring at room temperature for 24 h and low-temperature crystallization, led to isolation of the bis(amide) Th-$(OAr)_2(NH\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)_2$ (**5**) as a white powder in 92% yield (eq 5). No evidence was seen for the formation of any imido-containing thorium complexes.

$$Th(OAr)_2(CH_2SiMe_3)_2 + 2RNH_2 \xrightarrow[\text{24 h}]{\text{hexane}}$$
$$\mathbf{2}$$

$$Th(OAr)_2(NHR)_2 + 2SiMe_4 \quad (5)$$
$$\mathbf{5}$$

$$Ar = 2,6\text{-}t\text{-}Bu_2C_6H_3; R = 2,6\text{-}i\text{-}Pr_2C_6H_3$$

The closely related bis(arylamido) species $M(OAr)_2$-$(NHPh)_2$ (M = Zr, Hf) have been prepared by reaction of $Zr(OAr)_2Me_2$ with 2 equiv of aniline or of $Hf(CH_2Ph)_4$ with 2 equiv of aniline followed by 2 equiv of phenol, respectively.[15e,h]

A benzene solution of **2** reacts with dihydrogen (1.5 atm) over a period of 7 days to produce a thorium hydride complex with the empirical formula $ThH_2(OAr)_2$ in 33% yield after crystallization from hexane (eq 6).

$$Th(OAr)_2(CH_2SiMe_3)_2 \xrightarrow[\text{benzene, 7 days}]{H_2}$$
$$\mathbf{2}$$

$${}^1\!/_3[ThH_2(OAr)_2]_3 + 2SiMe_4 \quad (6)$$
$$\mathbf{6}$$

$$Ar = 2,6\text{-}t\text{-}Bu_2C_6H_3$$

An X-ray diffraction study (*vide infra*) shows **6** to be trimeric in the solid state, and the trimeric structure remains intact in solution, as demonstrated by a molecular weight determination in benzene (isopiestic method, calcd for trimer 1934, found 2061). The deuterated complex $[ThD_2(OAr)_2]_3$ (**6**-d_6) can be prepared in an analogous procedure using deuterium gas.

The hydride ligands in **6** undergo slow exchange with deuterium gas (1 atm, benzene-d_6, half-life ~36 h) to produce the perdeuterio complex **6**-d_6 (eq 7). The slow rate of H−D exchange in **6** is in marked contrast to the fast exchange observed in the dimeric hydride complex $[(\eta^5-C_5Me_5)_2Th(\mu-H)(H)]_2$.[21]

$$[ThH_2(OAr)_2]_3 \xrightarrow[\text{benzene}]{D_2} [ThD_2(OAr)_2]_3 \qquad (7)$$
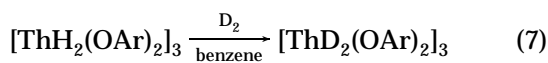
half-life ~36 h

The catalytic hydrogenation and polymerization activity of **2** toward α-olefins was also investigated. The ammonium salt $[HNMe_2Ph][B(C_6F_5)_4]$ was employed as a proton source to remove one alkyl ligand and form a cationic thorium complex with the noncoordinating tetrakis(perfluorophenyl)borate anion. Since attempts to characterize fully the presumed ionic species $[Th(OAr)_2(CH_2SiMe_3)][B(C_6F_5)_4]$ were unsuccessful, a mixture of **2** and $[HNMe_2Ph][B(C_6F_5)_4]$ was used *in situ* as the active catalyst. The addition of 1-hexene to an equimolar toluene solution of **2** and $[HNMe_2Ph][B-(C_6F_5)_4]$, followed by admission of 1 atm of dihydrogen, led to the catalytic hydrogenation of the olefin. Analysis of the volatile components from the reaction mixture by GC−MS, and quantification of the hexane present, allowed calculation of the turnover rate of 1 h^{-1}. The activity of **2**/$[HNMe_2Ph][B(C_6F_5)_4]$ is thus substantially lower than that of the bis(pentamethylcyclopentadienyl) methyl derivative $[(\eta-C_5Me_5)_2ThMe][B(C_6F_5)_4]$, for which a turnover rate of 16 450 h^{-1} has been reported,[22] but is only slightly lower than that of $(\eta-C_5Me_5)Th(OAr)(CH_2SiMe_3)_2$ (3 h^{-1}).[14]

An equimolar toluene solution of **2** and $[HNMe_2Ph]-[B(C_6F_5)_4]$ was found to be inactive as an ethylene polymerization catalyst, in contrast to the related pentamethylcyclopentadienyl complex $(\eta-C_5Me_5)Th(OAr)-(CH_2SiMe_3)_2$, which, in the presence of 1 equiv of $[HNMe_2Ph][B(C_6F_5)_4]$, showed an activity of 34 600 g h^{-1} atm^{-1} (mol catalyst)$^{-1}$ (N_t = 0.35 s^{-1}).[14]

The dihydride species $[ThH_2(OAr)_2]_3$ (**6**) was 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 3 h^{-1}. The activity of **6** is thus somewhat greater than that of the bis(pentamethylcyclopentadienyl) analog $[(\eta-C_5Me_5)_2Th-(\mu-H)(H)]_2$ (0.5 h^{-1})[21] but considerably lower than that of the "tied-back" derivative $[Me_2Si(\eta-C_5Me_4)_2Th(\mu-H)_2]_2$ (610 h^{-1})[23] and the mono(pentamethylcyclopentadienyl) complex $[(\eta-C_5Me_5)ThH_2(OAr)]_3$ (10 h^{-1}).[14]

Solid-State and Molecular Structures. Th(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_2$(CH$_2$SiMe$_3$)$_2$ (2). X-ray-quality crystals of

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Table 1. Summary of Crystallographic Data

	2	**6**
empirical formula	$C_{39}H_{64}O_2Si_2Th$	$C_{26}H_{32}O_2Th$
space group	$P2_1/c$	$P2_1/c$
cell dimens		
a, Å	11.779(2)	13.571(1)
b, Å	18.276(4)	26.610(3)
c, Å	20.276(4)	27.510(2)
β, deg	103.55(3)	96.716(3)
V, Å^3	4243.4	9866
Z (molecules/cell)	4	4
fw	853.1	2106.4
D_{calc}, g cm^{-3}	1.335	1.418
abs coeff, cm^{-1}	35.98	45.6
λ(Mo Kα)	0.710 69	0.710 69
temp, °C	−70	−100
2θ range, deg	2.0−45.0	5.0−45.0
no. of measd rflns	6217	15402
no. of unique intensities	5523	12789
no. of obsd rflns	3883 ($F > 4.0\sigma(F)$)	8144 ($F > 4.0\sigma(F)$)
$R(F)$[b]	0.0694	0.0460
$R_w(F)$ or wR2	0.0945[c]	0.0812[d]
goodness of fit	1.08	1.01

[a] **2** = Th(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_2$(CH$_2$SiMe$_3$)$_2$; **6** = Th$_3(\mu_3$-H)$_2(\mu_2$-H)$_4$(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_6$. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w(F) = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [d] wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0325P)^2$, with $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for Th(O-2,6-*t*-Bu$_2$C$_6$H$_3$)$_2$(CH$_2$SiMe$_3$)$_2$·C$_7$H$_8$ (2)

	10^4x	10^4y	10^4z	10^4U(eq),[a] Å^2
Th(1)	2325.5(5)	1502.6(3)	2049.2(3)	110(2)
Si(1)	−751(4)	1607(3)	874(2)	182(15)
C(1)	649(14)	2075(9)	1289(9)	272(63)
Si(2)	3695(4)	1190(3)	554(2)	180(16)
C(11)	3156(16)	775(9)	1240(8)	242(64)
O(1)	3570(9)	2341(5)	2456(5)	172(37)
C(21)	4312(13)	2798(9)	2906(7)	146(36)
C(22)	3975(13)	3530(9)	2935(8)	178(37)
C(23)	4717(14)	3967(9)	3405(8)	187(38)
C(24)	5743(17)	3730(10)	3794(9)	300(68)
C(25)	6088(17)	2999(10)	3725(8)	295(67)
C(26)	5366(14)	2520(9)	3268(7)	161(54)
C(27)	2845(14)	3832(9)	2477(8)	182(38)
C(31)	5812(15)	1741(10)	3182(9)	277(64)
O(2)	1715(8)	799(6)	2727(5)	127(23)
C(40)	1350(13)	362(8)	3199(7)	124(35)
C(41)	931(13)	702(9)	3709(7)	139(36)
C(42)	490(15)	244(10)	4143(9)	308(46)
C(43)	494(14)	−482(10)	4077(8)	242(40)
C(44)	946(13)	−822(9)	3589(8)	186(38)
C(45)	1392(12)	−417(9)	3135(7)	132(35)
C(46)	945(13)	1543(9)	3812(8)	171(36)
C(50)	1954(16)	−794(10)	2610(9)	279(67)

[a] Equivalent isotropic U, defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

2 were grown by cooling a concentrated toluene solution to −40 °C. A summary of data collection and crystallographic parameters is given in Table 1. Selected fractional coordinates are given in Table 2, 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 1. The overall molecular structure of **2** features a thorium metal center coordinated in a pseudotetrahedral fashion by two aryloxide and two alkyl ligands. The sterically demanding aryloxide ligands have a significantly larger angle between them (O(1)−Th(1)−O(2) = 119.2(4)°) than the somewhat smaller alkyl ligands (C(1)−Th(1)-C(11) = 101.4(6)°). Th−O bond distances in **2** are statistically indistinguishable (2.147(10) and 2.127(11) Å) and are
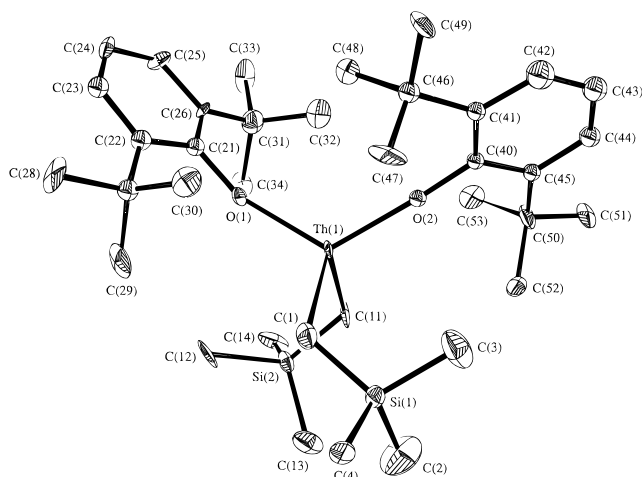
Figure 1. ORTEP representation (50% probability ellipsoids) of the molecular structure of Th(O-2,6-t-Bu$_2$C$_6$H$_3$)$_2$(CH$_2$SiMe$_3$)$_2$ (**2**), giving the atom-numbering scheme used in the tables.

Table 3. Selected Bond Distances (Å) and Angles (deg) for Th(O-2,6-t-Bu$_2$C$_6$H$_3$)$_2$(CH$_2$SiMe$_3$)$_2$·C$_7$H$_8$ (2)

Th(1)−O(1)	2.147(10)	Th(1)−O(2)	2.127(11)
Th(1)−C(1)	2.438(16)	Th(1)−C(11)	2.485(18)
O(1)−Th(1)−C(1)	108.4(5)	O(1)−Th(2)−C(11)	107.2(5)
O(2)−Th(1)−C(1)	108.8(5)	O(2)−Th(2)−C(11)	110.4(5)
O(1)−Th(1)−O(2)	119.2(4)	C(1)−Th(2)−C(11)	101.4(6)
Th(1)−C(1)−Si(1)	125.9(8)	Th(1)−C(11)−Si(2)	122.8(8)

comparable to those found in Th(O-2,6-t-Bu$_2$C$_6$H$_3$)$_2$(CH$_2$-py-6-Me)$_2$ (2.190(9) Å)[16b] and Th(O-2,6-t-Bu$_2$C$_6$H$_3$)$_4$ (2.189-(6) Å).[24] Th−C distances of 2.438(16) and 2.485(18) Å are similar to those found in other crystallographically characterized thorium alkyl complexes and can be compared to the average Th−C distances of 2.55(1), 2.47(1), 2.54(1), 2.49(2), and 2.58(1) Å found in Th(O-

2,6-t-Bu$_2$C$_6$H$_3$)$_2$(CH$_2$-py-6-Me)$_2$,[16b] (η-C$_5$Me$_5$)$_2$Th(CH$_2$-

SiMe$_2$CH$_2$),[25] (η-C$_8$H$_8$)(η-C$_5$Me$_5$)Th[CH(SiMe$_3$)$_2$],[26] (η-C$_5$Me$_5$)$_2$Th(CH$_2$SiMe$_3$)$_2$[27a] and (η-C$_5$Me$_5$)Th(CH$_2$C$_6$H$_5$)$_3$,[27b] respectively. Th−O−C angles are almost linear (162.1-(10) and 176.9(8)°) and are typical of those seen in other transition-metal complexes bearing bulky aryloxide ligands.[28] The Th−C−Si angles of 125.9(8) and 122.8-(8)° in **2** are larger than those typically found for sp^3-hybridized carbon atoms. Comparable Th−C−Si angles have precedence in the literature in the cyclopentadienyl complexes (η-C$_5$Me$_5$)$_2$Th(CH$_2$SiMe$_3$)$_2$ (Th−C−Si = 132.0(6) and 148.0(7)°),[27a] [Me$_2$Si(η-C$_5$Me$_4$)$_2$]Th(CH$_2$-SiMe$_3$)$_2$ (123.7(14) and 149.5(12)°),[23] and (η-C$_5$Me$_5$)Th-(OAr)(CH$_2$SiMe$_3$)$_2$ (120.0(4) and 139.8(6)°).[14] These large angles and the corresponding reduced coupling

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Table 4. Selected Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for [ThH$_2$(O-2,6-t-Bu$_2$C$_6$H$_3$)$_2$]$_3$ (6)

	10^4x	10^4y	10^4z	10^4U(eq),[a] Å^2
Th(1)	2930(1)	1858(1)	3056(1)	32(1)
Th(2)	2143(1)	3146(1)	3036(1)	31(1)
Th(3)	2348(1)	2482(1)	1822(1)	38(1)
O(1)	2122(5)	1171(3)	3141(2)	36(2)
O(2)	4371(5)	1720(2)	3441(2)	33(2)
O(3)	3004(5)	3827(3)	3170(2)	38(2)
O(4)	747(5)	3269(2)	3295(2)	30(2)
O(5)	1013(5)	2377(3)	1337(2)	40(2)
O(6)	3630(5)	2574(3)	1453(2)	40(2)
H(a)	1939(74)	3211(38)	2232(36)	80
H(b)	2819(73)	1844(38)	2310(36)	80
H(c)	3363(73)	2598(38)	3402(36)	80
H(d)	1833(73)	2359(39)	3357(35)	80
H(e)	1757(75)	2385(39)	2551(35)	80
H(f)	3179(74)	2666(39)	2561(36)	80

[a] Equivalent isotropic U, defined as one-third of the trace of the orthogonalized **U**$_{ij}$ tensor.

Table 5. Selected Bond Distances (Å) and Angles (deg) for [ThH$_2$(O-2,6-t-Bu$_2$C$_6$H$_3$)$_2$]$_3$ (6)

Th(1)−O(1)	2.159(7)	Th(1)−O(2)	2.143(7)
Th(2)−O(3)	2.164(7)	Th(2)−O(4)	2.126(7)
Th(3)−O(5)	2.139(7)	Th(3)−O(6)	2.127(7)
Th(1)−H(b)	2.04(10)	Th(1)−H(d)	2.23(10)
Th(1)−H(e)	2.43(10)	Th(1)−H(f)	2.58(10)
Th(2)−H(a)	2.20(10)	Th(2)−H(c)	2.34(10)
Th(2)−H(d)	2.33(10)	Th(2)−H(e)	2.45(10)
Th(2)−H(f)	2.40(10)	Th(3)−H(a)	2.34(10)
Th(3)−H(b)	2.21(10)	Th(3)−H(e)	2.26(10)
Th(3)−H(f)	2.26(10)	Th(2)−Th(3)	3.8176(6)
Th(1)−Th(2)	3.5884(6)	Th(1)−Th(3)	3.7806(6)
O(2)−Th(1)−O(1)	104.4(2)	O(4)−Th(2)−O(3)	107.4(2)
O(6)−Th(3)−O(5)	113.5(2)	Th(2)−Th(1)−Th(3)	62.34(1)
Th(1)−Th(2)−Th(3)	61.30(1)	Th(1)−Th(3)−Th(2)	56.36(1)

constant for the methylene carbon atom have been interpreted as evidence for α-agostic interactions, although mechanistic studies of alkane elimination from these complexes provide no evidence for α-hydrogen abstraction.[29]

Th$_3$(μ_3-H)$_2$(μ_2-H)$_4$(O-2,6-t-Bu$_2$C$_6$H$_3$)$_6$ (6). Crystals of **6** suitable for an X-ray diffraction study were grown by cooling a concentrated hexane solution to −40 °C. Selected fractional coordinates are given in Table 4, while selected bond lengths and angles are presented in Table 5. An ORTEP drawing giving the atom-numbering scheme used in the tables is shown in Figure 2. The basic structure of **6** consists of a triangular core of three thorium atoms with each thorium bonded to two terminal aryloxide ligands. Two of the located and refined hydride ligands cap the two faces of the trimer (μ_3-H), while the remaining four hydrides bridge the edges of the trimetallic core (μ_2-H). Two sides of the trimer are bridged by single μ_2-H ligands and display nonbonding Th−Th distances of 3.781(1) and 3.818(1) Å, while the third side has two μ_2-H ligands and a very short nonbonding Th−Th distance of 3.588(1) Å (*cf.* Th−Th distance in thorium metal, 3.59 Å).[30] The Th(1)−Th(2) separation appears to be the shortest yet documented in a molecular complex but is attributable primarily to the four bridging hydride interactions, which draw the metals into close proximity. The related

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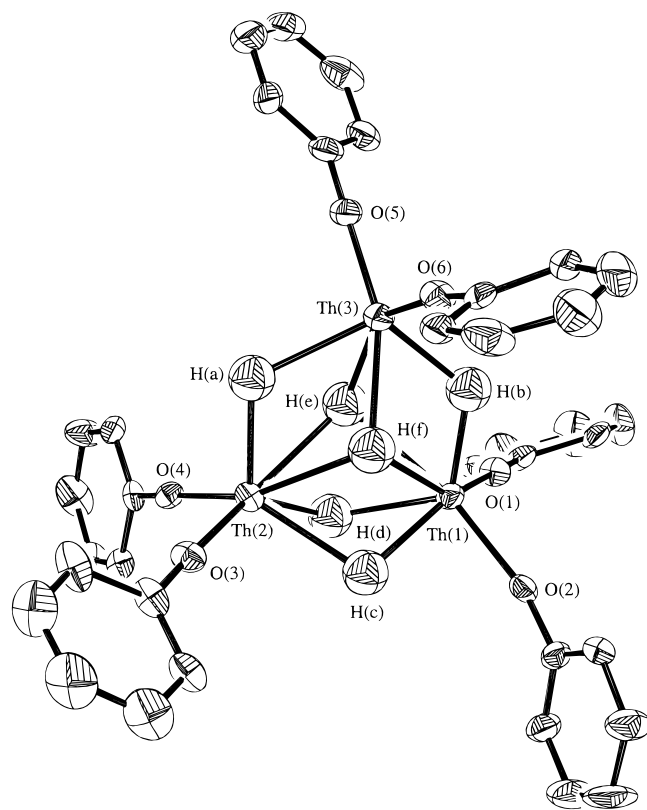
Figure 2. ORTEP representation (40% probability ellipsoids) of the molecular structure of $Th_3(\mu_3\text{-H})_2(\mu_2\text{-H})_4(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_6$ (**6**), giving the atom-numbering scheme used in the tables. *tert*-Butyl carbon atoms have been omitted for clarity.

bis(cyclopentadienyl) complex $\{[Me_2Si(\eta\text{-}C_5Me_4)_2]Th(\mu\text{-}H)_2\}_2$, which also features four bridging hydride ligands, exhibits a Th–Th distance of 3.632(2) Å.[23] Th–$(\mu_2$-H) distances (2.0(1)–2.3(1) Å) are found to be slightly shorter than the Th–$(\mu_3$-H) distances (2.3(1)–2.6(1) Å) and are in the range expected for bridging thorium-hydride interactions, as demonstrated by the neutron diffraction study of $[(\eta\text{-}C_5Me_5)_2Th(\mu\text{-}H)(H)]_2$ with Th–$(\mu_2$-H) distances of 2.29(3) Å.[31] Th–O distances of 2.126(7)–2.164(7) Å are directly comparable to those observed in **2** and related complexes (*vide supra*). The Th–O–C angles are also similar to those observed in **2**, ranging from 166.6(6) to 179.1(7)°.

The molecular geometry of **6** is highly unusual and is worthy of special note. The central $M_3(\mu_3\text{-H})_2(\mu_2\text{-H})_4$ core appears to be structurally unprecedented among metal hydride complexes, and we are aware of only three structurally characterized complexes among the later transition metals which feature triply bridging hydride ligands capping both faces of a trimetallic core.[32] The overall M_3X_{12} moiety may be considered as a derivative of the well-known M_3X_{11} structural type[33] formed by the addition of a single μ_2 ligand along one edge. The resulting $M_3(\mu_3\text{-}X)_2(\mu_2\text{-}X)_4X_6$ geometry appears to be a new structural type of triangular cluster.

Spectroscopic Studies. The ^{1}H NMR spectra of **1** and **2** showed resonances which were straightforwardly assignable to aryloxide and alkyl ligands in the expected ratios. In the proton-coupled ^{13}C NMR spectrum of **2**, the methylene carbon resonance appears as a triplet at δ 93.96 (J_{CH} = 98 Hz) with a C–H coupling constant which is significantly reduced from that of a typical sp^3-hybridized carbon atom. In the analogous cyclopentadienyl complexes $[Me_2Si(\eta\text{-}C_5Me_4)_2]Th(CH_2SiMe_3)_2$ and $(\eta\text{-}C_5Me_5)Th(OAr)(CH_2SiMe_3)_2$, similarly reduced coupling was observed and was attributed to α-agostic interactions with the metal.[14,23] Additional evidence for this interaction has also been observed in the solid-state structure of **2** (*vide supra*).

The ^{1}H NMR spectrum of **3** displays resonances assignable to two terminal aryloxide ligands in addition to a distinctive set of resonances in a 9:6:2 ratio which are characteristic of a cyclometalated di-*tert*-butylphenoxide ligand. The ^{1}H NMR spectrum of **4** exhibits two sets of resonances due to the metal-bound and carbon-bound CH_2SiMe_3 groups, together with resonances for the di-*tert*-butylphenoxide and (dimethylphenyl)imido groups. A resonance at 182.7 ppm in the ^{13}C NMR spectrum of **4** is consistent with insertion of the isocyanate O=C bond into the Th–C bond, as would be expected for an oxophilic actinide complex. The infrared spectrum of **4** contains a strong absorption at 1520 cm^{-1} assigned to the C=N stretching mode. This relatively low C=N stretching frequency is consistent with significant N→Th interaction, as shown schematically in resonance structure **C**. In contrast, a C=N stretching
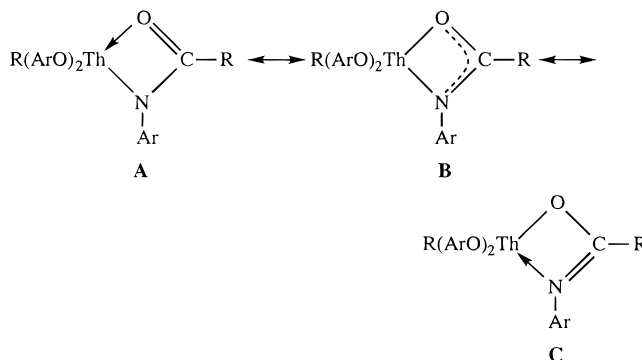
frequency of 1610 cm^{-1} was observed in the isocyanate insertion product $(\eta\text{-}C_5Me_5)_2Zr[C_4H_6(=N\text{-}t\text{-}Bu)O]$, which was shown to have no N→Zr interaction by means of an X-ray diffraction study.[34] Insertion of PhN=C=O into a Zr–C bond of Cp_2ZrMe_2 has been previously reported, and the bonding mode as determined by X-ray crystallography was best described by a delocalized structure analogous to that depicted in **B**.[35]

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The ^{1}H NMR spectrum of complex **6** has a resonance at 20.54 ppm, indicative of a thorium hydride species,[21,23] and this resonance shows only slight broadening at −90 °C in toluene-d_8. The IR spectrum of **6** (Nujol mull, KBr plates) displays ν(Th−H) stretches at 1336, 975, and 795 cm^{-1} which are shifted to 954, 705, and 560 cm^{-1}, respectively, upon deuteration. In the thorium hydrido complexes {[Me$_2$Si(η-C$_5$Me$_4$)$_2$]Th(μ-H)$_2$}$_2$ and [(η-C$_5$Me$_5$)$_2$Th(μ-H)(H)]$_2$, the bridging thorium hydrides show ν(Th−H) stretches in the region 1285−481 cm^{-1}, while terminal Th−H stretching frequencies were observed at 1404 and 1370 cm^{-1}.[21,23]

Concluding Remarks

We have shown that the sterically demanding 2,6-di-*tert*-butylphenoxide moiety serves as a useful ancillary ligand for thorium alkyl complexes. The aryloxide ligand may be readily introduced into the coordination sphere of the thorium metal center by selective metathesis reaction of ThBr$_4$(THF)$_4$ with KOAr to form ThBr$_2$-(OAr)$_2$(THF)$_2$ (**1**). Straightforward alkylation of **1** with a Grignard reagent subsequently allows access to the aryloxide-supported alkyl complex Th(OAr)$_2$(CH$_2$SiMe$_3$)$_2$ (**2**).

The reactivity of **2** provides some interesting comparisons both with cyclopentadienyl-supported thorium alkyls and also with analogous group 4 aryloxide−alkyl derivatives. Thus, the thermolysis of **2** in benzene at 60 °C leads to ligand redistribution and the isolation of the cyclometalated tris(aryloxide) complex $\overline{\text{Th(OC}_6\text{H}_3\text{-}}$

$t\text{-BuCMe}_2\text{CH}_2)(\text{OAr})_2$ (**3**). In contrast, thermolysis of M(OAr)$_2$(CH$_2$Ph)$_2$ (M = Ti, Zr) in toluene at 120 °C leads to elimination of toluene and the formation of the cyclometalated aryloxide−alkyl species $\overline{\text{M(OC}_6\text{H}_3\text{-}t\text{-}}$

$\text{BuCMe}_2\text{CH}_2)(\text{OAr})(\text{CH}_2\text{Ph})$, but ligand redistribution is not observed.[15i] However, heating the homoleptic alkyl Ti(CH$_2$SiMe$_3$)$_4$ to 80 °C with 2 equiv of HOAr is reported to produce a mixture of products, including the titanium analog of **3**, namely $\overline{\text{Ti(OC}_6\text{H}_3\text{-}t\text{-BuCMe}_2\text{CH}_2)}(\text{OAr})_2$.[15i]

Reaction of **2** with 2,6-dimethylphenyl isocyanate presented the possibility of an insertion reaction into either the Th−C bond of a (trimethylsilyl)methyl group or the Th−O bond of an aryloxide ligand, both reactions having ample literature precedence.[36] Although preferential insertion into a M−O bond rather than an M−C bond has been observed in an alkylzinc alkoxide,[37] it was expected in the case of **2** that the highly oxophilic thorium metal center would direct reactivity toward the Th−C bond. This was confirmed by a ^{1}H NMR study of the monoinsertion product **4**, which revealed that both aryloxide ligands remained equivalent while two sets of resonances due to metal-bound and carbon-bound alkyl groups were observed.

The reactivity of **2** toward 2 equiv of substituted aniline parallels that of the related zirconium complex Zr(OAr)$_2$Me$_2$, in that both alkyl ligands undergo facile aminolysis in hydrocarbon solvent to produce the bis-(arylamido) species M(OAr)$_2$(NHR)$_2$ (M = Zr, R = Ph;[15h]

M = Th, R = 2,6-i-Pr$_2$C$_6$H$_3$ (**5**)). Complex **2** thus differs considerably in its reactivity from that of the cyclopentadienyl-supported bis(alkyl) complex (η-C$_5$Me$_5$)$_2$UMe$_2$, which reacts with 2,6-diisopropylaniline to produce the imido species (η-C$_5$Me$_5$)$_2$U(N-2,6-i-Pr$_2$C$_6$H$_3$).[38] The zirconium complex Zr(OAr)$_2$(NHPh)$_2$ is also observed to undergo facile conversion to the imido derivative Zr-(OAr)$_2$(NPh)(py′) upon treatment with 1 equiv of 4-pyrrolidinopyridine (py′).[15h] All attempts to isolate a thorium imido species using similar methodologies were unsuccessful.

The overwhelming majority of transition-metal hydride complexes are supported by soft π-acceptor ligands such as carbon monoxide or phosphine, or π-bound carbocyclic ligands such as cyclopentadienyl, and the number of hydride complexes supported exclusively by π-donating alkoxides or aryloxide ligands is very small, with most of the known examples being based upon Mo, W, or Re metal centers.[39] Early-transition-metal alkoxide/hydride complexes are limited to the group 5 species Ta(OSi-t-Bu$_3$)$_3$H$_2$,[40a] [M(OSi-t-Bu$_3$)$_2$H$_2$]$_2$ (M = Nb,[40b] Ta[40a]), Nb(O-2,6-(C$_6$H$_{11}$)$_2$C$_6$H$_3$)$_4$H,[40c] and Ta(O-2,6-i-Pr$_2$C$_6$H$_3$)$_3$H$_2$L (L = phosphine ligand)[40d] and the titanium derivatives Ti$_4$(OEt)$_{13}$(H)[41] and Ti$_3$(OPh)$_6$(H),[42] which have been proposed only upon the basis of reactivity data. Complex **6** thus represents a rare example of an early-metal hydrido complex supported exclusively by aryloxide ligation. However, while Rothwell and co-workers have found aryloxide-supported hydrido derivatives of group 5 to be effective arene hydrogenation catalysts,[40d,43] the trimeric dihydride complex [ThH$_2$(OAr)$_2$]$_3$ (**6**) was found to exhibit only modest activity in the catalytic hydrogenation of 1-hexene (3 turnovers h^{-1} at 1 atm).

A most interesting reactivity comparison is provided by the ethylene polymerization activities of the bis(alkyl) complexes (η-C$_5$Me$_5$)$_2$ThMe$_2$, (η-C$_5$Me$_5$)Th(OAr)(CH$_2$-SiMe$_3$)$_2$, and Th(OAr)$_2$(CH$_2$SiMe$_3$)$_2$ (**2**) in the presence of 1 equiv of [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]. While the bis(pentamethylcyclopentadienyl) derivative [(η-C$_5$Me$_5$)$_2$ThMe]-[B(C$_6$F$_5$)$_4$] showed an extremely high activity of 3.6 × 10^6 g h^{-1} atm^{-1} (mol of catalyst)$^{-1}$ (N_t = 36 s^{-1}),[22] the mono(aryloxide) complex [(η-C$_5$Me$_5$)Th(OAr)(CH$_2$SiMe$_3$)]-[B(C$_6$F$_5$)$_4$] displayed a substantially lower activity of 3.46 × 10^4 g h^{-1} atm^{-1} (mol of catalyst)$^{-1}$ (N_t = 0.35 s^{-1})[14] and the bis(aryloxide) complex Th(OAr)$_2$(CH$_2$-SiMe$_3$)$_2$ (**2**) was found to be inactive. This trend in reactivity may be rationalized by the presence of the aryloxide ligands, which are capable of substantial π-donation to the metal center. It has been reported previously that the presence of alkoxide ligands in Cp*$_2$-Th(X)(Y) systems can significantly lower the rate of alkyl ligand hydrogenolysis by decreasing the electro-

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philicity of the metal center.[44] The presence of alkoxide ligands can also result in an increase in Th−R bond disruption enthalpies by 2−4 kcal mol⁻¹.[44]

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. $ThBr_4(THF)_4$ was prepared as described previously.[18] 2,6-Dimethylphenyl isocyanate and 2,6-diisopropylaniline were obtained from Aldrich and degassed prior to use. 2,6-Di-*tert*-butylphenol (Aldrich) was used as received. $KO-2,6-t-Bu_2C_6H_3$ was prepared from the reaction of 2,6-di-*tert*-butylphenol with potassium hydride in THF. $[HNMe_2Ph][B(C_6F_5)_4]$ was obtained from Quantum Design and used as received. Solvents were degassed and distilled from Na or Na/benzophenone ketyl under nitrogen. Benzene-d_6 was dried with Na/benzophenone ketyl and then trap-to-trap-distilled before use.

NMR spectra were recorded at 22 °C on a Brüker WM 300 spectrometer in benzene-d_6. All ¹H NMR chemical shifts are reported in ppm relative to the ¹H impurity in benzene-d_6 at δ 7.15. Infrared spectra were recorded on a BioRad FTS-40 spectrophotometer as Nujol mulls between KBr plates. 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.

$ThBr_2(O-2,6-t-Bu_2C_6H_3)_2(THF)_2$ (1). THF (70 mL) was added to a mixture of $ThBr_4(THF)_4$ (8.57 g, 10.2 mmol) and $KO-2,6-t-Bu_2C_6H_3$ (5.00 g, 20.4 mmol), and the mixture was stirred for 18 h at room temperature with much precipitate being formed. All solvent was removed under vacuum; the solid was extracted with toluene (3 × 25 mL) and filtered through a Celite pad. The filtrate was cooled to −40 °C, resulting in a solid mass of colorless crystals which were isolated by filtration and washed with hexane. Yield: 6.5 g (67%). ¹H NMR (300 MHz, benzene-d_6): δ 7.49 (d, $^3J_{HH} = 8$ Hz, 4 H, *meta* OAr), 6.85 (t, $^3J_{HH} = 8$ Hz, 2 H, *para* OAr), 3.11 (m, 8 H, α-THF), 1.69 (s, 36 H, *t*-Bu), 0.97 (m, 8 H, β-THF). IR (cm⁻¹): 1408 (s), 1314 (w), 1266 (m), 1231 (m), 1212 (s), 1193 (s), 1122 (m), 1003 (m), 882 (m), 845 (s), 820 (m), 799 (w), 754 (m), 724 (m), 663 (m). Anal. Calcd for $C_{36}H_{58}Br_2O_4Th$: C, 45.67; H, 6.18. Found: C, 45.89; H, 6.37.

$Th(O-2,6-t-Bu_2C_6H_3)_2(CH_2SiMe_3)_2$ (2). A diethyl ether solution of Me_3SiCH_2MgCl (1 M, 6.4 mL, 6.4 mmol) was added to a toluene (30 mL) solution of $ThBr_2(O-2,6-t-Bu_2C_6H_3)_2(THF)_2$ (2.54 g, 2.68 mmol), and this mixture was stirred for 3 min. Dioxane (2 mL) was added, resulting in much precipitation and the mixture was stirred for 2 h before the mixture was taken to dryness *in vacuo*. The solid was extracted with toluene (2 × 25 mL); the extracts were filtered through a Celite pad, concentrated to 10 mL, and cooled to −40 °C, resulting in colorless crystals. The crystals were isolated by filtration and washed with 2 × 3 mL of cold hexane. Yield: 1.34 g (61%). ¹H NMR (300 MHz, benzene-d_6): δ 7.21 (d, $^3J_{HH} = 8$ Hz, 4 H, *meta* OAr), 6.81 (t, $^3J_{HH} = 8$ Hz, 2 H, *para* OAr), 1.50 (s, 36 H, *t*-Bu), 0.50 (s, 4 H, ThCH_2), 0.30 (s, 18 H, $SiMe_3$). ¹³C NMR (75.5 MHz, benzene-d_6): 162.73, 137.44, 125.60, 120.31 (aromatic carbons), 93.96 (t, $J_{CH} = 98$ Hz, ThCH₂), 34.83 (*C*Me₃), 32.14 (C*Me₃*), 4.12 (Si*Me₃*). IR (cm⁻¹): 1411 (s), 1242 (m), 1219 (s), 1195 (w), 1124 (w), 1099 (w), 866 (s), 849 (s), 822 (m), 750 (m), 727 (m), 662 (m), 605 (w), 551 (w). Anal. Calcd for $C_{36}H_{64}O_2Si_2Th$: C, 52.92; H, 7.89. Found: C, 53.17; H, 7.38.

$Th(OC_6H_3-t-BuCMe_2CH_2)(O-2,6-t-Bu_2C_6H_3)_2$ (3). Th(O-2,6-*t*-Bu₂C₆H₃)₂(CH₂SiMe₃)₂ (2; 0.100 g, 0.122 mmol) and NEt₃ (0.020 g, 0.20 mmol) were dissolved in benzene-d_6 in an NMR tube and heated to 60 °C for 36 h. A ¹H NMR spectrum of the

reaction mixture showed one main product with a number of minor products. The solvent was allowed to evaporate from the NMR tube in the glovebox, resulting in an oil which formed crystals upon addition of 0.2 mL of hexane. The crystals were isolated by decantation of the solvent and were washed with a small amount of hexane, resulting in 0.025 g of product. Yield: 24%. ¹H NMR (300 MHz, benzene-d_6): δ 7.45 (d, $^3J_{HH} = 8$ Hz, 1 H, *meta* OAr), 7.31 (d, $^3J_{HH} = 8$ Hz, 1 H, *meta* OAr), 7.18 (d, $^3J_{HH} = 8$ Hz, 4 H, *meta* OAr), 6.94 (t, $^3J_{HH} = 8$ Hz, 1 H, *para* OAr), 6.79 (t, $^3J_{HH} = 8$ Hz, 2 H, *para* OAr), 1.76 (s, 6 H, ThCH₂C*Me₂*), 1.57 (s, 9 H, Th-*t*-BuC₆H₃), 1.50 (s, 36 H, *t*-Bu₂C₆H₃), 1.39 (s, 2 H, ThC*H₂*CMe₂). IR (cm⁻¹): 1407 (s), 1265 (m), 1221 (s), 1196 (m), 1123 (m), 1101 (w), 860 (s), 820 (m), 796 (w), 749 (s), 722 (m), 657 (m). Anal. Calcd for $C_{42}H_{62}O_3Th$: C, 59.56; H, 7.38. Found: C, 59.22; H, 7.03.

$Th(O-2,6-t-Bu_2C_6H_3)_2\{OC[=N(2,6-Me_2C_6H_3)]CH_2SiMe_3\}-(CH_2SiMe_3)$ (4). 2,6-Dimethylphenyl isocyanate (0.038 g, 0.257 mmol) in hexane (1 mL) was added to a hexane (8 mL) solution of **2** (0.200 g, 0.245 mmol), and the mixture was stirred at room temperature for 18 h. All solvent was removed under vacuum, 1 mL of hexane was added, and the resulting solution was cooled to −40 °C, resulting in colorless crystals. The crystals were isolated by filtration and washed with 0.5 mL of cold hexane. Yield: 0.167 g (67%). ¹H NMR (300 MHz, benzene-d_6): δ 7.25 (d, $^3J_{HH} = 8$ Hz, 4 H, *meta* OAr), 6.82 (m, 5 H, Ar), 2.14 (s, 6 H, NC₆H₃*Me₂*), 1.58 (s, 36 H, *t*-Bu), 1.38 (s, 2 H, ThOC*CH₂*), 0.46 (s, 2 H, ThC*H₂*), 0.32 (s, 9 H, SiMe₃), 0.00 (s, 9 H, SiMe₃). ¹³C NMR (75.5 MHz, benzene-d_6): δ −0.43 (SiMe₃), 4.07 (SiMe₃), 19.84 (NC₆H₃*Me₂*), 25.64 (C*CH₂*-SiMe₃), 32.21(C*Me₃*), 34.97 (*C*Me₃), 88.83 (ThCH₂), 120.12, 125.21, 125.66, 128.60, 131.46, 137.67, 144..06, 162.94 (aromatic carbons), 182.68 (Th*OC*). IR (cm⁻¹): 1520 (m), 1411 (s), 1378 (m), 1244 (m), 1220 (s), 1200 (m), 1165 (w), 1125 (w), 1117 (w), 1107 (w), 869 (br s), 828 (m), 780 (w), 759 (m), 732 (w) 625 (m), 562 (w). Anal. Calcd for $C_{44}H_{73}NO_3Si_2Th$: C, 56.05; H, 7.63; N, 1.45. Found: C, 55.45; H, 7.70; N, 1.22.

$Th(O-2,6-t-Bu_2C_6H_3)_2(NH-2,6-i-Pr_2C_6H_3)_2$ (5). A hexane solution (4 mL) of $H_2N-2,6-i-Pr_2C_6H_3$ (0.095 g, 0.490 mmol) was added to a cold (−78 °C) hexane solution (50 mL) of **1** (0.400 g, 0.490 mmol), and the reaction mixture was stirred for 1 h at −78 °C. The solution was warmed to room temperature and stirred for 2 h, after which all solvent was removed *in vacuo*. An NMR spectrum of the crude reaction mixture showed resonances assigned to the starting material in addition to signals consistent with mono- and bis(amide) products. A further 1 equiv of $H_2N-2,6-i-Pr_2C_6H_3$ (0.095 g, 0.490 mmol) in hexane (30 mL) was added to the crude reaction mixture, and the resulting solution was stirred for 24 h. The solution was concentrated to 1 mL and cooled to −40 °C, resulting in a white powder. Yield: 0.44 g (92%). ¹H NMR (300 MHz, benzene-d_6): δ 7.22 (d, $^3J_{HH} = 7$ Hz, 4 H, *meta* Ar), 7.03 (d, $^3J_{HH} = 8$ Hz, 4 H, *meta* Ar), 7.25 (m, 4 H, *para* Ar), 5.90 (s, 2 H, HN), 3.39 (septet, $^3J_{HH} = 7$ Hz, 4 H, C*H*Me₂), 1.60 (s, 36 H, *t*-Bu), 1.25 (d, $^3J_{HH} = 7$ Hz, 24 H, CH*Me₂*). IR (cm⁻¹): 1407 (s), 1326 (m), 1306 (w), 1263 (w), 1246 (w), 1268 (s), 1195 (s), 1117 (m), 1103 (w), 873 (m), 861 (s), 848 (s), 820 (m), 796 (w), 749 (s), 722 (m), 689 (w), 658 (m), 568 (w), 547 (w). Anal. Calcd for $C_{52}H_{78}N_2O_2Th$: C, 62.76; H, 7.90; N, 2.81. Found: C, 62.71; H, 7.77; N, 2.89.

$[ThH_2(O-2,6-t-Bu_2C_6H_3)_2]_3$ (6). Benzene (10 mL) was added to a 50 mL Kontes flask containing **2** (0.325 g, 0.40 mmol), and a hydrogen atmosphere (1.5 atm) was placed over the solution. The mixture was stirred for 3 days, and then all solvent was removed *in vacuo*. ¹H NMR spectra of the crude reaction mixture showed the presence of unreacted **2** and two products. Benzene (8 mL) and hydrogen (1.5 atm) were again added to the flask, and the solution was stirred an additional 4 days. All solvent was removed *in vacuo*, and upon addition of 1 mL of hexane, crystals were deposited. Yield: 0.085 g (33%). ¹H NMR (300 MHz, benzene-d_6): δ 20.54 (s, 2 H, ThH), 7.21 (d, $^3J_{HH} = 8$ Hz, 4 H, *meta* OAr), 6.79 (t, $^3J_{HH} = 8$ Hz, 2 H, *para* OAr), 1.59 (s, 36 H, *t*-Bu). IR (cm⁻¹): 1476 (m), 1437

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(w), 1409 (s), 1390 (m), 1356 (m), 1336 (w), 1263 (m), 1222 (s), 1195 (w), 1120 (s), 1101 (w), 975 (w), 866 (s), 922 (m), 795 (m), 748 (s), 662 (s). Anal. Calcd for $C_{28}H_{44}O_2Th$: C, 52.17; H, 6.88. Found: C, 52.27; H, 6.75.

Hydrogenation of 1-Hexene by 2. Toluene (5.6 mL) was added to a 100 mL flask containing **2** (0.019 g, 0.023 mmol) and $[HNMe_2Ph][B(C_6F_5)_4]$ (0.019 g, 0.023 mmol), and the resulting solution was stirred for 20 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 mixture was stirred for 1 h and then quenched with 1-propanol. All volatile components were vacuum transferred to a second flask and analyzed by GC–mass spectroscopy. The mass of hexane produced corresponded to a catalytic rate of 1 turnover h^{-1} (Th atom)$^{-1}$.

Hydrogenation of 1-Hexene by 6. Toluene (4.84 mL) was added to a 100 mL flask containing **6** (0.013 g, 0.023 mmol of Th). 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 mixture was stirred for 3 h and then quenched with 1-propanol. All volatile components were vacuum-transferred to a second flask, and the solution was analyzed by GC–mass spectroscopy. The mass of hexane produced corresponded to a catalytic rate of 3 turnover h^{-1} (Th atom)$^{-1}$.

H–D Exchange in 6. A benzene-d_6 solution of **6** was frozen in an NMR tube and that was then sealed under an atmosphere of deuterium. The hydride region was monitored periodically by ^1H NMR spectroscopy, and the hydride signal was found to decrease with a half-life of *ca.* 36 h.

Crystallographic Studies. Th(O-2,6-t-Bu$_2$C$_6$H$_3$)$_2$(CH$_2$-SiMe$_3$)$_2$·C$_7$H$_8$ (2). 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 $((\sin \theta)/\lambda)^2$ 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 chi ψ-scans. The structure was solved by routine Patterson and Fourier techniques and refined by full-matrix least squares. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms, except for part of the aryloxide ligands and the toluene of crystallization (C21–C23, C27, O2, C40–C46, C60–C61), and geometrical generation of hydrogen atoms, which were constrained to "ride" upon the appropriate carbon atoms, final refinement using 3883 unique observed ($F > 4\sigma(F)$) reflections converged at R = 0.069 and R_w = 0.095 (where $w = [\sigma^2(F) + 0.006(F)^2]^{-1}$). A final difference Fourier contained some residual electron density around the thorium atom, the largest peak being 2.42 e/Å^3. All calculations were performed using the Siemens SHELXTL PLUS computing package.[45]

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

Th$_3$(μ_3-H)$_2$(μ_2-H)$_4$(O-2,6-t-Bu$_2$C$_6$H$_3$)$_6$ (6). A light yellow block was attached to a thin glass fiber using silicone grease and placed under a nitrogen cold stream on a Siemens P4/PC diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.710 69 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 no systematic variation of intensities. Lattice determination and data collection were carried out using XSCANS Version 2.10b software. All data reduction, including Lorentz and polarization corrections, and structure solution and graphics were performed using SHELXTL PC Version 4.2/360 software.[45] The structure refinement was performed using SHELX 93 software. All data were corrected for absorption using the ellipsoid routine in the XEMP facility of SHELXTL PC.

The space group, $P2_1/c$, was uniquely determined by the systematic absences. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares. Non-hydrogen atoms were treated anisotropically, except for two severely disordered hexane molecules in the lattice, which were modeled using isotropic carbon atoms of partial occupancy. The carbon atom hydrogens were placed in fixed, idealized positions with their isotropic temperature factors set at 1.5 (methyl) or 1.2 (aromatic) times the equivalent isotropic U of the carbon atom they were bonded to. A high-angle refinement was used (the weighting function w was multiplied by $1 - \exp[-5((\sin \theta)/\lambda)^2]$ for all data) to locate the hydrogen atoms associated with the thorium cluster. (All subsequent refinements were performed using the standard weighting scheme.) All six hydrogen atoms associated with the thorium core appeared in the high-angle difference map as peaks with an average height of 0.80 e/Å^3 and were refined with isotropic temperature factors fixed at 0.08 Å^2. These hydrogen atom positions were refined without difficulty to their final positions. Analysis of the final difference map showed the residual peaks to be evenly distributed throughout the unit cell at constant height (0.53 e/Å^3). Moreover, none of these peaks were at chemically meaningful positions for a thorium–hydride bond. The large majority of the peaks were either within 1.0 Å of a thorium atom or at nonbonding positions in the unit cell. Two peaks were within 1.0 Å of H(a), but their Th–H distances did not correspond to a thorium–hydride bond. The final refinement converged to R1 = 0.0460 and wR2 = 0.0812.

Supporting Information Available: Tables of fractional atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **2** and **6** (22 pages). Ordering information is given on any current masthead page.

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