# Synthesis of Coordinatively Unsaturated Tetravalent Actinide Complexes with η^5 Coordination of Pyrrole

Rami J. Batrice, Natalia Fridman, and Moris S. Eisen*

Schulich Faculty of Chemistry, Institute of Catalysis Science and Technology, Technion-Israel Institute of Technology, Technion City, 3200008 Israel

S *Supporting Information*

ABSTRACT: The synthesis of new actinide complexes utilizing bridged α-alkyl-pyrrolyl ligands is presented. Lithiation of the ligands followed by treatment with 1 equiv of actinide tetrachloride (uranium or thorium) produces the desired complex in good yield. X-ray diffraction studies reveal unique η^5:η^5 coordination of the pyrrolyl moieties; when the nonsterically demanding methylated ligand is used, rapid addition of the lithiated ligand solution to the metal precursor forms a bis-ligated complex that reveals η^5:η^1 coordination as determined by crystallographic analysis.
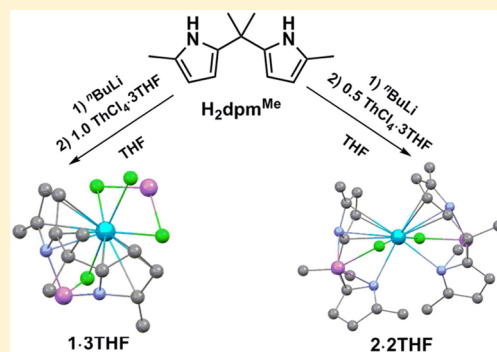
INTRODUCTION

The actinide metallocenes have long been the cornerstone of 5f-block coordination chemistry. Since the earliest reports of cyclopentadienyl-actinide complexes,[1−4] this class of complexes has drawn the attention of numerous studies focusing on the preparation of various Cp analogues,[5−12] as well as their reactivity in diverse stoichiometric[13−21] and catalytic reactions.[8,11,22−35] One of the most attractive features of the pentamethylcyclopentadienyl (Cp*) ligands in particular is the considerable thermal stability that they impart upon the resulting organoactinide complex;[36] however, despite this, relatively little work has been done exploring similar ligands containing heteroatoms within the ring structure. Of the possibilities, pyrrole emerges as the most suitable substitute for Cp* largely owing to its isoelectronic properties. As compared to other common heterocycles, pyrrole is highly susceptible to facile deprotonation to generate a monoanionic species because of the acidity of the N−H proton (pK_a = 23.0 in DMSO),[37] in contrast to other protic heterocycles; moreover, the electronegativity of the nitrogen in competition with the π-system of the heterocycle results in a considerable resonance stabilization energy of 29.6 kcal mol^{-1}.[38] The combination of these factors suggests that pyrrole possesses the capacity to form an aromatic system capable of forming a pentahapto coordination pattern to a metal center, similar to that seen in cyclopentadienyl ligands.

While pyrrole is widely used in coordination complexes incorporating virtually all metals of the transition block, most of these show pyrrole to be bound in an η^1 fashion, directly forming a nitrogen−metal bond.[39−47] Interestingly, there are still many examples of η^5-bound pyrrole in transition metal chemistry; however, it is often seen that such ligation is vulnerable to substitution reaction or haptotropic shifts.[48−50] The selected

examples in which these side reactions are absent are mainly seen in early transition metal chemistry, and studies of such complexes elucidate the highly electrophilic nature of the metal and steric environment that are required to yield the pentahapto pyrrolyl-metal moiety.[51,52] Although studies of actinide-pyrrolyl complexes date as far back as 1974 with Marks' preparation of tetrakis(2,5-dimethylpyrrolyl)uranium(IV),[53] it is only in the past decade that pyrrolyl ligands have been reintroduced into actinide chemistry and the focus of continued investigation.[54] In the first of these studies, Boncella et al. revealed a U^{VI} center coordinated to a bridged dipyrrolylmethane (dpm) ligand. Salt metathesis of the dipotassium ligand with U($\equiv$N^{t}Bu)$_2$I$_2$(THF)$_2$ yielded the η^1:η^1-bound ligand; when the 1,9-bis(arylated) ligand is employed using similar reaction conditions, the coordination mode of the ligand is found to favor the π-coordinated η^5:η^5 motif (Scheme 1).[55]

In addition, Cloke and co-workers have unveiled a trivalent uranium complex displaying η^5 coordination of 2,3,4,5-tetramethylpyrrole.[56] By the salt metathesis reaction of the dipotassium salts of a substituted cyclooctatetraene and the potassium salt of tetramethylpyrrole with uranium(III) iodide, a
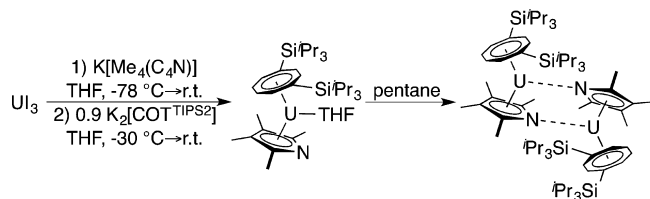
**Scheme 1. Synthesis of U(VI)-Dipyrrolylmethane Complexes**

A
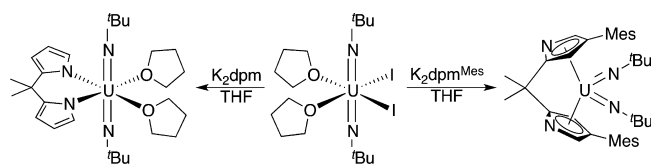
bimetallic complex bearing π-coordination of both ligands is formed, which upon solvation with THF yields the monometallic complex (Scheme 2).

Scheme 2. Synthesis of the Uranium(III) Mixed-Sandwich Complex

A recent study by Arnold et al. utilized pyrrolic macrocyclic ligands bound to a uranium(IV) center. With this considerably electrophilic metal center ($5f^2 6d^0$), the pyrrolyl moieties of the ligand bind in a pentahapto manner; however, reduction of the uranium center using potassium-graphite provides a more electron rich metal and results in isomerization of the ligand coordination mode to an $\eta^1 : \eta^1$ configuration (Scheme 3).[57]

Scheme 3. Synthesis of the U(IV) Pyrrolyl-Macrocyclic Complex and Its Subsequent Reduction to a U(III) Analogue
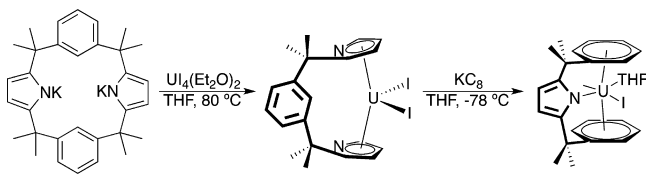

The ability to form pentahapto pyrrolyl bonding to an actinide center was further demonstrated by Gambarotta and co-workers with the preparation of a [(-CH$_2$-]4-calix[4]tetrapyrrolyl uranium complex and a uranium(III) polypyrrolide complex.[58,59] The polypyrrolides displayed η^5 coordination of two of the four pyrroles present, and retention of a solvated potassium or lithium counterion; however, more impressive was the catalytic behavior exhibited by these complexes, showing C–H bond activation, solvent deoxygenation and fragmentation, polysilanol depolymerization, and dinitrogen cleavage.[59,60] In addition, it has been shown that reduction of a thorium(IV) bis-pyrrolide complex using potassium metal in a coordinating solvent results in the formation of a thorium(III) center displaying $\eta^5 : \eta^5$ coordination to the pyrrolic moieties.[61]

Although the investigation of pyrrolyl-actinides is limited, these studies show extraordinary behavior and provide insight into the influences of the ligand substitution and metal center, which facilitate the divergent coordination modes of the pyrrolic moiety. The six-electron donation to the metal center achieved through the π-bonding interactions of pyrrole would be expected to stabilize the metal in a manner similar to cyclopentadienyl ligation. Inspired by this, we have pursued the preparation of a
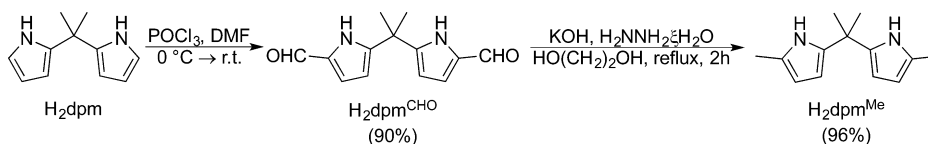
series of uranium(IV) and thorium(IV) *ansa*-bridged dipyrrolyl complexes that inherently incorporate coordinative unsaturation of the metal sphere, making subsequent functionalization or reactivity studies of the metal complex readily achievable. Herein, we report the synthesis of 1,9-dialkyl-dipyrrolylmethane ligands (H$_2$dpm^R; R = Me, ^{t}Bu, or Ad), the methyl analogue being prepared according to previously reported methods, and the synthesis of the corresponding organoactinides by salt metathesis with the dilithiated ligands. The formed complexes are studied by spectroscopic and crystallographic techniques and reveal unusual pentahapto coordination of the pyrrolic fragment of the ligand. We demonstrate the suitability of the dpm^R motif to stabilize the U(IV) or Th(IV) center with a preference of forming an *ansa*-bridged structure analogous to cyclopentadienyl systems. Investigation of the bond lengths reveals differences in the electronic nature of the pyrrole that show promise for future functionalization and reactivity studies.

■ RESULTS AND DISCUSSION

Ligand Synthesis. The methylated dipyrrolylmethane ligand (H$_2$dpm^{Me}) was prepared according to previously reported methods. Beginning from H$_2$dpm, Vilsmeier–Haack formylation[62] selectively formed the 1,9-bisformyl-dipyrrolylmethane in 90% isolated yield. Successive Wolff–Kishner reduction[63] yielded the target ligand in 96% yield after workup (Scheme 4).

To prepare the *tert*-butyl and 1-adamantyl derivatives of the H$_2$dpm ligand, a dissimilar synthetic protocol was employed. The 2-alkylpyrroles were prepared by Friedel–Crafts alkylation according to published methods;[64,65] using the α-substituted pyrroles, acid-catalyzed condensation was achieved in dichloromethane with 2,2-dimethoxypropane (DMP) and pyridinium *p*-toluenesulfonate (PPTS) as the acid source, yielding the desired ligands after column chromatography on silica gel with an eluent of 5% ethyl acetate in hexane (eq 1).

(1)
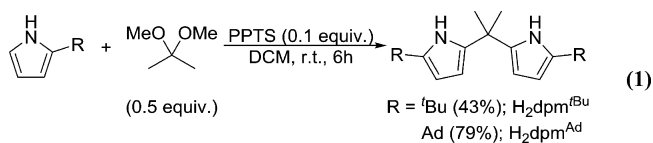
Synthesis of (dpm^R)$_n$An(IV) Complexes. The ligands were deprotonated *in situ* using 2 equiv of 1.6 M ^{n}BuLi to yield the dilithium salt (Li$_2$dpm^R). The reaction between the dilithiated ligand solution and an equimolar amount of actinide tetrachloride (UCl$_4$ or ThCl$_4$·3THF) was performed in THF at ambient temperature for up to 2 days or 12 h, respectively. After workup and filtration through Celite to remove the LiCl generated, samples were recrystallized in either a toluene solution or a mixture of toluene and ethyl ether, furnishing structures 1−4 (Table 1). Each of the complexes showed the retention of solvated lithium ions, similar to the molecular structure seen for previous actinide polypyrrolide complexes.[59] Conversely, the structures can be considered as bonding of a

Scheme 4. Synthesis of 1,9-Dimethyl(dipyrrolylmethane)

Table 1. Crystal Data and Structure Analysis Results

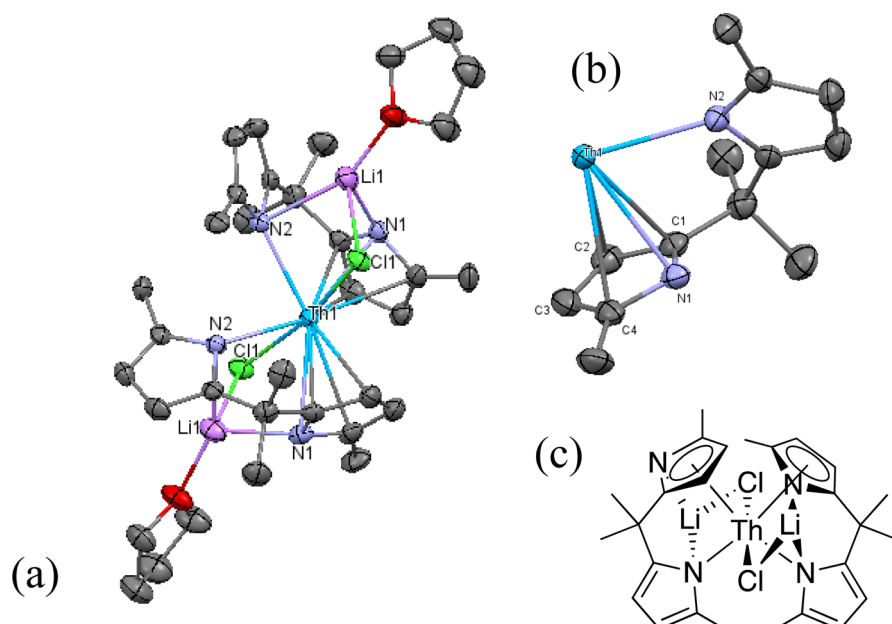|	1	2	3	4
formula	$C_{34}H_{48}Cl_2Li_2N_4O_2Th$	$C_{28}H_{40}Cl_4Li_2N_2O_3Th$	$C_{34}H_{48}Cl_2Li_2N_4O_2U$	$C_{31}H_{48}Cl_4Li_2N_2O_3U$
fw	861.58	840.34	867.57	890.42
space group	monoclinic, $C2/c$	triclinic, $P\bar{1}$	monoclinic, $P2_1/c$	triclinic, $P\bar{1}$
a (Å)	20.753(4)	8.745(18)	17.3080(8)	10.2600(3)
b (Å)	10.150(6)	9.35(4)	11.5880(5)	11.2090(3)
c (Å)	17.081(3)	15.89(5)	17.456(1)	17.8490(6)
α (deg)	90	74.50(3)	90	96.878(1)
β (deg)	98.180(13)	76.40(4)	97.7620(17)	99.668(1)
γ (deg)	90	67.87(6)	90	110.1340(16)
V (Å³)	3561(2)	1147(7)	3469.0(3)	1864.61(10)
Z	4	2	4	2
radiation ($K\alpha$, Å)	0.71073	0.71073	0.71073	0.71073
T (K)	200	200	200	200
D_{calcd} (g cm⁻³)	1.607	2.433	1.661	1.586
μ_{calcd} (cm⁻¹)	4.372	7.010	4.869	4.670
R1, wR2	0.0295, 0.0746	0.0775, 0.1950	0.0598, 0.1458	0.0683, 0.1857
GOF	1.094	1.032	1.034	1.222

Figure 1. Solid state structure of **1** (thermal ellipsoids are drawn at 50% probability). (a) Full molecular structure and (b) condensed structure showing only the ligand binding mode with hydrogen atoms removed for the sake of clarity. (c) Molecular structure of **1** with coordinated THF molecules removed for the sake of clarity. Selected bond distances (angstroms) and angles (degrees): Th1−N1, 2.748(3); Th1−C1, 2.778(2); Th1−C2, 2.915(3); Th1−C3, 2.956(3); Th1−C4, 2.876(2); Th1−N2, 2.516(7); Th1−$[\eta^5\text{-}C_4N]_{cent}$, 2.601(5); Th1−Cl1, 2.816(7); $[\eta^5\text{-}C_4N]_{cent}$−Th1−N2, 85.83(8); Cl1−Th1−Cl1, 170.25(4).

lithium pyrrolide to the actinide center with accompanying chloride ion and stabilizing solvent.

In the reaction of the actinide precursors with Li_2dpm^{Me}, it is seen with the thorium analogue that rapid addition of the ligand solution results in a mixture of mono- and bis-dpm^{Me} complexes. However, either of these products can be formed selectively by the addition of 2 equiv of the ligand solution to ThCl₄·3THF to yield $Li_2(dpm^{Me})_2ThCl_2$·2THF (**1**), or slow addition of 1 equiv of the ligand to a cooled solution of thorium tetrachloride (−35 °C) to yield $Li_2(dpm^{Me})ThCl_4$·3THF (**2**). Single crystals of these complexes were prepared from saturated THF solutions layered with *n*-hexane at −35 °C in a nitrogen-filled glovebox. The X-ray diffraction pattern from the bis complex (**1**) revealed the molecular structure shown in Figure 1.

The molecular structure obtained shows a highly symmetric metal complex with each dpm^{Me} ligand bound in an $\eta^1{:}\eta^5$ fashion and 2 equiv of lithium chloride and two molecules of THF. Several interesting features are apparent in this structure, one of the most notable being the bond lengths to the atoms of the η^5-pyrrole; the ring structure is found to be disposed with the nitrogen atom of the π-bound heterocycle closer to the thorium metal center at a distance of 2.748(3) Å, with the carbon atoms growing more distant from the α- to β-carbons up to a length of 2.956(3) Å, and a centroid distance of 2.601(5) Å. Via comparison of the Th−N bond distances between two nitrogens of the bridged pyrrols, the pentahapto pyrrole nitrogen is found to be 0.232 Å farther from the metal center than from the η^1 pyrrole (Th1−N2, 2.516 Å), a reasonable observation given the strong σ-donation that is absent from the η^5 heterocycle. The
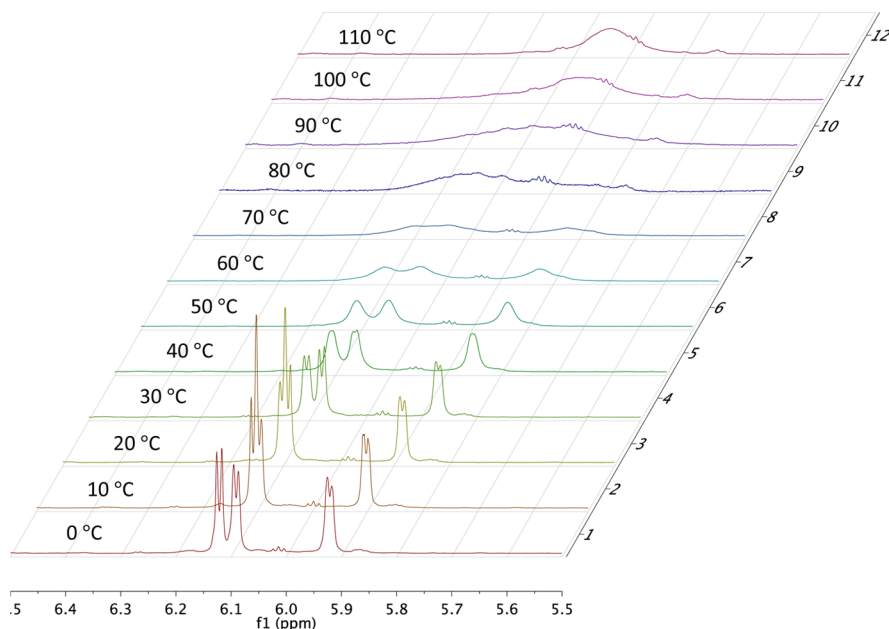
Figure 2. Variable-temperature NMR spectra of $[(dpm^{Me})_2ThCl_2][Li_2(THF)_2]$ with the pyrrolic region shown. Coalescence is observed at 80 °C.
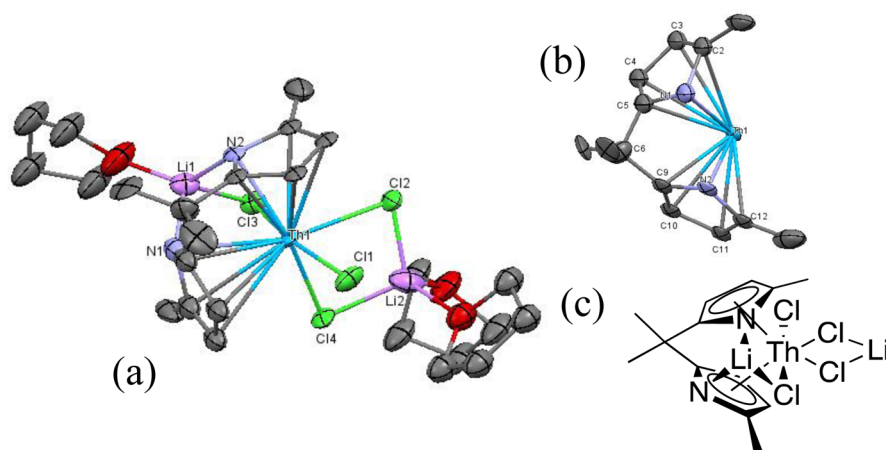

Figure 3. Solid state structure of **2** (thermal ellipsoids are drawn at 50% probability). (a) Full molecular structure and (b) condensed structure showing only the ligand binding mode with hydrogen atoms removed for the sake of clarity. (c) Molecular structure of **2** with coordinated THF molecules removed for the sake of clarity. Selected bond distances (angstroms) and angles (degrees): Th1−N1, 2.446(1); Th1−C2, 2.713(1); Th1−C3, 2.782(2); Th1−C4, 2.742(2); Th1−C5, 2.522(9); Th1−N2, 2.258(2); Th1−C9, 2.341(1); Th1−C10, 2.560(1); Th1−C11, 2.631(1); Th1−C12, 2.533(1); Th1−Cl1, 2.428(8); Th1−Cl2, 2.478(6); Th1−Cl3, 2.543(8); Th1−Cl4, 2.269(8); Th1−$[\eta^5$-$C_4N]_{cent(ave)}$, 2.265(2); $[\eta^5$-$C_4N1]_{cent}$−Th1−$[\eta^5$-$C_4N2]_{cent}$, 105.66(2); Cl1−Th1−Cl2, 84.3(2); Cl3−Th1−Cl4, 82.8(1); Cl1−Th1−Cl3, 164.4(1); Cl1−Th1−Cl4, 86.5(2); Cl2−Th1−Cl3, 82.7(1); Cl2−Th1−Cl4, 80.2(1).

geometry of the resultant molecule is arranged with the two chloride moieties in a *trans* configuration (Cl−Th−Cl, 170.38°), and the pentahapto pyrrols *cis* to each other ($[\eta^5$-$C_4N]_{cent}$−Th−$[\eta^5$-$C_4N]_{cent}$) at an angle of 112.09°. Line-shape analysis of the pyrrolic proton signals in ^{1}H NMR spectrum shows that the ligand isomerizes between the η^5 and η^1 modes of coordination with an enthalpic barrier of 20.1(1) kcal mol^{-1}, and coalescence occurs at 80 °C (Figure 2). The entropy calculated by the exchange rates of these peaks was found to be 7.3(4) eu, suggesting that the ligand isomerization occurs by decoordination/coordination rather than by a highly ordered twisting mechanism.

Conversely, the molecular structure of **2**, prepared by the slow addition of a Li$_2$dpm^{Me} solution to a cooled solution of ThCl$_4$· 3THF, revealed a single ligand coordinated to the thorium center

in an η^5:η^5 fashion (Figure 3), resembling the previously reported *ansa*-bridged metallocenes.[10]

Similar to the structure of complex **1**, the pyrrole rings in **2** are found to be disposed with the π-bound nitrogen closer to the thorium center; however, the bond distances from the actinide center to the pyrrole centroid (2.265 Å) are significantly shorter than those of the bis-ligated complex (**1**) and in fact are shorter than the Th−Cp*$_{cent}$ bond distance (2.53 Å),[66] suggesting higher covalency to dpm^{Me} and the possibility of augmented thermal stability. It is worth noting that the difference in bond lengths between the two thorium−nitrogen bonds is 0.188 Å; however, the proton NMR signals for the pyrrolic hydrogens are found to be degenerate for this complex in solution. This indicates that the asymmetry seems to be a structural phenomenon arising from the solid state structure that is lost upon dissolution at ambient
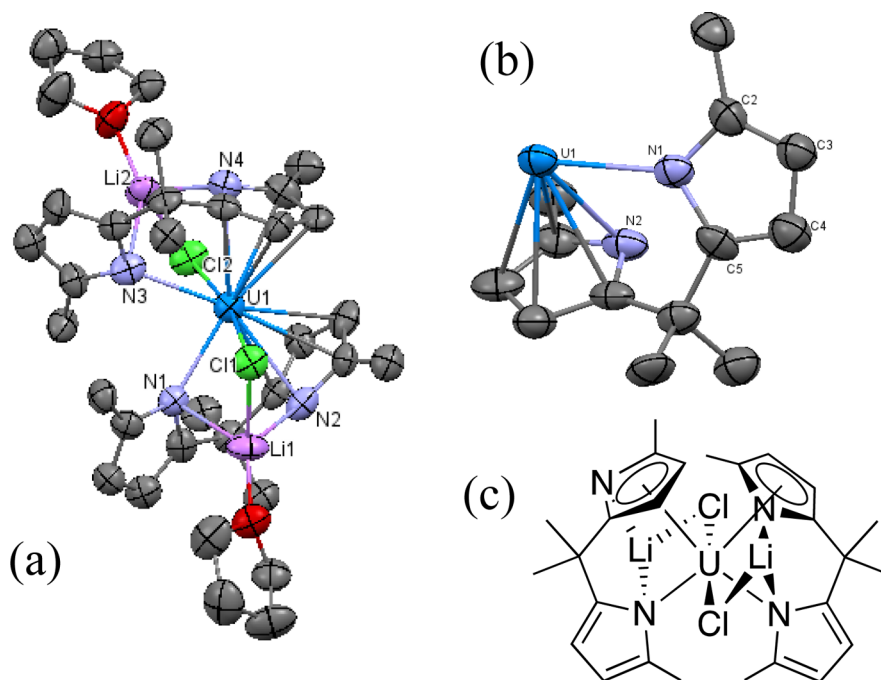
Figure 4. Solid state structure of **3** (thermal ellipsoids are drawn at 50% probability). (a) Full molecular structure and (b) condensed structure showing only the ligand binding mode with hydrogen atoms removed for the sake of clarity. (c) Molecular structure of **3** with coordinated THF molecules removed for the sake of clarity. Selected bond distances (angstroms) and angles (degrees): U1–N1, 2.436(8); U1–N2, 2.731(9); U1–C10, 2.84(1); U1–C11, 2.90(1); U1–C12, 2.85(1); U1–C13, 2.73(1); U1–[η^5-C$_4$N2]$_{cent}$, 2.547(9); U1–N3, 2.462(9); U1–N4, 2.715(9); U1–C27, 2.84(1); U1–C28, 2.91(1); U1–C29, 2.88(1); U1–C30, 2.73(1); U1–[η^5-C$_4$N4]$_{cent}$, 2.553(9); U1–Cl1, 2.751(3); U1–Cl2, 2.742(3); [η^5-C$_4$N2]$_{cent}$–U1–N1, 86.19(3); [η^5-C$_4$N4]$_{cent}$–U1–N3, 85.44(7); [η^5-C$_4$N2]$_{cent}$–U1–[η^5-C$_4$N4]$_{cent}$, 111.46(8); Cl1–U1–Cl2, 170.3(1).

temperature, likely arising from the rapid thermal motion of the thorium center within the binding pocket of the bidentate ligand. Via comparison of the thorium–centroid bond lengths to those found for the thorium(III) bis-pyrrolides presented by Gambarotta et al.,[61] one can assume that the higher electrophilicity of the thorium(IV) center leads to a stronger bonding interaction to the heterocycle. Seeing the markedly short Li2–Cl2 bond length [1.859(2) Å], we can consider the structure as retaining 1 equiv of lithium chloride rather than forming an anionic actinide complex. The lithium–pyrrole bonds [1.72(2) and 1.79(1) Å] are significantly shorter than those seen for previous actinide pyrrolides (2.05 Å),[59] also suggesting the presence of a lithium pyrrolide moiety rather than a lithium ion balancing an anionic complex.

During the salt metathesis reaction of Li$_2$dpm^{Me} with UCl$_4$, the limited solubility of the uranium precursor, even in ethereal solvent, proved to be problematic for the desired synthesis. After workup and crystallization, the molecular structure found by X-ray diffraction revealed a bis-ligated complex of the formula Li$_2$(dpm^{Me})$_2$UCl$_2$·2THF (**3**) (Figure 4). No indication of the monoligated complex is found, informing us that the chloride displacement by the lithiated ligand occurs more rapidly than the dissolution of uranium tetrachloride as the reagent is consumed. The structure is seen to be isomorphous with complex **1** with only slightly longer bond lengths, consistent with the smaller ionic radius of U(IV) compared to that of Th(IV).[67]

Using larger alkyl substituents on the dpm backbone was studied to sterically crowd the actinide center sufficiently to form the target monoligated complex. Similar salt metathesis reactions were performed with H$_2$dpm^{tBu} and H$_2$dpm^{Ad} with both actinide precursors, and single crystals isolated from the reaction of Li$_2$dpm^{tBu} with UCl$_4$. The molecular structure revealed that even

given the aforementioned low solubility of UCl$_4$, the monoligated complex of the formula Li$_2$(dpm^{tBu})UCl$_4$·3THF (**4**) is produced selectively (Figure 5).

The structure reveals a distorted octahedral geometry with both pyrrole rings maintaining the previously seen η^5 coordination mode. Upon comparison to the average bond length of the uranium–pyrrole centroid (2.566 Å), the lengths are found to be longer than the uranium–centroid bond in bis(pentamethylcyclopentadienyl)uranium dichloride (2.47 Å); however, they are found to be remarkably similar to the centroid lengths seen in previous pentahaptic pyrrolyl–uranium moieties (2.55 Å).[58] Additionally, the observed bond lengths reveal a high level of symmetry, particularly evident in the uranium–nitrogen and –carbon bond lengths of the pyrrolic moieties. Although crystal structures of the other (dpm^R)uranium complexes would aid in a systematic study of the effects of alkyl substitution, unfortunately attempts to form single crystals of the 1-adamantyl analogue have thus far been unsuccessful. However, examining the data obtained thus far would suggest that the sterically encumbering *tert*-butyl groups create additional crowding about the metal center that forces the pyrrole rings to be situated farther from the uranium atom.

Although attempts to crystallize the samples prepared with the thorium analogue bearing dpm^{tBu} or dpm^{Ad} provided only clusters of crystals, ^{1}H NMR spectroscopy and combustion analysis were useful in proposing the nature of the complexes obtained. In both thorium complexes bound to either the *tert*-butyl- or 1-adamantyl-substituted ligands, similar chemical shifts and splitting patterns are seen for the pyrrolic protons, as well as chemical shifts consistent with coordinated THF molecules, suggesting that according to the previously seen structures and their respective spectra, these compounds are isostructural to
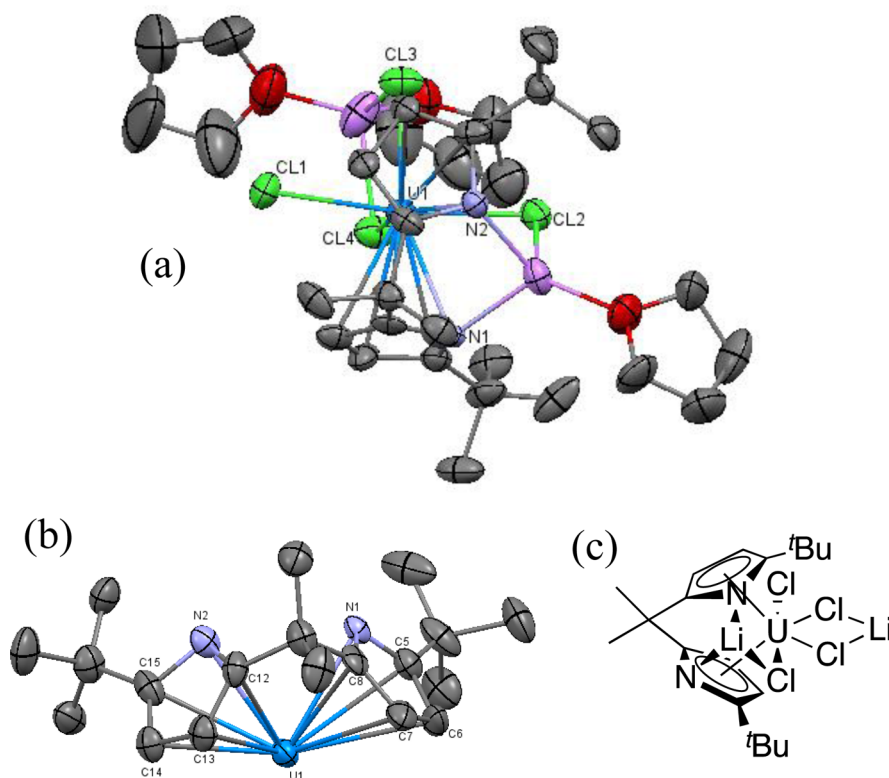
Figure 5. Solid state structure of **4** (thermal ellipsoids are drawn at 50% probability). (a) Full molecular structure and (b) condensed structure showing only the ligand binding mode with hydrogen atoms removed for the sake of clarity. (c) Molecular structure of **4** with coordinated THF molecules removed for the sake of clarity. Selected bond distances (angstroms) and angles (degrees): U1−N1, 2.753(3); U1−C5, 2.946(8); U1−C6, 2.959(5); U1−C7, 2.831(7); U1−C8, 2.687(1); U1−N2, 2.749(6); U1−C12, 2.711(1); U1−C13, 2.810(1); U1−C14, 2.904(5); U1−C15, 2.928(2); U1−Cl1, 2.663(7); U1−Cl2, 2.721(6); U1−Cl3, 2.724(2); U1−Cl4, 2.702(9); U1−$[\eta^5$-C$_4$N$]_{cent(ave)}$, 2.566(3); $[\eta^5$-C$_4$N1$]_{cent}$−U1−$[\eta^5$-C$_4$N2$]_{cent}$, 101.31(3); Cl1−U1−Cl2, 162.15(1); Cl3−U1−Cl4, 76.37(4); Cl1−U1−Cl3, 81.93(9); Cl1−U1−Cl4, 80.71(4); Cl2−U1−Cl3, 84.79(1); Cl2−U1−Cl4, 84.62(1).

complex **1**. In addition, the elemental analyses showed percent compositions of carbon, hydrogen, and nitrogen consistent with the proposed molecular formulas, further supporting formation of the desired compounds; while these data are useful in proposing the aforementioned structures, further analysis, namely, single-crystal diffraction studies, is needed to definitively identify the molecular structure of these compounds.

■ CONCLUSIONS

A set of actinide-dipyrrolylmethane complexes have been prepared and show the unusual η^5 coordination of pyrrole. When methyl groups are introduced at positions 1 and 9 of the ligand, a mono- or bis-ligated complex may be obtained selectively for the thorium complex by salt metathesis with the dilithiated ligand. Conversely, the analogous reaction performed with UCl$_4$ generated only the bis(dpm^{Me}) complex because of the low solubility of the uranium precursor. The 1,9-di-*tert*-butyldipyrrolylmethane was additionally reacted with uranium tetrachloride after lithiation and, after crystal structure determination, showed that the use of larger alkyl groups favored the formation of the mono(dpm) complex. The coordinative unsaturated monoligated complexes show the structural potential to serve as possible precatalysts for future organic transformations. Functionalization and reactivity studies are currently under investigation in our group.

■ EXPERIMENTAL SECTION

Materials and Methods. All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware or J-Young Teflon valve-sealed NMR tubes on a dual-manifold Schlenk line interfaced with a high-vacuum (10^{-5} Torr) line, or in a nitrogen-filled Innovative Technologies glovebox with a medium-capacity recirculator (1−2 ppm of O$_2$). Argon and nitrogen were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Hydrocarbon solvents benzene-d_6 (Cambridge Isotopes), toluene-d_8 (Cambridge Isotopes), toluene (Bio-Lab), THF (Bio-Lab), and diethyl ether (BioLab) were distilled under vacuum from Na/K alloy or purified by passage through an activated alumina column under a nitrogen atmosphere. Pyrrole was purified by distillation on a rotary evaporator and then dried by refluxing over CaH$_2$ and distilling. UCl$_4$,[68] ThCl$_4$·2DME,[69] H$_2$dpm^{Me},[62] 2-*tert*-butylpyrrole,[64] and 2-adamantylpyrrole were prepared according to previously reported methods.[65] ThCl$_4$·3THF was prepared by passage of carbon tetrachloride vapor under a stream of helium over thoria in a tube furnace heated to 750 °C, followed by heating of the ThCl$_4$ produced in THF and precipitation with *n*-hexane.
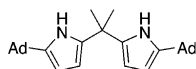
NMR spectra of crude reaction mixtures were recorded on a Bruker Avance 300, Bruker Avance III 400, or Bruker Avance 500 spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR are referenced to internal protio solvent and reported relative to tetramethylsilane. *J* values are reported for ^{1}H NMR coupling constants in Hertz. Known products were compared to previously reported data. Elemental analyses were performed on a Thermo Scientific Flash 2000 CHNS OEA instrument.

Synthetic Procedures. *Synthesis of 5,5′-(Propane-2,2-diyl)bis[2-(tert-butyl)pyrrole] (H2dpm^{tBu}).* 2-*tert*-Butylpyrrole (3.6 g, 29.7 mmol)
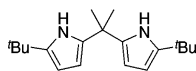
was dissolved in 100 mL of DCM, and 1.8 mL of 2,2-dimethoxypropane (14.8 mmol) was added to the solution. The solution was sparged with dinitrogen for 5 min, and then 750 mg of PPTS was added (3.0 mmol) and the solution stirred at room temperature for 6 h, resulting in a rapid color change of the solution to orange. The solution was then passed through a plug of Celite and the filtrate evaporated, and the solids were purified by column chromatography on silica gel with a 5% solution of ethyl acetate in hexane to yield 1.8 g of an orange waxy solid as the desired product (43%): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.49 (bs, 2H, NH), 5.97 (t, J = 3.0 Hz, 2H, pyrrole CH), 5.84 (t, J = 3.0 Hz, 2H, pyrrole CH), 1.63 (s, 6H, CH_3), 1.23 [s, 18H, C(CH_3)$_3$]; ^{13}C NMR (101 MHz, CDCl3) δ 141.22, 137.78, 103.20, 101.79, 35.80, 31.41, 30.59, 29.71; mp 58−60 °C; HRMS (APCI) [M + H]* observed m/z 287.2479, calcd for C$_{19}$H$_{31}$N$_2$ m/z 287.2487. Anal. Calcd for C$_{19}$H$_{30}$N$_2$: C, 79.66; H, 10.56; N, 9.78. Found: C, 79.45; H, 10.46; N, 10.09.

Synthesis of 5,5′-(Propane-2,2-diyl)bis[2-(1-adamantyl)pyrrole] (H$_2$dpm^{Ad}). A 500 mL Schlenk flask was loaded with 9.4 g (46.7 mmol) of 2-(1-adamantyl)pyrrole, 250 mL of DCM, and 2.8 mL of 2,2-dimethoxypropane (22.9 mmol). The solution was sparged with nitrogen for 5 min, and then 1.17 g of PPTS (4.7 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 24 h, then filtered through a plug of Celite, and dried under vacuum. The solids were purified by column chromatography on silica gel with a 5% solution of ethyl acetate in hexane to yield 7.95 g of an orange oil that solidified upon standing (79%): ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.53 (bs, 2H, NH), 5.96 (t, J = 3.0 Hz, 2H, pyrrole CH), 5.81 (t, J = 3.0 Hz, 2H, pyrrole CH), 2.02 (bs, 12H, adamantyl CH_2), 1.81 (d, J = 2.2 Hz, 12H, adamantyl CH_2), 1.72 (q, J = 12.2 Hz, 6H, adamantyl CH), 1.61 (s, 6H, CH_3); ^{13}C NMR (101 MHz, CDCl$_3$) δ 141.98, 137.44, 103.20, 101.09, 42.94, 36.89, 35.82, 33.30, 29.75, 28.67; mp 121−123 °C; HRMS (APCI) [M + H]* observed m/z 443.3430, calcd for C$_{31}$H$_{43}$N$_2$ m/z 443.3426. Anal. Calcd for C$_{31}$H$_{42}$N$_2$: C, 84.11; H, 9.56; N, 6.33. Found: C, 84.38; H, 9.31; N, 6.31.

Synthesis of Li$_2$(η^5:η^1-dpm^{Me})$_2$ThCl$_2$·2THF (1). A THF solution of the ligand (170 mg, 840 μmol) was cooled to −35 °C, followed by the addition of 2 equiv of ^{n}BuLi as a 1.6 M solution in hexane (1.05 mL, 1.68 mmol). The solution was warmed to room temperature and stirred for 2 h. A second solution of ThCl$_4$·3THF (248 mg, 420 μmol) in THF was prepared, and both solutions were cooled to −35 °C, followed by the rapid addition of the ligand solution to the thorium solution. The mixture was warmed to room temperature and stirred overnight. The solution was then evaporated to dryness and dissolved in toluene, followed by filtration and evaporation, yielding 299 mg of a beige solid (84%): ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 7.31 (d, J = 2.7 Hz, 2H, η^5-pyrrole CH), 6.21 (d, J = 2.8 Hz, 2H, η^5-pyrrole CH), 6.18 (d, J = 2.7 Hz, 2H, η^1-pyrrole CH), 6.01 (dd, J = 2.8, 0.7 Hz, 2H, η^1-pyrrole CH), 3.59 (t, J = 6.5 Hz, 12H, THF CH_2), 2.58 (s, 6H, CH_3), 2.34 (s, 6H, CH_3), 2.25 (s, 6H, CH_3), 1.66 (s, 6H, CH_3), 1.33−1.21 (m, 12H, THF CH_2); ^{13}C NMR (126 MHz, C$_6$D$_6$) δ 156.82 (C), 150.42 (C), 145.12 (C), 138.71 (C), 121.91 (CH), 117.49 (CH), 108.27 (CH), 105.52 (CH), 68.14 (CH_2), 39.33 (C), 34.82 (CH_3), 30.20 (CH_3), 25.54 (CH_2), 18.18 (CH_3), 16.63 (CH_3). Anal. Calcd for C$_{34}$H$_{48}$Cl$_2$Li$_2$N$_4$O$_2$Th: C, 47.40; H, 5.62; N, 6.50. Found: C, 47.02; H, 5.97; N, 6.88.

Synthesis of Li$_2$(η^5:η^1-dpm^{Me})$_2$UCl$_2$·2THF (3). A THF solution of the ligand (198 mg, 979 μmol) was cooled to −35 °C, followed by the addition of 2 equiv of ^{n}BuLi as a 1.6 M solution in hexane (1.22 mL, 1.96 mmol). The solution was warmed to room temperature and stirred for 2 h. A second solution of UCl$_4$ (372 mg, 979 μmol) in THF was prepared, and both solutions were cooled to −35 °C, followed by the slow addition of the ligand solution to the uranium solution. The mixture was warmed to room temperature and stirred for 3 days. The solution was then evaporated to dryness and dissolved in toluene, followed by filtration

and evaporation, yielding 577 mg of a dark red solid occurring from coordination of 2 equiv of ligand (69%): ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 20.77 (s, 6H), 20.44 (s, 6H), 15.17 (s, 2H), 4.16 (s, 18H), 1.73 (s, 2H), 1.48 (s, 18H), −1.15 (s, 2H), −1.60 (s, 6H), −5.55 (s, 6H), −8.84 (s, 6H), −31.84 (s, 2H), −33.91 (s, 6H). ^{13}C NMR is silent except for THF resonances. Anal. Calcd for C$_{34}$H$_{48}$Cl$_2$Li$_2$N$_4$O$_2$U: C, 47.07; H, 5.58; N, 6.46. Found: C, 47.55; H, 6.08; N, 6.27.

Synthesis of Li$_2$(η^5:η^5-dpm^{Me})ThCl$_4$·3THF (2). An ethyl ether solution of the ligand (288 mg, 1.42 mmol) was cooled to −35 °C, followed by the addition of 2 equiv of ^{n}BuLi as a 1.6 M solution in hexane (1.78 mL, 2.85 mmol). The solution was warmed to room temperature and stirred for 2 h. A second solution of ThCl$_4$·3THF (840 mg, 1.42 mmol) in THF was prepared, and both solutions were cooled to −35 °C, followed by the slow addition of the ligand solution to the thorium solution. The mixture was warmed to room temperature and stirred overnight. The solution was evaporated to dryness and dissolved in a mixture of toluene and ethyl ether, followed by filtration and evaporation, yielding 869 mg of a beige solid (77%): ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 6.90 (d, J = 2.5 Hz, 2H, pyrrole CH), 6.62 (d, J = 2.5 Hz, 2H, pyrrole CH), 3.59 (t, J = 6.5 Hz, 12H, THF CH_2), 2.86 (s, 6H, CH_3), 1.71 (s, 6H, CH_3), 1.33−1.21 (m, 12H, THF CH_2); ^{13}C NMR (126 MHz, C$_6$D$_6$) δ 146.62 (C), 145.80 (C), 120.13 (CH), 119.13 (CH), 68.14 (CH_2), 25.54 (CH_2), 24.26 (CH_3), 18.56 (CH_3). Anal. Calcd for C$_{25}$H$_{40}$Cl$_4$Li$_2$N$_2$O$_3$Th: C, 37.33; H, 5.01; N, 3.48. Found: C, 37.18; H, 4.90; N, 3.37.

Synthesis of Li$_2$(η^5:η^5-dpm^{tBu})UCl$_4$·3THF (4). A THF solution of the ligand (201 mg, 702 μmol) was cooled to −35 °C, followed by the addition of 2 equiv of ^{n}BuLi as a 1.6 M solution in hexane (877 μL, 1.40 mmol). The solution was warmed to room temperature and stirred for 2 h. A second solution of UCl$_4$ (267 mg, 702 μmol) in THF was prepared, and both solutions were cooled to −35 °C, followed by the slow addition of the ligand solution to the uranium solution. The mixture was warmed to room temperature and stirred for 3 days. The solution was then evaporated to dryness and dissolved in toluene, followed by filtration and evaporation, yielding 408 mg of a dark red solid (66%): ^{1}H NMR (300 MHz, C$_6$D$_6$) δ 19.17 (s, 1H), 18.78 (s, 1H), 16.67 (s, 6H), 15.86 (s, 1H), 14.41 (s, 1H), 13.54 (s, 1H), 7.16 (s, 7H), 1.61 (s, 3H), 1.33 (s, 2H), 1.06 (s, 7H), 0.98 (s, 1H), −9.89 (s, 18H), −13.41 (s, 3H). ^{13}C NMR was silent. Anal. Calcd for C$_{31}$H$_{52}$Cl$_4$Li$_2$N$_2$O$_3$U: C, 41.63; H, 5.86; N, 3.13. Found: C, 42.05; H, 6.14; N, 2.79.

Synthesis of Li$_2$(η^5:η^5-dpm^{tBu})ThCl$_4$·3THF. A solution of H$_2$dpm^{tBu} (327 mg, 1.14 mmol) in THF (3 mL) was cooled to −35 °C, and then 1.463 mL of a 1.6 M ^{n}BuLi solution was added at the reduced temperature. The solution was warmed to room temperature, stirred for 3 h, and then added to a cooled (−35 °C) solution of ThCl$_4$·2DME (632 mg, 1.14 mmol) in THF. The reaction mixture was warmed to room temperature and stirred for 8 h, followed by removal of solvent *in vacuo*. The residue was dissolved in toluene, filtered through a plug of Celite, and evaporated, yielding 730 mg of a light orange powder (73%): ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 7.15 (m, 2H, pyrrole CH), 6.83 (m, 2H, pyrrole CH), 3.63 (bs, 12H, THF CH_2), 2.80 (s, 6H, CH_3), 1.67 [s, 18H, C(CH_3)$_3$], 1.36 (s, 12H, THF CH_2); ^{13}C NMR (126 MHz, C$_6$D$_6$) δ 164.24 (C), 142.18 (C), 122.67 (CH), 116.41 (CH), 69.80 (C), 68.19 (CH_2), 59.30 (C), 25.22 (CH_2), 23.42 (CH_3), 21.07 (CH_3). Anal. Calcd for C$_{31}$H$_{52}$Cl$_4$Li$_2$N$_2$O$_3$Th: C, 41.91; H, 5.90; N, 3.15. Found: C, 42.26; H, 5.85; N, 2.82.

Synthesis of Li$_2$(η^5:η^5-dpm^{Ad})ThCl$_4$·3THF. A solution of 490 mg of H$_2$dpm^{Ad} (1.107 mmol) in 4 mL of THF was cooled to −35 °C, followed by the addition of 2 equiv of ^{n}BuLi as a 1.6 M solution in hexane (1.384 mL, 2.214 mmol). The solution was warmed to room temperature, stirred for 3 h, and then added to a cooled solution (−35 °C) of 613 mg (1.107 mmol) of ThCl$_4$·2DME dissolved in THF. The reaction mixture was warmed to room temperature and stirred overnight, at which point the volatiles were removed under vacuum. The residue was dissolved in a mixture of ethyl ether and toluene, then filtered through a plug of Celite, and evaporated under vacuum to yield 644 mg of a pale orange powder (56%): ^{1}H NMR (500 MHz, C$_6$D$_6$) δ 6.23 (t, J = 3.0 Hz, 2H, pyrrole CH), 6.06 (t, J = 3.0 Hz, 2H, pyrrole CH), 3.61 (bs, 12H, THF CH_2), 1.87−1.82 (m, 12H, adamantyl CH_2), 1.73 (d, J = 2.4 Hz, 12H, adamantyl CH_2), 1.66 (s, 6H, CH_3), 1.58 (bs, 6H,

adamantyl CH), 1.39 (bs, 12H, THF CH_2); ^{13}C NMR (126 MHz, C$_6$D$_6$) δ 141.18 (C), 136.91 (C), 103.78 (CH), 101.93 (CH), 70.64 (CH$_2$), 58.93 (C), 42.66 (C), 36.53 (CH), 29.73 (CH), 28.52 (CH$_2$), 25.31 (CH$_2$), 13.94 (CH$_3$). Anal. Calcd for C$_{43}$H$_{64}$Cl$_4$Li$_2$N$_2$O$_3$Th: C, 49.44; H, 6.18; N, 2.68. Found: C, 49.18; H, 5.92; N, 2.60.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02853.

CIF file providing crystallographic data for **1** (CIF)
CIF file providing crystallographic data for **2** (CIF)
CIF file providing crystallographic data for **3** (CIF)
CIF file providing crystallographic data for **4** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: chmoris@tx.technion.ac.il. Telephone: +972-4-8292680.

Notes

The authors declare no competing financial interest.

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