Synthesis, Characterization, and Organometallic Derivatives of Diamidosilyl Ether Thorium(IV) and Uranium(IV) Halide Complexes

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The high-yield synthesis and spectroscopic and structural characterization of two new dimeric uranium(IV) and thorium(IV) halide complexes $\{[^{tBu}NON]AnCl_2\}_2$ (An = U (**1**), Th (**2**)) supported by the doubly deprotonated diamidosilyl ether ligand $[(CH_3)_3CNH(Si(CH_3)_2)]_2O$ ($[^{tBu}NON]^{2-}$) are reported. The reaction of $^1/_2$ equiv of **1** or **2** with 2 equiv of $LiCH_2Si(CH_3)_3$ or C_3H_5MgCl generates stable organoactinides of the form $[^{tBu}NON]AnR_2$ (R = C_3H_5, An = U (**3**), Th (**4**); R = $CH_2Si(CH_3)_3$, An = U (**5**), Th (**6**)). The reaction of $^1/_2$ equiv of **1** or **2** with 1 equiv of $Na(C_5(CH_3)_5)$ results in $[^{tBu}NON]An(\eta^5\text{-}C_5(CH_3)_5)Cl$ (An = U (**7**), Th (**8**)), which can be converted to the mixed amido/Cp complex $[^{tBu}NON]An(C_5(CH_3)_5)CH_3$ (An = U (**9**), Th (**10**)) by reaction with CH_3MgBr. The uranium(IV) complexes were characterized by paramagnetically shifted ^1H NMR spectra; the U−CH_2 and U−CH_3 resonances for **5** and **9** are at δ −148.9 and −146.3, respectively. The ^1H and $^{13}C\{^1H\}$ NMR spectra of the thorium(IV) complexes are also consistent with these formulations; the Th−CH_2 resonances in **6** are at δ 0.0 and 85.58 for ^1H and $^{13}C\{^1H\}$, respectively. The variable-temperature magnetic susceptibilities of the uranium(IV) halide dimer **1** and monomer **7** are also reported.

Introduction

Organoactinide centers typically require sterically demanding ligands to achieve stabilization. The ubiquitous cyclopentadienyl (Cp) and pentamethylcyclopentadienyl ($C_5(CH_3)_5$) ligands have proven to be effective in attaining this stabilization and have played a prominent role in organoactinide chemistry.[1−3] To broaden the scope beyond Cp-based systems, amido and other nitrogen donor ligands have recently been utilized on actinide centers. The macrocyclic tetrapyrrole tetraanion $\{[(-CH_2-)_5]_4\text{-calix}[4]\text{tetrapyrrole}\}$ has been effective in stabilizing trivalent uranium.[4] The research on amido actinides thus far has focused primarily on monodentate bis(trimethylsilyl)amido-type ligands.[5−20] This ligand set is extremely effective for stabilizing actinide centers, and their complexes exhibit a rich and varied chemistry. More recently, the tetradentate triamidoamine ligands $[N(CH_2CH_2NR)_3]^{3-}$ have been used to prepare actinide amido complexes.[21−23] These systems engage in exciting reaction chemistry such as mixed-valent U(III)/U(IV) complexes[24] and the first actinide dinitrogen complex.[25] It is clear that altering the steric bulk and/or the number of amido donors is one key to accessing different reactivities and stabilities of amido actinide complexes.

Dianionic chelating diamido ether and diamido-donor ligands, for which Zr(IV) and Ti(IV) complexes have been studied with respect to alkene polymerization,[26−37] have never been explored with respect to actinide

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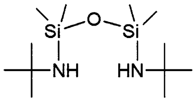
centers. In particular, due to the oxophilic nature of actinide centers, the diamido ether ligands that we and others have developed are exemplary frameworks to support organoactinide complexes.[38] Herein we report two dimeric actinide halide complexes stabilized by the chelating diamido ether ligand $[(CH_3)_3CNH(Si(CH_3)_2)]_2O$ ($H_2[^{tBu}NON]$)[27,39] and their subsequent alkylation with a range of organic substituents to yield stable amido-based organoactinide complexes.

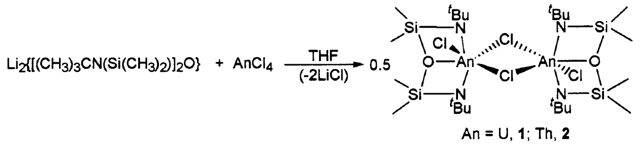


$H_2[^{tBu}NON]$

Results and Discussion

Synthesis and Characterization of $\{[^{tBu}NON]AnCl_2\}_2$. As depicted in Scheme 1, treatment of a THF slurry of $AnCl_4$ with $Li_2[^{tBu}NON]$[27,39] (1 equiv) at −30 °C affords $\{[^{tBu}NON]AnCl_2\}_2$ (An = U (**1**), Th (**2**)) in over 90% isolated yield. The only other known diamidoactinide complexes, obtained by reacting the diamidoamine ligand $Li_2[(CH_3)_3SiN\{CH_2CH_2NSi(CH_3)_3\}_2]$ with UCl_4 and $ThCl_4$, resulted in a mixture of mono- and bis(diamidoamine) complexes.[40]

Scheme 1. Synthesis of Complexes 1 and 2



As shown in Figure 1, the ^1H NMR spectrum of **1** at 293 K displayed paramagnetically shifted peaks, as anticipated for a U(IV) species,[41] and was assigned on the basis of integration of the signals. The $-C(CH_3)_3$ protons are assigned to the singlet at δ 68.9. Two broad upfield peaks at δ −17.7 and −23.8 correspond to the $-Si(CH_3)_2$ groups. The presence of two resonances for the $-Si(CH_3)_2$ substituents is consistent with the dimeric nature of the complex in toluene-d_8. A variable-temperature NMR study between 293 and 353 K showed that the two resonances became increasingly broad as the temperature increased, coalescing at 353 K. As illustrated in Scheme 2, either the rapid interconversion of the bridging and terminal chlorides or a monomer−dimer equilibrium could yield equivalent ligand silyl methyl moieties.

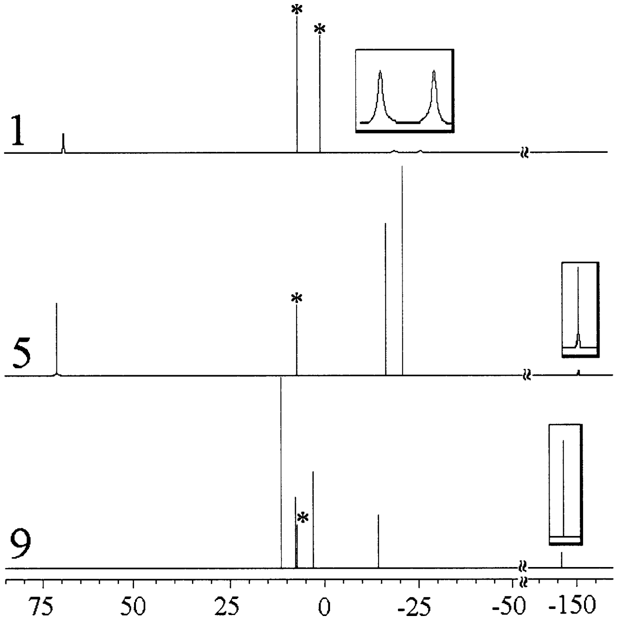
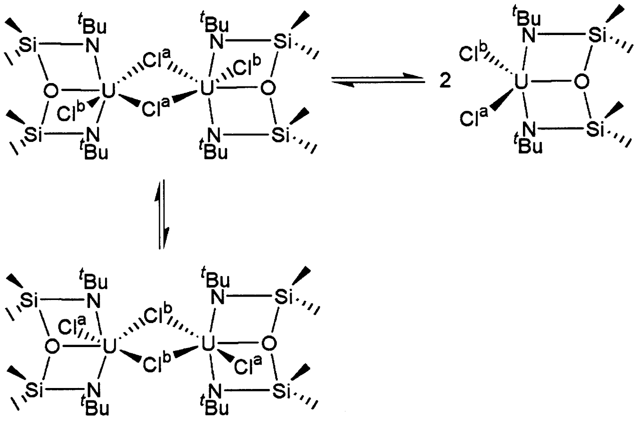


Figure 1. Paramagnetically shifted ^1H NMR spectra for complexes **1** (500 MHz, 293 K), **5**, and **9** (400 MHz, 294 K). The inset for **1** is the expansion around δ −20, and the insets for **5** and **9** are expansions around δ −150 (asterisks indicate toluene-d_8 for **1** and benzene-d_6 for **5** and **9**).

Scheme 2. Possible Mechanism for the Dynamic Behavior of 1 in Toluene-d_8



The ^1H NMR spectrum of **2**, recorded at 294 K, also showed two inequivalent $-Si(CH_3)_2$ groups at δ 0.30 and 0.27, again consistent with the complex remaining in a dimeric state in toluene-d_8. The $^{13}C\{^1H\}$ chemical shifts of **2** at 294 K were confirmed through the use of a {C,H} 2D-COSY experiment. Both the ^1H and ^{13}C signals of **2** are similar to those of other diamagnetic transition-metal and main-group complexes containing the $[^{tBu}NON]$ ligand backbone.[39,42]

Solid-State Structure of $\{[^{tBu}NON]ThCl_2\}_2$ (2) and $\{[^{tBu}NON]UBr_{1.46}Cl_{0.54}\}_2$ (1′). Single crystals of **2**

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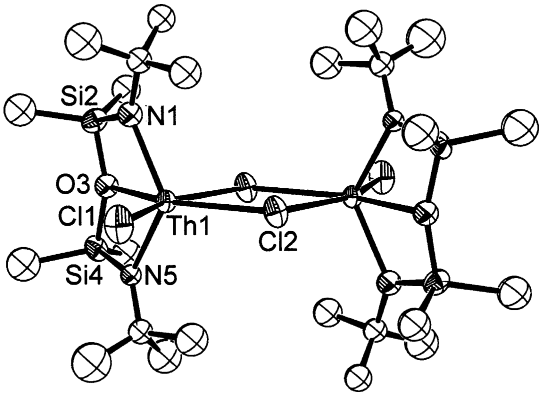

Figure 2. Molecular structure and numbering scheme of **2** (ORTEP, 40% probability ellipsoids).

Table 1. Summary of Crystallographic Data

	1′[a]	**2**[b]
empirical formula	$UBr_{1.46}Cl_{0.54}N_2Si_2OC_{12}H_{30}$	$ThCl_2N_2Si_2OC_{12}H_{30}$
fw	648.4	577.5
cryst dimens, mm^3	0.60 × 0.33 × 0.48	0.18 × 0.21 × 0.18
T, K	293	293
cryst syst	orthorhombic	monoclinic
space group	*Pbca*	$P2_1/c$
a, Å	14.343(2)	8.712(3)
b, Å	16.922(3)	19.087(5)
c, Å	18.654(3)	13.488(4)
β, deg		100.30(3)
V, Å^3	4527.6	2206.9
Z	8	4
d_{calcd}, g cm^{-3}	1.902	1.738
μ, cm^{-1}	95.2	250.44
no. of obsd data	1094 ($>2.5\sigma(I)$)	1674 ($>3\sigma(I)$)
no. of params	126	107
$R(F)$[c]	0.0384	0.0598
$R_w(F)$[d]	0.0308	0.0664

[a] Additional conditions: Enraf-Nonius CAD-4 diffractometer, Mo Kα radiation ($\lambda = 0.7093$ Å), graphite monochromator. [b] Additional conditions: Rigaku RAXIS-Rapid curved image plate area detector, Cu Kα radiation ($\lambda = 1.5419$ Å), graphite monochromator. [c] $R(F) = \sum||F_o| - |F_c|/\sum|F_o|$. [d] $\sum w(|F_o| - |F_c|)^2$ was the function minimized, where $w^{-1} = \sigma^2(F_o) + 0.0001F_o^2$. $R_w(F) = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1′ and 2

bond, angle	$\{[^tBuNON]UX_2\}_2$[e]	$\{[^tBuNON]ThCl_2\}_2$
U1−X1; Th1−Cl1	2.772(2)	2.670(7)
U1−X2; Th1−Cl2	2.913(3)	2.850(6)
An1−O3	2.479(11)	2.531(17)
An1−N1	2.145(16)	2.29(2)
An1−N5	2.130(18)	2.291(19)
N1−An−N5	124.7(6)	121.4(7)
X1−U−X2; Cl1−Th−Cl2	89.91(8)	85.6(2)
O3−U−X1; O3−Th−Cl1	109.5	121.3(4)
O3−U−X2; O3−Th−Cl2	160.6(3)	153.1(4)

[e] Where X(1) = Br(1)/Cl(1) = 0.85/0.15 and X(2) = Br(2)/Cl(2) = 0.62/0.38.

suitable for X-ray diffraction were obtained by slow evaporation of a toluene solution of **2**. The overall structure of **2** (Figure 2 and Table 2) is dimeric with a pseudooctahedral coordination about each thorium center, with one chelating diamido ether ligand and two bridging and one terminal chloride.

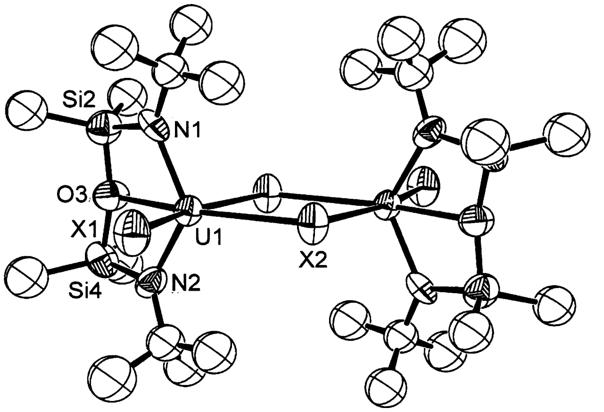

Figure 3. Molecular structure and numbering scheme of **1′** (ORTEP, 33% probability ellipsoids), where X(1) = Br(1)/Cl(1) = 0.85/0.15 and X(2) = Br(2)/Cl(2) = 0.62/0.38.

The silyl ether oxygen donor, with a Th1−O3 bond length of 2.531(17) Å, is located cis to one bridging chloride and trans to the other. This Th−O distance is nearly identical with one of the thorium−THF oxygen distances in $[(C_5(CH_3)_5)_2Th(CH_3)(THF)_2]BPh_4$[43] and is similar to other Th−O bond distances;[44−47] it is shorter than in a similar iron(III) chloride-bridged dimer, $\{[^{tBu}NON]Fe(\mu\text{-}Cl)\}_2$, which has an Fe−O distance of 2.597(4) Å.[48] This is surprising, due to the much larger covalent radius of thorium compared to that of iron, and is most likely attributable to the thorium center having a higher degree of oxophilicity than the iron.[49]

As expected, the Th1−Cl2 bridging distance of 2.858(6) Å is considerably longer than the terminal Th1−Cl1 distance of 2.670(7) Å. These distances are slightly shorter than in the seven-coordinate diphosphinoamido−thorium chloride-bridged dimer $[\{ThCl_2[N(CH_2CH_2PPr^i{}_2)_2]\}_2]$, which has bridging Th−Cl distances of 2.871(3) and 2.965(6) Å and a terminal Th−Cl distance of 2.702(4) Å.[50] The shorter distances in **2** may be due to the lower coordination number and resulting lower steric strain at the thorium metal center compared to $[\{ThCl_2[N(CH_2CH_2PPr^i{}_2)_2]\}_2]$.

In an attempt to methylate **1**, 2 equiv of CH_3MgBr was added at −78 °C to a THF solution of $\{[^{tBu}NON]UCl_2\}_2$, but upon filtration and extraction with toluene, green crystals of $\{[^{tBu}NON]UBr_{1.46}Cl_{0.54}\}_2$ (**1′**), a halide redistribution product, were obtained by slow evaporation in toluene. X-ray analysis showed that **1′** is isostructural with the thorium analogue **2** (Figure 3 and Table 2).

The halide sites consist of partial chlorine and partial bromine occupancy in **1′**. The U1−O3 distance of 2.479(11) Å is considerably smaller than the Th1−O3 distance of 2.531(17) Å, which can be explained by the smaller covalent radius of U(IV) compared to Th(IV).[49,51] In addition, while the Th1−Cl2 bridge is symmetric within

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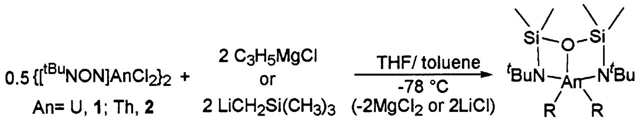
error, the U1−Br2 bridge possesses two slightly different bond lengths, presumably due to the chloride/bromide disorder in the structure. This disorder precludes a meaningful discussion of structural parameters relating to the U−X atoms.

Organometallic Derivatives. Synthesis and Characterization of $[^{tBu}NON]An(\eta\text{-}C_3H_5)_2$. Treatment of $^1/_2$ equiv of **1** or **2** with C_3H_5MgCl (2 equiv) afforded the disubstituted allyl complexes $[^{tBu}NON]An(\eta\text{-}C_3H_5)_2$ (An = U (**3**), Th (**4**)) in good yields (Scheme 3).

Scheme 3. Synthesis of Complexes 3−6



3-6

R = C_3H_5; An = U, **3**; Th, **4**
R = $CH_2Si(CH_3)_3$; An = U, **5**; Th, **6**

To assist in deciphering the hapticity of the allyl ligand in both **3** and **4**, ^1H NMR studies were completed from 183 to 353 K in toluene-d_8. The 294 K spectrum of **4** displayed both a quintet at δ 6.90 ($CH(CH_2)_2^-$), in accordance with an A_4X pattern, and a very broad resonance at δ 3.5. Upon heating, this broad resonance develops into a doublet and the quintet at δ 6.90 begins to broaden into the baseline. Even at 353 K the doublet is not fully resolved. When the sample is cooled to 248 K, the broadened resonance at 294 K of δ 3.5 is resolved into two doublets at δ 3.74 and 3.21. Further cooling results in the doublets broadening into the baseline. Unfortunately, the collapse of the allyl linkage, into either an η^1 or η^3 linkage, was not observed at either temperature extreme. The dynamic process in the variable-temperature NMR is complex, possibly because there are two allyl resonances present, potentially of different binding modes and different fluxional rates. Further experiments will be carried out to assist in determining the binding mode of both allyl ligands on the thorium center. For **3**, heating in toluene-d_8 shifted all of the allyl resonances upfield, consistent with the χ_m value of the complex lowering with increasing temperature. The broad resonances of δ 29.7 and 11.4 for $CH(CH_2)_2^-$, observed at 294 K, begin to shift together as the temperature is increased. Two broad peaks are still observed at 313 K; further heating to 353 K results in one single resonance observed. When **3** was cooled, the allyl resonances broadened into the baseline, as expected for a paramagnetic complex. Again, the hapticity information is ambiguous.

Additional information about the hapticity of the allyl ligands was obtained using IR spectroscopy. The most characteristic absorption band for an actinide η^1-allyl complex is $\nu_{C=C}$ at approximately 1610−1640 cm^{-1}; this band is absent in η^3-allyl structures.[52−55] Weak bands are observed at 1617 and 1615 cm^{-1} for complexes **3** and **4**, respectively. Additional bands are also present at 1552 and 1503 cm^{-1} for **3** and 1548 and 1494 cm^{-1} for **4**, indicating CH_2 deformations or antisymmetric C−C−C stretching modes. These IR spectra are similar to those of other actinide η^1-allyl complexes[52,53] and differ from those of actinide η^3-allyl complexes.[54,55] Thus, in the solid state, at least one allyl ligand is likely bound in an η^1 fashion to the actinide center. Unfortunately, despite numerous attempts, X-ray-quality crystals could not be obtained.

Synthesis and Characterization of $[^{tBu}NON]An(CH_2Si(CH_3)_3)_2$. Treatment of $^1/_2$ equiv of either **1** or **2** with 2 equiv of $LiCH_2Si(CH_3)_3$ in toluene at −78 °C resulted in the formation of $[^{tBu}NON]An(CH_2Si(CH_3)_3)_2$ (An = U (**5**), Th (**6**)) in greater than 90% isolated yield (Scheme 3). The reaction is sensitive to the choice of solvent, and the use of toluene resulted in **5** and **6** being obtained in the highest purity and yield.

Differing from the dimeric starting materials **1** and **2**, which both displayed two separate resonances for the $-Si(CH_3)_2$ protons of the ligand backbone, **5** and **6** both show one sharp singlet for this resonance at 294 K, consistent with a monomeric structure in solution. The ^1H NMR spectrum of **5** is sharp and is paramagnetically shifted, consistent with a U(IV) species (Figure 1).[41] There is a significant upfield shift for the $U-CH_2-$ resonance, observed at δ −148.9. This large shift is attributed to the close proximity of these protons to the paramagnetic uranium center. The postulated structure of **6** was supported by its ^1H NMR spectrum, with singlets in a 9:9:6:2 ratio corresponding to the $-C(CH_3)_3$, $-Si(CH_3)_3$, $-Si(CH_3)_2$, and $-CH_2-$ groups, respectively. The $Th-CH_2-$ resonance is at δ 0.00. The ^{13}C resonances of **6** were assigned with the assistance of a {C, H} 2D-COSY spectrum. The $Th-CH_2-$ resonance appears at δ 85.58; this is similar to that observed in $Th(O\text{-}2,6\text{-}t\text{-}Bu_2C_6H_3)_2(CH_2Si(CH_3)_3)_2$.[56] In the proton-coupled ^{13}C NMR of **6**, the $Th-CH_2-$ resonance appears as a sharp triplet with a coupling constant of $^1J_{CH} = 104$ Hz. The observed coupling is significantly reduced from that which is expected for a typical sp^3-hybridized carbon atom and suggests the existence of an α-agostic interaction of the methylene group with the thorium center. Similar reduced values for J_{CH}, attributed to the same α-agostic interaction, have been observed for $(C_5(CH_3)_5)Th(OAr)(CH_2Si(CH_3)_3)_2$ (Ar = 2,6-t-$Bu_2C_6H_3$) ($^1J_{CH} = 100$ Hz)[57] and $(CH_3)_2Si[\eta^5\text{-}(CH_3)_4C_5]_2Th[CH_2Si(CH_3)_3]_2$ ($^1J_{CH} = 99$ Hz).[58] Although attempts to crystallize **5** and **6** were unsuccessful, due to both complexes' exceptionally high solubility in most solvents, including hexanes and hexamethyldisiloxane, the spectroscopic and microanalytical data support the formation of the new actinide bis(alkyl) complexes as described.

Synthesis and Characterization of $[^{tBu}NON]An(\eta^5\text{-}C_5(CH_3)_5)Cl$ and $[^{tBu}NON]An(\eta^5\text{-}C_5(CH_3)_5)CH_3$. While there are a plethora of bis(pentamethylcyclopentadienyl)actinide complexes known,[59−64] monosubstitu-

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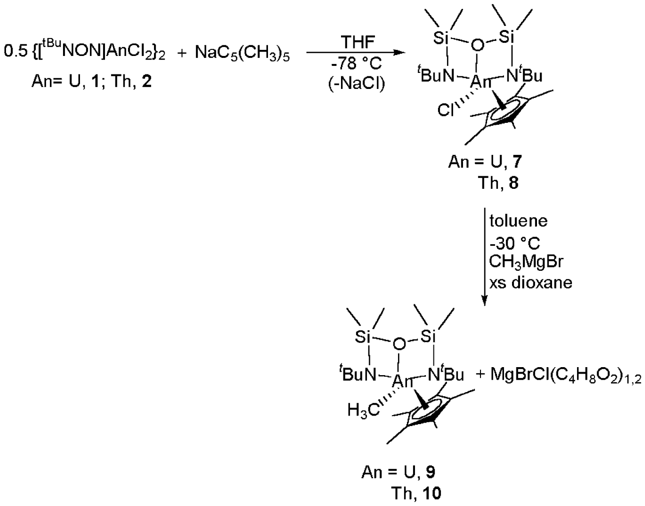
Scheme 4. Synthesis of Complexes 7−10



ted pentamethylcyclopentadienyl complexes are less common.[54,57,65−70] Placing a single $C_5(CH_3)_5^-$ unit on **1** or **2** permits further substitution chemistry to be carried out at the remaining chloride site. Presumably due to the steric bulk of the [^{tBu}NON] ligand, attempts to yield diamido $(C_5(CH_3)_5)^-{}_2$ complexes were unsuccessful. However, $(C_5(CH_3)_5)^-$ complexes of the form [^{tBu}NON]-An($C_5(CH_3)_5$)Cl (An = U (**7**), Th (**8**)) were readily synthesized in high yield by treating a THF solution of {[^{tBu}NON]AnCl$_2$}$_2$ with 2 equiv of NaC$_5$(CH$_3$)$_5$ (Scheme 4).

Despite numerous attempts, significant disorder in crystals of **7** and **8** limited the refinement to a crude connectivity, which revealed η^5-$C_5(CH_3)_5$ and [^{tBu}NON]$^{2-}$ ligands bound to the actinide centers. The ^{1}H NMR spectrum of **7** displayed sharp, shifted peaks, as anticipated for a U(IV) paramagnetic species.[41] Spectra of both **7** and **8** indicated two different environments for the silyl methyl groups, readily identified by endo and exo sides of the [^{tBu}NON] ligand relative to the $C_5(CH_3)_5^-$ ligand plane. In both **7** and **8**, the presence of only one resonance in the ^{1}H NMR spectrum for the $C_5(CH_3)_5^-$ moiety suggests an η^5 binding mode.[71−74]

Also indicative of a η^5-$C_5(CH_3)_5$ binding mode are the characteristic IR stretches at 1018 and 793 cm^{-1} for **7** and at 1024 and 793 cm^{-1} for **8**.[1,61,75] Finally, the molecular ion peaks with the correct isotropic signature for both compounds were observed at *m*/*z* 683 and 678 for **7** and **8**, respectively. Both complexes show the loss of a chloride ligand as the first fragment, and the mass fragmentation patterns were identical for both compounds.

Further reaction of **7** and **8** with 1 equiv of CH$_3$MgBr and excess *p*-dioxane resulted in chloride for methyl substitution to give [^{tBu}NON]An($C_5(CH_3)_5$)CH$_3$ (An = U (**9**), Th (**10**)) in high yield. The 294 K ^{1}H NMR of **9** displayed sharp, paramagnetically shifted resonances (Figure 1). As in **5**, the U−C*H*$_3$ resonance is upfield, in this instance at δ −146.34. The NMR spectra of **10** are also consistent with the proposed structure, with the Th−*C*H$_3$ resonances at δ 0.43 and 57.63 in the ^{1}H and ^{13}C{^{1}H} NMR, respectively. The chemical shift values are in good agreement with other actinide complexes containing both a −$C_5(CH_3)_5$ and a −CH$_3$ unit.[76]

In addition to the single −C$_5$(C*H*$_3$)$_5$ resonance in the ^{1}H NMR for all complexes, indicative of an η^5 binding mode, the characteristic IR stretches at 1019 and 803 cm^{-1} for **9** and at 1025 and 802 cm^{-1} for **10** verify an η^5-$C_5(CH_3)_5$ binding mode to the actinide center.[1,61,75] Both **9** and **10** were found to be unstable under electron impact conditions and lost methyl fragments to give *m*/*z* 648 and 642, respectively.

Magnetism. Apart from obtaining the room-temperature magnetic moments using the Evans method,[77] solid-state variable-temperature magnetic studies were performed on {[^{tBu}NON]UCl$_2$}$_2$ (**1**) and [^{tBu}NON]U-($C_5(CH_3)_5$)Cl (**7**). The magnetic behavior of actinides is complicated, due to these systems existing in a situation such that the crystal field splittings are of approximately the same magnitude as the spin−orbit coupling parameter, both of which are greater than kT.[78,79] This is in contrast to the lanthanides, where the spin−orbit coupling parameter dominates the single-ion magnetism. The result is a deficiency in a well-defined coupling scheme for the actinides. Russell−Saunders coupling, typically employed for the first-row transition metals, breaks down but is not replaced by *jj* coupling.[79] Considering the actinides, the term "spin-only" often holds little meaning due to the large spin−orbit coupling and crystal field terms mixing into the free ion, and the magnetic moment reflects this mixing, especially at lower temperatures.[80]

With this in mind, the values of μ_{eff} from 5 to 300 K for **1** and **7** are shown in Figure 4. The μ_{eff} value for monometallic **7** is 2.80 μ_B at 300 K, similar to that observed for related tetrakis(amido)uranium(IV) complexes.[81] This value is much lower than 3.58 μ_B, the theoretical value for a 5f^2 free-ion system, which has a

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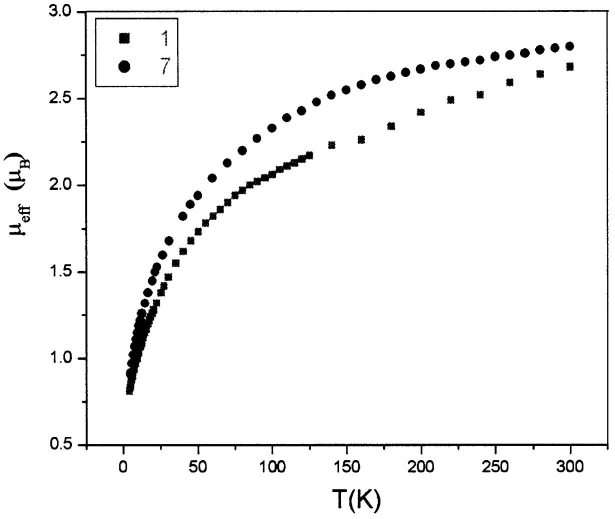

Figure 4. Plot of μ_{eff} vs T for **1** and **7**.

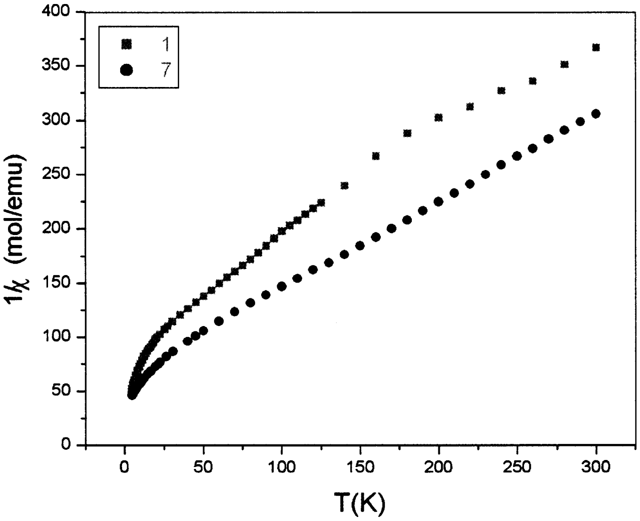

Figure 5. Plot of $1/\chi$ vs T for **1** and **7**.

nominal $^3H_4$ ground state (*jj* coupling).[82] This lower value is likely a reflection of covalency in the bonding interactions and also a reduction in symmetry; both factors lower the overall orbital contribution to the magnetic moment by removing orbital degeneracies. The μ_{eff} value for **7** decreases to 0.91 μ_B at 5 K. This decrease is due solely to the single-ion effects at the uranium(IV) center, as the ground state for U(IV) is an orbital singlet.[78] In this case, the $1/\chi_m$ vs T plots (Figure 5) indicate that these uranium(IV) systems may have nearly degenerate ground states.

Similar to **7**, the μ_{eff} value for dinuclear **1** is 2.63 μ_B at 300 K and decreases to 0.81 μ_B at 2 K; again, this decrease is due to the single-ion magnetism of the uranium(IV) centers. However, in addition to this factor, a portion of the μ_{eff} drop could, for **1**, be attributed to weak antiferromagnetic interactions between the two uranium(IV) centers, mediated by the chloride bridges. The slightly sharper decrease of the μ_{eff} value for dinuclear **1** with temperature, compared to mononuclear **7** (Figure 4), might qualitatively indicate that such weak antiferromagnetic interactions are present in **1**, but the significant change in covalency and symmetry upon changing $C_5(CH_3)_5^-$ for a chloride ligand may also be responsible. In any case, any antiferromagnetic interactions in **1** are clearly very weak in magnitude. Such qualitative determinations of magnetic coupling interactions in the presence of strong single-ion magnetic effects have been useful in heterobimetallic lanthanide/transition metal, actinide/transition metal, and lanthanide/organic radical complexes.[83-86]

Concluding Remarks. The synthesis and spectroscopic properties of the two new dimeric uranium(IV) and thorium(IV) halide complexes $\{[^{tBu}NON]AnCl_2\}_2$ (An = U (**1**), Th (**2**)), supported by the chelating diamidosilyl ether ligand $[(CH_3)_3CNH(Si(CH_3)_2)]_2O$ ($H_2[^{tBu}NON]$), have been described. The exemplary steric and electronic properties of the chelating diamidosilyl ether ligand ($H_2[^{tBu}NON]$) have facilitated the stabilization of both U(IV) and Th(IV) centers. These complexes presented an excellent opportunity for further substitution chemistry at the chloride sites. The syntheses and spectroscopic properties of the resulting substituted complexes $[^{tBu}NON]AnR_2$ (R = η-C_3H_5, $CH_2Si(CH_3)_3$), $[^{tBu}NON]An(C_5(CH_3)_5)Cl$, and $[^{tBu}NON]An(C_5(CH_3)_5)CH_3$ (An = U, Th) have been described. This new class of organoactinide complexes was readily synthesized in good yield. Solid-state magnetic measurements of **1** and **7** have shown that both complexes exhibit a decrease in μ_{eff} with decreasing temperature and may be explained by the single-ion magnetism of the uranium(IV) centers. We are presently exploring the reactivity of these new organonactinides.

Experimental Section

General Procedures and Techniques. All reactions and manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen using either an Mbraun Labmaster 130 glovebox or standard Schlenk and vacuum-line techniques. All glassware was dried at 160 °C overnight prior to use. Toluene and hexanes (Fisher) were purified using an MBraun solvent purification system connected to the glovebox and were passed through one column of activated alumina and one column of activated copper catalyst under nitrogen pressure. Diethyl ether (Et_2O; Caledon) and 1,4-dioxane (Aldrich) distillations were performed from a sodium/benzophenone solution. The tetrahydrofuran (THF; Fisher) distillation was performed from a potassium/benzophenone solution. All distillations were done under a nitrogen atomosphere. Deuterated solvents (Cambridge Isotope Laboratories) were distilled from a sodium/benzophenone solution and stored under nitrogen. Uranium tetrachloride[87] and $[(CH_3)_3CNH(Si(CH_3)_2)]_2O$[27,39] ($H_2[^{tBu}NON]$) were prepared in accordance with the literature procedures. Anhydrous thorium tetrachloride (Strem), ^{n}BuLi (1.6 M hexane solution, Acros), C_3H_5MgCl (2.0 M solution in THF, Aldrich), CH_3MgBr (1.4 M toluene/THF (75:25) solution, Aldrich), and $NaC_5(CH_3)_5$ (0.5 M THF solution, Aldrich) were used as received. The pentane was removed in vacuo from $(CH_3)_3SiCH_2Li$ (1.0 M, Aldrich) prior to use.

NMR spectra were recorded at 294 K, unless otherwise stated, on a 400 MHz Brüker AMX spectrometer in either benzene-d_6 or toluene-d_8, as specified below. NMR data for **1**

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were recorded on a 500 MHz Varian Unity spectrometer. All ^{1}H and ^{13}C chemical shifts are reported in ppm relative to the ^{1}H or the ^{13}C impurity of the internal solvent: specifically, benzene-d_6 at δ 7.15 (^{1}H) and δ 128.39 (^{13}C) and toluene-d_8 at δ 2.09 (^{1}H) and δ 20.40 (^{13}C). Elemental analyses (C, H, N) were performed at Simon Fraser University by Mr. Miki Yang employing a Carlo Erba EA 1110 CHN elemental analyzer. Infrared spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR spectrometer. Mass spectrometry measurements were carried out on a HP-5985 GC-MS EI/CI instrument operating at 70 eV. The variable-temperature magnetic susceptibilities of crystalline samples were measured over the range 2−300 K at a field of 1 T using a Quantum Design MPMS-5S SQUID magnetometer. The airtight sample holder, made of PVC, was specifically designed to possess a constant cross-sectional area. The data were corrected for the diamagnetism of the constituent atoms and of the sample holder using Pascal's constants.[88]

$\{[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{UCl}_2\}_2$ (1). $\mathrm{H_2}[^{\mathrm{tBu}}\mathrm{NON}]$ (0.250 g, 0.90 mmol) was dissolved in 10 mL of diethyl ether, and 2 equiv of ^{n}BuLi (1.13 mL, 1.80 mmol) was added dropwise at −78 °C. The resulting solution was stirred for 40 min at room temperature and subsequently added dropwise at −35 °C to a 35 mL THF solution of $\mathrm{UCl_4}$ (0.365 g, 0.95 mmol), yielding a dark green solution. After the reaction mixture was stirred for 1 h at room temperature, the solvent was removed under reduced pressure. The resulting product was extracted with toluene and filtered through a Celite-padded medium-porosity glass frit. Removal of toluene under reduced pressure gave analytically pure **1** as a green powder. Yield: 0.482 g (91%). Anal. Calcd for $\mathrm{C_{12}H_{30}N_2Cl_2OSi_2U}$: C, 24.70; H, 5.18; N, 4.80. Found: C, 24.47; H, 5.33; N, 4.43. $\mu_{\mathrm{eff}} = 2.4\ \mu_{\mathrm{B}}$ per U center at 294 K (Evans method). ^{1}H NMR (293 K, toluene-d_8): δ 68.94 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$), −17.7 (br s, 6H, $\mathrm{Si(C}\mathit{H}_3)_2$), −23.8 (br s, 6H, $\mathrm{Si(C}\mathit{H}_3)_2$). MS (CI): *m/z* 584 (monomer), 569 ($-\mathrm{CH_3}$). IR (cm^{-1}, KBr): 2963 (s), 2904 (sh), 1360 (m), 1260 (vs), 1198 (m), 1101 (m), 1035 (s), 977 (s), 857 (m), 795 (vs), 760 (m), 529 (w), 430 (m).

$\{[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{ThCl}_2\}_2$ (2). $\mathrm{H_2}[^{\mathrm{tBu}}\mathrm{NON}]$ (0.281 g, 1.02 mmol) was dissolved in 10 mL of diethyl ether, and 2 equiv of ^{n}BuLi (1.34 mL, 2.04 mmol) was added dropwise at −78 °C. The reaction mixture was stirred for 40 min at room temperature and subsequently added dropwise to a 60 mL THF solution of $\mathrm{ThCl_4}$ (0.400 g, 1.07 mmol), resulting in a colorless reaction mixture. After the resulting reaction mixture was stirred for 1 h, the solvent was removed under reduced pressure. The product was then extracted with toluene and filtered through a Celite-padded medium-porosity glass frit. Removal of toluene under reduced pressure gave analytically pure **2** as a white powder. Yield: 0.566 g (96%). Clear, colorless crystals were afforded by slow evaporation in toluene. Anal. Calcd for $\mathrm{C_{12}H_{30}N_2Cl_2OSi_2Th}$: C, 24.96; H, 5.24; N, 4.85. Found: C, 25.31; H, 5.25; N, 4.53. ^{1}H NMR (toluene-d_8): δ 1.42 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$), 0.30 (s, 6H, $\mathrm{Si(C}\mathit{H}_3)_2$), 0.27 (s, 6H, $\mathrm{Si(C}\mathit{H}_3)_2$). ^{13}C{^{1}H} NMR (toluene-d_8): δ 52.14 (s, $\mathit{C}\mathrm{(CH_3)_3}$), 33.80 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 5.20 (s, $\mathrm{Si(}\mathit{C}\mathrm{H_3)_2}$), 4.90 (s, $\mathrm{Si(}\mathit{C}\mathrm{H_3)_2}$). IR (cm^{-1}, KBr): 2961 (m), 2858 (w), 1468 (m), 1385 (m), 1359 (vs), 1265 (s), 1201 (s), 1098 (m), 980 (w), 725 (m), 649 (m), 527 (s), 499 (s), 433 (vs).

$[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{U}(\eta\text{-}\mathrm{C_3H_5})_2$ (3). $\{[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{UCl}_2\}_2$ (0.175 g, 0.15 mmol) was dissolved with stirring in 35 mL of THF, and 4 equiv of $\mathrm{C_3H_5MgCl}$ (0.30 mL, 0.60 mmol) was added dropwise at −78 °C. The color turned from green to red immediately upon addition. The solution was warmed to room temperature, and the THF was removed under reduced pressure. The product was subsequently extracted with hexanes and filtered through a Celite-padded medium-porosity glass frit. Removal of the hexanes under reduced pressure resulted in analytically pure **3** as a red solid. Yield: 0.133 g (75%.) Anal. Calcd for $\mathrm{C_{18}H_{40}N_2OSi_2U}$: C, 36.35; H, 6.78; N, 4.71. Found: C, 36.21; H, 7.14; N, 4.50. $\mu_{\mathrm{eff}} = 2.9\ \mu_{\mathrm{B}}$ 294 K (Evans method). ^{1}H NMR (toluene-d_8): δ 72.84 (2H, $\mathrm{C}\mathit{H}\mathrm{(CH_2)_2}$), 29.7 (br 4H, $\mathrm{CH(C}\mathit{H}_2)_2$), 11.4 (br 4H, $\mathrm{CH(C}\mathit{H}_2)_2$), −13.59 (s, 12H, $\mathrm{Si(C}\mathit{H}_3)_2$), −21.50 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$). MS (EI): *m/z* 595 (M$^+$), 554 ($\mathrm{M^+ - C_3H_5}$), 513 ($\mathrm{M^+ - 2C_3H_5}$). IR (cm^{-1}, KBr): 3064 (w), 2962 (m), 2858 (m), 1617 (w), 1552(w), 1503 (w), 1461 (w), 1384 (w), 1358 (s), 1252 (s), 1198 (s), 1040 (m), 991 (m), 856 (w), 800 (w), 748 (w), 716 (w), 676 (w), 641 (w), 588 (m), 550 (w), 524 (s), 496 (s), 436 (s), 427 (s).

$[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{Th}(\eta\text{-}\mathrm{C_3H_5})_2$ (4). The same procedure was used as in the preparation of **3**. Reaction of $\{[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{ThCl}_2\}_2$ (0.150 g, 0.13 mmol) with $\mathrm{C_3H_5MgCl}$ (0.26 mL, 0.52 mmol) gave analytically pure **4** as a light yellow powder. Yield: 0.110 g (72%). Anal. Calcd for $\mathrm{C_{18}H_{40}N_2OSi_2Th}$: C, 36.72; H, 6.85; N, 4.76. Found: C, 36.35; H, 6.70; N, 4.44. ^{1}H NMR (benzene-d_6): δ 6.90 (quint, $^3J = 12.5$ Hz, 1H, $\mathrm{C}\mathit{H}\mathrm{(CH_2)_2}$), 3.5 (v br 4H, $\mathrm{CH(C}\mathit{H}_2)_2$), 1.10 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$), 0.22 (s, 12H, $\mathrm{Si(C}\mathit{H}_3)_2$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 155.48 (s, $\mathit{C}\mathrm{H(CH_2)_2}$), 82.90 (s, $\mathrm{CH(}\mathit{C}\mathrm{H_2)_2}$), 52.65 (s, $\mathit{C}\mathrm{(CH_3)_3}$), 33.67 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 5.20 (s, $\mathrm{Si(}\mathit{C}\mathrm{H_3)_2}$). IR (cm^{-1}, KBr): 3054 (w), 2961 (m), 2926 (m sh), 2893 (m sh), 2857 (m), 1615 (w), 1548 (m), 1494 (w), 1463 (w), 1383 (w), 1358 (s), 1252 (s), 1202 (s), 1091 (w sh), 1053 (s), 1014 (m sh), 982 (s), 907 (w), 857 (m), 857 (m), 796 (m), 781 (m), 747 (m), 721 (m), 707 (m), 669 (m), 683 (w), 583 (w), 524 (m), 494 (m), 432 (s).

$[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{U(CH_2Si(CH_3)_3)_2}$ (5). $\{[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{UCl}_2\}_2$ (0.175 g, 0.15 mmol) was dissolved with stirring in 30 mL of toluene, and 4 equiv of a toluene solution of $\mathrm{LiCH_2Si(CH_3)_3}$ (0.057 g, 0.60 mmol) was added dropwise at −78 °C. Upon addition the solution immediately turned from green to orange. As soon as the reaction mixture was warmed to room temperature, the solvent was removed under reduced pressure. The residue was then extracted with toluene and filtered through a Celite-padded medium-porosity glass frit, yielding analytically pure **5** as a dark orange oil. Yield: 0.190 g, (92%). Anal. Calcd for $\mathrm{C_{20}H_{52}N_2OSi_4U}$: C, 34.97; H, 7.63; N, 4.08. Found: C, 35.26; H, 7.31; N, 3.93. $\mu_{\mathrm{eff}} = 2.8\ \mu_{\mathrm{B}}$ at 294 K (Evans method). ^{1}H NMR (benzene-d_6): δ 71.25 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$), −16.49 (s, 12H, $\mathrm{Si(C}\mathit{H}_3)_2$), −20.84 (s, 18H, $\mathrm{Si(C}\mathit{H}_3)_3$), −148.94 (s, 4H, $\mathrm{C}\mathit{H}_2\mathrm{Si(CH_3)_3}$).

$[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{Th(CH_2Si(CH_3)_3)_2}$ (6). The same procedure was used as in the preparation of **5**. Reaction of $\{[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{ThCl}_2\}_2$ (0.400 g, 0.35 mmol) with $\mathrm{LiCH_2Si(CH_3)_3}$ (0.130 g, 1.38 mmol) afforded **6** as a light beige oil. Yield: 0.430 g, (91%). Anal. Calcd for $\mathrm{C_{20}H_{52}N_2OSi_4Th}$: C, 35.27; H, 7.70; N, 4.11. Found: C, 35.12; H, 7.57; N, 3.69. ^{1}H NMR (benzene-d_6): δ 1.39 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$), 0.29 (s, 18H, $\mathrm{Si(C}\mathit{H}_3)_3$), 0.23 (s, 12H, $\mathrm{Si(C}\mathit{H}_3)_2$), 0.00 (s, 4H, $\mathrm{C}\mathit{H}_2\mathrm{Si(CH_3)_3}$). ^{13}C{^{1}H} NMR (benzene-d_6): δ 85.58 (s, $\mathit{C}\mathrm{H_2Si(CH_3)_3}$), 52.17 (s, $\mathit{C}\mathrm{(CH_3)_3}$), 34.21 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 6.03 (s, $\mathrm{Si(}\mathit{C}\mathrm{H_3)_2}$), 3.60 (s, $\mathrm{Si(}\mathit{C}\mathrm{H_3)_3}$).

$[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{U}(\eta^5\text{-}\mathrm{C_5(CH_3)_5})\mathrm{Cl}$ (7). $\{[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{UCl}_2\}_2$ (0.250 g, 0.21 mmol) was dissolved with stirring in 35 mL of THF, and 2 equiv of $\mathrm{NaC_5(CH_3)_5}$ (0.86 mL, 0.43 mmol) was added dropwise at −78 °C. When the mixture was warmed to room temperature, the color changed from green to red. The THF was removed under reduced pressure, the residue was extracted with hexanes, and the extracts were filtered through a Celite-padded medium-porosity glass frit. Yield: 0.264 g (90%). Dark red crystalline bars of **7** were formed by slow evaporation of a hexane solution of **7**. Anal. Calcd for $\mathrm{C_{22}H_{45}N_2ClOSi_2U}$: C, 38.67; H, 6.64; N, 4.10. Found: C, 38.93; H, 6.54; N, 4.40. $\mu_{\mathrm{eff}} = 2.3\ \mu_{\mathrm{B}}$ at 294 K (Evans method). ^{1}H NMR (benzene-d_6): δ 15.58 (s, 18H, $\mathrm{C(C}\mathit{H}_3)_3$), 6.35 (s, 6H, $\mathrm{Si(C}\mathit{H}_3)_2$), 4.53 (s, 15H, $\mathrm{C_5(C}\mathit{H}_3)_5$), −20.12 (s, 6H, $\mathrm{Si(C}\mathit{H}_3)_2$). MS (CI): *m/z* 683 (M$^+$), 648 ($\mathrm{M^+ - Cl}$). IR (cm^{-1}, KBr): 2963 (vs), 2906 (m), 2866 (m), 1453 (w), 1413 (m), 1353 (w), 1264 (s), 1195 (w), 1105 (s), 1018 (s), 940 (w), 907 (w), 863 (m), 819 (s), 793 (s), 783 (m), 742 (w), 685 (m), 661 (m), 527 (m), 497 (vs), 450 (s).

$[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{Th}(\eta^5\text{-}\mathrm{C_5(CH_3)_5})\mathrm{Cl}$ (8). The same procedure was used as in the preparation of **7**. Reaction of $\{[^{\mathrm{tBu}}\mathrm{NON}]\mathrm{ThCl}_2\}_2$ with $\mathrm{NaC_5(CH_3)_5}$ (0.61 mL, 0.30 mmol) gave analytically pure

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(88) Kahn, O. *Molecular Magnetism*; VCH: Weinheim, Germany, 1993.

8 as a light yellow solid. Yield: 0.198 g, (96%). Colorless crystals of **8** were afforded at −30 °C overnight in toluene. Anal. Calcd for $C_{22}H_{45}N_2ClOSi_2Th$: C, 39.02; H, 6.70; N, 4.13. Found: C, 39.26; H, 6.60; N, 3.97. ^1H NMR (benzene-d_6): δ 2.25 (s, 15H, $C_5(CH_3)_5$), 1.33 (s, 18H, $C(CH_3)_3$), 0.35 (s, 6H, $Si(CH_3)_2$), 0.17 (s, 6H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 126.59 (s, $C_5(CH_3)_5$), 52.11 (s, $C(CH_3)_3$), 34.60 (s, $C(CH_3)_3$), 11.83 (s, $C_5(CH_3)_5$), 6.86 (s, $Si(CH_3)_2$), 6.28 (s, $Si(CH_3)_2$). MS (CI): m/z 678 (M^+), 643 ($M^+ - Cl$). IR (cm^{-1}, KBr): 2958 (m), 2906 (m), 2856 (m), 1467 (w), 1385 (w), 1358 (vs), 1258 (s), 1197 (s), 1097 (s), 1038 (s), 1024 (m), 923 (w), 856 (m), 806 (m), 793 (s), 746 (s), 726 (vs), 675 (m), 645 (w), 557 (m), 525 (s), 496 (vs), 434 (vs), 423 (w).

[^{tBu}NON]U(η^5-$C_5(CH_3)_5$)CH_3 (9). [^{tBu}NON]U($C_5(CH_3)_5$)Cl (0.291 g, 0.43 mmol) was dissolved with stirring in 50 mL of toluene and cooled to −30 °C. CH_3MgBr (0.40 mL, 0.55 mmol) was added dropwise, and stirring was continued at room temperature for 2 h, during which time a color change from red to dark orange occurred. Dioxane (0.15 mL, 1.70 mmol) was subsequently added dropwise, affording a cloudy orange reaction mixture that was stirred at room temperature for 4 h. The resulting product was filtered through a Celite-padded medium-porosity glass frit. Yield: 0.257 g (91%). Orange needle-shaped crystals were afforded by slow evaporation on a hexanes solution of **9**. Anal. Calcd for $C_{23}H_{48}N_2OSi_2U$: C, 41.68; H, 7.30; N, 4.23. Found: C, 41.41; H, 6.85; N, 3.92. $\mu_{eff} = 2.7\ \mu_B$ at 294 K (Evans method). ^1H NMR (benzene-d_6): δ 11.36 (s, 18H, $C(CH_3)_3$), 7.65 (s, 6H, $Si(CH_3)_2$), 2.80 (s, 15H, $C_5(CH_3)_5$), −14.40 (s, 6H, $Si(CH_3)_2$), −146.34 (s, 3H, CH_3). MS (EI): m/z 648 ($M - CH_3$). IR (cm^{-1}, KBr): 2968 (s), 2917 (m), 2863 (m), 1465 (w), 1385 (w), 1358 (s), 1251 (vs), 1213 (w), 1192 (s), 1115 (w), 1033 (m), 1019 (m), 948 (s), 858 (s), 835 (m), 803 (m), 789 (s), 749 (m), 719 (w), 677 (w), 562 (w), 523 (w), 496 (w), 426 (w).

[^{tBu}NON]Th(η^5-$C_5(CH_3)_5$)CH_3 (10). The same procedure was used in the preparation of **9**. Reaction of [^{tBu}NON]Th($C_5(CH_3)_5$)Cl (0.194 g, 0.29 mmol) with CH_3MgBr (0.25 mL, 0.34 mmol) and dioxane (0.07 mL, 0.86 mmol) gave **10** as a pale yellow solid. Yield: 0.180 g (96%). Anal. Calcd for $C_{23}H_{48}N_2OSi_2Th$: C, 42.06; H, 7.37; N, 4.26. Found: C, 41.70; H, 7.20; N, 3.89. ^1H NMR (benzene-d_6): δ 2.29 (s, 15H, $C_5(CH_3)_5$), 1.33 (s, 18H, $C(CH_3)_3$), 0.43 (s, 3H, CH_3), 0.40 (s, 6H, $Si(CH_3)_2$), 0.28 (s, 6H, $Si(CH_3)_2$). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 124.62 (s, $C_5(CH_3)_5$), 57.63 (s, CH_3), 51.99 (s, $C(CH_3)_3$), 34.91 (s, $C(CH_3)_3$), 11.89 (s, $C_5(CH_3)_5$), 7.31 (s, $Si(CH_3)_2$), 6.76 (s, $Si(CH_3)_2$). MS (EI): m/z 642 ($M - CH_3$). IR (cm^{-1}, KBr): 2965 (vs), 2913 (s), 2863 (m), 1466 (m), 1444 (w), 1411 (w), 1384 (w), 1358 (s), 1252 (vs), 1197 (s), 1039 (m), 1025 (w), 941 (m), 922 (m), 858 (s), 802 (m), 790 (s), 748 (w), 724 (w), 674 (w), 557 (w), 523 (w), 495 (m), 430 (w).

Crystallographic Details of {[^{tBu}NON]$UBr_{1.46}Cl_{0.54}$}$_2$ (1′) and {[^{tBu}NON]$ThCl_2$}$_2$ (2). Crystallographic data for both complexes are given in Table 1. The structures were solved using SIR92 and refined in CRYSTALS.[89] Complex scattering factors for neutral atoms[90] were used in the calculation of structure factors. All diagrams were made using ORTEP-3.[91]

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Supporting Information Available: Text and tables giving crystallographic details for **1′** and **2**, including refinement details, final coordinates, thermal parameters, and bond distances and bond angles; these data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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