Extremely Stable Thorium(IV) Dialkyl Complexes Supported by Rigid Tridentate 4,5-Bis(anilido)xanthene and 2,6-Bis(anilidomethyl)pyridine Ligands

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A new NON-donor ligand, 4,5-bis(2,6-diisopropylanilino)-2,7-di-*tert*-butyl-9,9-dimethylxanthene (H_2-[XA_2], **1**), was prepared by palladium-catalyzed coupling of 2,6-diisopropylaniline with the appropriate dibromoxanthene precursor. Stable $K_2(dme)_2[XA_2]$ (**2**) and $Na_2[XA_2]$ (**3**) salts were accessible by deprotonation of $H_2[XA_2]$ with KH in dme or NaH in toluene. The thermally unstable lithium salt of McConville's 2,6-bis(2,6-diisopropylanilidomethyl)pyridine ligand (Li_2[BDPP], **4**) was isolated by deprotonation with *n*BuLi or $LiCH_2SiMe_3$ in hexanes at low temperature. Reaction of $[ThCl_4(dme)_2]$ with Li_2[BDPP] or $M_2(dme)_n[XA_2]$ resulted in the formation of pentagonal bipyramidal $[LThCl_2(dme)]$ complexes (L = BDPP, **5**; XA_2, **6**). Subsequent reaction of **5** or **6** with $LiCH_2SiMe_3$ gave base- and salt-free dialkyl complexes, $[LTh(CH_2SiMe_3)_2]$ (L = BDPP, **7**; XA_2, **8**), which are stable for days in solution at 90 and 70 °C, respectively. Complexes **5**, **7**, and **8** were also accessible by initial combination of 2 or 4 equiv of $LiCH_2SiMe_3$ with $[ThCl_4(dme)_2]$, followed by addition of H_2L. These reactions likely proceed by alkane elimination, but dialkyl or tetraalkyl thorium intermediates were not identified. The X-ray crystal structure of **8** suggests the presence of α-agostic C−H−Th interactions for both alkyl groups. In solution, **7** and **8** exhibit temperature-dependent $^1J_{C,H}$ coupling constants for Th*CH*$_2$, demonstrating the presence of α-agostic interactions which become increasingly favored at lower temperature. Reaction of **5** with Li_2[BDPP] at 0 °C or **7** with H_2[BDPP] at 100 °C resulted in the formation of extremely sterically encumbered $[Th(BDPP)_2]$ (**9**), which adopts a highly distorted six-coordinate geometry with the four anilido groups arranged in an approximate tetrahedron around thorium. Bis-ligand complexes were not accessible with the XA_2 platform, presumably due to increased ligand rigidity.

Introduction

Complexes of the early actinide elements, of which only thorium and uranium are naturally abundant and readily available, are unique due to the potential for significant covalency and f-orbital involvement in bonding.[1,2] Actinides also tend to form complexes of high Lewis acidity and possess ionic radii that are similar or larger than those of the lanthanide ions and significantly larger than those for transition metals in the same oxidation state.[3] These properties, in addition to the distinctly non-lanthanide-like variety of oxidation states accessible for several of the early actinides (e.g., U(III)−U(VI)],[1,4] lead to the potential for early actinide complexes to facilitate unusual reactivity[5] that may not be accessible elsewhere in the periodic table.

To date, organoactinide chemistry has been dominated by the use of carbocyclic ancillaries such as C_5R_5 and related ligands,[6,7] the tetramethylphospholyl anion,[8] dianionic C_8R_8 or pentalene[9] ligands, carboranes,[10] arenes,[11] and the cycloheptatrienyl trianion.[12] In contrast, the chemistry of non-carbocycle-supported organoactinide complexes is much less developed, but is of great interest due to the enormous structural and electronic versatility afforded by such ligands.

Non-cyclopentadienyl actinide(IV) bis-hydrocarbyl (alkyl, aryl, or allyl) complexes are particularly rare and generally rely on the coordination of monoanionic ancillaries such as alkoxy/aryloxy (Th/U),[13−15] amidinate (U),[16] and tris(pyrazolyl)borate (U)[17] ligands. Other ancillaries such as the popular β-diketiminato anion[18] have not been reported to be effective in the

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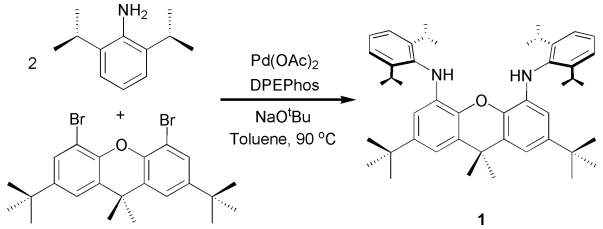
preparation of actinide(IV) dialkyls,[19−21] perhaps due to provision of insufficient electronic saturation, a relatively small metal binding pocket, and a tendency toward ligand degradation reactions[19] under a variety of conditions.[22] The only dialkyl actinide(IV) complexes bearing a single dianionic, non-carbocyclic supporting ligand are [(^{DIPP}NCOCN)U(CH_2SiMe_3)$_2$] and [(^{tBu}NON)M(R)$_2$] (M = Th or U; R = C_3H_5 or CH_2SiMe_3) reported very recently by Leznoff [^{DIPP}NCOCN = O(CH_2CH_2-NAr)$_2$; ^{tBu}NON = O($SiMe_2N$*t*Bu)$_2$; Ar = 2,6-diisopropylphenyl].[23,24]

Scheme 1. Synthesis of Proligand H_2XA_2 (1)



We are interested in the preparation of non-carbocyclic organoactinide complexes as a result of their largely untapped potential in both traditional organometallic catalysis and the development of novel reactivity. Of particular interest are thorium(IV) dialkyl complexes of sufficient thermal stability to allow investigation of reactivity over a wide temperature range and to serve as precursors for the synthesis of new, highly reactive organometallic derivatives. With this goal in mind, we have focused our efforts on the use of *extremely rigid and planar* tridentate ancillary ligands, and in particular those that provide a binding pocket of a suitable size to accommodate a large actinide metal and contain only robust structural elements (e.g., avoidance of isolated imine groups).[25,26]

Our preference for rigid ligands stems from the expectation that they will (a) allow access to coordination environments that are dictated by design rather than the preferences of the central metal and/or coligands and (b) ensure that well-intentioned steric bulk is not positioned in such a way as to significantly limit its effectiveness. As a result, various modes of decomposition are expected to become less favorable, especially those involving sterically hindered transition states or the formation of dinuclear or bis-ligand complexes. Rigid ligands are also expected to be more amenable to steric tuning since the effects of steric bulk are not easily mitigated by alterations in the ligand geometry or hapticity and are, therefore, more predictable.

Herein we report the preparation of uniquely robust base- and salt-free thorium(IV) dialkyls, as well as dichloro and bis-ligand complexes, using the 2,6-bis(2,6-diisopropylanilidomethyl)pyridine dianion (BDPP, Scheme 1) and a new, extremely rigid and planar NON-donor, 4,5-bis(2,6-diisopropylanilido)-2,7-di-*tert*-butyl-9,9-dimethylxanthene (XA_2, Scheme 2).

Results and Discussion

Ligand Synthesis. The new NON-donor proligand $H_2[XA_2]$ (**1**) was synthesized in 86% isolated yield by Hartwig−

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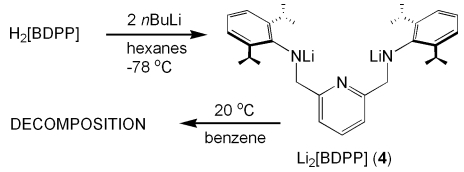
Scheme 2. Preparation and Thermal Stability of 4



Buchwald coupling of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene with 2,6-diisopropylaniline (Scheme 1). Stirring $H_2[XA_2]$ with excess KH in 1,2-dimethoxyethane (dme) at room temperature for 5 h gave base-stabilized $K_2(dme)_2[XA_2]$ (**2**) in 81% yield. Alternatively, base-free $Na_2[XA_2]$ (**3**) is accessible by refluxing $H_2[XA_2]$ with excess NaH in toluene for several days.

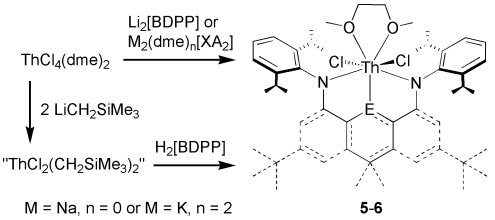
The NNN-donor ligand H_2[BDPP] was prepared as reported by McConville et al. This ligand has previously been employed in titanium, zirconium, and tantalum chemistry, using amine (H_2[BDPP] + [$M(NR_2)_n$]) or chlorotrimethylsilane (BDPP-$(SiMe_3)_2$ + [MCl_n]) elimination to effect ligand attachment.[27−29] An alkali or alkaline earth metal salt of the BDPP dianion, which would allow direct access to chloro complexes by salt metathesis, has not been reported. However, we found that reaction of H_2[BDPP] with 2 equiv of an alkyl lithium reagent ($LiCH_2SiMe_3$ or *n*BuLi) in hexanes at −78 °C resulted in precipitation of base-free Li_2[BDPP] (**4**), which is isolated in 87% yield as a bright yellow solid (Scheme 2). This compound is unusually temperature sensitive, decomposing in minutes in benzene at room temperature.[30] Solid **4** is also significantly decomposed after several hours at room temperature, but can be stored for weeks without appreciable decomposition at −30 °C.

Both the BDPP and XA_2 ligands are structurally related to the diamidoamine ligand $[(Me_3SiN(CH_2CH_2NSiMe_3)_2]^{2-}$ previously employed by Cloke et al. for the synthesis of dichloro and bis(ligand) thorium(IV) complexes.[31] However, the rigidity of the ligand backbone increases dramatically in the order $[(Me_3SiN(CH_2CH_2NSiMe_3)_2]^{2-}$ < BDPP < XA_2.

Dichloride Complexes. Reaction of 1 equiv of Li_2[BDPP] (**4**) with [$ThCl_4(dme)_2$] in benzene[30] at 0 °C gave [(BDPP)-$ThCl_2$(dme)] (**5**) in 51% yield. Similarly, [$(XA_2)ThCl_2$(dme)] (**6**) was isolated by reaction of $Na_2[XA_2]$ (**3**) with [$ThCl_4(dme)_2$] in toluene at room temperature (69% yield; Scheme 3). In contrast, base-coordinated $K_2(dme)_2[XA_2]$ (**2**) is considerably less reactive than **3**, despite similar solubilities (of **2** and **3** in C_6H_6 or C_7H_8), and the reaction is complete only after refluxing in toluene for 12 h.

Complex **5** could also be prepared by reaction of 2 equiv of $LiCH_2SiMe_3$ with [$ThCl_4(dme)_2$] for 1 h at 0 °C, followed by cooling to −78 °C and addition of H_2BDPP. In this case, ligand attachment likely proceeds by alkane elimination from a source of "$ThCl_2(CH_2SiMe_3)_2$". However, the reaction of $LiCH_2SiMe_3$ with [$ThCl_4(dme)_2$] forms a mixture of products, the nature of which has not been determined (Scheme 3). Nevertheless, this is the preferred route for the synthesis of **5** due to greater simplicity and an improved yield (85%). By contrast, attempts to prepare **6** by this method gave solutions containing $H_2[XA_2]$ and $SiMe_4$ as the only soluble products, presumably due to thermal decomposition of the alkyl thorium precursor in preference to reaction with the rigid $H_2[XA_2]$ proligand.

Scheme 3. Synthesis of Dichloro Complexes 5 and 6



^{1}H NMR spectra of **5** and **6** between 20 and −90 °C show the presence of one molecule of symmetrically coordinated dme and a lone C*H*Me_2 signal, consistent with C_{2v} symmetric pentagonal bipyramidal products. Single crystals of [(BDPP)-$ThCl_2(\kappa^2$-dme)]·2toluene were grown by slow diffusion of hexanes into a toluene solution of **5** at −30 °C. The X-ray crystal structure of **5** (Figure 1, Table 1) confirms a distorted pentagonal bipyramidal geometry with the two chloride anions occupying apical positions [Cl(1)−Th−Cl(2) = 156.38(10)°; Th−Cl = 2.698(3) and 2.686(3) Å]. As anticipated, the BDPP ligand is approximately planar and binds thorium via short $Th-N_{anilido}$ contacts [2.305(9) and 2.321(8) Å] and a longer $Th-N_{py}$ bond [2.568(9) Å]. However, while N(1), N(3), O(1), O(2), and Th lie in a plane, the metal is located 0.33(1) Å above the N(1)−N(2)−N(3) plane of the BDPP ligand. In this way, only one chloro ligand is positioned directly between the bulky isopropyl groups, while the other is located in a more open region of the thorium coordination sphere. To accommodate the more sterically contentious chloride anion, both 2,6-diisopropylphenyl rings rotate to give C(14)···C(26) = 6.35(2) Å and C(17)···C(29) = 7.26(2) Å.

The dme molecule is κ^2-coordinated in the pentagonal plane and is bound via long and unequal Th−O contacts {Th−O(1) = 2.674(8) Å and Th−O(2) = 2.724(8) Å}, likely due to steric pressure at the metal; cf. 2.564(8)−2.620(8) Å in [$ThBr_4(\kappa^2$-dme)$_2$],[32] 2.620(5) Å in [$LTh(NH_2)(\kappa^1$-dme)]$^-$, and 2.613(3) Å in [$LTh(Cl)(\kappa^1$-dme)]$^-$ {L = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenolate)}.[33] In contrast, the $Th-N_{py}$ bond {2.568(9) Å} is atypically short. For example, Th−N is 2.72(1)−2.80(1) Å in [Th(quiolinolate)$_4$(dmf)],[34] 2.730(6) Å in [{$Th(OCHEt_2)_3$-(μ-$OCHEt_2$)(Py)}$_2$], 2.752(7) Å in *cis*-[$Th(OtBu)_4(Py)_2$],[35] and 2.662(8), 2.696(8) Å in *cis*-[$Th(OC_6H_3Me_2$-2,6)$_4(Py)_2$].[36] The only $Th-NC_5R_5$ bonds of comparable length are found in [Th-$(OC_6H_3t$Bu-2,6)$_2$(*C*,*N*-2,6-lutidinyl)$_2$] {2.61(1) Å}[15] and [Th-(BDPP)$_2$] (**9**) {2.615(6) Å, *vide infra*}. The former is a special case since significant delocalization of negative charge to the N-donor can occur. Therefore, the short $Th-N_{py}$ bond lengths observed in this work are likely a result of incorporation of the pyridine unit into a rigid ligand framework and perhaps the

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(30) Li_2[BDPP] (**4**) shows similar thermal stability in both benzene and THF (extensive decomposition in minutes at room temperature) and is considerably less stable in toluene (decomposition occurs rapidly even at −30 °C). The thermal decomposition of **4** in benzene is not clean, and a mixture of unidentified air-sensitive products is formed.

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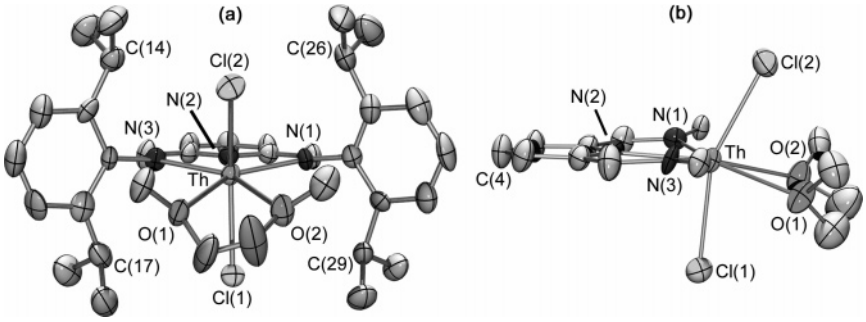


Figure 1. Molecular structure of **5**·2toluene with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent omitted for clarity. In view b, only the N-C_{ipso} carbon atoms of the N-*Aryl* rings are shown.

Table 1. Crystallographic Data Collection and Refinement Parameters and Selected Bond Distances (Å) for Complexes 5, 8, and 9

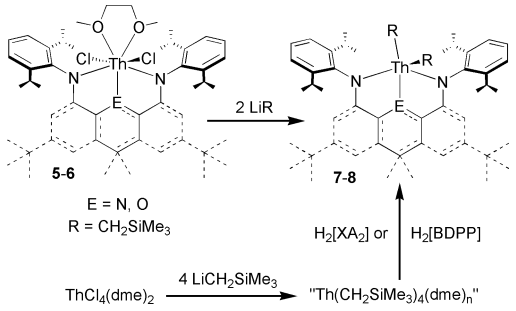
	5·2toluene	**8**·toluene	**9**
formula	$C_{91}H_{126}Cl_4N_6O_4Th_2$	$C_{62}H_{92}N_2OSi_2Th$	$C_{62}H_{82}N_6Th$
fw	1973.86	1169.60	1143.38
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*P*2(1)/*n*	*C*2/*c*
a (Å)	28.7133(8)	16.6445(5)	14.901(15)
b (Å)	15.8253(5)	22.5599(7)	17.895(17)
c (Å)	21.3589(7)	16.8509(5)	21.354(16)
α (deg)	90	90	90
β (deg)	107.398(2)	107.928(2)	106.72(3)
γ (deg)	90	90	90
volume (Å^3)	9261.4(5)	6020.2(3)	5453(9)
Z	4	4	4
density (calcd; mg/m^3)	1.449	1.288	1.393
μ (mm^{-1})	3.374	2.555	2.779
F(000)	4074	2408	2344
cryst size (mm^3)	0.22 × 0.22 × 0.18	0.10 × 0.08 × 0.01	0.12 × 0.10 × 0.03
θ range for collection (deg)	1.49 to 27.54	1.50 to 27.49	1.83 to 25.50
no. of reflns collected	40 216	32 615	20 838
no. of indep reflns	10 567	13 480	5071
completeness to θ_{max}	98.9%	97.5%	100.0%
max. and min. transmn	0.55 and 0.455	0.98 and 0.8200	0.920 and 0.711
GOF on F^2	1.003	1.002	1.100
final R_1 [$I > 2\sigma(I)$][a]	0.0705	0.0570	0.0698
Th−N_{amido}	2.305(9), 2.321(8)	2.291(4), 2.312(4)	2.373(7), 2.488(7)
Th−E (E = N_{py} or O_{xant})[b]	2.568(9)	2.535(4)	2.614(7)
Th−Cl or Th−C	2.686(3), 2.698(3)	2.467(6), 2.484(6)	
Th−O_{dme}	2.674(8), 2.724(8)		

[a] For **5**, **8**, and **9**: T = 173(2) K, wavelength = 0.71073 Å, absorption correction = semiempirical from equivalents, and refinement method = full-matrix least-squares on F^2. [b] E = the central neutral donor of the BDPP and XA_2 ligands.

enhanced donor properties of N_{py} (relative to an unsubstituted pyridine) as a result of 2,6-dialkyl substitution. All other metal−ligand bonds are in the usual range. For comparison, Th−$N_{anilido}$ is 2.327(6)−2.378(7) Å in $[L_2ThCl]^-$ {L = 1,3-bis(2,6-diisopropylanilido)propane}[37] and 2.299(7), 2.304(6) Å in [Th{$N(SiMe_3)_2$}$_2$($NMePh)_2$],[38] while Th−Cl is 2.620(6)−2.697(1) Å in $[L_2ThCl_2]$ {L = Tp, $ArC(NSiMe_3)_2$, and $HC(CPhNSiMe_3)_2$; Ar = $C_6H_2(CF_3)_3$-2,4,6}[20,39] and 2.673(1), 2.721(2) Å in [L′$ThCl_2$(THF)] {L′ = $Me_3SiN(C_2H_4NSiMe_3)_2$}.[31]

Dialkyl Complexes. Reaction of the dichlorides, **5** and **6**, with 2 equiv of $LiCH_2SiMe_3$ gave the base- and salt-free dialkyl complexes [L$Th(CH_2SiMe_3)_2$] {L = BDPP (**7**) and XA_2 (**8**)} in quantitative yield by ^{1}H NMR (68% and 63% isolated yields, respectively). However, a more straightforward route to these complexes involved reaction of $[ThCl_4(dme)_2]$ with 4 equiv of $LiCH_2SiMe_3$ at 0 °C, followed by addition of H_2[BDPP] or H_2-[XA_2]. Using this method, which likely proceeds by alkane elimination[40] from a source of "$Th(CH_2SiMe_3)_4(dme)_n$", tan **7** and white **8** may be isolated in 82% and 49% yield, respectively (Scheme 4).

Scheme 4. Synthesis of Dialkyl Complexes 7 and 8



The initial reaction between $[ThCl_4(dme)_2]$ and $LiCH_2SiMe_3$ proceeds cleanly and reproducibly to form a product or mixture of products giving rise to a single set of O*Me*, O*C*H_2, Si*Me*$_3$,

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(40) Propene elimination from the reaction of $[U(allyl)_4]$ with 2 ROH (R = Et, $CHMe_2$, or CMe_3) has been reported: see ref 14d.

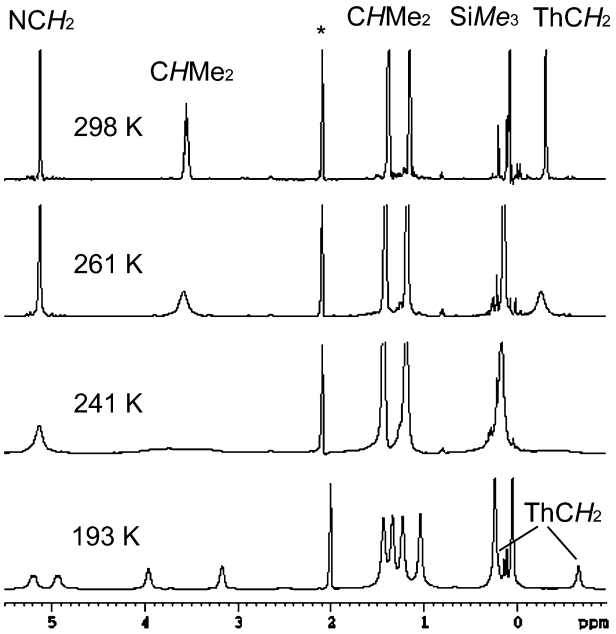

Figure 2. Variable-temperature ^{1}H NMR spectra of **7** in d_8-toluene (* = toluene).

and C*H*$_2$SiMe$_3$ signals in the ^{1}H NMR spectrum at 20 °C, with no change down to −90 °C. Unfortunately, the oily nature and thermal instability (decomposition is complete after 1.5 h at 20 °C) of this material precluded its isolation. However, the formation of a tetraalkyl derivative[41−44] under the conditions described above seems likely given that [Th(CH$_3$)$_4$(dmpe)$_2$],[41] [Th(CH$_2$Ph)$_4$],[44] [Th(CH$_2$C$_6$H$_3$Me$_2$-3,5)$_4$],[43] and [Th(C$_3$H$_5$)$_4$][43] are formed in related reactions of [ThCl$_4$L$_x$] {L$_x$ = (dmpe)$_2$ or (THF)$_3$} with 4 equiv of LiR at temperatures below 0 °C. That said, the involvement of ate-complexes structurally related to [MeTh(μ-Me)$_6${Li(TMEDA)}$_3$][45] and [UR$_6$Li$_2$L$_x$][46] or *in-situ* ligand deprotonation by remaining LiCH$_2$SiMe$_3$ cannot be ruled out.

At 60 °C in d_8-toluene, the ^{1}H and ^{13}C NMR spectra of complexes **7** and **8** exhibit a single set of Th*CH*$_2$ and *CH*Me$_2$ resonances; the Th*CH*$_2$ resonance is located at −0.32 (**7**) or −0.17 (**8**) ppm in the ^{1}H NMR and 89 (**7**) or 97 (**8**) ppm in the ^{13}C NMR. However, upon cooling to −80 °C, the ^{1}H and ^{13}C NMR spectra of both complexes show two distinct CH$_2$SiMe$_3$ groups, two *CH*Me$_2$ signals, and ligand backbone resonances consistent with loss of top-bottom symmetry to give a C_s symmetric product. The Th*CH*$_2$ resonances are located at 0.31 and −0.70 (**7**) or 0.52 and −0.68 (**8**) ppm in the ^{1}H NMR and 78 and 98 (**7**) or 90 and 103 (**8**) ppm in the ^{13}C NMR (Figure 2).

X-ray-quality single crystals of [(XA$_2$)Th(CH$_2$SiMe$_3$)$_2$]·toluene were grown by cooling a saturated toluene solution of **8** from room temperature to −30 °C, and to the best of our knowledge, **8** represents the first structurally characterized thorium dialkyl complex supported by a multidentate noncarbocyclic ancillary. In the solid state (Figure 3, Table 1), **8** is pentacoordinate and adopts a square pyramidal geometry that is strongly distorted in the square plane as a result of XA$_2$ ligand rigidity; the XA$_2$ ligand backbone is approximately planar, but thorium is located 0.475(6) Å above the NON ligand plane. Consistent with the low-temperature ^{1}H and ^{13}C NMR spectra of **8**, the two alkyl groups are distinct; one is located approximately in the NON plane, while the other is located directly above the plane. This arrangement, in conjunction with rotation of the two 2,6-diisopropylphenyl groups to give C(34)···C(44) = 7.514(9) Å and C(30)···C(48) = 4.995(9) Å, is adopted in order to minimize unfavorable steric interactions between metal−alkyl and ligand−isopropyl groups. Similar behavior has been observed in other five-coordinate dialkyl complexes in which a metal is flanked by bulky 2,6-diisopropylphenyl substituents.[26,27,47]

As expected, the Th−N$_{anilido}$ {2.292(4), 2.312(4) Å} bond lengths in **8** are very similar to those observed in complex **5**, and the Th−C {2.468(6), 2.485(6) Å} bond lengths fall within the range observed for the other crystallographically characterized thorium(IV) trimethylsilylmethyl complexes: 2.48(2) and 2.54(2) Å in [{Me$_2$Si(C$_5$Me$_4$)$_2$}ThR$_2$],[48] 2.47(3) Å in [Cp*$_2$Th(CH$_2$*t*Bu)R],[49] 2.438(16) and 2.485(18) Å in [(2,6-*t*Bu$_2$H$_3$C$_6$O)$_2$ThR$_2$],[13] and 2.488(2) and 2.460(9) Å in [Cp*(2,6-*t*Bu$_2$H$_3$C$_6$O)ThR$_2$][50] (R = CH$_2$SiMe$_3$). Structurally characterized thorium diaryl ether or even aryl ether complexes have not previously been reported. However, the Th−O bond length in **8** {2.534(3) Å} is similar to those observed for coordinated dme {2.564(8)−2.620(8) Å}[32,33] or THF {e.g., 2.53(1), 2.58(1) Å in [(COT)ThCl$_2$(THF)][51] and 2.520(7), 2.526(7) Å in [Cp*$_2$Th(NXyl)(THF)][52]}. This is perhaps surprising since a diaryl ether should be a considerably less effective donor than dme or THF. However, a short bond between thorium and the neutral donor of the ligand backbone was also observed in **5**, and this feature is likely a consequence of tridentate binding and BDPP and XA$_2$ ligand rigidity.

Of particular note are the Th−C−Si bond angles in **8** {127.6(3)° and 126.8(3)°}, which are both significantly larger than is typically observed for an sp^3-hybridized carbon atom. Similar increases in M−C−Si or M−C−C (M = Th or U) bond angles have been observed in other trimethylsilylmethyl or neopentyl complexes and are attributed to α-agostic C−H−Th interactions.[13,23,48−50] Further evidence for the presence of agostic interactions is provided by a $^1J_{C,H}$ of 102 Hz for the rapidly exchanging *CH*$_2$SiMe$_3$ groups in the ^{1}H-coupled ^{13}C NMR spectrum of **8** in d_8-toluene at 50 °C. This value is significantly lower than typically observed for an sp^3-hybridized carbon atom and compares well with literature values for related complexes: 104 Hz in Leznoff's [(^{t}BuNON)ThR$_2$],[24] 100 Hz in [Cp*(2,6-*t*Bu$_2$H$_3$C$_6$O)ThR$_2$],[50] 99 Hz in [{Me$_2$Si(C$_5$Me$_4$)$_2$}ThR$_2$],[48]

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(52) Straub, T.; Haskel, A.; Neyroud, T. G.; Kapon, M.; Botoshansky, M.; Eisen, M. S. *Organometallics* **2001**, *20*, 5017.

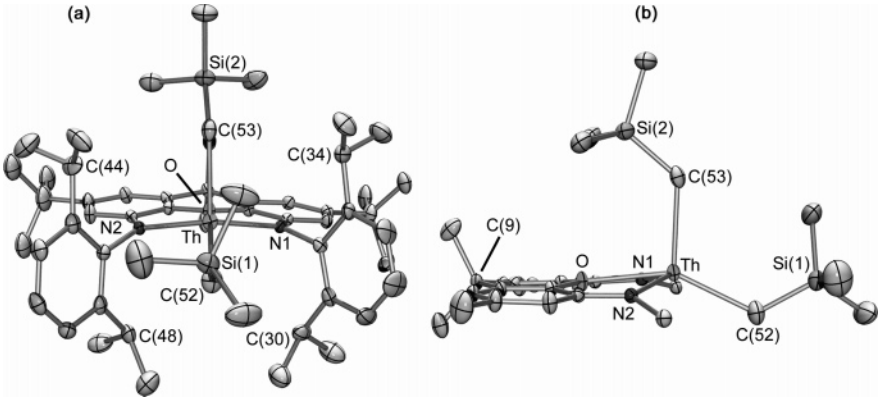

Figure 3. Molecular structure of dialkyl complex **8**·toluene with thermal ellipsoids at the 50% probability level. Hydrogen atoms and solvent omitted for clarity. In view b, C*Me*$_3$ groups have been removed and only the N-C_{ipso} carbon atoms of the N-*Aryl* rings are shown.

and 98 Hz in $[(2,6\text{-}t\text{Bu}_2\text{H}_3\text{C}_6\text{O})_2\text{ThR}_2]$[13] (R = CH_2SiMe_3). A $^1J_{C,H}$ value of 103 Hz is observed for the CH_2SiMe_3 groups in **7** (60 °C, C_7D_8).

Interestingly, upon lowering the temperature to −80 °C, separate $^1J_{C,H}$ coupling constants for each CH_2SiMe_3 group were observed by fully coupled HSQC NMR. These values (88 and 91 Hz for **7** and 81 and 88 Hz for **8**) are considerably reduced relative to those obtained at 60 °C and suggest that for both complexes in solution an equilibrium exists between products participating in α-agostic C−H−Th bonding to a greater or lesser extent (up to four α-agostic C−H−Th interactions[49] could occur in either **7** or **8**) and that entropy favors less agostic products. Consequently, as the temperature is lowered, the equilibrium shifts toward more agostic products, resulting in a decrease in the average $^1J_{C,H}$ coupling constant.[53]

The weak and nonstatic nature of α-agostic interactions has previously been discussed,[49,54] and temperature-dependent $^1J_{E,H}$ coupling constants as a result of an equilibrium between an agostic and a nonagostic isomer have been reported for several related complexes. For example, $^1J_{C,H}$ for α-*CH*R$_2$ in [(κ^3-Tp′)NbCl(cyclopropyl)(C_2Me_2)] varies from 102 Hz at 20 °C to 93 Hz at −80 °C,[55] and $^1J_{Si,H}$ in [$Cp_2Ti(t\text{Bu}C_2SiHMe_2)$] varies from 123 Hz at 30 °C to 93 Hz at −80 °C.[56] A temperature-dependent $^1J_{C,H}$ constant was also observed for α-CH_2Me in [(P_2N_2)Ta(Et)(C_2H_4)] (123 Hz at 77 °C and 134 Hz at −40 °C), but in this case it is due to a greater contribution from a β-agostic structure (versus an α-agostic structure) at lower temperature.[57]

Dialkyl Complex Stability. Both dialkyl complexes exhibit remarkable thermal stability; [(BDPP)Th(CH_2SiMe_3)$_2$] (**7**) is stable for days in toluene at 90 °C and is only fully decomposed after 3 days at 110 °C, while [(XA_2)Th(CH_2SiMe_3)$_2$] (**8**) is stable at 70 °C, but decomposes over several hours at 90 °C. Tetramethylsilane was the only soluble product observed when the thermal decomposition of **7** or **8** was monitored by ^{1}H NMR spectroscopy. The greater stability of **7** could be a result of decreased ligand rigidity, allowing the ligand to form a more optimal metal binding pocket. However, Th−N_{amido} bond lengths in **8** are very similar to those observed in the dichloro BDPP complex (**5**), and in both cases, the ligand is approximately planar. Therefore, the greater stability of **7** is more likely due to improved donor properties of a pyridine versus a diaryl ether neutral donor, leading to increased electronic saturation at the metal center.

The stability of **7** is particularly remarkable and highlights the suitability of rigid tridentate ligands such as BDPP for the stabilization of organoactinide complexes. The thermal stability of most other non-cyclopentadienyl thorium(IV) dialkyl complexes has not been reported. However, for comparison, [Th($OC_6H_3t\text{Bu}_2$-2,6)$_2$(CH_2SiMe_3)$_2$] decomposes over 36 h at 60 °C,[13] [Cp*Th($OC_6H_3t\text{Bu}_2$-2,6)$_2$(CH_2SiMe_3)$_2$] decomposes over 12 h at 60 °C,[50] [Cp*$_2$Th(CH_2SiMe_3)$_2$] decomposes over 36 h at 85 °C,[49] and [{$Me_2Si(C_5Me_4)_2$}Th(CH_2SiMe_3)$_2$] decomposes at 60 °C.[7] In fact, only [Cp*$_2$ThMe$_2$] is of similar thermal stability, being 50% decomposed after 1 week at 100 °C.[58] In addition, while [(C_5R_5)$_2$ThR$_2$] complexes are reported to be extremely air sensitive,[48,59] exposure of toluene solutions of **7** to air for 5 min resulted in only 20−30% decomposition.[60] By contrast, solid samples of **7** and **8** are more sensitive, being entirely decomposed after 5 min of exposure to air.

Bis-ligand Complexes. Addition of 1 equiv of H_2[BDPP] to a solution of [(BDPP)Th(CH_2SiMe_3)$_2$] (**7**) followed by heating to 100 °C for 24 h in a sealed reaction vessel resulted in $SiMe_4$ elimination to form the bis-ligand complex [Th(BDPP)$_2$] (**9**) as a pale greenish-yellow solid in 37% isolated yield (Scheme 5). Alternatively, **9** may be synthesized by addition of benzene[30] to 2 equiv of Li_2[BDPP] (**4**) and [$ThCl_4$(dme)$_2$] at −78 °C followed by warming to room temperature.

Solution NMR spectra of **9** between 20 and −35 °C (d_5-bromobenzene) are consistent with a highly symmetrical product containing a single C*H*Me$_2$ environment. Crystals of **9** suitable for X-ray diffraction were grown by cooling a saturated toluene solution of **9** from room temperature to −30 °C (Figure 4, Table 1). Complex **9** adopts an unusual six-coordinate geometry in which the four amido donors form a distorted tetrahedron around thorium while the pyridine units are directed

(53) An alternative explanation in which the *strength* of E−H−M interactions are strongly affected by temperature has been found not to be responsible for the observed temperature-dependent $^1J_{E,H}$ coupling constants in related Ti and Nb complexes (see ref 56).

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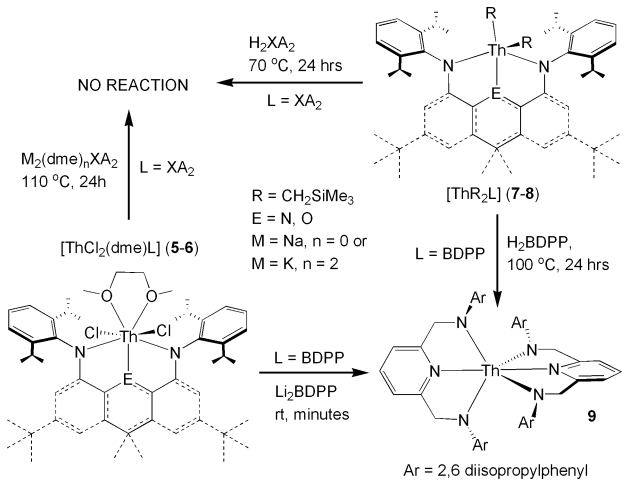
(60) The rate at which benzene solutions of **8** decompose upon exposure to air was not reproducible (25−100% decomposition after 5 min), perhaps as a result of variations in atmospheric humidity.

Scheme 5. Bis-ligand Complex 9 Formation by Salt Metathesis or Alkane Elimination



toward two of the edges (N2···N3 and N2′···N3′) of the tetrahedron but offset toward the center of the two smaller faces (N1 is offset toward the N3, N3′, N2 face, and N1′ is offset toward the, N3, N3′, N2′ face). Above each of the two larger faces (defined by N2, N2′, X, where X = N3 or N3′) of the tetrahedron are located three of the eight isopropyl groups (Figure 4b). In order to adopt such a distorted geometry, the two identical BDPP ligands are considerably twisted away from planarity and the C(4)−N(1)−Th angle is far from linear (165°). This situation likely arises due to severe steric crowding at the metal, resulting in a geometry influenced more strongly by the anionic N_{amido} donors than the neutral pyridine units. Steric pressure at the metal center is also considered to be responsible for the significant difference in Th−$N_{anilido}$ bond lengths {Th−N3 = 2.368(7) Å and Th−N2 = 2.488(6) Å}, as well as Th−$N_{anilido}$ and Th−N_{py} bonds {Th−N_{py} = 2.615(6) Å}, which are considerably longer than those observed in the structures of the dichloro BDPP (**5**) and dialkyl XA_2 (**8**) complexes.

Attempts to prepare the analogous [Th$(XA_2)_2$] complex by either alkane elimination or salt metathesis were unsuccessful: [$(XA_2)ThCl_2$(dme)] (**6**) failed to react with K_2(dme)$_2$[XA_2] (**2**) or Na_2[XA_2] (**3**) at temperatures up to 110 °C, and [(XA_2)Th$(CH_2SiMe_3)_2$] (**8**) did not react with H_2[XA_2] (**1**) at temperatures (≤70 °C) below the onset of thermal decomposition. A lack of reactivity was also observed in attempts to prepare the mixed ligand derivative [Th(BDPP)(XA_2)] by salt metathesis ([Th(BDPP)Cl_2(dme)] + Na_2[XA_2], up to 110 °C) or alkane elimination ([Th(BDPP)$(CH_2SiMe_3)_2$] + H_2[XA_2], up to 110 °C) in toluene. This marked difference in BDPP and XA_2 ligand reactivity presumably stems from the enhanced rigidity of κ^3-coordinated XA_2, which does not permit the type of ligand twisting observed in [Th$(BDPP)_2$] (**9**). As a result, κ^3-*N,O,N*- or even κ^2-*N,N*-donation, which would likely allow the xanthene backbone of XA_2 to adopt a butterfly conformation,[61] must be rendered sterically inaccessible, precluding bis-ligand complex formation.

Summary and Conclusions

A new, extremely rigid and planar NON-donor ligand, H_2-XA_2 (**1**), was prepared and is conveniently deprotonated to form stable disodium or dipotassium salts (**2**, **3**). The thermally unstable dilithium salt of a structurally related 2,6-bis(2,6-diisopropylanilidomethyl)pyridine ligand (Li_2BDPP; **4**) was also isolated, and its availability is expected to extend the utility of this ligand, which until now could only be installed using amine or Me_3SiCl elimination.

For both the BDPP and XA_2 ligands, pentagonal bipyramidal [$LThCl_2$(dme)] (**5**, **6**) and five-coordinate [L Th$(CH_2SiMe_3)_2$] (**7**, **8**) complexes were prepared by either salt metathesis or apparent alkane elimination. Alkane elimination has not previously been employed as a means of primary ancillary ligand attachment in actinide chemistry[40] but has the potential to serve as a valuable tool for the direct synthesis of thorium dichloro and dialkyl complexes, especially when salt metathesis proves ineffective.

Despite a coordination number of only five, complexes **7** and **8** are remarkably robust, showing no sign of decomposition after several days at 90 and 70 °C, respectively. In fact, no other bis-trimethylsilylmethyl or bis-neopentyl thorium complexes, including [Cp^*_2Th$(CH_2EMe_3)_2$] (E = Si or C), have been reported to be of comparable thermal stability to **7**. The availability of **7** and **8** is expected to provide a unique opportunity to study the reactivity and catalytic potential of non-carbocyclic dialkyl and related thorium complexes over a significant temperature range.

The greater stability of **7** is suspected to result from reduced Lewis acidity as a result of the enhanced donor properties of the central pyridine unit in BDPP, relative to the diarylether group of XA_2. However, while the bis-ligand complex [Th(BDPP)$_2$] (**9**) is readily obtained by either alkane elimination or salt metathesis, [Th$(XA_2)_2$] proved inaccessible, likely due to the greater rigidity of XA_2. Since ligand redistribution (to form a complex containing more than one ancillary ligand as well as a more highly alkylated product) is a common decomposition pathway for early transition metal and f-block dialkyl complexes at elevated temperatures,[13,62] the XA_2 ligand represents an important step in the design of ligands suitable for the formation of uniquely robust thorium dialkyls.

Future work will investigate the potential of **7** and **8** and closely related thorium dialkyl complexes in catalysis and as starting materials for the preparation of dihydride complexes and cationic alkyls. Efforts toward a new ligand that combines the rigidity of the XA_2 ligand with the more effective donor properties of BDPP are also underway.

Experimental Section

General Details. An argon-filled MBraun UNIlab glove box was employed for the manipulation and storage of all oxygen- and moisture-sensitive compounds (**2**−**9**), and all thermally unstable compounds were stored in a −30 °C freezer within the glovebox. Reactions were performed on a double-manifold high-vacuum line using standard techniques,[63] and all reaction products were thor-

(61) Xantphos, the neutral 4,5-bis(diphenylphosphino) analogue of XA_2, is typically *cis* κ^2-*P,P*-coordinated with the xanthene backbone adopting a butterfly conformation: Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Acc. Chem. Res.* **2001**, *34*, 895. However, a planar xanthene backbone has been observed in cationic complexes where κ^3-*P,O,P*-coordination is favored: (a) Zuideveld, M. A.; Swennenhuis, B. H. G.; Boele, M. D. K.; Guari, Y.; van Strijdonck, G. P. F.; Reek, J. N. H.; Kamer, P. C. J.; Goubitz, K.; Fraanje, J.; Lutz, M.; Spek, A. L.; van Leeuwen, P. W. N. M. *Dalton Trans.* **2002**, 2308. (b) Sandee, A. J.; van der Veen, L. A.; Reek, J. N. H.; Kamer, P. C. J.; Lutz, M.; Spek, A. L.; van Leeuwen, P. W. N. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3231.

(62) For example: (a) Ernst, R. D.; Kennelly, W. J.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2656. (b) Woodman, T. J.; Schormann, M.; Hughes, D. L.; Bochmann, M. *Organometallics* **2004**, *23*, 2972. (c) Bambirra, S.; Brandsma, M. J. R.; Brussee, E. A. C.; Meetsma, A.; Hessen, B.; Teuben, J. H. *Organometallics* **2000**, *19*, 3197. (d) Emslie, D. J. H.; Piers, W. E.; Parvez, M.; McDonald, R. *Organometallics* **2002**, *21*, 4226. (e) Trifonov, A. A.; Lyubov, D. M.; Fukin, G. K.; Baranov, E. V.; Kurskii, Y. A. *Organometallics* **2006**, *25*, 3935. (f) Duncan, A. P.; Mullins, S. M.; Arnold, J.; Bergman, R. G. *Organometallics* **2001**, *20*, 1808.

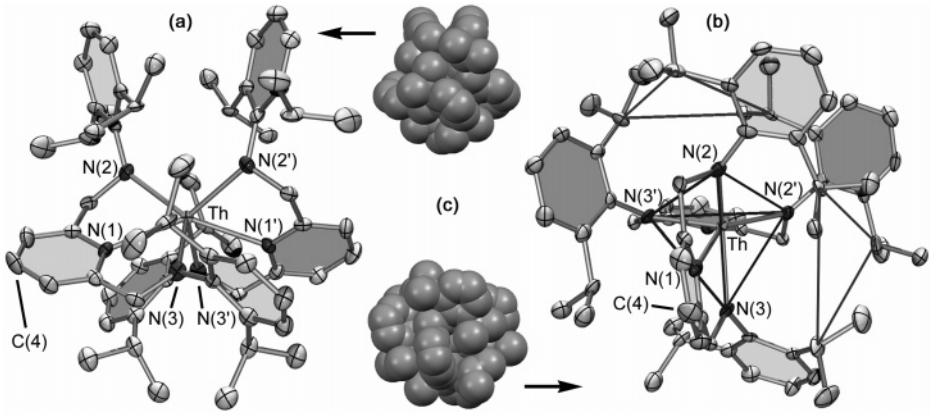


Figure 4. Molecular structure of bis-ligand complex **9** with hydrogen atoms omitted for clarity. (a and b) ORTEPs with thermal ellipsoids at the 50% probability level. (c) Space filling diagrams. Part b highlights the distorted tetrahedral arrangement of $N_{anilido}$ donors around Th and the position of three isopropyl groups above each of the larger faces of the tetrahedron.

oughly dried *in vacuo*. Commonly utilized specialty glassware includes the swivel frit assembly, J-Young NMR tubes, and thick walled flasks equipped with Teflon stopcocks. A Fisher Scientific Ultrasonic FS-30 bath was used to sonicate reaction mixtures where indicated. Residual oxygen and moisture were removed from the argon stream by passage through an Oxisorb-W scrubber from Matheson Gas Products. Anhydrous 1,2-dme and diethyl ether were purchased from Aldrich. Hexanes, toluene, and THF were initially dried and distilled at atmospheric pressure from CaH_2, sodium, and sodium benzophenone ketal, respectively. Unless otherwise noted, all proteo solvents were stored over an appropriate drying agent (1,2-dme, OEt_2, THF, toluene, C_6H_6 = Na/Ph_2CO; hexanes, $O(SiMe_3)_2$ = Na/Ph_2CO/tetraglyme) and introduced to reactions via vacuum transfer with condensation at −78 °C. Deuterated solvents (ACP Chemicals) were dried over CaH_2 (CD_2Cl_2, C_6D_5Br) or Na/Ph_2CO (C_6D_6, d_8-toluene, d_8-THF).

$Th(NO_3)_4(H_2O)_4$ was purchased from Strem Chemicals. $SOCl_2$, $O(SiMe_3)_2$, 2,6-bis(bromomethyl)pyridine, tetraglyme, xanthone, $AlMe_3$ (2 M in toluene), $Pd(OAc)_2$, NaO*t*Bu, DPEPhos [bis{2-(diphenylphosphino)phenyl} ether], NaH, KH (30 wt % in mineral oil), $LiCH_2SiMe_3$ (1.0 M in pentane), *n*BuLi (2.0 M in cyclohexane),[64] Fe powder, and Br_2 were purchased from Sigma-Aldrich. 2,6-Diisopropylaniline was purchased from Lancaster. Prior to use, solid $LiCH_2SiMe_3$ was obtained by removal of pentane *in vacuo*, solid KH was obtained by filtration and washing with hexanes, 2,6-diisopropylaniline was distilled from CaH_2, and tetraglyme was distilled from sodium/benzophenone ketal. H_2[BDPP],[29] 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene,[65] and $ThCl_4(dme)_2$[37] were prepared by literature procedures.

NMR spectroscopy (^{1}H, $^{13}C\{^1H\}$, DEPT-135, COSY, HSQC, HMBC) was performed on Bruker DRX-500 and AV-600 spectrometers. All ^{1}H NMR and ^{13}C NMR spectra were referenced relative to $SiMe_4$ through a resonance of the employed deuterated solvent or proteo impurity of the solvent: C_6D_6 (δ 7.15 ppm), C_7D_8 (δ 7.09, 7.00, 6.98, 2.09 ppm), C_6D_5Br (δ 7.30, 7.02, 6.94 ppm), d_8-THF (3.58, 1.73 ppm), CD_2Cl_2 (5.32 ppm) for ^{1}H NMR, and C_6D_6 (δ 128.0 ppm), C_7D_8 (δ 137.86, 129.24, 128.33, 125.49, 20.4 ppm), C_6D_5Br (δ 130.9, 129.3, 126.1, 122.3 ppm), d_8-THF (67.57, 25.37 ppm), CD_2Cl_2 (54.0 ppm) for ^{13}C NMR.

(63) Burger, B. J.; Bercaw, J. E. Vacuum Line Techniques for Handling Air-Sensitive Organometallic Compounds. In *Experimental Organometallic Chemistry−A Practicum in Synthesis and Characterization*; American Chemical Society: Washington, D.C., 1987; Vol. 357, p 79.

(64) *n*BuLi solutions were titrated using *N*-benzylbenzamide (Sigma-Aldrich) in THF at −45 °C: Burchat, A. F.; Chong, J. M.; Nielsen, N. *J. Organomet. Chem.* **1997**, *542*, 281.

(65) Nowick, J. S.; Ballester, P.; Ebmeyer, F.; Rebek, J. *J. Am. Chem. Soc.* **1990**, *112*, 8902.

Combustion elemental analyses were performed on a Thermo EA1112 CHNS/O analyzer by Dr. Steve Kornic of this department. X-ray crystallographic analyses were performed on suitable crystals coated in Paratone oil and mounted on a P4 diffractometer with a Bruker Mo rotating-anode generator and a SMART1K CCD area detector in the McMaster Analytical X-Ray (MAX) Diffraction Facility. Herein, Q = quaternary, Ar = 2,6-diisopropylphenyl, the *ipso* carbon refers to the carbon attached to nitrogen, Py and Xanth refer to the pyridine and xanthene backbones of the BDPP and XA_2 ligands, respectively, and CH^1 and CH^3 refer to the 1- and 3-positions of the xanthene backbone (*para* and *ortho*, respectively, to the amido group in XA_2).

$H_2(XA_2)$ (1). 4,5-Dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (10.00 g, 20.82 mmol), 2,6-diisopropylaniline (7.85 mL, 41.64 mmol), NaO*t*Bu (5.60 g, 58.30 mmol), $Pd(OAc)_2$ (40 mg, 0.21 mmol), and DPEPhos (167 mg, 0.31 mmol) in toluene (150 mL) were heated to 100 °C for 16 h. The reaction mixture was then quenched with water, extracted into toluene (3 × 50 mL), dried over $MgSO_4$, and concentrated to approximately 30 mL. Recrystallization from a hot ethanol/toluene (10:1) solution gave **1** as a white solid (12.02 g, 17.86 mmol) in 86% yield. ^{1}H NMR (C_6D_6, 600 MHz): δ 7.26−7.21 (m, 6H, Ar-*H*), 6.99 (d, 2H, *J* 1.94 Hz, C*H*^{3}), 6.51 (d, 2H, *J* 1.94 Hz, C*H*^{1}), 5.93 (s, 2H, N*H*), 3.47 (sept, 4H, *J* 6.88 Hz, C*H*Me$_2$), 1.98 (s, 18H, C*Me*$_3$), 1.68 (s, 6H, C*Me*$_2$), 1.18 (d, 12H, *J* 6.88 Hz, CH*Me*$_2$), 1.14 (d, 12H, *J* 6.88 Hz, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 150 MHz): δ 147.8 (Ar-C_{ipso}), 146.1, 136.4, 135.9 (Xanth-*Q*), 136.2 (Ar-C_{ortho}), 129.4 (Ar-CH_{para}), 124.3 (Ar-CH_{meta}), 111.9 (*C*H^3), 108.1 (*C*H^1), 35.1 (*C*Me$_2$), 34.8 (*C*Me$_3$), 32.9 (C*Me*$_2$), 31.7 (C*Me*$_3$), 28.7 (*C*HMe$_2$), 24.7, 23.5 (CH*Me*$_2$). Anal. Calcd for $C_{47}H_{64}N_2O$: C, 83.88; H, 9.58; N, 4.16. Found: C, 83.91; H, 9.64; N, 4.00.

$K_2(dme)_2[XA_2]$ (2). KH (0.120 g, 3.00 mmol) and $H_2[XA_2]$ (0.750 g, 1.11 mmol) in dme (60 mL) were stirred at room temperature for 5 h. The solution was filtered to remove excess KH. Solvent was removed *in vacuo*, and hexamethyldisiloxane (30 mL) was added, followed by sonication. The solution was cooled to −78 °C and filtered on a precooled frit to obtain 0.756 g (0.81 mmol, 73%) of **2** as a white solid. ^{1}H NMR (C_6D_6, 600 MHz): δ 7.29 (d, 4H, *J* 7.53 Hz, Ar-*H*), 7.14 (t, 2H, *J* 7.53 Hz, Ar-*H*), 6.57 (d, 2H, *J* 1.95 Hz, C*H*^{3}), 6.18 (d, 2H, *J* 1.95 Hz, C*H*^{1}), 3.00 (sept, 4H, *J* 6.90 Hz, C*H*Me$_2$), 2.97 (s, 8H, OC*H*$_2$), 2.83 (s, 12H, OC*H*$_3$), 1.90 (s, 6H, C*Me*$_2$), 1.40 (s, 18H, C*Me*$_3$), 1.29 (d, 12H$_2$, *J* 6.77 Hz, CH*Me*), 1.16 (d, 12H, *J* 7.04 Hz, CH*Me*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 150 MHz): δ 154.1 (Ar-C_{ipso}), 149.2 (Ar-C_{ortho}), 147.7, 143.0, 138.6, 132.9 (Xanth-*Q*), 124.3 (Ar-CH_{para}), 120.6 (Ar-CH_{meta}), 109.1 (*C*H^1), 100.8 (*C*H^3), 71.7 (O*C*H$_2$), 58.7 (O*Me*), 36.4 (*C*Me$_2$), 35.6 (C*Me*$_3$), 32.8 (*C*Me$_3$), 31.2 (C*Me*$_2$), 28.7 (*C*HMe$_2$), 25.5, 24.8

(CH*Me*$_2$). Anal. Calcd for $C_{55}H_{82}N_2O_5K_2$: C, 71.07; H, 8.89; N, 3.01. Found: C, 71.16; H, 8.86; N, 3.10.

$Na_2[XA_2]$ (3). NaH (0.100 g, 4.17 mmol) and $H_2[XA_2]$ (0.700 g, 1.04 mmol) were refluxed in toluene (60 mL) for 2−12 days.[66] The solution was then filtered to remove excess NaH, solvent was removed *in vacuo*, and hexamethyldisiloxane (30 mL) was added. Sonication and filtration gave 0.555 g (0.866 mmol, 84%) of **3** as a white solid. ^{1}H NMR (C_6D_6, 600 MHz): δ 7.28 (d, 4H, *J* 7.65 Hz, Ar-*H*), 7.19 (t, 2H, *J* 7.6 Hz, Ar-*H*), 6.67 (d, 2H, *J* 2.0 Hz, C*H*^{3}), 6.34 (d, 2H, *J* 2.0 Hz, C*H*^{1}), 2.98 (sept, 4H, *J* 6.9 Hz, C*H*Me$_2$), 1.81 (s, 6H, C*Me*$_2$), 1.35 (s, 18H, C*Me*$_3$), 1.29 (d, 12H, *J* 6.8 Hz, CH*Me*$_2$), 0.99 (d, 12H, *J* 7.1 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 151.8, 148.8, 146.2, 133.0 (Xanth-*Q*), 137.4 (Ar-C_{ipso}), 128.6 (Ar-C_{ortho}), 125.0 (Ar-CH_{meta}), 121.2 (Ar-CH_{para}), 109.4 (*C*H^3), 101.2 (*C*H^1), 35.8 (*C*Me$_2$), 34.4 (*C*Me$_3$), 31.4 (C*Me*$_3$), 28.3 (C*Me*$_2$), 27.7 (*C*HMe$_2$), 24.0, 23.4 (CH*Me*$_2$). Anal. Calcd for $C_{47}H_{62}N_2Na_2O$: C, 78.73; H, 8.72; N, 3.91. Found: C, 79.09; H, 8.65; N, 3.96.

Li_2[BDPP] (4). *n*BuLi (2.0 M) in cyclohexane (2.20 mL, 4.37 mmol) was added dropwise to 2,6-bis(2,6-diisopropylanilinomethyl)pyridine (1.00 g, 2.19 mmol) in hexanes (30 mL) at −78 °C. After stirring at −78 °C for 5 min the solution was warmed to −45 °C for 5 min to give a yellow-brown solution with large amounts of yellow precipitate. The mixture was then recooled to −78 °C and filtered quickly on a precooled frit to provide **4** as a yellow solid (0.898 g, 1.91 mmol) in 87% yield. ^{1}H NMR (d_8-THF,[30] −30 °C, 500 MHz): δ 7.58 (t, 1H, *J* 7.3 Hz, py-C*H*), 7.44 (d, 2H, *J* 7.3 Hz, py-C*H*), 6.71 (d, 4H, *J* 7.3 Hz, Ar-*H*), 6.23 (t, 2H, *J* 7.3 Hz, Ar-*H*), 4.78 (s, 4H, NC*H*$_2$), 3.73 (sept, *J* 6.9 Hz, C*H*Me$_2$), 1.11 (d, 24H, *J* 6.7 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (d_8-THF, −30 °C, 125 MHz): δ 166.4 (Py-C_{ortho}), 160.1 (Ar-C_{ipso}), 138.5 (Ar-C_{ortho}), 133.0 (Py-CH_{para}), 120.8 (Ar-CH_{meta}), 115.9 (Py-CH_{meta}), 110.2 (Ar-CH_{para}), 62.4 (NCH_2), 25.5 (*C*HMe$_2$), 21.0 (CH*Me*$_2$). Anal. Calcd for $C_{31}H_{41}N_3Li_2$: C, 79.29; H, 8.80; N 8.95. Found: C, 79.15; H, 9.21; N, 8.49.

[(BDPP)ThCl$_2$(dme)] (5): Method A. $ThCl_4(dme)_2$ (0.600 g, 1.08 mmol) and $LiCH_2SiMe_3$ (0.204 g, 2.17 mmol) in toluene (60 mL) were stirred for 1 h at −78 °C followed by 1 h at 0 °C. A solution of 2,6-bis(2,6-diisopropylanilinomethyl)pyridine (0.620 g, 1.35 mmol) in toluene (10 mL) was then added dropwise. The solution was allowed to warm to room temperature over ca. 2 h, stirred for an additional 12 h, and then filtered to remove lithium salts. Solvent was removed *in vacuo*, and hexanes (30 mL) were added, followed by sonication and filtration to give **5** as a white solid (0.781 g, 0.92 mmol) in 85% yield. **Method B.** $ThCl_4(dme)_2$ (0.140 g, 0.25 mmol) in benzene (10 mL) was placed in an ice−water bath (the majority of the solution does not freeze, despite the 6 °C freezing point of benzene). A solution of Li_2[BDPP] (0.119 g, 0.25 mmol) in benzene[30] (5 mL) was added dropwise (over 1−2 min). The solution was stirred for 1 h, followed by filtration and removal of solvent *in vacuo*. Hexanes (10 mL) were added, followed by sonication and filtration to give **5** as a white solid (0.109 g, 0.13 mmol) in 51% yield. ^{1}H NMR (C_6D_5Br, 600 MHz): δ 7.24 (t, 1H, *J* 7.6 Hz, py-C*H*), 7.17 (m, 6H, Ar-*H*), 6.85 (d, 2H, *J* 7.6 Hz, py-C*H*), 5.27 (s, 4H, NCH_2), 4.19 (sept, *J* 6.7 Hz, C*H*Me$_2$), 3.42 (s, 2H, OCH_2), 2.38 (s, 3H, OCH_3), 1.42, 1.15 (d, 24H, *J* 6.7 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 165.0 (Py-C_{ortho}), 148.1 (Ar-C_{ipso}), 147.6 (Ar-C_{ortho}), 137.4 (Py-CH_{para}), 125.3 (Ar-CH_{meta}), 116.8 (Py-CH_{meta}), 124.2 (Ar-CH_{para}), 70.6 (NCH_2), 27.8 (*C*HMe$_2$), 27.0, 24.3 (CH*Me*$_2$). Anal. Calcd for $C_{35}H_{51}Cl_2N_3O_2Th$: C, 49.53; H, 6.06; N 4.95. Found: C, 49.85; H, 6.35; N, 4.37.

[(XA_2)ThCl$_2$(dme)] (6). $ThCl_4(dme)_2$ (0.416 g, 0.75 mmol) and $K_2(dme)_2[XA_2]$ (0.700 g, 0.75 mmol) in toluene (60 mL) were stirred for 16 h at 100 °C. The solution was cooled to room temperature and filtered, and the solvent was removed *in vacuo*. Hexanes (30 mL) were added, followed by sonication and filtration to give **6** as a white solid (0.378 g, 0.36 mmol) in 59% yield. ^{1}H NMR (C_6D_6, 600 MHz): δ 7.31 (m, 4H, *J* 7.5 Hz, Ar-*H*), 7.25 (m, 2H, *J* 7.5 Hz, Ar-*H*), 6.85 (d, 2H, *J* 1.8 Hz, C*H*^{3}), 5.89 (d, 2H, *J* 1.8 Hz, C*H*^{1}), 4.06 (sept, 4H, *J* 6.8 Hz, C*H*Me$_2$), 3.04 (s, 4H, OCH_2), 2.25 (s, 6H, OCH_3), 1.70 (s, 6H, C*Me*$_2$), 1.47 (d, 12H, *J* 6.7 Hz, CH*Me*$_2$), 1.25 (s, 18H, C*Me*$_3$), 1.09 (d, 12H, *J* 6.9 Hz, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 149.4 (Ar-C_{ortho}), 147.1, 145.9, 141.3 (Xanth-*Q*), 142.0 (Ar-C_{ipso}), 127.3 (Ar-CH_{para}), 125.4 (Ar-CH_{meta}), 111.7 (*C*H^1), 111.4 (*C*H^3), 71.0 (OCH_2), 61.3 (O*Me*), 34.9 (*C*Me$_3$), 34.1 (*C*Me$_2$), 33.8 (C*Me*$_2$), 31.7 (C*Me*$_3$), 28.1 (*C*HMe$_2$), 27.2, 24.8 (CH*Me*$_2$). Anal. Calcd for $C_{51}H_{72}Cl_2N_2O_3Th$: C, 57.57; H, 6.82; N, 2.63. Found: C, 57.76; H, 6.89; N, 2.49.

[(BDPP)Th(CH$_2$SiMe$_3$)$_2$] (7): Method A. $ThCl_4(dme)_2$ (0.750 g, 1.35 mmol) and $LiCH_2SiMe_3$ (0.510 g, 5.41 mmol) in toluene (60 mL) were stirred for 1 h at −78 °C followed by 1 h at 0 °C. The cloudy, colorless solution was then recooled to −78 °C, and a solution of 2,6-bis(2,6-diisopropylanilinomethyl)pyridine (0.620 g, 1.35 mmol) in toluene (10 mL) was added dropwise. The solution was allowed to warm to room temperature over ca. 2 h, stirred for an additional 12 h, and then filtered to remove lithium salts. Solvent was removed *in vacuo* and hexamethyldisiloxane (30 mL) was added, followed by sonication and filtration to afford **7** as an off-white solid (0.949 g, 1.10 mmol) in 82% yield. **Method B.** [(BDPP)$ThCl_2$(dme)] (0.150 g, 0.18 mmol) and $LiCH_2SiMe_3$ (0.033 g, 0.35 mmol) in toluene (15 mL) were stirred for 30 min at room temperature. The solution was filtered, and solvent was removed *in vacuo*. Hexamethyldisiloxane (10 mL) was added, followed by sonication and filtration to afford **7** as an off-white solid (0.106 g, 0.12 mmol) in 68% yield. ^{1}H NMR (C_6D_6): δ 7.24 (m, 6H, Ar-*H*), 6.90 (t, 1H, *J* 7.7 Hz, py-C*H*), 6.49 (d, 2H, *J* 7.7 Hz, py-C*H*), 5.24 (s, 4H, NCH_2), 3.75 (sept, 4H, *J* 6.8 Hz, C*H*Me$_2$), 1.52 (d, 12H, *J* 6.8 Hz, CH*Me*$_2$), 1.26 (d, 12H, *J* 6.8 Hz, CH*Me*$_2$), −0.02 (s, 18H, Si*Me*$_3$), −0.32 (s, 4H, ThCH_2). ^{13}C{^{1}H} NMR (C_6D_6, 150 MHz): δ 164.8 (Py-C_{ortho}), 148.1 (Ar-C_{ipso}), 141.9 (Ar-C_{ortho}), 138.4 (Py-CH_{para}), 126.8 (Ar-CH_{meta}), 125.0 (Ar-CH_{para}), 117.8 (Py-CH_{meta}), 89.9 (ThCH_2), 68.7 (NCH_2), 28.7 (C*H*Me$_2$), 27.3, 24.9 (CH*Me*$_2$), 3.8 (Si*Me*$_3$). Anal. Calcd for $C_{39}H_{63}N_3Si_2Th$: C, 54.33; H, 7.37; N, 4.87. Found: C, 54.10; H, 7.35; N, 4.69.

[(XA_2)Th(CH$_2$SiMe$_3$)$_2$] (8): Method A. Complex **8** was prepared in a similar fashion to **7** (method A) using 0.750 g (1.35 mmol) of $ThCl_4(dme)_2$, 0.510 g (5.41 mmol) of $LiCH_2SiMe_3$, and 0.909 g (1.35 mmol) of $H_2[XA_2]$. However, the crude filtered product was sonicated in hexanes (20 mL) before filtration to give 0.710 g of **8** as a white solid (0.711 g, 0.66 mmol) in 49% yield. **Method B.** Complex **8** was prepared in a similar fashion to **7** (method B) using [(XA_2)$ThCl_2$(dme)] (0.250 g, 0.25 mmol) and $LiCH_2SiMe_3$ (0.048 g, 0.51 mmol). However, the crude filtered product was sonicated in hexanes (10 mL) before filtration to afford **8** as a white solid (0.175 g, 0.16 mmol) in 65% yield. ^{1}H NMR (d_8-toluene, 600 MHz): δ 7.26 (m, 6H, Ar-*H*), 6.77 (d, 2H, *J* 1.5 Hz, C*H*^{3}), 6.00 (d, 2H, *J* 1.5 Hz, C*H*^{1}), 3.54 (sept, 4H, *J* 7.0 Hz, C*H*Me$_2$), 1.66 (s, 6H, C*Me*$_2$), 1.40 (d, 12H, *J* 7.0 Hz, CH*Me*$_2$), 1.16 (d, 12H, *J* 7.0 Hz, CH*Me*$_2$), 0.03 (s, 18H, Si*Me*$_3$), −0.17 (s, 4H, ThCH_2). ^{13}C{^{1}H} NMR (d_8-toluene, 150 MHz): δ 146.2 (Ar-C_{ortho}), 148.5 (Xanth-*Q*), 142.6 (Ar-C_{ipso}), 130.3 (Ar-CH_{para}), 129.7 (Ar-CH_{meta}), 110.7 (*C*H^1), 110.9 (*C*H^3), 35.6 (*C*Me$_3$), 35.5 (*C*Me$_2$), 31.4 (C*Me*$_2$), 32.1 (C*Me*$_3$), 29.5 (*C*HMe$_2$), 26.8, 25.5 (CH*Me*$_2$), 3.4 (Si*Me*$_3$). Note: ThCH_2 was not observed at room temperature but was observed at +50 or −80 °C (see main text). Anal. Calcd for $C_{55}H_{84}N_2OSi_2Th$: C, 61.31 H, 7.86; N, 2.60. Found: C, 61.41; H, 8.06; N, 2.37.

[Th(BDPP)$_2$] (9): Method A. [(BDPP)Th(CH$_2$SiMe$_3$)$_2$] (**7**) (0.200 g, 0.23 mmol) and 2,6-bis(2,6-diisopropylanilinomethyl)-pyridine (0.106 g, 0.23 mmol) in benzene (15 mL) were heated at 100 °C for 24 h in a sealed flask. Upon cooling, the reaction mixture

(66) The reaction time was not reproducible. Typically, no reaction is observed for days, but once the reaction begins, it takes less than 24 h to reach completion.

was filtered and the solvent was reduced to ca. 1 mL *in vacuo*. Addition of hexamethyldisiloxane (10 mL) and sonication afforded **9** as a pale greenish-yellow solid (0.097 g, 0.085 mmol) in 37% isolated yield. **Method B.** $ThCl_4(dme)_2$ (0.100 g, 0.18 mmol) and Li_2BDPP (0.170 g, 0.36 mmol) in benzene[30] (15 mL) were stirred at 0 °C for 1 h (the majority of the solution does not freeze, despite the 6 °C freezing point of pure benzene). The reaction mixture was then warmed to room temperature and filtered, and the solvent was removed *in vacuo*. Addition of hexanes (5 mL) and sonication gave a brown solid, which was collected by filtration and washed with hexanes several times. Recrystallization by cooling a hot, concentrated toluene solution of **9** to −30 °C afforded the product as a pale greenish-yellow solid (0.109 g, 0.095 mmol) in 26% isolated yield. ^{1}H NMR (C_6D_6, 600 MHz): δ 7.10 (m, 12H, Ar-*H*), 6.81 (t, 2H, *J* 7.7 Hz, py-C*H*), 6.48 (d, 4H, *J* 7.7 Hz, py-C*H*), 4.87 (s, 8H, NCH_2), 3.00 (sept, 8H, *J* 6.5 Hz, C*H*Me_2), 1.01 (d, 24H, *J* 6.5 Hz, CHMe_2), 0.97 (d, 24H, *J* 6.6 Hz, CHMe_2). ^{13}C{^{1}H} NMR (CD_2Cl_2, 150 MHz): δ 167.5 (Py-C_{ortho}), 156.1 (Ar-C_{ortho}), 146.2 (Ar-C_{ipso}), 138.0 (Py-CH_{meta}), 123.9 (Ar-CH_{meta}), 123.4 (Ar-CH_{para}), 117.5 (Py-CH_{para}), 68.0 (NCH_2), 29.5 (*C*HMe_2), 27.7, 24.1 (CHMe_2). Anal. Calcd for $C_{62}H_{82}N_6Th$: C, 65.13; H, 7.23; N, 7.35. Found: C, 65.22; H, 7.36; N, 7.02.

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Supporting Information Available: X-ray crystallographic data in PDF format and CIF files are available free of charge via the Internet at http://pubs.acs.org.

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