FULL PAPER

Synthesis and structure of diamido ether uranium(IV) and thorium(IV) halide "ate" complexes and their conversion to salt-free bis(alkyl) complexes

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The high-yield synthesis, spectroscopic and structural determination of three new uranium(IV) and thorium(IV) "ate" complexes supported by three different diamido ether ligands are reported. The reaction of $Li_2[2,6^{-1}Pr_2PhN(CH_2CH_2)]_2O(Li_2[^{DIPP}NCOCN])$ with 1 equiv. of UCl₄ in THF generates [^{DIPP}NCOCN]UCl_3Li(THF)₂ (1), while reaction in toluene/ether gives salt-free [^{DIPP}NCOCN]UCl₂· $\frac{1}{2}C_7H_8$ (2), which was identified by para-magnetically shifted ¹H NMR. Reaction of 0.5 equiv. of {[^{^{1Bu}NON]}UCl₂} ([^{^{1Bu}NON]} = [(CH₃)₃CN(Si(CH₃)₂)]₂O²⁻) with 3.5 equiv. LiI in toluene and a minimal amount of THF results in [^{^{1Bu}NON]}UI₃Li(THF)₂ (3) and is very similar in structure to 1. {[^{Mes}NON]ThCl₃Li(THF)]₂ (4), a dimeric complex with a Th₂Li₂Cl₆ core, is prepared by reaction of Li₂[2,4,6-Me₃PhN(Si(CH₃)₂)]₂O (Li₂[^{Mes}NON]) with ThCl₄ in THF. The analogous reaction in toluene did not yield the salt-free complex but rather a sterically crowded diligated compound, [^{Mes}NON]₂Th (5), which was also structurally characterized. Complex **5** was prepared rationally by reacting 2 equiv. Li₂[^{Mes}NON] with ThCl₄ in toluene. The reaction of 1 and 3 with 2 equiv. of LiCH₂Si(CH₃)₃ (7). Complex **6** was structurally characterized. The value of the viability of "ate" complexes as useful synthetic precursors.

Introduction

Amido ligands are ideal for stabilizing mid-valent actinide centers due to their strong π -donating ability and the ease of synthetically modifying the steric and electronic properties by varying the organic substituent on the amido nitrogen.¹ Monodentate bis(trimethylsilyl)amido-type ligands are excellent ligand frameworks for actinides, supporting rich and varied actinide systems.²⁻¹⁷ Bulky tetradentate triamidoamine ligands have also been explored,^{18,19} resulting in the first actinide-dinitrogen complex²⁰ and mixed-valent U(III)/U(IV) systems.²¹ Recently, the triamidoamine ligand Li₃[N(CH₂CH₂NSi⁴Bu(CH₃)₂)₃] was reacted with UO₂Cl₂(THF)₃ to give dinuclear U(VI)/U(V) oxo– imido systems.²²

We recently reported two An(IV) (An = Th, U) chloridebridged dimers supported by the tridentate diamido ether ligand $\{[(CH_3)_3CN(Si(CH_3)_2)]_2O\}^{2-}$ $([^{1Bu}NON])^{23,24}$ and their subsequent metathesis reactions to form a series of alkyl complexes.²⁵ Surprisingly, none of these complexes retained any solvent-salt molecules, i.e., "ate"-type complexes were not formed. "Ate" complex formation is commonly seen with the lanthanides²⁶⁻³⁴ and early transition metals.³⁵⁻⁴⁰ Similar retention of solvent-salt adducts has also been reported for actinide complexes containing ansa-cyclopentadienyl-amido ligands,⁴¹ cyclopentadienyl-type ligands,⁴²⁻⁴⁵ permethylindenyl⁴⁶ and [(-CH₂-)₅]-4-calix[4]tetrapyrrole ligands.⁴⁷ Such "ate" complexes are often perceived as synthetically exhausted due to their relative coordinative saturation, and by extension have been considered less interesting than salt-free systems. There are only a few examples of uranium(IV) and thorium(IV) "ate" complexes acting as precursors for further reaction chemistry. Specifically, [Me2Si(C5Me4)2]AnCl2·2LiCl·n(solvent) $(An = Th(IV), U(IV))^{48,49}$ undergo substitution chemistry to form bis(alkyl) complexes. Also, the reaction of [Li(TMEDA)][(Cp*2U(NC6H5)Cl] with the two-electron oxidative atom transfer reagent, $PhN_3,$ results in a salt-free bis(organoimido)uranium(vI) complex.^{44}

Herein we report a series of U(IV) and Th(IV) "ate" complexes stabilized by three different chelating diamido ether ligands (Fig. 1). The U(IV) "ate" analogues were further subjected to alkylation to yield two stable *salt-free* uranium bis(alkyl) complexes, further illustrating the viability of "ate" complexes as useful synthetic precursors.



Fig. 1 Chelating diamido ether ligands used in the synthesis of complexes 1–7.

Results and discussion

Synthesis and characterization of $[^{DIPP}NCOCN]UCl_3Li(THF)_2$ (1) and $[^{DIPP}NCOCN]UCl_2 \cdot \frac{1}{2}C_7H_8$ (2)

As depicted in Scheme 1, treatment of a THF solution of UCl₄ with $Li_2[^{DIPP}NCOCN]^{50}$ (1 equiv.) at -30 °C affords $[^{DIPP}NCOCN]UCl_3Li(THF)_2$ (1) in over 90% isolated yield.

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Scheme 1 Synthesis of complexes 1, 2 and 6.

Single crystals of 1 suitable for X-ray diffraction were obtained from a hexanes/toluene solution of 1 at -30 °C. The structure of 1 (Fig. 2 and Table 1) contains a single U(IV) center with pseudooctahedral coordination geometry, consisting of the tridentate, chelating diamido ether ligand, a terminal chloride and two additional chlorides which bridge to a charge-balancing lithium cation. The lithium is also complexed by two THF ligands to yield a pseudo-tetrahedral coordination geometry.



Fig. 2 Molecular structure and numbering scheme of **1** (ORTEP, 33% probability ellipsoids).

The ether oxygen donor has a U1–O1 distance of 2.432(12) Å, which falls within bonding range (sum of the van der Waals radii for U and O is 3.38 Å)⁵¹ and is very similar to the silyl ether U–O distance of 2.479(11) Å in the chelating diamidosilyl

 Table 1
 Selected bond lengths (Å) and angles (°) for 1

U1-Cl1	2.700(5)	U1-Cl3	2.648(5)
U1-Cl2	2.707(5)	U1-N1	2.183(15)
U1-N2	2.192(15)	U1-O1	2.432(12)
C1-N1	1.496(19)	C4-N2	1.44(2)
C2-O1	1.420(19)	C3-O1	1.401(19)
C1-C2	1.47(2)	C3-C4	1.50(2)
$\begin{array}{c} N2{-}U1{-}N1\\ N2{-}U1{-}C11\\ N2{-}U1{-}C12\\ N2{-}U1{-}C13\\ C12{-}U1{-}C13\\ C12{-}U1{-}C13\\ N2{-}U1{-}O1\\ O1{-}U1{-}C13\\ O1{-}U1{-}C11\\ L1{-}C12{-}U1 \end{array}$	$135.1(5) \\115.1(4) \\88.9(4) \\90.1(4) \\81.07(16) \\171.80(15) \\68.6(5) \\82.6(3) \\173.6(3) \\92.1(10)$	N1-U1-C11 N1-U1-C12 N1-U1-C13 C13-U1-C11 N1-U1-O1 O1-U1-C12 Li1-C11-U1 C11-Li1-C12 C2-O1-C3	109.6(4) 93.9(4) 92.5(3) 92.00(17) 67.4(5) 104.5(3) 90.9(10) 95.9(15) 116.7(14)

ether complex {[^{18u}NON]UCl₂}₂.²⁵ The amido donors have U–N bond distances⁵² of 2.183(15) and 2.192(15) Å, which are shorter than the amido-U bond lengths in related mono-amido,^{7,8,53} diamidoamine⁵⁴ and triamidoamine^{13,55} uranium(IV) complexes, but slightly longer than in the mono-amido complex U(NEt₂)(*O*-2,6-¹Bu₂C₆H₃)₃ (2.16(1) Å)⁵⁶ and the diamidosilyl ether complex {[^{18u}NON]UCl₂}₂ (2.145(16) and 2.130(18) Å).²⁵ As is commonly observed, the terminal U1–Cl3 bond length of 2.648(5) Å is shorter than the bridging chloride distances of 2.700(5) and 2.707(5) Å for U1–Cl1 and U1–Cl2, respectively.

The ¹H NMR spectrum of 1 at 294 K contains a large number of sharp to very broad, paramagnetically shifted resonances, suggesting that complex 1 retains its asymmetric structure in toluene- d_8 ; specific peak assignments cannot be easily made.

However, upon heating to 373 K, five pairs of resonances merge into five single peaks. This is not simply a coalescence as the final spectrum obtained after cooling back to 294 K retains this higher-symmetry peak pattern, *i.e.*, the original 294 K spectrum is not regenerated. This increase in symmetry is consistent with the loss of LiCl from 1 upon heating, to yield a salt-free complex which may be either mononuclear or dinuclear with bridging chlorides. Two resonances at δ –5.66 and –11.61 that appear in the 373 K spectrum are broadened into the baseline in the 294 K spectrum taken after the heating process but could be attributed to a U(IV)-bound THF molecule, the THF having been liberated from the LiCl(THF)₂ adduct upon heating. In both structures, the crude integrations and number of peaks present suggest that there is restricted rotation about the N–C(aryl) bond.

The putative solvent-salt free complex [DIPPNCOCN]UCl₂ (2) that was observed by NMR spectroscopy can be synthesized on a preparative scale in high yield by the reaction of Li_2 [DIPPNCOCN] with a room temperature toluene slurry of UCl₄. Complex 2 is brownish-orange in color, markedly different to the greenish-orange appearance of 1. Consistent with the variable-temperature NMR spectroscopy experiment, the 294 K ¹H NMR spectrum of 2 is very similar to the spectrum of 1 after heating; the small differences are attributable to the absence of a uranium-bound THF molecule in 2 compared with 1.

Synthesis, characterization and structural determination of [^{IBu}NON]UI₃Li(THF)₂ (3)

[^{IBu}NON]UI₃Li(THF)₂ (**3**) was initially isolated as a green crystalline minor byproduct from an attempt to form a U(III) diamido ether complex employing Li_2 [^{IBu}NON] and UI₃(THF)₄. This complex can also be synthesized in high yield (Scheme 2) by reacting 0.5 equiv. of {[^{IBu}NON]UCl₂}₂ with 3.5 equiv. of anhydrous LiI in toluene and a minimal amount of THF.



Scheme 2 Synthesis of complexes 3 and 7.

Table 2Selected bond lengths (Å) and angles (°) for 3

U1–I1	3.161(2)	U1–I2	3.123(2)
U1–I3	3.039(3)	U1-N1	2.179(17)
U1-N2	2.194(16)	U1-01	2.494(16)
I1–Li1	2.90(6)	I2–Li1	2.79(6)
Sil-N1	1.707(19)	Si2–N2	1.701(19)
Si1–O1	1.643(19)	Si2-O1	1.654(19)
N2-U1-N1	125.8(7)	I2-U1-I1	84.79(6)
I3–U1–I1	92.23(8)	I3-U1-I2	176.74(9)
Li1–I1–U1	87.4(11)	Li1-I2-U1	90.1(12)
N1-U1-I1	116.6(5)	N2-U1-I1	117.5(5)
N1-U1-I2	89.8(5)	N2-U1-I2	92.5(4)
N1-U1-I3	90.4(5)	N2-U1-I3	90.1(4)
O1–U1–I1	171.6(4)	O1–U1–I2	86.8(4)
O1–U1–I3	96.2(4)	01-U1-N1	63.2(6)
01-U1-N2	62.9(6)	Si1-O1-Si2	165.1(11)

Crystals of **3** suitable for X-ray analysis were obtained from a concentrated toluene solution of **3** at -30 °C. This structure (Fig. 3 and Table 2) has one chelating diamidosilyl ether ligand, one terminal and two bridging iodides. Similar to **1**, the complex is coordinated in a pseudo-octahedral fashion with a Li(THF)₂ moiety attached to the bridging iodides. Despite changing the halide from chloride to iodide, and altering the ancillary diamido ether ligand substantially from a flexible carbon backbone with aryl-amido groups to a silyl ether backbone with 'Bu-amido groups, the structures of **1** and **3** are very similar.



Fig. 3 Molecular structure and numbering scheme of **3** (ORTEP, 33% probability ellipsoids).

The U1–O1 distance of 2.494 (16) Å in **3** is slightly longer than that in **1** and {[^{1Bu}NON]UCl₂}₂.²⁵ The N2–U1–N1 bite angle of 125.8(7)° is comparable with the analogous angle in {[^{1Bu}NON]UCl₂}₂ (124.7(6)°) but is *ca*. 10° smaller than that found in **1**. The larger angle in **1** is most likely attributed to the steric factors ascribed to the ligand, namely that the longer and more flexible backbone of (H₂[^{DIPP}NCOCN]) in **1** facilitates the larger bite angle. The U1–N1 and U1–N2 distances are 2.179(17) and 2.194(16) Å, respectively. Similar to **1**, the terminal halide has a shorter U–I bond length than that of the bridging iodides. The same trend was also seen in the dinuclear complex, [U{ κ^3 -H(μ -H)B(pz^{1Bu,Me})₂}(Hpz^{1Bu,Me})I(μ -I])₂, which has a terminal U–I length of 3.116(2) Å and bridging U–I bond lengths of 3.216(2) and 3.238(2) Å.⁵⁷

The ¹H NMR spectrum of 3 is sharp and paramagnetically shifted, as is usually observed for a U(IV) species.⁵⁸ The–C(CH_3)₃ protons are assigned to the singlet at δ 81.84. Two broad signals at δ 0.31 and -3.57 are assigned to the protons on the THF rings. The resonance at δ –3.57 is more broad and shifted than that at δ 0.31, and may thus be inferred to correspond to the α -THF protons. The shifted THF resonances also suggest that the structure is retained in a solution of benzene- d_6 . The –Si(CH_3)₂ protons are assigned to a single resonance at δ –16.75; the obser-

vation of a single resonance for the silvl methyl group suggests that rapid interconversion of the bridging and terminal iodides in benzene- d_6 may be occurring²⁵ but even upon cooling to 233 K in toluene- d_8 this fluxional process could not be frozen out.

$\label{eq:synthesis, characterization, and structural determination of $$ {[^{Mes}NON]ThCl_3Li(THF)}_2$ (4) and $$ [^{Mes}NON]_2Th$ (5)$

As depicted in Scheme 3, treatment of a THF solution of $ThCl_4$ with Li_2 [MesNON]⁵⁹ (1 equiv.) at room temperature results in {[MesNON]ThCl_3Li(THF)}₂ (4) in 94% isolated yield.



Scheme 3 Synthesis of complex 4.

X-Ray quality crystals of **4** (Fig. 4, Table 3) were obtained by slow evaporation of a hexanes solution of **4**. The structure is dimeric, in which each thorium center is seven-coordinate, and the dimer is held together by six bridging chlorides. The monomeric unit possesses one [^{Mes}NON] ligand coordinating to



Fig. 4 Molecular structure and numbering scheme of **4** (ORTEP, 33% probability ellipsoids).

Table 3Selected bond lengths (Å) and angles (°) for 4

Th1–Cl1 Th1–Cl3 Th1–O1 Si1–N1	2.736(5) 2.710(5) 2.663(13) 1.743(10)	Th1-Cl2 Th1-N1 Th1-Si1 Si1-O1	2.957(2) 2.290(9) 3.260(3) 1.654(5)
Cl2-Th1-Cl1 Cl3-Th1-Cl2 Si1-Th1-Cl2 N1-Th1-Cl3 N1-Th1-Si1 O1-Th1-Cl3 O1-Th1-Cl3 O1-Th1-Cl2 O1-Th1-Cl1 Th1-Cl2-Th1 ^b Li1-Cl2-Th1	81.71(9) 81.50(8) 162.87(7) 93.2(2) 30.7(3) 127.9(3) 136.71(15) 72.6(3) 110.35(13) 85.09(6)	Cl3-Th1-Cl1 Si1-Th1-Cl1 Si1-Th1-Cl3 OI-Th1-Si1 N1-Th1-O1 N1-Th1-Cl2 N1-Th1-Cl1 N1-Th1-N1" Li1-Cl1-Th1 Si1"-O1-Si1	$\begin{array}{c} 159.51(15)\\ 82.12(12)\\ 115.47(11)\\ 30.35(9)\\ 60.8(3)\\ 159.8(3)\\ 98.6(2)\\ 109.4(5)\\ 98.12(16)\\ 149.1(8)\end{array}$

 $^{a}x, -y, z. ^{b}-x, y, -z.$

the Th(iv) center in a chelating fashion *via* the amido nitrogens, three bridging chlorides and a Li(THF) adduct. Thus, the molecule contains an unusual Th₂Li₂Cl₆ core. The Li1–Cl1 distance of 2.330(4) Å is short enough to constitute a bonding interaction, however the Li1–Cl2 and Li1–Cl3 distances of 2.7111(8) and 2.957(2) are longer than the sum of the effective ionic radii of both elements (Li: 0.590 Å, Cl: 1.81 Å),⁵¹ suggesting the presence of a weak electrostatic interaction at best. Thus, there are three distinct chloride ligands: Cl1 is bridging the thorium and lithium, Cl2 is pseudo-trigonal, bridging the two thorium atoms and interacting with the lithium, and Cl3 is essentially terminal from the thorium center.

The Th–Cl1 and Th–Cl3 distances are 2.736(5) and 2.710(5) Å and are shorter than the Th1–Cl2 distance of 2.957(2) Å; the Cl2 atom is bridging two thorium centers while the other two chlorides bridge to lithium centers. The amido-thorium distance of 2.290(9) Å is similar to other chelating diamido amine and diamido ether Th–N distances,^{25,54} but the Th–O1 distance of 2.663(13) Å is longer than the Th–O bonds in $[(Cp*_2Th(CH_3)(THF)_2]*BPh_4^- (2.531(9), 2.628(8) Å)^{60}$ and $[(Cp*_2Th[OC(CH_2-t-Bu)C(P(CH_3))O](Cl) (2.340(9), 2.256(8) Å).^{61}$ This may be attributed to the steric crowding of the mesityl groups limiting access of the silyl ether donor ligand backbone to the metal center.

The ¹H and ¹³C NMR spectra of **4** are similar to those of other diamagnetic transition metal, actinide and main-group complexes containing related chelating diamidosilyl ether ligand backbones.^{24,25,62} The ¹³C{H} resonances of **4** were assigned with the assistance of a {C, H} 2D-COSY spectrum. The ⁷Li NMR spectrum shows a broad resonance at $\delta - 0.2$ in toluene- d_8 .

An attempt to synthesize the related solvent-salt free complex was carried out by adding $Li_2[^{Mes}NON]$ (1 equiv.) to a room temperature toluene slurry of ThCl₄. Unlike the clean synthesis of salt-free **2** via the analogous route, this reaction resulted in a mixture of products: the major product was a diligated compound, [^{Mes}NON]₂Th (**5**), with a minor product presumed to be the desired {[^{Mes}NON]ThCl₂₂, also apparent in the ¹H NMR spectrum. The formation of **5** instead of {[^{Mes}NON]ThCl₂₂ is likely due to the low solubility of ThCl₄ in toluene; the solubility of UCl₄ is comparatively higher. Complex **5** can be rationally synthesized in high yield by reacting $Li_2[^{Mes}NON]$ (2 equiv.) with a room temperature toluene slurry of ThCl₄ (Scheme 4).



Scheme 4 Synthesis of complex 5

The single crystal structure of **5** (Fig. 5, Table 4) confirms that two chelating diamidosilyl ether ligands are bound to the Th(IV) center. In addition to the amido donors, the silyl ether donors

Fable 4 Selected bond lengths (A) and angles (°)	for	5
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Th1-O11	2.741(2)	Th-O21	2.726(2)
Th1-N11	2.343(2)	Th1-N41	2.329(2)
Th1-N51	2.336(3)	Th-N81	2.333(2)
Si21-N11	1.715(3)	Si31-N41	1.720(3)
Si61-N51	1.715(3)	Si71-N81	1.703(3)
N11-Th1-N41	108.73(9)	N51-Th1-N81	108.47(9)
N41-Th1-N51	104.52(9)	N11-Th1-N81	102.62(9)
N51-Th1-N41	104.52(9)	N51-Th1-N11	114.50(9)
N41-Th1-N81	118.42(9)	O11-Th1-O21	131.10(6)
N11-Th1-O11	59.99(7)	N41-Th1-O21	158.60(8)
N51-Th1-O21	60.07(7)	N81-Th1-O21	59.91(8)
Si21-O11-Si31	141.64(15)	Si61-O21-Si71	143.59(15)



Fig. 5 Molecular structure and numbering scheme of **5** (ORTEP, 33% probability ellipsoids).

in the ligand backbone are bound to the Th(IV) center (Th–O 2.741(2), 2.726(2) Å) resulting in a pseudo-octahedral geometry. The Th–O distances for **5** are significantly longer than in **4** and other known Th–O bonds.^{25,60,61,63} The Th–N distances for **5** (2.343(2), 2.336(3), 2.329(2), 2.333(2) Å) are also longer than in **4**. These elongations are most likely a result of the significant steric crowding about the thorium center created by the binding of two sterically demanding ancillary ligands.

Organometallic derivatives. Synthesis and characterization of [^{DIPP}NCOCN]U(CH₂Si(CH₃)₃)₂ (6) and [^{IBu}NON]U(CH₂Si(CH₃)₃)₂ (7)

Treatment of **1** with two equiv. of LiCH₂Si(CH₃)₃ in toluene at -30 °C resulted in the formation of [^{DIPP}NCOCN]U-(CH₂Si(CH₃)₃)₂ (**6**) in high yield (Scheme 1).

Single crystals of $\mathbf{6}$ were obtained by slow evaporation of a solution of $\mathbf{6}$ in pentane. The structure is a monomeric, lithium chloride-free molecule (Fig. 6 and Table 5). To the best of our



Fig. 6 Molecular structure and numbering scheme of 6 (ORTEP, 33% probability ellipsoids). Isopropyl groups have been omitted for clarity.

Table 5	Selected bond	lengths (A	A) and	angles (°) for 6
					/

U1–N1 U1–O1 U1–C30 Si2–C30 C4–N2 C3–C4 C3–O1	2.241(16) 2.535(12) 2.44(2) 1.841(19) 1.44(2) 1.45(3) 1.43(2)	U1–N2 U1–C29 Si1–C29 C1–N1 C1–C2 C2–O1	2.257(18) 2.40(2) 1.84(2) 1.45(3) 1.50(3) 1.41(2)
N1-U1-O1 N2-U1-N1 N2-U1-O1 C29-U1-O1 C29-U1-N1 C29-U1-N2 C30-U1-C29	67.2(5) 130.6(5) 66.1(5) 102.4(6) 103.0(6) 101.6(7) 110.8(6)	U1-C29-Si1 U1-C30-Si2 C30-U1-O1 C30-U1-N1 C30-U1-N2 C2-O1-C3	129.7(10) 127.0(11) 146.8(6) 104.5(6) 105.7(7) 114.3(17)

knowledge this is the first example of a structurally characterized uranium compound with a $-CH_2Si(CH_3)_3$ group. The facile loss of the lithium chloride–THF adduct may perhaps be attributed to the high combined steric bulk of the chelating diamido ether backbone and the $CH_2Si(CH_3)_3$ ligands, thus increasing the propensity to eliminate LiCl.

The U(IV) center has a five-coordinate geometry. The U–N bond lengths of 2.241(16) and 2.257(18) Å, and the U–O distance of 2.535(12) Å are all slightly longer that those of **1**. The U1–C29 and U1–C30 distances are 2.40(2) and 2.44(2) Å, respectively and are very similar to the uranium-CH₃ distances reported for $[(1,3-(CH_3)_3Si)_2C_5H_3]_2U(CH_3)_2$ (2.42(2) Å)⁶⁴ and Cp*₂U(CH₃)₂ (2.424(7), 2.414(7) Å)⁶⁵ as well as the U–CH₂ distance in Cp*₃U(*n*-butyl) (2.426(23) Å).⁶⁶

The U–C–Si bond angles in 6 are 129.7(10) and 127.0(11)° and can be compared with related thorium(IV) complexes such as $Cp*_{2}Th[CH_{2}C(CH_{3})_{3}][CH_{2}Si(CH_{3})_{3}]$, which has a large Th–C– Si bond angle of $150(3)^{\circ}$.⁶⁷ Other thorium complexes containing two -CH₂Si(CH₃)₃ substituents usually have one Th-C-Si angle substantially larger than the other.^{68,69} For example $(CH_3)_2Si[\eta^5-$ (CH₃)₄C₅]₂Th[CH₂Si(CH₃)₃]₂ has Th-C-Si angles of 123.7(14) and 149.5(12)°.48 These large Th-C-Si angles have been thought to provide evidence for some degree of α -agostic interaction between the methylene hydrogens and the actinide center. The structure of Cp*2Th[CH2C(CH3)3]2 was determined by neutron diffraction analysis and was concluded to exhibit a-agostic interactions based on Th-Ca-Cb angles of 132.1(3) and 158.2(3)° and Th-C-H bond angles of 84.4(5) and 87.1(5)°; the decreased latter two angles resulted from the a-hydrogens bending towards the thorium center.⁶⁷ Unfortunately the α-hydrogens for 6 could not be located through X-ray diffraction and the comparatively acute U–C–Si angles of $<130^{\circ}$ in 6 do not provide definitive evidence for the presence of an α -agostic interaction.

In addition, although such interactions are often characterized by unusually low v_{C-H} stretching vibrations in the IR spectrum,⁷⁰ no such peaks were observed for **6**. There were also no low v_{C-H} stretching vibrations observed for Cp*Th(OAr)[CH₂Si(CH₃)₃]₂ (Ar = 2,6-*t*-Bu₂C₆H₃)⁶⁸ and Cp*₂Th[CH₂C(CH₃)₃]₂,⁶⁷ for which the presence of α -agostic interactions were suggested from the ¹H NMR and structural data.

The ¹H NMR spectrum of **6** is paramagnetically shifted, but was assignable on the basis of the integration of the signals. The NCH₂CH₂O resonances of the ligand framework are seen as two singlets at δ 66.72 and -41.33. Two broad resonances at δ 27.5 and 13.4 correspond to the CH(CH₃)₂ and CH(CH₃)₂ resonances, respectively. The *para*- and *meta*-proton shifts of the aromatic ring are observed at δ 20.85 and -17.60, respectively, while the Si(CH₃)₃ resonates as a sharp singlet at δ -17.52. The U-CH₂ is assigned to the very broad resonance at *ca*. δ -140.

Reaction of [^{IBu}NON]UI₃Li(THF)₂ with 2 equiv. LiCH₂Si-(CH₃)₃ resulted in the formation of the bis(alkyl) complex [^{IBu}NON]U(CH₂Si(CH₃)₃)₂ (7) in high yield. This product was previously synthesized from an alternate route involving the reaction of {[^{IBu}NON]UCl₂}₂ and 4 equiv. of LiCH₂Si(CH₃)₃.²⁵ The ¹H NMR spectrum of 7 prepared by both routes is identical; the C(CH₃)₃ resonance appears downfield at δ 71.17 and the two silvl methyl resonances occur upfield at δ –16.62 and –20.84 for Si(CH₃)₂ and Si(CH₃)₃, respectively. Similar to **6**, the U– CH₂-resonance is significantly upfield at δ –148.92. Attempts to alkylate the thorium ate-complex **4** resulted in a mixture of inseparable products.

Magnetism

The magnetic susceptibilities of the uranium(IV) complexes **1** and **3** from 2–300 K were measured and the resulting plots of μ_{eff} vs. *T* are shown in Fig. 7. For **1**, $\mu_{\text{eff}} = 2.86 \,\mu_{\text{B}}$ at 300 K and is similar to that observed for related tetrakis(amido)uranium(IV) complexes⁷¹ and also to {[I^{Bu}NON]UCl₂}.²⁵ Complex **3** has a



Fig. 7 Plot of μ_{eff} vs. T for 1 and 3.

higher μ_{eff} of 3.46 μ_{B} at 300 K. A decrease in μ_{eff} with decreasing temperature is observed for both complexes and can be solely attributed to single ion effects at the uranium(IV) center. The small μ_{eff} values at low temperature are consistent with the typically observed non-magnetic ground state for uranium(IV) complexes.⁷²

Concluding remarks

Three sterically and electronically different ligands, which also encompass two different ligand backbone lengths and flexibilities, have been used to stabilize uranium(IV) and thorium(IV) centers. There appears to be a greater propensity to form actinide ate-complexes with the less-basic arylamido donors than with the alkylamido chelate, as exemplified by the fact that salt metathesis reactions performed in THF resulted in salt-free U(IV) and Th(IV) complexes containing the [^{IBu}NON] ligand.²⁵ In any case, the fact that the uranium ate-complexes can be cleanly alkylated to yield salt-free bis-alkyl complexes illustrates the viability of "ate" complexes as useful synthetic precursors, thereby providing a useful route to organoactinide systems.

Experimental

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. The diethyl ether (Et₂O) (Caledon) distillation was 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 atmosphere. Benzene- d_6 (Aldrich) and toluene d_8 (Cambridge Isotope Laboratories) were dried over activated 4 Å molecular sieves (Acros) and stored under nitrogen. Deuterium oxide (Isotec) was used as received. Anhydrous pentane (Aldrich) was dried with KH (Aldrich) and filtered over dried alumina, neutral Brockmann activity I, 60-325 mesh (Fisher) and stored under a nitrogen atmosphere. Uranium tetrachloride,73 $[2,4,6-Me_3PhNH(Si(CH_3)_2)]_2O$ (H₂[^{Mes}NON]),⁵⁹ [2,6-Pr2PhNH(CH2CH2)]2O (H2[DIPPNCOCN])74 and {[1BuNON]- $UCl_2\}_2$,²⁵ ([^{IBu}NON] = [(CH_3)_3CN(Si(CH_3)_2)]_2O)^{23,24} were prepared in accordance with the literature procedures. Anhydrous thorium tetrachloride (Strem), anhydrous lithium

iodide (Aldrich) and "BuLi (1.6 M hexane solution, Acros) were used as received. The pentane was removed in vacuo from (CH₃)₃SiCH₂Li (1.0 M, Aldrich) prior to use. NMR spectra were recorded at 294 K, unless otherwise stated, in benzene- d_6 or toluene-d₈ employing a 500 MHz Varian Unity spectrometer. NMR data for 1 were recorded on a 400 MHz Bruker AMX spectrometer. Variable temperature data for 3 were recorded on a 400 MHz Bruker AMX spectrometer. All ¹H and ¹³C chemical shifts are reported in ppm relative to the ¹H or the ¹³C impurity of the internal solvent, specifically, benzene- d_6 , δ 7.15 (¹H) and δ 128.39 (¹³C) and toluene- d_8 , δ 2.09 (¹H). ⁷Li NMR data for 4 was recorded on a 400 MHz Bruker AMX spectrometer referenced to external LiI (0.41 M in D₂O, δ 0.00). Determination of μ_{eff} in solution was conducted using Evans method.⁷⁵ 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 with a 1 cm⁻¹ resolution. The variable temperature magnetic susceptibility of microcrystalline samples was measured over the range 2-300 K at a field of 1 T using a Quantum Design MPMS-XL7 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, using Pascal's constants, and of the sample holder.⁷⁶

[^{DIPP}NCOCN]UCl₃Li(THF)₂ (1)

H₂[^{DIPP}NCOCN] (0.425 g, 1.00 mmol) was dissolved in 15 mL of diethyl ether, and 2 equiv. of "BuLi (1.32 mL, 2.11 mmol) was added dropwise at -78 °C. The resulting solution was stirred for 40 min at room temperature and subsequently added dropwise to a 30 mL -35 °C THF solution of UCl₄ (0.400 g, 1.05 mmol), vielding a green-orange 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 mediumporosity glass frit. Removal of the toluene under reduced pressure gave 1 as a greenish-orange powder. Yield: 0.861 g (94%). X-Ray quality crystals were afforded overnight from a hexanes/toluene solution cooled at -30 °C. Anal. Calc. for C₃₆H₅₈N₂Cl₃LiO₃U: C, 47.09; H, 6.37; N, 3.05. Found: C, 46.76; H, 6.23; N, 3.14%. IR (cm⁻¹, KBr): 3051 (w), 2961 (vs), 2928 (s), 2868 (s), 1460 (s), 1430 (s), 1382 (w), 1360 (w), 1315 (w), 1242 (m), 1184 (m), 1085 (s), 1045 (s), 954 (w), 932 (m), 905 (m), 889 (m), 836 (w), 820 (w), 799 (s), 759 (m), 730 (vw), 695 (w), 519 (w), 428 (w). ¹H NMR (toluene-d₈, 294 K, approximate integrations where possible): δ 49.0 (v br), 45.9 (br, 2H), 43.7 (s, 2H), 23.7 (s, 2H), 22.2 (s, 2H), 18.0 (s, 1H), 16.6 (s, 1H), 12.4–12.3 (v br, s, 12H total), 6.2 (s, 6H), 4.7 (s, 6H), -1.3 (v br), -42.2 (s, 2H), -44.2 (s, 2H). ¹H NMR (toluene- d_8 , 313 K): δ 46.5 (br, 2H), 44.9 (s, 2H), 41.9 (s, 2H), 22.7 (s, 2H), 21.6 (s, 2H), 17.3 (s, 1H), 16.2 (s, 1H), 12.4 (v br, 6H), 11.7 (s, 6H), 5.7 (s, 8H), 4.6 (s, 8H), -0.8 (br s, 3H), -8.2 (br s, 2H), -40.3 (s, 2H), -41.7 (s, 2H). ¹H NMR (toluene-d₈, 373 K): δ 46.64 (s, 2H), 36.67 (s, 2H), 20.83 (s, 4H), 15.78 (s, 2H), 10.64 (s, 12H), 3.11 (s, 12H), -5.66 (s, 4H, THF β-H), -11.61 (br s, 4H, THF α-H), -35.58 (s, 4H). ¹H NMR (toluene- d_8 , 294 K, after cooling): δ 45.23 (s, 2H), 43.93 (s, 2H), 22.03 (s, 2H), 16.49 (s, 1H), 12.22 (s, 6H), 6.36 (s, 6H), 4.87 (s, 1H), 1.18 (s, 2H), -41.9 (s, 2H). μ_{eff} (solution) = 2.6 μ_{B} at 294 K.

$[^{\text{DIPP}}\text{NCOCN}]\text{UCl}_2 \cdot \frac{1}{2}\text{C}_7\text{H}_8$ (2)

 $H_2[^{DIPP}NCOCN]$ (0.425 g, 1.00 mmol) was dissolved in 15 mL of diethyl ether, and 2 equiv. of "BuLi (1.32 mL, 2.11 mmol) was added dropwise at -78 °C. The resulting solution was stirred for 40 min at room temperature and subsequently added dropwise to a 75 mL room temperature toluene solution of UCl₄ (0.400 g, 1.05 mmol), yielding a dark brown–orange solution. After the reaction mixture was stirred for 15 h at room temperature, the

product was filtered through a Celite-padded medium-porosity glass frit. Removal of the volatiles under reduced pressure gave **2** as a brownish-orange powder. Yield: 0.696 g (90%). Anal. Calc. for $C_{28}H_{42}N_2Cl_2OU \cdot {}_2^{1}C_7H_8$: C, 48.65; H, 5.96; N, 3.60. Found: C, 48.94; H, 6.21; N, 3.54%. IR (cm⁻¹, KBr): 2960 (vs), 2923 (m), 2867 (m), 1463 (s), 1444 (m), 1383 (m), 1360 (m), 1313 (w), 1250 (m), 1237 (m), 1177 (m), 1087 (s), 1050 (m), 930 (w), 900 (m), 800 (vs), 761 (s), 578 (s), 463 (vs), 431 (vs). ¹H NMR (toluene-*d*₈, 294 K): δ 56.0 (br, 2H), 45.1 (br, 2H), 25.41 (s, 4H), 18.72 (s, 2H), 14.26 (s, 12H), 6.6 (br, 2H), 5.9 (br, 2H), 4.4 (br mult, 5H, C₆*H*₅CH₃), 1.34 (s, 3H, C₆*H*₅C*H*₃), -1.8 (br s, 12H), -46.0 (s, 4H). ¹H NMR (toluene-*d*₈, 373 K): δ 63.7 (s, 2H), 36.8 (br s, 2H), 23.9 (s, 4H), 17.8 (s, 2H), 12.0 (s, 12H), 7.00–6.90 (br mult, 5H, C₆*H*₅CH₃), 3.0 (br, 2H), 2.6 (br, 2H), 2.06 (s, 3H, C₆*H*₅C*H*₃), -1.56 (s, 12H), -38.7 (s, 4H). μ_{eff} (solution) = 2.4 μ_B at 294 K.

$[^{tBu}NON]UI_{3}Li(THF)_{2}$ (3)

 $\{[^{1Bu}NON]UCl_2\}_2$ (0.400 g, 0.343 mmol) was dissolved with stirring in 45 mL of toluene and LiI (0.321 g, 2.40 mmol) in 1.83 mL THF was added dropwise. Upon addition the reaction mixture turned lighter green in color. The resulting reaction mixture was stirred overnight and subsequently filtered through a Celite-padded medium-porosity glass frit. Removal of the solvent under reduced pressure resulted in 3 as a light green powder. Yield: 0.698 g (97%). X-Ray quality green needle-shaped crystals were obtained from a -30 °C concentrated toluene solution of 3. Anal. Calc. for $C_{20}H_{46}N_2I_3LiO_3Si_2U$: C, 23.00; H, 4.44; H, 2.68. Found: C, 22.86; H, 4.38; N, 2.66%. IR (cm⁻¹, KBr): 2963 (m), 2887 (m), 1469 (m), 1401 (vw), 1385 (w), 1359 (s), 1342 (w), 1296 (vw), 1252 (vs), 1228 (s), 1196 (vs), 1040 (m), 973 (m), 861 (w), 799 (m), 759 (m), 734 (m), 676 (vw), 652 (m), 548 (vw), 527 (s), 502 (vs), 427 (m). ¹H NMR (benzene- d_6): δ 81.84 (s, 18H, C(CH₃)₃), 0.31 (br s, 8H, THF β -H), -3.57 (br s, 8H, THF α -H), -16.75 (s, 12H, Si(CH₃)₂). μ_{eff} (solution) = 2.5 $\mu_{\rm B}$ at 294 K.

{[MesNON]ThCl₃Li(THF)}₂ (4)

H₂[MesNON] (0.503 g, 1.26 mmol) was dissolved with stirring in 30 ml of diethyl ether, and 2 equiv. of "BuLi (1.57 mL, 2.51 mmol) was added dropwise at -78 °C. The reaction mixture was stirred for 1 h at room temperature and subsequently added dropwise to a 60 mL THF solution of ThCl₄ (0.494 g, 1.32 mmol), resulting in a colorless reaction mixture. After the resulting reaction mixture was stirred overnight, 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 the toluene under reduced pressure gave 4 as an off-white powder. Yield: 1.008 g (94%). X-Ray quality clear, colorless crystals were afforded from slow evaporation of a hexanes solution of 4. Anal. Calc. for C₂₉H₄₉N₂Cl₃LiO₂Si₂Th (crystal): C, 40.54; H, 5.75; N, 3.26. Found: C, 39.97; H, 5.56; N, 2.96%. IR (cm⁻¹, KBr): 2953 (s), 2919 (s), 2856 (m), 2728 (w), 1729 (w), 1468 (s), 1373 (w), 1300 (m), 1255 (vs), 1221 (vs), 1156 (s), 1099 (w), 1041 (w), 989 (m), 953 (w), 904 (m), 796 (s), 777 (m), 723 (w), 711 (m), 671 (w), 637 (w), 588 (w), 566 (m), 542 (m), 523 (s), 507 (w), 463 (vw), 422 (m). ¹H NMR (benzene- d_6): δ 6.89 (s, 4H, Ar-H), 3.54 (br s, 4H, THF α -H), 2.78 (s, 6H, *p*-C*H*₃), 2.36 (s, 12H, *o*-C*H*₃), 1.34 (br s, 4H, THF β-*H*), 0.31 (s, 6H, Si(CH₃)₂), 0.27 (s, 6H, Si(CH₃)₂). ${}^{13}C{}^{1}H{}$ NMR (benzened₆): δ 132.16 (s, Ar-C), 129.29 (s, Ar-C), 129.15 (s, Ar-C), 128.31 (s, *m* Ar-*C*), 68.98 (s, THF α-*H*), 25.27 (s, THF β-*H*), 20.88 (s, o Ar-CH₃), 20.80 (s, p Ar-CH₃), 3.69 (s, Si(CH₃)₂), 3.01 (s, Si(CH₃)₂). ⁷Li NMR (toluene- d_8): δ –0.2 (br).

$[^{Mes}NON]_2Th$ (5)

 H_2 [^{Mes}NON] (0.713 g, 1.78 mmol) was dissolved with stirring in 30 ml of diethyl ether, and "BuLi (2.34 mL, 3.74 mmol) was added dropwise at -78 °C. The reaction mixture was stirred

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for 1 h at room temperature and subsequently added dropwise to a 75 mL toluene slurry of ThCl₄ (0.350 g, 0.936 mmol), resulting in a colorless reaction mixture. After the reaction mixture was stirred for 15 h, the product was filtered through a Celite-padded medium-porosity glass frit. Removal of the toluene under reduced pressure gave 5 as an off-white powder. Yield: 0.803 g (83%). X-Ray quality clear, colorless crystals were obtained by slow evaporation of a toluene solution of 5. Anal. Calc. for C44H68N4O2Si4Th: C, 51.34; H, 6.66; N, 5.44. Found: C, 51.66; H, 6.71; N, 5.56. IR (cm⁻¹, KBr): 2993 (m), 2951 (s), 2916 (s), 2855 (m), 2724 (w), 1927 (w), 1724 (w), 1610 (w), 1474 (vs), 1440 (m), 1370 (w), 1301 (s), 1254 (s), 1219 (vs), 1158 (vs), 1033 (w), 969 (s), 951 (s), 909 (s), 853 (m), 824 (w), 795 (m), 759 (m), 713 (s), 660 (w), 633 (w), 588 (w), 568 (w), 535 (s), 519 (vs), 444 (w), 416 (s). ¹H NMR (benzene- d_6): δ 6.85 (s, 8H, Ar-H), 2.38 (s, 24 H, o-CH₃), 2.27 (s, 12H, p-CH₃), 0.05 (s, 24 H, Si(CH₃)₂). ¹³C{¹H} NMR (benzene- d_6): δ 144.36 (s, Ar-C), 131.44 (s, Ar-C), 130.29 (s, Ar-C), 129.59 (s, Ar-C), 21.21 (s, Ar-CH₃), 20.70 (s, Ar-CH₃), 3.83 (s, Si(CH₃)₂).

$[^{DIPP}NCOCN]U(CH_2Si(CH_3)_3)_2 (6)$

[DIPPNCOCN]UCl₃Li(THF)₂ (0.400 g, 0.436 mmol) was dissolved with stirring in 100 mL of toluene, and 2 equiv. of a -30 °C toluene solution of LiCH₂Si(CH₃)₃ (0.082 g, 0.871 mmol) was added dropwise at -30 °C. Within 5 min of stirring the solution turned from green-orange to red-brown in color. Stirring was continued for 30 min at room temperature and the resulting reaction slurry was reduced to a volume of 45 mL and filtered over a Celite-padded medium-porosity glass frit. Removal of the toluene under reduced pressure yielded 6 as a red-orange powder. Yield: 0.328 g (90%). X-Ray quality orange crystals were obtained by slow evaporation of a pentane solution of 6. Anal. Calc. for C₃₆H₆₄N₂OSi₂U: C, 51.78; H, 7.72; N, 3.35. Found: C, 51.44; H, 7.51; N, 3.81%. IR (cm⁻¹, KBr): 3053 (vw), 2959 (m), 2868 (m), 1585 (w), 1456 (s), 1429 (s), 1383 (m), 1362 (m), 1310 (m), 1240 (vs), 1190 (m), 1098 (s), 1083 (vs), 1048 (s), 947 (w), 939 (w), 852 (m), 793 (m), 756 (m), 733 (w), 705 (m), 690 (m), 665 (w), 517 (m), 431 (m). ¹H NMR (benzene- d_6): δ 66.7 (br, 4H, CH₂), 27.5 (v br, 4H, CH(CH₃)₂), 20.85 (s, 2H, p-H), 13.4 (v br, 24H, CH(CH₃)₂), -17.52 (s, 18H, Si(CH₃)₃), -17.60 (s, 4H, *m*-H), -41.3 (br, 4H, CH₂), ca. -140 (vv br, 4H, $CH_2Si(CH_3)_3$). μ_{eff} (solution) = 2.7 μ_B at 294 K.

Table 6 Summary of crystallographic data

[^{tBu}NON]U(CH₂Si(CH₃)₃)₂ (7)

[^{IBu}NON]UI₃Li(THF)₂ (0.108 g, 0.103 mmol) was dissolved with stirring in 30 mL of toluene, and 2 equiv. of a -30 °C toluene solution of LiCH₂Si(CH₃)₃ (0.020 g, 0.207 mmol) was added dropwise at -30 °C. Upon addition the solution turned yellow in colour. As soon as the reaction mixture was warmed to room temperature, the toluene was removed under reduced pressure. The residue was then extracted with hexanes and filtered over a Celite-padded medium-porosity glass frit. Removing the solvent under reduced pressure yielded 7 as a dark orange oil. Yield: 0.060 g (85%). ¹H NMR (benzene-*d*₆): δ 71.17 (s, 18H, C(CH₃)₃), -16.62 (s, 12H, Si(CH₃)₂), -20.84 (s, 18H, Si(CH₃)₃), -148.92 (s, 4H, CH_2 Si(CH₃)₃). μ_{eff} (solution) = 2.8 μ_B at 294 K. This ¹H NMR data matches analytically pure 7 prepared by a different route.²⁵

X-Ray crystallographic analysis of $[^{DIPP}NCOCN]UCl_3Li(THF)_2$ (1), $[^{IBu}NON]UI_3Li(THF)_2$ (3), $\{[^{Mes}NON]ThCl_3Li(THF)\}_2$ (4), $[^{Mes}NON]_2$ Th (5) and $[^{DIPP}NCOCN]U(CH_2Si(CH_3)_3)_2$ (6)

Crystallographic data for all structures are in Table 6. The crystals of complexes 1, 3, 4 and 6 were sealed into glass capillaries under an atmosphere of nitrogen. Complex 5 was coated with oil (Paratone 8277, Exxon) and collected on top of the nylon fiber of a mounted CryoLoopTM (diameter of the nylon fiber: 10 microns; loop diameter 0.1–0.2 mm; Hampton Research, USA) under a microscope. The crystal was then mounted onto a goniometer head, which was quickly transferred to the N₂ cold stream. Crystal descriptions and measurements for each compound are as follows: 1 was a green block (0.40 × 0.30 × 0.20 mm³); 3 was a green plate (0.36 × 0.15 × 0.09 mm³); 4 was a colorless block (0.45 × 0.30 × 0.15 mm³); 5 was a colorless block (0.25 × 0.20 × 0.18 mm³); 6 was an orange plate (0.75 × 0.45 × 0.09 mm³).

For compounds 1, 3 and 6 the following data ranges were recorded employing an Enraf Nonius CAD4F diffractometer with the diffractometer control program DIFRAC:⁷⁷ 1, $4 \le 2\theta \le 39^{\circ}$; 3, $4 \le 2\theta \le 50^{\circ}$; 6, $4 \le 2\theta \le 50^{\circ}$. The programs used for empirical absorption corrections (psi-scan) and data reduction, including Lorentz and polarization corrections for 1, 3 and 6 were from the NRCVAX Crystal Structure System⁷⁸ and the structures were solved using SIR92 and refined in *CRYSTALS*.⁷⁹ Diagrams for all complexes were made using Ortep-3.⁸⁰ Complex

	1 ^{<i>a</i>}	3ª	$4 \cdot \tfrac{1}{2} \mathbf{C}_6 \mathbf{H}_{14}{}^{\boldsymbol{b}}$	5 ^c	6 ^{<i>a</i>}
Empirical formula	UCl ₃ O ₃ N ₂ C ₃₆ LiH ₅₈	UI ₃ Si ₂ O ₃ N ₂ C ₂₀ LiH ₄₆	ThSi ₂ Cl ₃ O ₂ N ₂ C ₂₉ LiH ₄₉	ThSi ₄ O ₂ N ₄ C ₄₄ H ₆₈	USi ₂ ON ₂ C ₃₆ H ₆₄
$M_{\rm w}$	918.2	1044.5	859.2	1029.42	835.1
Cryst. dimens./mm	$0.20 \times 0.30 \times 0.40$	$0.09 \times 0.15 \times 0.36$	$0.15 \times 0.30 \times 0.45$	$0.18 \times 0.20 \times 0.25$	$0.09 \times 0.45 \times 0.75$
Τ/K	293	293	293	173	293
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	Pn	C2/m	$P2_{1}/c$	Pbca
a/Å	13.266(3)	11.259(3)	24.157(5)	11.0190(1)	11.4344(13)
b/Å	19.914(2)	13.222(4)	17.397(4)	20.3090(2)	20.050(5)
c/Å	16.697(3)	12.012(3)	9.239(2)	21.6470(3)	35.450(6)
β/°	106.697(3)	92.45(2)	99.17(2)	98.4250(4)	90
$V/Å^3$	4223.4(13)	1786.5(8)	3833.2(15)	4791.99(9)	8127(3)
Ζ	4	2	8	4	8
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.444	1.942	1.448	1.427	1.338
μ/cm^{-1}	38.66	69.59	146.41	32.50	37.94
Independent reflns.	$3693; 1736 (> 2.5\sigma(I_0))$	3294; 1673 (>2.5 $\sigma(I_0)$)	$3531; 2355 (> 3\sigma(I_0))$	13945; 10814 (> $2\sigma(I_0)$)	7203; 2613 (>2.5 $\sigma(I_0)$)
No. of params.	238	188	187	516	316
R	0.0390^{d}	0.0337 ^d	0.0469^{d}	0.0368 ^e	0.0525 ^d
<i>R</i>	0.0389/	0.0380	0.0597 ^f	0.0683 ^g	0.0686

^{*a*} Enraf-Nonius CAD-4 diffractometer, Mo-Ka radiation ($\lambda = 0.71073$ Å), graphite monochromator. ^{*b*} Rigaku RAXIS-Rapid curved image plate area detector, Cu-Ka radiation ($\lambda = 1.5419$ Å), graphite monochromator. ^{*c*} Nonius Kappa CCD 4-Circle Kappa FR540C diffractometer, Mo-Ka radiation ($\lambda = 0.71073$ Å), graphite monochromator. ^{*d*} $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^{*e*} $R(F) = \sum |F_o^2 - F_c^2| / \sum F_o^2$. ^{*f*} Function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = [\sigma^2(F_o) + (P_1F_o)^2]^{-1}$, 1: $P_1 = 0.025$, 4: $P_1 = 0.026$, 6: $P_1 = 0.03$, $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{\frac{1}{2}}$. ^{*s*} Function minimized $\sum w(F_o^2 - F_c^2)^2$ where $w = [\sigma^2(F_o^2) + (0.011P)^2 + 6.63P]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$, $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum F_o^4]^{\frac{1}{2}}$.

scattering factors for neutral atoms⁸¹ were used in the calculation of structure factors. The data were corrected for the effects of absorption using the following transmission ranges: **1**, 0.3281– 0.6508; **3**, 0.2539–0.3569; **6**, 0.2675–0.6725. Final unit-cell dimensions were determined on the basis of the following wellcentered reflections: **1**, 22 reflections with range $28 \le 2\theta \le 30^{\circ}$; **3**, 32 reflections with range $29 \le 2\theta \le 31^{\circ}$; **6**, 46 reflections with range $35 \le 2\theta \le 38^{\circ}$.

For compound 4 data was acquired on a Rigaku RAXIS-Rapid curved image plate area detector with graphite monochromated utilizing Cu-Ka radiation. Indexing was performed from four 5° oscillations that were exposed for 80 s. The data was collected to a maximum 2θ value of 136.5°. A total of 27 oscillation images were collected. A sweep of data was done using ω scans from 50.0 to 230.0° in 20.0° steps, at $\chi = 50.0^{\circ}$ and $\phi = 0.0^{\circ}$. A second sweep was performed using ω scans from 50.0 to 230.0° in 20.0° steps, at $\chi = 50.0^{\circ}$ and $\phi = 90.0^{\circ}$. A final sweep was performed using ω scans from 50.0 to 230.0° in 20.0° steps, at $\chi = 50.0^{\circ}$ and $\phi = 180.0^{\circ}$. The exposure was 80 s/° The crystal-to-detector distance was 127.40 mm. Of the 15225 reflections that were collected, 3531 were unique ($R_{int} = 0.0992$); equivalent reflections were merged. The data was processed and corrected for Lorentz and polarization effects and absorption with the relative transmission range 0.66-1.00.82

For 5, all measurements were made on a Nonius KappaCCD 4-Circle Kappa FR540C diffractometer using monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). An initial orientation matrix and cell was determined from 10 frames using ϕ scans (1° per frame, 20 s exposures per degree for a 10° rotation at a detector distance of 35 mm). Data were measured using ϕ - and ω -scans and two sets of frames were collected (1.5° rotation per frame; exposure per frame: 30 s; detector distance of 30 mm). A total of 26815 reflections were collected. Cell parameters were initially retrieved using the COLLECT⁸³ software, refined with the HKL DENZO and SCALEPACK software⁸⁴ using 13782 observed reflections (mosaicity: 0.451(1)°). Data reduction was performed with the HKL DENZO and SCALEPACK software,85 which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarization effects. A multi-scan absorption correction was applied.⁸⁴ Transmission coefficients were calculated using SHELXL97-2.85 Of the 26815 collected reflections, 24 were rejected. The remaining reflections were merged (all symmetry equivalents and Friedel opposites; $R_{int} = 0.0397$) to provide 13945 reflections, all of which were unique ($R_{sigma} = 0.0563$), and 10814 observed reflections $(I > 2\sigma(I))$. The ranges of indices were $-15 \le h \le 15, -28 \le k \le 28, -30 \le l \le 30$ corresponding to a $\theta\text{-range}$ of 2.86–30.02.85

For 1 and 3 coordinates, anisotropic displacement parameters for the non-carbon and non-hydrogen atoms and isotropic thermal parameters for carbon and lithium atoms were refined. For 4 coordinates and anisotropic displacement parameters for all non-hydrogen atoms, with the exception of the lithium, hexanes and THF carbons, were refined. For 6 coordinates and anisotropic displacement parameters for all non-hydrogen atoms, with the exception of the methylene carbon in -CH₂Si(CH₃)₃ and all methyl groups, were refined. In all cases, hydrogen atoms were placed in calculated positions (d_{C-H} = 0.950 Å), and refined using a riding model. Initially, isotropic thermal parameters for the hydrogen atoms were assigned to be 1.2 times the equivalent isotropic thermal parameters of their respective carbon atoms. Subsequently, isotropic thermal parameters for sets of similar C-H hydrogen atoms were constrained to have identical shifts during refinement. An extinction parameter⁸⁶ was included in the final cycles of fullmatrix least-squares refinement of 6. The Flack enantiopole parameter⁸⁷ (0.023(17)) was included in the final cycles of fullmatrix least-squares refinement of 3. For 4, the lithium atom, with its coordinated THF molecule is 50:50 disordered over two positions associated with chlorine atoms from different adjacent molecules, related by a two-fold rotational symmetry.

For 5 the structure was solved by direct methods using SIR-97⁸⁸ and refined by full-matrix least-squares method on F^2 with SHELXL97-2.85 The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at geometrically idealized positions (C-H bond distances 0.95/0.98 Å) and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 times that of the preceding carbon atom. The mean square atomic displacements parameters for the carbon atom C(48) are slightly higher. However, refinement of this atom using the split-atom model failed. The final cycle of full-matrix least squares refinement using F^{2} ,⁸⁵ was based on 13945 reflections, 516 variable parameters and converged (largest parameter shift was 0.002 times its esd) with an unweighted factor of R1 = 0.0368 for $I > 2\sigma(I)$. The standard deviation of an observation of unit weight (goodness-of-fit) was 1.028. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.711 and $-1.023 e^- Å^{-3}$ (close to Th), respectively. Selected bond lengths and angles for 1, 3, 4, 5 and 6 are found in Tables 1, 2, 3, 4 and 5, respectively.

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See http://dx.doi.org/10.1039/b506180f for crystallographic data in CIF or other electronic format.

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