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Synthesis of Thorium Amide Complexes *via* Halide Metathesis and Transamination Procedures: X-ray Structure of $Th[N(SiMe_3)_2]_2(NMePh)_2$

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Reaction of $ThBr_4(THF)_4$ with 4 equiv of potassium diphenylamide in THF produces the THF adduct $Th(NPh_2)_4(THF)$ (**1**) in 61% yield. Use of 4 or 5 equiv of the less bulky potassium *N*-methylanilide in an analogous reaction allows the isolation of the bis-THF adduct $Th(NMePh)_4(THF)_2$ (**2**) or the salt $K[Th(NMePh)_5]$ (**3**), respectively. The transamination reaction of the metallacycle $\{[(Me_3Si)_2N]_2\overline{Th(CH_2SiMe_2N}SiMe_3)\}$ with 4 equiv of *N*-methylaniline in refluxing toluene produces the four-coordinate amide species $Th[N(SiMe_3)_2]_2(NMePh)_2$ (**4**). An X-ray crystal structure determination of **4** revealed a distorted tetrahedral environment about the metal center, with Th−N distances averaging 2.308(7) Å. Close approach of the methyl groups within the *N*-methylanilide ligands to the metal center is suggestive of an agostic interaction, with Th−C distances of 3.073(10) and 3.064(10) Å. Crystal data for **4** (at −70 °C): monoclinic space group $P2_1/c$, $a = 17.091(3)$ Å, $b = 11.825(2)$ Å, $c = 16.981(3)$ Å, $\beta = 90.24(3)°$, $V = 3431.9$ Å^3, $Z = 4$, $d_{calc} = 1.481$ g cm^{-3}, $R(F) = 0.0378$, $R_w(F) = 0.0391$.

Introduction

During our recent studies of the alkoxide chemistry of the lanthanide and early actinide elements, we have frequently employed the alcoholysis of lanthanide and actinide amide complexes as a synthetic route to produce alkoxide compounds of differing nuclearities.[2] In the case of the early actinide elements thorium and uranium, we employed almost exclusively the metallacyclic amide complex $\{[(Me_3Si)_2N]_2\overline{An(CH_2SiMe_2N}SiMe_3)\}$,[3] which may be prepared both in good yield and on a large scale from the reaction of either $ThBr_4(THF)_4$[2c] or UCl_4[7b,c] with 4 equiv of sodium bis(trimethylsilyl)amide in refluxing toluene. During a search for alternative actinide amide starting materials, however, it became clear that this area of f-block chemistry has not been extensively studied and that the paucity of reported compounds is more noticeable in the case of thorium[4] than it is for uranium.[5] Indeed, a search of crystallographic databases revealed the surprising fact that, while a small number of thorium complexes containing bis(trimethylsilyl)amide,[6,7a] tris(pyrazolyl)borate,[8] and monoalkylamide[9] ligands have been structurally characterized, no structural data currently exist for thorium compounds containing dialkyl- or diarylamide ligation. We report here the synthesis and characterization of several thorium amido complexes, in addition to an X-ray crystallographic study of the four-coordinate species $Th[N(SiMe_3)_2]_2(NMePh)_2$.

Results and Discussion

Synthesis and Reactivity. Addition of 4 equiv of solid potassium diphenylamide to a THF solution of $ThBr_4(THF)_4$ results in the immediate formation of an off-white precipitate. Stirring at room temperature for 24 h, followed by filtration and workup of the filtrate from toluene, provides a white solid formulated as the mono-THF adduct $Th(NPh_2)_4(THF)$ (**1**) as shown in eq 1.

Microanalytical data and ^1H NMR integration support the proposed stoichiometry with one molecule of THF per thorium

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[9] One of the two resonance structures of $(\eta\text{-}C_5Me_5)_2\overline{ThCl[NHC(Me)NC}(Me)CHCN]$ contains a formal Th−NRR′ interaction, while the other features a dative Th←N(=R)R′ bond: Sternal, R. S.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1987**, *109*, 7920.

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$$\mathrm{ThBr_4(THF)_4 + 4KNPh_2 \xrightarrow{THF} Th(NPh_2)_4(THF) + 4KBr} \qquad (1)$$

atom. **1** is virtually insoluble in hexane but soluble in benzene, toluene, and THF. Attempts to grow X-ray quality crystals led only to the deposition of white powders.

Treatment of $ThBr_4(THF)_4$ with 4 equiv of the less bulky potassium *N*-methylanilide in THF was also successful with respect to the replacement of all four bromide substituents with the amide functionality. Workup from toluene, followed by cooling of the solution to −40 °C, yielded colorless crystals of $Th(NMePh)_4(THF)_2$ (**2**) (eq 2). The formulation of **2** with two THF molecules is based upon both ^1H NMR integration and microanalytical data.

$$\mathrm{ThBr_4(THF)_4 + 4KNMePh \xrightarrow{THF} Th(NMePh)_4(THF)_2 + 4KBr} \qquad (2)$$

Reaction of $ThBr_4(THF)_4$ with 5 equiv of potassium *N*-methylanilide produced the salt complex $K[Th(NMePh)_5]$ (**3**), which is insoluble in toluene but quite soluble in THF (eq 3).

$$\mathrm{ThBr_4(THF)_4 + 5KNMePh \xrightarrow{THF} K[Th(NMePh)_5] + 4KBr} \qquad (3)$$

Formulation of this complex with no coordinated THF ligands is based upon both microanalytical data and the absence of significant THF resonances in a concentrated ^1H NMR sample of **3** in THF-d_8. Integration of the minor THF resonances visible in the spectrum revealed that <<1 equiv of protio-THF was present, and this was assigned to the residual protons within the deuterated solvent.

In an attempt to obtain a homoleptic thorium amide complex, the metallacycle $\{[(Me_3Si)_2N]_2Th(CH_2SiMe_2NSiMe_3)\}$ was refluxed in toluene with 4 equiv of *N*-methylaniline for 18 h. Removal of solvent and crystallization of the residue from toluene led to the formation of large pale yellow crystals of the mixed amido species $Th[N(SiMe_3)_2]_2(NMePh)_2$ (**4**). Thus the reaction is seen to proceed according to the stoichiometry of eq 4.

$$\mathrm{[(Me_3Si)_2N]_2Th(CH_2SiMe_2NSiMe_3) \xrightarrow{2HNMePh} Th[N(SiMe_3)_2]_2(NMePh)_2 + HN(SiMe_3)_2} \qquad (4)$$

Solid State and Molecular Structure. $Th[N(SiMe_3)_2]_2(NMePh)_2$ (4). Crystals of **4** suitable for an X-ray diffraction study were grown by slow evaporation of a toluene solution in the drybox atmosphere, and the structure of **4** was determined from data collected at −70 °C. A summary of data collection and crystallographic parameters is given in Table 1. Atomic positional parameters are given in Table 2, while selected bond lengths and angles are given in Table 3. A ball-and-stick view of the solid state structure giving the atom-numbering scheme used in the tables is shown in Figure 1.

Table 1. Summary of Crystallographic Data

compound	$Th[N(SiMe_3)_2]_2(NMePh)_2$
empirical Formula	$C_{26}H_{52}N_4Si_4Th$
color; habit	Clear block
crystal dimens, mm	0.20 × 0.20 × 0.25
space group	$P2_1/c$ (No. 14)
a, Å	17.091(3)
b, Å	11.825(2)
c, Å	16.981(3)
β, deg	90.24(3)
volume, Å^3	3431.9
Z (molecules/cell)	4
formula weight	765.1
D_{calc}, g cm^{-3}	1.481
abs coeff, cm^{-1}	46.53
λ(Mo Kα)	0.710 73
temperature, °C	−70
2θ range, deg	2.0−55.0
no. of measd reflns	8484
no. of unique intensities	7830
no. of obsd reflns	4867 ($F > 4.0\sigma(F)$)
$R(F)$[a]	0.0378
$R_w(F)$[b]	0.0391
goodness-of-fit	1.59

[a] $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $R_w(F) = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients for $Th[N(SiMe_3)_2]_2(NMePh)_2$ (**4**)

	10^5x	10^5y	10^5z	10^4U(eq),[a] Å^2
Th(1)	24865(1)	−339(3)	30848(1)	172(1)
Si(1)	22402(14)	18836(20)	16276(13)	275(7)
Si(2)	37570(14)	23096(20)	25095(14)	281(7)
Si(4)	27347(14)	−21283(20)	17652(13)	280(7)
Si(3)	12437(14)	−24720(20)	27040(14)	282(7)
N(1)	29072(36)	15256(54)	23652(36)	241(20)
N(2)	20776(34)	−16732(51)	24823(34)	207(19)
N(3)	15882(35)	5183(57)	40165(35)	246(20)
N(4)	34013(39)	−4773(56)	40317(39)	246(21)
C(1)	13459(51)	9653(84)	17982(56)	354(30)
C(2)	19129(66)	33986(98)	16539(62)	425(36)
C(3)	25915(74)	15614(99)	6005(57)	491(40)
C(4)	36011(65)	33652(89)	33110(66)	435(35)
C(5)	40807(63)	31558(110)	16401(64)	534(40)
C(6)	45666(51)	13233(90)	27664(68)	383(33)
C(7)	4154(56)	−14728(90)	29112(62)	390(32)
C(8)	8931(68)	−33699(96)	18767(69)	499(38)
C(9)	14336(62)	−34184(79)	35665(66)	422(34)
C(10)	30676(59)	−36194(83)	18989(59)	383(32)
C(11)	36162(62)	−12007(86)	18610(57)	335(31)
C(12)	23641(65)	−19387(98)	7295(61)	423(37)
C(13)	15033(62)	−4157(82)	45721(57)	348(30)
C(14)	11831(42)	15005(69)	41983(43)	227(23)
C(15)	13295(51)	24831(77)	37521(49)	309(27)
C(16)	9391(62)	34708(84)	38894(61)	429(35)
C(17)	3610(70)	35378(99)	44717(72)	557(42)
C(18)	2386(70)	26083(112)	49220(67)	564(43)
C(19)	6275(51)	15723(80)	47996(51)	332(28)
C(20)	34856(56)	5305(78)	45348(61)	332(29)
C(21)	37805(46)	−14328(70)	42949(46)	259(25)
C(22)	43070(52)	−14500(77)	49393(49)	286(27)
C(23)	46740(56)	−24370(84)	51664(54)	399(31)
C(24)	45422(68)	−34279(94)	47853(71)	526(40)
C(25)	40184(65)	−34574(86)	41548(68)	514(39)
C(26)	36313(56)	−24822(78)	39105(53)	346(29)

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

The overall molecular structure of **4** consists of a central thorium atom coordinated in a distorted tetrahedral fashion by the four nitrogen atoms of two bis(trimethylsilyl)amide and two *N*-methylanilide ligands. No significant difference is observed in Th−N distances between the Th−$N(SiMe_3)_2$ and Th−NMePh groups, the average value being 2.308(7) Å. This value is comparable with the average Th−N distances of 2.34(1) Å in $(\eta\text{-}C_8H_8)Th[N(SiMe_3)_2]_2$[6] and 2.32(2) Å in $(\eta^3\text{-}BH_4)Th[N(SiMe_3)_2]_3$,[7a] while being significantly shorter than the Th−N distance of 2.46(1) Å (average) in $(\eta\text{-}C_5Me_5)_2ThCl[NHC(Me)NC(Me)CHCN]$.[9] N−Th−N angles about thorium are generally close to the 109.5° value for an ideal tetrahedron, with the exception of the N(1)−Th(1)−N(2) angle, which is opened out to 121.9(2)°, and the N(3)−Th(1)−N(4) angle, which is 92.2-

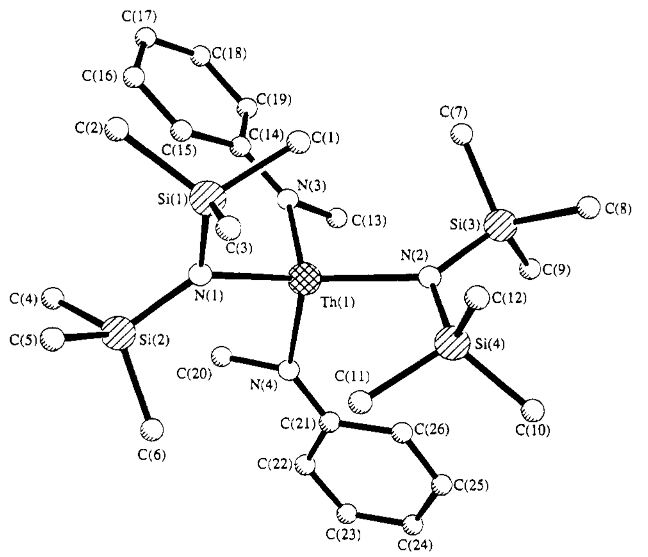

Figure 1. Ball and stick drawing of the solid state structure of Th[$N(SiMe_3)_2]_2(NMePh)_2$ (**4**) giving the atom-numbering scheme used in the tables.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $Th[N(SiMe_3)_2]_2(NMePh)_2$ (**4**)

Th(1)−N(1)	2.328(6)	Th(1)−N(2)	2.299(6)
Th(1)−N(3)	2.304(6)	Th(1)−N(4)	2.299(7)
Th(1)−C(13)	3.073(10)	Th(1)−C(20)	3.064(10)
Th(1)-Si(1)	3.381(2)	Th(1)-Si(4)	3.368(2)
Si(1)−N(1)	1.742(7)	Si(2)−N(1)	1.739(7)
Si(4)−N(2)	1.745(6)	Si(3)−N(2)	1.752(6)
N(3)−C(13)	1.460(12)	N(4)−C(20)	1.473(12)
N(3)−C(14)	1.388(10)	N(4)−C(21)	1.376(11)

N(1)−Th(1)−N(2)	121.9(2)	N(2)−Th(1)−N(3)	110.0(2)
N(1)−Th(1)−N(3)	110.1(2)	N(2)−Th(1)−N(4)	108.9(2)
N(1)−Th(1)−N(4)	109.7(2)	N(3)−Th(1)−N(4)	92.2(2)
N(1)−Si(1)−C(1)	106.0(4)	N(1)−Si(1)−C(2)	114.1(4)
N(1)−Si(1)−C(3)	113.9(4)	N(1)−Si(2)−C(4)	109.7(4)
N(1)−Si(2)−C(5)	115.1(4)	N(1)−Si(2)−C(6)	108.6(4)
N(2)−Si(4)−C(10)	113.8(4)	N(2)−Si(4)−C(11)	106.2(4)
N(2)−Si(4)−C(12)	113.6(4)	N(2)−Si(3)−C(7)	108.4(4)
N(2)−Si(3)−C(8)	113.9(4)	N(2)−Si(3)−C(9)	110.6(4)
Th(1)−N(1)−Si(1)	111.5(3)	Si(1)−N(1)−Si(2)	121.0(4)
Th(1)−N(1)−Si(2)	127.4(3)	Th(1)−N(2)−Si(3)	127.2(3)
Th(1)−N(2)−Si(4)	112.0(3)	Th(1)−N(3)−C(13)	107.3(5)
Si(4)−N(2)−Si(3)	120.7(4)	Th(1)−N(3)−C(14)	136.4(5)
Th(1)−N(4)−C(21)	137.1(5)	Th(1)−N(4)−C(20)	106.6(5)

(2)°. One noticeable feature of the structure is the relatively close approach to the metal center of the methyl groups within the *N*-methylanilide ligands. Th−C distances to these methyl groups are 3.073(10) Å in the case of C(13) and 3.064(10) Å for C(20). These Th−C distances may be compared with those of 3.09(2) Å in the uranium(III) alkyl $U[CH(SiMe_3)_2]_3$, for which a γ-agostic interaction was proposed.[10] The extent to which these methyl groups interact with the metal center is apparent from a study of the Th−N−C bond angles within the *N*-methylanilide groups. Thus the Th(1)−N(3)−C(14) and Th(1)−N(4)−C(21) angles (to the *ipso* phenyl carbon atoms) are 136.4(5) and 137.1(5)°, respectively, while the Th(1)−N(3)−C(13) and Th(1)−N(4)−C(20) (methyl carbon) angles are only 107.3(5) and 106.6(5)°, respectively. We do note, however, that since the methyl groups of these amide ligands have a smaller steric requirement than the phenyl groups, the dissimilarity in Th−N−C angles may be explained partly by steric arguments. The shortest Th−C distances to methyl groups within the bis(trimethylsilyl)amide ligands are 3.152(10) Å to C(1) and 3.160(10) Å to C(11). The closest approaches of any of the located and refined hydrogen atoms to the metal center are 2.959 Å in the case of H(13C) and 2.948 Å for H(20B).

There are now a number of examples in the literature of lanthanide and actinide complexes for which solid state agostic interactions have been proposed between the metal center and either a trimethylsilyl group of an amide $[N(SiMe_3)_2]$ or alkyl $[CH(SiMe_3)_2]$ ligand[11−14] or the methylene group of a neopentoxide ligand.[2g] Such γ-agostic or β-methyl interactions between trimethylsilyl groups and f-block metals were recently the subject of a detailed study by Schaverien.[15]

Concluding Remarks

The four new complexes described here expand considerably upon the few examples of well-characterized thorium amido compounds previously described in the literature. A number of workers have prepared bis(trimethylsilyl)amide derivatives of thorium,[3,6,7,16,17] while the only known examples of dialkylamide complexes are the homoleptic species $Th(NR_2)_4$ (R = Et,[18] *n*-Pr,[19] *n*-Bu[19]) and some cyclopentadienyl derivatives.[20]

The isolation of the mono-THF adduct $Th(NPh_2)_4(THF)$ (**1**) supports the recent findings of Van der Sluys *et al.* concerning the reactivity of the uranium(IV) diphenylamido complex $U(NPh_2)_4$ toward Lewis bases.[21] This study concluded that while the formation of the mono-THF adduct $U(NPh_2)_4(THF)$ does take place in solution, the preponderance of evidence suggests that a bis-THF adduct does not form. In contrast, Watt[18] and Edelstein[19] have reported the isolation of base-free tetrakis(dialkylamido) complexes of thorium containing sterically nondemanding ligands such as NEt_2 and N-*n*-Bu_2, despite the fact that the preparations were carried out in a coordinating solvent (diethyl ether). In these cases, however, the products were sublimed under high vacuum at *ca.* 100 °C, and presumably any coordinated ether was lost during this process.

Although the solid state structure of the mono-THF adduct $Th(NPh_2)_4(THF)$ (**1**) could not be determined by an X-ray crystallographic study, we tentatively propose a trigonal bipyramidal geometry with the THF ligand occupying an axial site, by analogy with the five-coordinate thorium alkoxide complex Th(OCH-*i*-$Pr_2)_4$(quin) (quin = quinuclidine),[22] which has been structurally characterized. Similarly, an analogy may be drawn between the bis-THF adduct $Th(NMePh)_4(THF)_2$ (**2**) and the structurally characterized alkoxide complexes $Th(OR)_4(py)_2$ (R = *t*-Bu,[2f] 2,6-$Me_2C_6H_3$[2e]) and ThI(OCH-*i*-$Pr_2)_3(py)_2$.[22] In all

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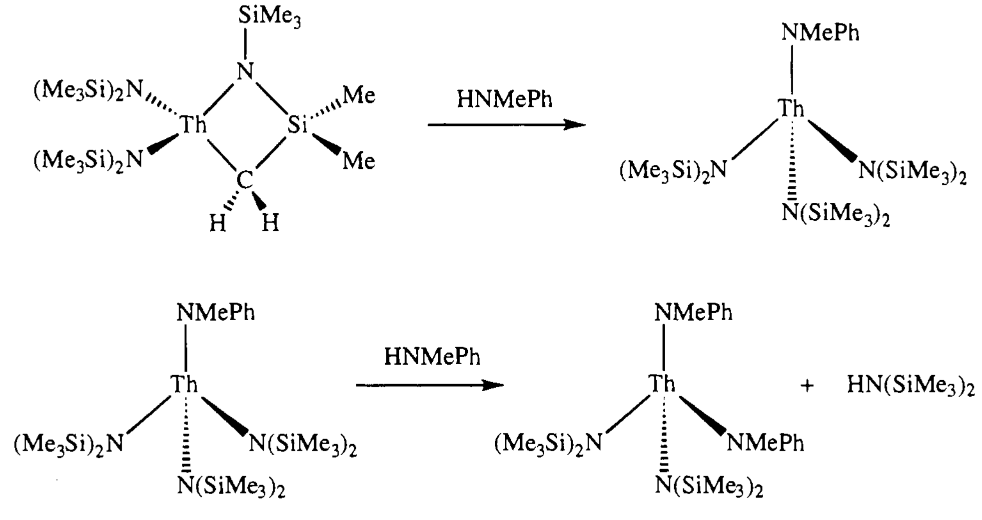
Scheme 1



(4)

cases, the alkoxide species adopt a pseudooctahedral geometry with pyridine ligands assuming a *cis* orientation.

In the case of K[Th(NMePh)$_5$] (**3**), the absence of THF in the coordination sphere of either thorium or potassium leads to a question as to the nature of the coordination environment of the potassium cation. For example, reaction of UI$_3$(THF)$_4$ with 5 equiv of potassium 2,6-diisopropylanilide leads to the formation of the salt [K(THF)$_2$]$_2$[U(NH-2,6-*i*-Pr$_2$C$_6$H$_3$)$_5$], in which each potassium cation is coordinated by two THF ligands as well as interacting in an η^6-fashion with the arene rings of two amido groups.[23] We have also observed potassium cations interacting *exclusively* with arene rings in the solid state structures of K[Ln(O-2,6-*i*-Pr$_2$C$_6$H$_3$)$_4$] (Ln = La, Nd, Sm, Er),[2d,24] despite the preparative reactions being carried out in THF. Thus we speculate that the solid state structure of **3** may contain potassium cations coordinated primarily by π-arene interactions with the NMePh ligands.

The X-ray crystallographic study of Th[N(SiMe$_3$)$_2$]$_2$(NMePh)$_2$ (**4**), described above, provides the first structural data for a thorium metal center within a four-coordinate all-nitrogen environment and is also, somewhat surprisingly, the first solid state structure of a thorium complex which contains alkylamide, as opposed to bis(trimethylsilyl)amide, ligands.[9] The only other structurally characterized example of an actinide metal bound only by four nitrogen atoms is provided by U(NPh$_2$)$_4$.[5d] Additional structural data for thorium in all-nitrogen coordination environments are found for the octakis(thiocyanato)thorium complex [NEt$_4$]$_4$[Th(NCS)$_8$][25] and for bis(phthalocyanine) and bis(tetraphenylporphyrin) compounds.[26–29] Despite the fact that a solid state agostic interaction was suggested by the relatively short Th–C(13) and Th–C(20) distances in **4**, no spectroscopic evidence could be obtained to support the preservation of this structure in solution. Thus the observation of *solution* spectroscopic evidence for f-element agostic interactions is still extremely rare.[2g]

On the basis of previous experimental observations with alcohol and thiol reagents,[2e,14] we propose that the formation of Th[N(SiMe$_3$)$_2$]$_2$(NMePh)$_2$ (**4**) occurs *via* the stepwise protonation sequence shown in Scheme 1. The thorium–carbon bond in $\{[(Me_3Si)_2N]_2\overline{Th(CH_2SiMe_2N}SiMe_3)\}$ would be expected to be the initial site for protonation, to produce the intermediate Th[N(SiMe$_3$)$_2$]$_3$(NMePh). Protonation by a further equivalent of HNMePh then yields **4** plus an equivalent of hexamethyldisilazane.

Reactivity studies of the new complexes are currently in progress.

Experimental Details

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)$_4$[2c] and {[(Me$_3$Si)$_2$N]$_2$Th(CH$_2$SiMe$_2$NSiMe$_3$)}[3,7b,c] were prepared as described previously.[2e] Diphenylamine was purchased from Aldrich and used without further purification. *N*-Methylaniline was purchased from Aldrich and degassed prior to use. Potassium amide salts (KNPh$_2$ and KNMePh) were prepared by refluxing HNPh$_2$ and HNMePh, respectively, with potassium hydride in toluene for 48 h. Solvents were degassed and distilled from Na/K alloy under nitrogen. Benzene-*d*$_6$ and THF-*d*$_8$ were degassed, dried over Na/K alloy, and then trap-to-trap distilled before use. Solvents were taken into the glovebox and small amounts tested with a solution of sodium benzophenone in THF. Solvents that failed to maintain a purple coloration from this test were not used.

NMR spectra were recorded at 22 °C on a Bruker AF 250 or WM 300 spectrometer in benzene-*d*$_6$ or THF-*d*$_8$. All ^{1}H NMR chemical shifts are reported in ppm relative to the ^{1}H impurity in benzene-*d*$_6$ or THF-*d*$_8$ set at δ 7.15 or 1.73, respectively. Infrared spectra were recorded on a Perkin-Elmer 1500 spectrophotometer interfaced with a 1502 Central Processor, 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.

Syntheses. Th(NPh$_2$)$_4$(THF) (1). In the drybox, 2.18 g (2.60 mmol) of ThBr$_4$(THF)$_4$ was dissolved in 50 mL of THF and then 2.05 g (10.4 mmol) of solid potassium diphenylamide added over a period of 5 min. A white precipitate formed as the addition took place. After being stirred at room temperature for 24 h, the suspension was filtered through Celite to give a clear, colorless filtrate. All solvent was removed *in vacuo* and the white solid residue dissolved in 50 mL of

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toluene. The solution was filtered through Celite and all solvent removed to leave a white powder, which was washed with hexane (10 mL) and hexane/toluene (1:1, 10 mL). Yield: 1.79 g (70%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.03 (m, 4 H, meta NPh_2), 6.91 (m, 4 H, ortho NPh_2), 6.73 (t, $J = 8$ Hz, 2 H, para NPh_2), 3.53 (m, 1 H, α-THF), 1.06 (m, 1 H, β-THF). IR (Nujol, cm^{-1}): 1582 (m), 1565 (m), 1460 (s), 1378 (s), 1279 (m), 1254 (m), 1186 (m), 1073 (w), 840 (m), 746 (m), 699 (m), 493 (s). Anal. Calcd for $C_{52}H_{48}N_4OTh$: C, 63.93; H, 4.95; N, 5.73. Found: C, 64.69; H, 5.21; N, 5.78.

$Th(NMePh)_4(THF)_2$ (2). In the drybox, 2.00 g (2.38 mmol) of $ThBr_4(THF)_4$ was dissolved in 50 mL of THF and then 1.20 g (8.26 mmol) of solid potassium *N*-methylanilide added over a period of 5 min to produce an off-white precipitate. This suspension was stirred at room temperature for 18 h before being filtered through Celite to give a clear, pale yellow filtrate. All solvent was removed *in vacuo* to leave an off-white solid residue which was dissolved in 25 mL of toluene. The solution was filtered through Celite, and the filtrate was cooled to −40 °C, resulting in colorless crystals, which were isolated by filtration. Yield: 0.25 g (15%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.21 (m, 2 H, meta Ph), 7.01 (m, 2 H, ortho Ph), 6.76 (t, $J = 6$ Hz, 1 H, para Ph), 3.59 (m, 2 H, α-THF), 3.05 (s, 3 H, Me), 1.00 (m, 2 H, β-THF). IR (Nujol, cm^{-1}): 1590 (s), 1565 (m), 1343 (w), 1299 (s), 1261 (s), 1185 (m), 1155 (m), 1079 (w), 1036 (w), 1016 (w), 980 (s), 829 (m), 802 (s), 755 (s), 723 (m), 691 (s), 621 (m), 612 (m), 524 (w). Anal. Calcd for $C_{36}H_{48}N_4O_2Th$: C, 53.99; H, 6.04; N, 7.00. Found: C, 55.14; H, 6.23; N, 7.58.

$KTh(NMePh)_5$ (3). In the drybox, 1.12 g (1.33 mmol) of $ThBr_4(THF)_4$ was dissolved in 40 mL of THF and then 0.97 g (6.69 mmol) of solid potassium *N*-methylanilide was added over a period of 5 min to produce an off-white precipitate. This suspension was stirred at room temperature for 18 h before being filtered through Celite to give a clear, pale yellow filtrate. Toluene (20 mL) was added to the flask, resulting in precipitation of a white powder which was isolated by filtration. Yield: 0.90 g (84%). ^{1}H NMR (300 MHz, C_4D_8O): δ 6.86 (m, 2 H, meta Ph), 6.71 (m, 2 H, ortho Ph), 6.24 (t, $J = 7$ Hz, 1 H, para Ph), 2.82 (s, 3 H, Me). IR (Nujol, cm^{-1}): 1566 (m), 1548 (m), 1311 (w), 1294 (w), 1260 (m), 1188 (w), 1155 (m), 1078 (w), 1038 (w), 980 (s), 760 (s), 690 (s), 618 (m), 595 (m), 522 (w). Anal. Calcd for $C_{35}H_{40}N_5KTh$: C, 52.43; H, 5.03; N, 8.73. Found: C, 52.42; H, 5.09; N, 7.92.

$Th[N(SiMe_3)_2]_2(NMePh)_2$ (4). To a Schlenk vessel containing a solution of 0.68 g (0.96 mmol) of $\{[(Me_3Si)_2N]_2\overline{Th(CH_2SiMe_2N}SiMe_3)\}$ in 30 mL of toluene was added 0.41 g (3.83 mmol) of *N*-methylaniline. The vessel was attached to a reflux condenser, and the contents were allowed to reflux under argon for 18 h. After the mixture was cooled to room temperature, all solvent was removed *in vacuo* to leave a sticky pale yellow solid. The residue was washed with 10 mL of hexane and then dissolved in 20 mL of toluene. The solution was concentrated to 3 mL and cooled to −40 °C, resulting in colorless crystals. A second crop was collected after concentrating and cooling. Yield: 0.088 g (12%). ^{1}H NMR (300 MHz, C_6D_6): δ 7.28 (t, $J = 8$ Hz, 2 H, meta Ph), 6.94 (d, $J = 7$ Hz, 2 H, ortho Ph), 6.78 (t, $J = 7$ Hz, 1 H, para Ph), 2.92 (s, 3 H, Me), 0.32 (s, 18 H, Si*Me*$_3$). IR (Nujol, cm^{-1}): 1590 (s), 1568 (m), 1495 (s), 1302 (s), 1270 (s), 1246 (s), 1185 (w), 1160 (w), 1039 (w), 1017 (m), 985 (m), 930 (s), 874 (m), 834 (s), 803 (s), 774 (m), 751 (s), 690 (m), 654 (m), 606 (s), 516 (w). Anal. Calcd for $C_{26}H_{52}N_4Si_4Th$: C, 40.82; H, 6.85; N, 7.32. Found: C, 40.98; H, 6.72; N, 6.89.

Crystallographic Studies. A small pale yellow block measuring 0.2 × 0.2 × 0.25 mm was selected under a microscope using an argon purge. It was affixed to the end of a glass fiber using silicone grease and transferred to the goniometer head of a Siemens R3m/V diffractometer with graphite-monochromated Mo Kα radiation, where it was cooled to −70 °C for characterization and data collection. Unit cell parameters were determined from the least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 50 accurately centered reflections. Two reflections were chosen as intensity standards and were measured every 7200 s of X-ray exposure time, and two orientation controls were measured every 250 reflections.

The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction based on azimuthal scans was applied. The structure was readily solved by Patterson methods and subsequent difference Fourier maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in difference maps and refined positionally using fixed isotropic temperature factors. Final refinement using 4867 unique observed $[F > 4.0\sigma(F)]$ reflections converged at $R = 0.0378$, $R_w = 0.0391$ $\{$where $w = [\sigma^2(F) + 0.0001(F)^2]^{-1}\}$. All calculations were performed using the SHELXTL PLUS suite of computer programs (Siemens Analytical X-ray Instruments, Inc, 1990). A final difference Fourier map was essentially featureless, with the largest peak being of magnitude 0.91 e/Å^3.

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Supplementary Material Available: Tables of fractional coordinates and isotropic thermal parameters, bond distances, bond angles, and anisotropic thermal parameters for **4** (5 pages). Ordering information is given on any current masthead page.

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