Organometallic chemistry of the actinides. Part 3
Novel 1-aza-allyl- and β-diketiminatothorium chlorides; X-ray structures of [{ $\overline{Th(LL')}_2$ (μ_3-Cl)(μ-Cl) $_2$ K(OEt$_2$)}$_\infty$] and [$\overline{Th(LL)}_2$ Cl$_2$] [LL' = N(SiMe$_3$) C(Bu^t) C(H) SiMe$_3$; LL = {N(SiMe$_3$) C(Ph)}$_2$CH] [1]

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Abstract

Treatment of ThCl$_4$ with (i) $2/n[\{K(LL')\}_n]$ in Et$_2$O or (ii) $2/m[\{K(LL)\}_m]$ in THF yielded (i) the crystalline, polymeric, heterobimetallic bis(1-aza-allyl)dichlorothorium(IV)–KCl complex [{ $\overline{Th(LL')}_2$ (μ_3-Cl)(μ-Cl)$_2$K(OEt$_2$)}$_\infty$] 1, or (ii) the crystalline, mononuclear bis(β-diketiminato)thorium(IV) chloride [$\overline{Th(LL)}_2$Cl$_2$] 2 [LL' = N(SiMe$_3$)C(Bu^t)C(H)SiMe$_3$, LL = {N(SiMe$_3$)C(Ph)}$_2$CH, THF = OC$_4$H$_8$]. Details of the NMR spectra of 1 (in C$_5$D$_5$N) and 2 (in [^{2}H$_8$]toluene), and results of single crystal X-ray diffraction data for both 1 and 2 are presented. While complex 1 was resistant to reduction by K/Na alloy in THF, 2 afforded an unidentified paramagnetic Th(III) complex, g_{av} 2.003 at 300 K in PhMe. © 1997 Elsevier Science S.A.

Keywords: Thorium; 1-Aza-allyl; β-Diketiminates; Crystal structure

1. Introduction

This paper impinges on two areas of chemistry which have been of interest to us: organothorium compounds and metal 1-aza-allyls and β-diketiminates.

In Part 1 of this series, we described the synthesis, spectroscopic properties and crystal structures of [AcCp$_2''$Cl$_2$] (Ac = Th or U) and [UCp$_2''$X$_2$] (X = Br, I or BH$_4$) [1], while in Part 2 we reported on two monocyclopentadienylthorium(IV) and seven bis(cyclopentadienyl)thorium(IV) complexes: [{(ThCp'''Cl$_3$)$_2$NaCl(OEt$_2$)}$_2$], [ThCp'''Cl$_3$(PMDETA)], [ThCp$_2''$Cl$_2$(OEt$_2$)], [ThCp$_2''$Cl$_2$], [ThCp$_2^*$Br$_2$(THF)], [ThCp$_2''$Cl$_2$], [ThCp$_2''$Cl$_2$(DMPE)], [ThCp$_2''$(Cl)-{CH(SiMe$_3$)$_2$}] and [ThCp$_2''$(acac)Cl] [Cp'' = η^5-C$_5$H$_3$(SiMe$_3$)$_2$-1,3; Cp''' = η^5-C$_5$H$_2$(SiMe$_3$)$_3$-1,2,4; Cp* = η^5-C$_5$Me$_5$; Cp$''$ = η^5-C$_5$H$_3$(SiMe$_2$Bu^t)$_2$-1,3; PMDETA = MeN(CH$_2$CH$_2$NMe$_2$)$_2$; DMPE = (Me$_2$PCH$_2$)$_2$; acacH = {MeC(O)}$_2$CH$_2$] [2]. The common thorium(IV) precursor in each case was ThCl$_4$,

which was initially treated with an appropriate lithium or sodium cyclopentadienyl, alkyl or acetylacetonate. Earlier publications on organothorium chemistry, as preliminary communications, have dealt with thorocene(IV) aryloxides [3]; and the as yet sole X-ray characterised thorium(III) complex [ThCp$_3''$] [4] (obtained from [ThCp$_2''$Cl$_2$] and K/Na), which was shown to have a 6d^1 (ESR active at 300 K, g_{av} 1.9010 in methylcyclohexane) electronic ground state [5].

The synthesis, structures and reactions of alkali metal, in particular lithium, 1,3-bis(trimethylsilyl)-1-aza-allyls and β-diketiminates, including their role as precursors for preparing unusual transition metal and main group element complexes, have recently been reviewed [6]. The compounds [{Li(LL')}$_2$] I [7] and [{Li(LL)}$_2$] II [8] were the first members of these series to be obtained [LL' = N(SiMe$_3$)C(Bu^t)C(H)SiMe$_3$, LL = {N(SiMe$_3$)C(Ph)}$_2$CH], Eq. (1). Compound I has already been employed to obtain [{K(LL')}$_n$] III [7], *rac*-[$\overline{Zr(LL')}_2$Cl$_2$] [7], *rac*-[$\overline{Yb(LL')}_2$] [9] and [$\overline{Zr(LL')}$Cl$_3$] [10]; experiments are in hand on derivatives of tin(II), lead(II), iron(II) and cobalt(II), using [LL']$^-$ or a closely related ligand [11]. Compound II likewise has

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been used as a ligand transfer reagent, giving rise to inter alia [{K(LL)}$_m$] **IV** [8], [SnCl(Me)$_2$(LL)] [8], [Co(LL)$_2$] [6] and [{ U(LL)Cl(NSiMe$_3$)(μ-Cl)}$_2$] [U(LL)Cl$_2${N(SiMe$_3$)C(Ph)NC (Ph)C(H)SiMe$_3$)]$_2$ **A** [12], and experiments are in progress on derivatives of tin(II), nickel(II), copper(II), copper(I) and zirconium(IV) [11]; [Zr{N(SiMe$_3$)C(Ph)C(H)C(Bu^t)N - SiMe$_3$}Cl$_3$] has been shown to be mononuclear [7].

We have previously noted that the β-diketiminato ligand [LL]$^-$ is sterically extremely demanding and has some η^5-character, thus being somewhat analogous to extremely bulky cyclopentadienyls and of potential use as a kinetically inert 'spectator' ligand [6,11]; the 1-aza-allyl ligand [LL']$^-$ is significantly less bulky, but may have a similar role.

In this paper, we focus on the reactions of the potassium compounds **III** and **IV** with thorium(IV) chloride.

(1)
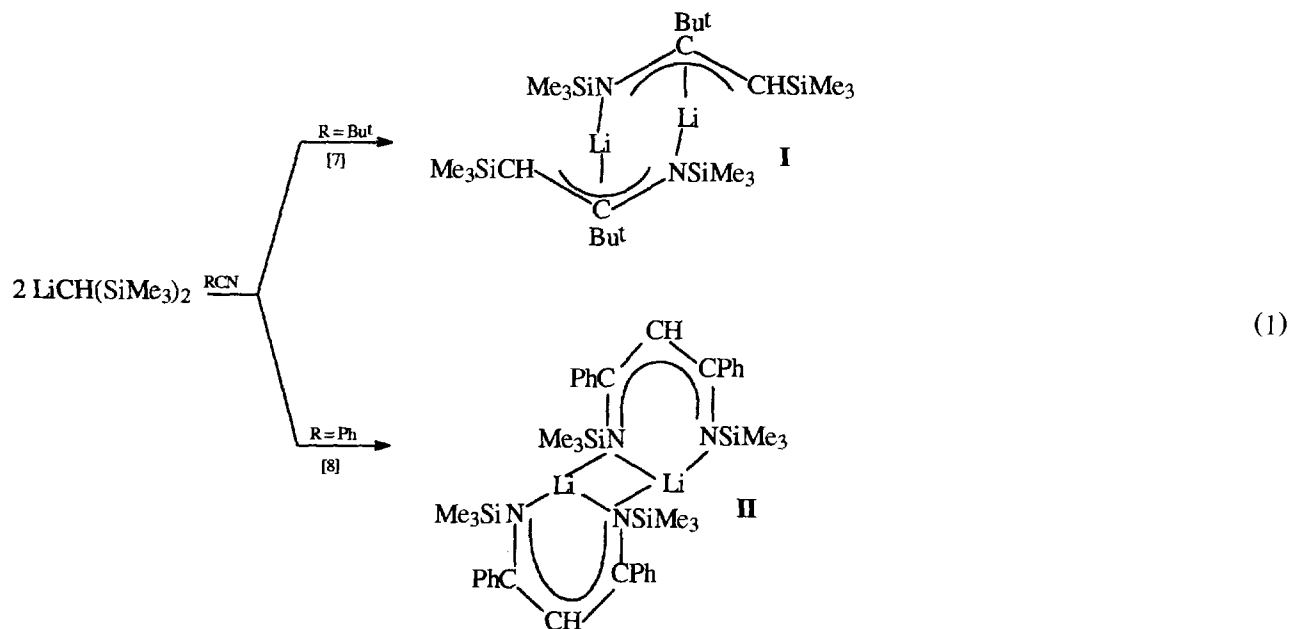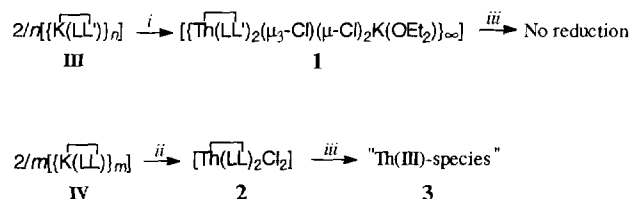
2. Results and discussion

2.1. Synthetic studies

Treatment of thorium(IV) chloride with two equivalents of the potassium 1-aza-allyl [{K(LL')}$_n$] **III** in diethyl ether at ambient temperature yielded (i in Scheme 1) the colourless, crystalline, polymeric, heterobimetallic bis(1-aza-allyl)dichlorothorium(IV)–potassium chloride complex [{ Th(LL')$_2$(μ$_3$-Cl)(μ-Cl)$_2$K(OEt$_2$)}$_∞$] **1** in good yield. Likewise, from ThCl$_4$ and two equivalents of the potassium β-diketiminate [{K(LL)}$_m$] **IV** in tetrahydrofuran under similarly mild conditions there was obtained (ii in Scheme 1) the crystalline, mononuclear bis(β-diketiminato)thorium(IV) chloride **2** in excellent yield.

Compounds **1** and **2** gave satisfactory analytical results, details of which, with yields and some other data, are shown in Table 1. While **2** was soluble even in hydrocarbons, **1** was only sparingly soluble in toluene but dissolved in the donor solvents diethyl ether or pyridine. Similarly, an EI mass spectrum was not ob-

tainable for **1**, but **2** gave the parent molecular ion as well as various fragment ions.

The ^{1}H NMR spectra of **1** and **2** gave the appropriate signals and signal intensities for the organic ligands, as shown in Table 2.

A combination of these data clearly pointed to the monocular bis(β-diketiminato)dichlorothorium(IV) structure **2**, but an X-ray study was still undertaken (Section 2.3) because no example of an [M(LL)$_2$ Cl$_2$] molecule (e.g. M = Zr or U) was known, and attempts to make such a uranium(IV) compound, from UCl$_4$ and

2/n[{K(LL')}$_n$] $\xrightarrow{i}$ [{Th(LL')$_2$(μ$_3$-Cl)(μ-Cl)$_2$K(OEt$_2$)}$_∞$] $\xrightarrow{iii}$ No reduction
III   **1**

2/m[{K(LL)}$_m$] $\xrightarrow{ii}$ [Th(LL)$_2$Cl$_2$] $\xrightarrow{iii}$ "Th(III)-species"
IV   **2**   **3**

Scheme 1. Reagents and conditions: (i) ThCl$_4$, Et$_2$O, 48h, ca. 25°C; (ii) ThCl$_4$, THF, 48h, ca. 25°C; (iii) excess K/Na alloy, THF, 48h, ca. 25°C.

Table 1
Yields, colours, analytical and mass spectral data for complexes **1–3** and ESR spectral data for **3**

Compound	Yield [a] (%)	Colour	Analysis [b] (%)	Electron impact mass spectrum, m/z
1	72	colourless	C 34.8 (35.9) H 7.0 (7.1) N 3.3 (3.0)	[c]
2	85	yellow	C 48.7 (48.8) H 5.6 (5.7) N 5.3 (5.4)	1034 (M$^+$)
3 [d]	[c]	violet–red	C 46.0 H 5.9 N 4.3 Cl < 0.3	1512 (highest ion)

[a] Not optimised.
[b] Calculated values in parentheses.
[c] Not applicable.
[d] ESR spectral data, g_{av} 2.003 in THF at 300 K.

Table 2
NMR spectral chemical shifts δ with assignments for complexes **1** and **2** at 305 K [a]

Compound	^{1}H	^{31}C{^{1}H}	Solvent
1	−0.14 (9H, s, SiMe$_3$) 0.56 (9H, s, SiMe$_3$) 0.63 (9H, s, SiMe$_3$) 0.67 (9H, s, SiMe$_3$) 1.45 (9H, s, Bu^t) 1.65 (9H, s, Bu^t) 5.32 (1H, s, CH) 5.63 (1H, s, CH) 1.11 (6H, t, ^3J [7.03 Hz], [CH_3CH$_2$]$_2$O) 3.33 (4H, q, ^3J [7.03 Hz], [CH$_3$CH_2]$_2$O)		C$_5$D$_5$N
2	0.35 (18H, s, SiMe$_3$) 5.29 (1H, s, CH) 6.92–7.30 (10H, m, phenyl)	4.07, SiMe$_3$; 97.61, CH 171.77, CN 127.86, 142.77, 130.24 130.73, phenyl	C$_7$D$_8$

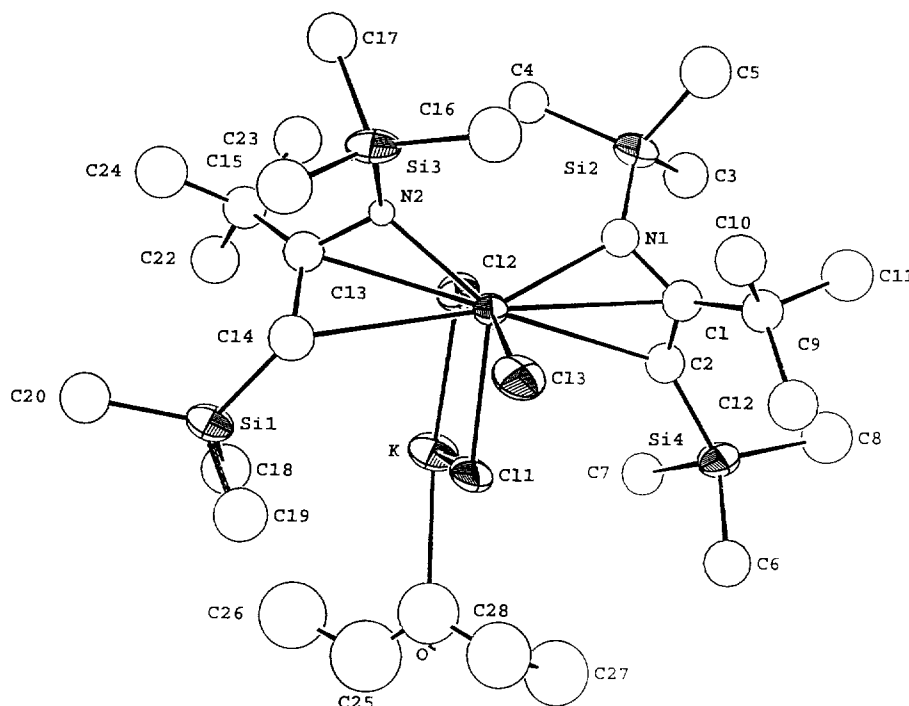[a] At 360.1 MHz for ^{1}H and 62.9 MHz for ^{13}C{^{1}H} NMR.

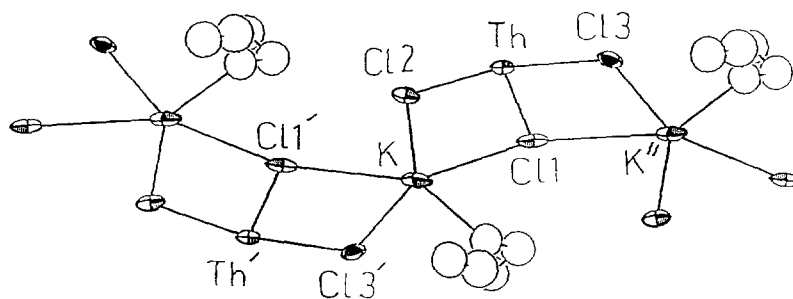Fig. 1. Molecular structure and atom numbering scheme for complex **1**.

Fig. 2. Polymeric structure and atom numbering scheme for complex 1 with [LL′]⁻ omitted for clarity.

$2/m[\{K(LL)_m\}]$ **IV**, had led to a partially rearranged product, the $[\{U(VI)\}_2][U(III)]_2$ salt **A** (see Section 1) [12]. It is therefore noteworthy that the corresponding Th reaction (ii in Scheme 1) gave $[\overline{Th(LL)}_2Cl_2]$. The rearrangement in the U^{4+} case may have been due to a steric effect, which for the larger Th^{4+} analogue was less significant.

For **1**, a crystal structure determination (Section 2.2) was even more crucial, because the data of Table 1 were inadequate to propose a structure. Additionally, a heterobimetallic Th/K complex had no precedent in 5f element chemistry. Although chloride-bridging between an f-block or Group 3 element and lithium or sodium is well documented, the first such complex was $[Y(\eta^5-C_5H_4SiMe_3)_2(\mu-Cl)_2Li(THF)_2]$ [13], potassium ana-

logues remain a rarity for organolanthanides and are unknown in organoactinide chemistry [14], presumably because of the greater ionic character for the heavier alkali metal.

Attempts to reduce complex **1** with an excess of K/Na alloy in THF was unsuccessful, complex **1** being recovered from such experiments.

Reduction of the yellow complex **2** with an excess of K/Na alloy in THF (iii in Scheme 1; cf. the corresponding reaction of $[ThCp''_2Cl_2] \rightarrow [ThCp''_3]$ [3]) yielded a deep blue solution. When the reduction was carried out in toluene solution, the product was dark green. Both solutions gave a violet–red solid after filtration and removal of solvent. Extraction of the violet–red solid with diethyl ether afforded a purple solution, from
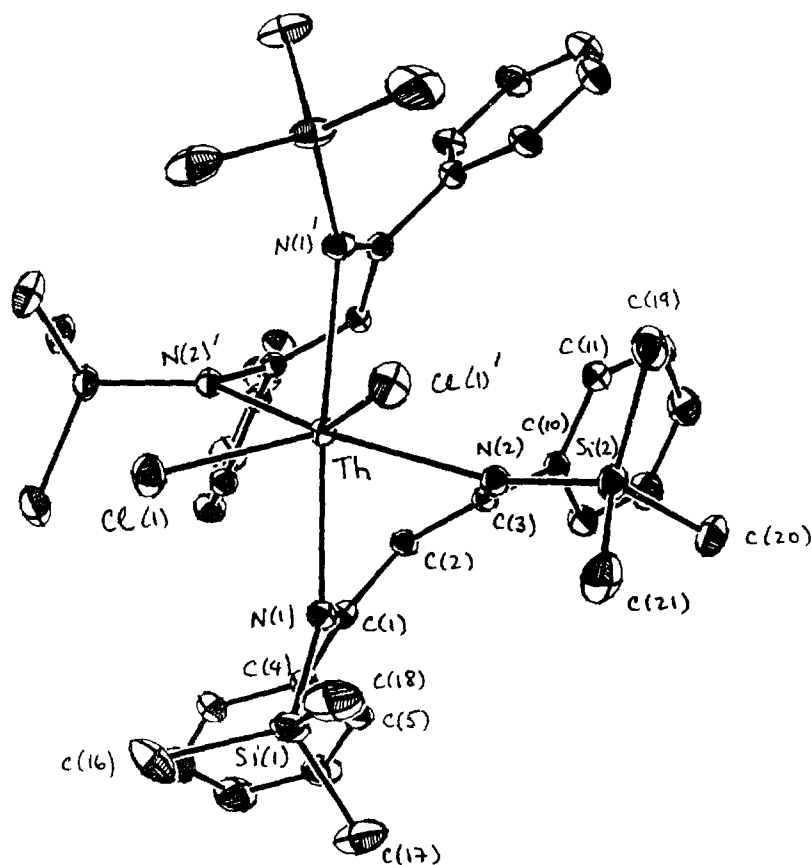

Fig. 3. Molecular structure and atom numbering scheme for complex 2.

which a violet–red microcrystalline solid **3** was obtained upon concentration and cooling to −30 °C. The two products were identical according to their mass spectra. Attempts to obtain X-ray quality single crystals were unsuccessful. The mass spectrum showed the highest ion at m/z 1512; the starting material was absent. The ^{1}H NMR spectrum showed **3** to be paramagnetic. The ESR spectrum in THF showed g_{av} 2.003 at 300 K, consistent with its containing a $6d^1$ Th(III) species. The analytical results (Table 1) are inconsistent with **3** being either [$\overline{\text{Th(LL)}}_3$] or [$\overline{\text{Th(LL)}}_2\text{Cl}$].

2.2. The X-ray crystal structure of 1

A single crystal X-ray diffraction study of **1** revealed the structure to be as shown in Figs. 1 and 2. Selected bond lengths and angles are listed in Table 3 and atomic coordinates in Table 4. The polymeric structure (Fig. 2) consists of an infinite chain of $\overline{\text{Th(LL')}}_2(\mu_3\text{-Cl})(\mu\text{-Cl})_2\text{K(OEt}_2)$ units (Fig. 1), which extend along the crystal b axis.

Each thorium centre is coordinated by three chlorides

Table 3
Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [{ $\overline{\text{Th(LL')}}_2(\mu_3\text{-Cl})(\mu\text{-Cl})_2\text{K(OEt}_2)\}_\infty$] **1**

Bond distance		Angle	
Th–N(1)	2.25(2)	Cl(1)–Th–Cl(2)	95.7(2)
Th–N(2)	2.16(2)	Cl(1)–Th–Cl(3)	72.5(2)
Th–C(1)	2.87(2)	Cl(1)–Th–N(1)	125.1(5)
Th–C(13)	2.89(2)	Cl(1)–Th–N(2)	123.1(5)
Th–Cl(1)	2.413(6)	Cl(2)–Th–Cl(3)	168.2(1)
Th–Cl(3)	3.204(6)	Cl(2)–Th–N(2)	88.6(5)
Th–C(2)	2.91(2)	Cl(2)–Th–N(1)	88.0(5)
Th–C(14)	2.99(2)	Cl(3)–Th–N(1)	99.3(5)
Th–Cl(2)	3.093(8)	Cl(3)–Th–N(2)	97.2(5)
K···Cl(1)	3.750(10)	N(1)–Th–N(2)	111.7(7)
K···Cl(1)′	4.159(11)	Cl(1)–K–Cl(1)′	154.5(2)
K–Cl(3)′	2.938(9)	Cl(1)–K–Cl(3)′	149.1(2)
K–Cl(2)	2.618(7)	Cl(1)′–K–Cl(2)	76.5(2)
K–O	2.79(2)	Cl(1)–K–Cl(2)	78.1(2)
K···C(7)	3.49(2)	Cl(1)–K–O	59.0(5)
K···C(18)	4.04(2)	Cl(1)′–K–Cl(3)′	53.6(2)
N(1)–C(1)	1.33(3)	Cl(1)′–K–O	146.4(5)
N(2)–C(13)	1.37(3)	Cl(2)–K–O	137.1(6)
C(13)–C(14)	1.48(3)	Cl(2)–K–Cl(3)′	127.9(3)
C(1)–C(2)	1.24(3)	Cl(3)′–K–O	93.4(5)
		Th–Cl(1)–K	87.1(2)
		K–Cl(1)–K″	163.6(2)
		Th–Cl(3)–K″	124.7(2)
		Th–Cl(1)–K″	108.9(2)
		Th–Cl(2)–K	99.1(3)
		C(14)–Th–N(2)	48(1)
		C(2)–Th–N(1)	44(1)
		C(14)–C(13)–N(2)	103(2)
		C(2)–C(1)–N(1)	106(2)

Primed atoms are related to unprimed ones by $0.5 - x$, $-0.5 + y$, z. Double primed atoms are related to unprimed ones by $0.5 - x$, $0.5 + y$, z.

Table 4
Atomic coordinates and isotropic displacement parameters for **1**

Atom	x	y	z	U_{iso}
Th	0.04220(1)	0.20820(1)	0.12330(1)	0.032(1) *
K	0.3137(4)	0.0411(5)	0.1332(1)	0.059(4) *
Cl1	0.2129(4)	0.2706(5)	0.1292(1)	0.049(4) *
Cl2	0.1141(4)	0.0157(5)	0.1266(2)	0.047(4) *
Cl3	0.0170(4)	0.4164(4)	0.1226(2)	0.046(4) *
Si1	0.1588(5)	0.2601(5)	0.2142(2)	0.042(5) *
Si2	−0.0956(5)	0.0704(6)	0.0698(2)	0.045(5) *
Si3	−0.1619(5)	0.2377(6)	0.1656(2)	0.050(5) *
Si4	0.2185(5)	0.2231(6)	0.0423(2)	0.041(5) *
O	0.4480(18)	0.1839(14)	0.1374(5)	0.092(7)
N1	−0.0331(14)	0.1765(12)	0.0794(4)	0.032(5)
N2	−0.0607(13)	0.1828(13)	0.1602(4)	0.014(5)
C1	0.0211(17)	0.2227(17)	0.0599(5)	0.036(6)
C2	0.1116(16)	0.1958(17)	0.0618(5)	0.035(6)
C3	−0.0287(19)	−0.0170(16)	0.0454(5)	0.051(8)
C4	−0.1246(17)	0.0033(16)	0.1049(5)	0.039(7)
C5	−0.2028(20)	0.0983(18)	0.0501(6)	0.058(9)
C6	0.2764(18)	0.3489(16)	0.0460(5)	0.047(7)
C7	0.2922(17)	0.1267(16)	0.0615(5)	0.042(7)
C8	0.2097(19)	0.1859(19)	0.0024(5)	0.060(9)
C9	−0.0115(16)	0.3122(16)	0.0399(5)	0.036(6)
C10	−0.0929(19)	0.3610(18)	0.0525(6)	0.050(8)
C11	−0.0308(20)	0.2603(16)	0.0088(6)	0.055(8)
C12	0.0547(19)	0.3986(16)	0.0342(6)	0.050(7)
C13	−0.0013(17)	0.1600(16)	0.1843(5)	0.035(6)
C14	0.0658(15)	0.2374(13)	0.1888(4)	0.043(6)
C15	−0.1576(19)	0.3414(17)	0.1946(6)	0.055(8)
C16	−0.1995(19)	0.2903(19)	0.1292(5)	0.058(8)
C17	−0.2506(19)	0.1475(17)	0.1777(5)	0.050(7)
C18	0.2603(19)	0.1808(17)	0.2078(5)	0.053(8)
C19	0.1912(19)	0.3973(17)	0.2056(6)	0.054(8)
C20	0.1318(20)	0.2569(16)	0.2541(5)	0.052(8)
C21	−0.0106(18)	0.0626(17)	0.2025(5)	0.041(7)
C22	0.0769(19)	0.0171(18)	0.2114(6)	0.053(8)
C23	−0.0620(19)	−0.0195(17)	0.1841(5)	0.052(8)
C24	−0.0653(20)	0.0928(18)	0.2304(6)	0.059(8)
C25	0.5161(31)	0.1709(27)	0.1581(9)	0.126(16)
C26	0.4984(27)	0.1107(24)	0.1826(8)	0.113(14)
C27	0.5228(28)	0.1953(23)	0.0910(7)	0.106(12)
C28	0.4640(28)	0.2466(22)	0.1146(8)	0.103(13)

* U_{iso} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

in an approximate T-shaped geometry. Two 1-aza-allyl ligands $[\text{LL'}]^-$ are η^3-bonded to thorium (the distance Th to the central C of the 1-aza-allyl is marginally shorter than that to the terminal C), forming a sandwich structure with a T-shaped 'ThCl$_3$' moiety in between. The two 1-aza-allyl $[\text{N(SiMe}_3)\text{C(Bu}^t)\text{CH(SiMe}_3)]^-$ ($\equiv$ $[\text{LL'}]^-$) ligands are aligned so that the two Bu^t groups point away from one another; therefore the unit $\overline{\text{Th(LL')}}_2(\mu_3\text{-Cl})(\mu\text{-Cl})_2\text{K(OEt}_2)$ is a *rac*-diastereoisomer with two chiral centres at C(14) and C(2). The overall coordination geometry around Th in each $\overline{\text{Th(LL')}}_2\text{Cl}_3$ unit may be regarded as distorted trigonal bipyramidal or square pyramidal, if each $[\text{LL'}]^-$ is taken as occupying a single equatorial or basal site.

Table 5

Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for [Th(LL)₂Cl₂] **2**

Bond distance		Angle	
Th–Cl	2.697(1)	Cl(1)–Th–Cl(1)′	80.38(6)
Th–N(2)	2.462(3)	Cl(1)–Th–N(1)′	109.43(9)
Th–N(1)	2.472(4)	Cl(1)–Th–N(2)′	82.77(9)
N(1)–C(1)	1.318(5)	Cl(1)–Th–N(1)	81.50(8)
N(2)–C(3)	1.332(5)	Cl(1)–Th–N(2)	143.25(9)
C(1)–C(2)	1.427(6)	N(1)–Th–N(1)′	166.1(2)
C(2)–C(3)	1.418(6)	N(1)–Th–N(2)	73.7(1)
		N(1)–Th–N(2)′	100.0(1)
		N(2)–Th–N(2)′	127.5(2)
		Th–N(2)–C(3)	98.1(2)
		Th–N(1)–C(1)	100.0(3)
		N(2)–C(3)–C(2)	122.3(4)
		N(1)–C(1)–C(2)	121.8(4)
		C(1)–C(2)–C(3)	127.0(4)

Primed atoms are related to unprimed ones by − x, y, 0.5 − z.

Considering compound **1** from the standpoint of its polymeric structure (Fig. 2), each Th is linked to K(OEt₂) units through chloride bridges, so that each K has four Cl⁻ nearest neighbours from two adjacent ThCl₂ moieties. The two doubly bridging chlorides Cl(2) and Cl(3) in **1** have close K · · · Cl contacts of 2.618(7) and 2.938(9) Å, which are shorter than in

Table 6

Atomic coordinates and equivalent istropic displacement parameters for **2**

Atom	x	y	z	U_{eq} [a]
Th	0.0000	0.10903(1)	0.2500	0.033(1)
Cl(1)	0.04255(10)	0.00141(6)	0.16737(7)	0.061(1)
Si(1)	0.28292(11)	0.06501(8)	0.28085(9)	0.061(1)
Si(2)	0.04929(10)	0.14479(7)	0.46352(7)	0.049(1)
N(1)	0.1817(3)	0.1247(2)	0.2685(2)	0.042(2)
N(2)	0.0493(2)	0.1659(2)	0.3701(2)	0.039(2)
C(1)	0.1865(3)	0.1930(2)	0.2615(2)	0.039(2)
C(2)	0.1165(3)	0.2385(2)	0.2853(2)	0.036(2)
C(3)	0.0694(3)	0.2290(2)	0.3464(2)	0.035(2)
C(4)	0.2623(3)	0.2288(3)	0.2257(2)	0.044(2)
C(5)	0.3055(3)	0.2915(3)	0.2536(3)	0.053(2)
C(6)	0.3743(4)	0.3242(3)	0.2204(3)	0.071(3)
C(7)	0.4001(4)	0.2964(4)	0.1589(3)	0.088(4)
C(8)	0.3583(4)	0.2356(4)	0.1301(3)	0.081(4)
C(9)	0.2885(4)	0.2013(3)	0.1636(3)	0.060(3)
C(10)	0.0369(3)	0.2938(2)	0.3799(2)	0.037(2)
C(11)	−0.0567(3)	0.2958(2)	0.3982(2)	0.044(2)
C(12)	−0.0883(4)	0.3542(3)	0.4308(3)	0.057(3)
C(13)	−0.0272(4)	0.4108(3)	0.4459(3)	0.069(3)
C(14)	0.0654(4)	0.4102(3)	0.4275(3)	0.067(3)
C(15)	0.0970(4)	0.3524(2)	0.3937(3)	0.051(2)
C(16)	0.3147(5)	0.0275(4)	0.1957(4)	0.106(4)
C(17)	0.3943(4)	0.1081(3)	0.3342(4)	0.093(4)
C(18)	0.2459(5)	−0.0077(3)	0.3351(4)	0.091(4)
C(19)	−0.0777(4)	0.1226(3)	0.4776(3)	0.069(3).
C(20)	0.1037(4)	0.2151(3)	0.5276(3)	0.065(3)
C(21)	0.1348(5)	0.0700(3)	0.4859(3)	0.078(3)

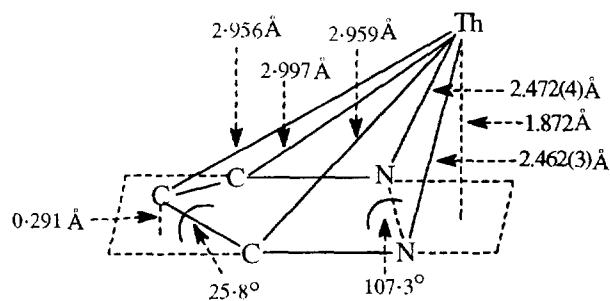[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Fig. 4. A simplified bonding pattern for complex **2**.

crystalline KCl, 3.138 Å [15]; whereas the corresponding Th–Cl bond lengths of 3.093(8) and 3.204(6) Å are considerably longer than those in [{(ThCp‴Cl₃)₂NaCl(OEt₂)}₂], 2.600(4)–2.888(3) Å [2]. Conversely, the triply bridging chloride Cl(1) has a short Th–Cl bond, 2.413(6) Å, but weak K · · · Cl contacts of 3.750(10) and 4.159(11) Å. These Th–Cl distances may also be compared with those in [Th(LL)₂Cl₂] **2**, 2.621(16) Å, or those mentioned in Section 2.3.

2.3. The X-ray molecular structure of crystalline 2

A single crystal X-ray diffraction study of **2** revealed the molecular structure to be as shown in Fig. 3. Selected bond lengths and angles are listed in Table 5 and atomic coordinates in Table 6. The β-diketiminato ligands [LL]⁻ are bonded to the metal in a quasi-η⁵-manner (cf. a cyclopentadienyl, as in [ThCp″₂Cl₂] [1]), as illustrated schematically in Fig. 4; a similar bonding mode has been observed in other β-diketiminates derived from [LL]⁻, see Section 1 [6,8,11,12] and demonstrates the very considerable steric requirements of [LL]⁻. Fig. 4 shows (i) the central carbon of the NC-CCN skeletal unit of [LL]⁻ to be out of the plane of the other four atoms; (ii) the distances Th–N, Th–C and Th-to-the-N₂C₂ plane; and (iii) two dihedral angles.

If, on the contrary, [LL]⁻ is regarded as an N,N-chelating ligand, then the coordination geometry around the central thorium approximates to octahedral, the two chloride ligands occupying cis-positions. The Th–Cl distance of 2.697(1) Å in **2** is slightly longer than the 2.632(2) Å in [ThCp″₂Cl₂] [1] or the 2.621(16) Å in [ThCl₂{N(SiMe₃)C(Ar)N(SiMe₃)}₂] [AR = C₆H₂(CF₃)-2,4,6] [16]; the latter has Th–N distances of 2.466(13) Å compared with 2.467(3) Å in **2**.

3. Experimental details

All manipulations were carried out under argon using a high vacuum manifold and conventional Schlenk techniques. Solvents were distilled over appropriate drying

agents and were thoroughly degassed prior to use. NMR spectra were recorded on a Bruker WM 360 or AC-250SY instrument, and mass spectra were obtained with a Fisons VG Autospec instrument. Elemental analyses were determined by Medac Ltd., Brunel University.

The compounds [{K(LL′)}$_n$] **III** [1] and [{K(LL)}$_m$] **IV** [2] were prepared according to literature methods. Others were purchased, and purified by standard procedures.

3.1. Preparation of [{ $\overline{Th(LL')}_2(\mu_3\text{-}Cl)(\mu\text{-}Cl)_2K(OEt_2)$ }$_\infty$] 1

Solid $1/n[\{K(LL')\}_n]$ **III** (1.084 g, 4.02 mmol) was added to a stirred slurry of ThCl$_4$ (0.75 g, 2.01 mmol) in diethyl ether (ca. 40 ml) at 0 °C. The resultant mixture was stirred at ambient temperature for two days, and then filtered. The concentrated filtrate gave clear colourless crystals of compound **1** (1.36 g, 72%).

3.2. Preparation of [$\overline{Th(LL)}_2Cl_2$] 2

A solution of $1/m[\{K(LL)\}_m]$ (3.1 g, 7.76 mmol) in tetrahydrofuran (50 ml) was added to a stirred suspension of ThCl$_4$ (1.43 g, 3.84 mmol) in tetrahydrofuran (100 ml) at room temperature and the mixture was stirred for two days, leaving a yellow solution and a pale yellow precipitate which was filtered off. Solvent was removed from the filtrate in vacuo and the yellow residue was extracted with toluene (2 × 100 ml). The volume of the extract was reduced to ca. 15 ml and cooled to −30 °C to yield the yellow crystalline compound **2** (3.38 g, 85%).

3.3. Reduction of [$\overline{Th(LL)}_2Cl_2$] 2 with Na / K

An excess of K/Na alloy (Na 0.2 g and K 0.6 g) was added to a solution of [$\overline{Th(LL)}_2$ Cl$_2$] **2** (1.5 g, 1.45 mmol) in tetrahydrofuran (100 ml). There was an immediate colour change from yellow to green, and finally an intense blue. The mixture was stirred at room temperature for two days and filtered. Tetrahydrofuran was removed from the filtrate in vacuo and the resultant red–violet residue was extracted with diethyl ether (50 ml). The extract was filtered and the filtrate concentrated to ca. 10 ml. Cooling to −30 °C afforded a red–violet powder (1.0 g).

3.4. X-ray structure determination of crystalline 1 and 2

In each case, data sets were collected on an Enraf–Nonius CAD4 diffractometer with monochromated Mo Kα radiation ($\lambda = 0.7107$ Å for **1** and **2**). For **1**, data were measured at 173 K using a crystal coated in oil; and for **2**, at room temperature using a crystal sealed in a Lindemann capillary under argon. Data were corrected

Table 7
X-ray crystal structure details for complexes **1, 2**

Parameter	1 [a]	2 [a]
Formula	C$_{28}$H$_{66}$Cl$_3$KN$_2$OSi$_4$Th	C$_{42}$H$_{58}$Cl$_2$N$_4$Si$_4$Th
M	936.7	1034.2
Crystal system	Orthorhombic	Monoclinic
Space group	*Pbca*	*C2/c*
a (Å)	12.885(3)	13.728(2)
b (Å)	15.309(6)	19.142(4)
c (Å)	44.945(10)	18.573(4)
U (Å^3)	8866(5)	4795.9
Z	8	4
D_{calc} (g cm^{-3})	1.40	1.43
μ(Mo Kα) (cm^{-1})	38.8	34.6
Θ_{max} for data (°)	25	25
Unique reflections	8601	4350
Reflections with $I > 2\sigma(I)$	3644	3571
R	0.094	0.029
R'	0.086	0.031
T (K)	173	293

[a] Details in common: $R = \Sigma\|F_o| - |F_c\|/\Sigma|F_o|$;

$$R' = \left[\Sigma w\left(|F_o| - |F_c|\right)^2/\Sigma w\left(|F_o|^2\right)\right]^{1/2}$$

for Lorentz and polarization effects (Lp), and also for absorption using DIFABS [17]. Each structure was solved using the heavy atom routines of SHELXS-86 [18] and refined by full-matrix least-squares. Refinement was based on F using XRAY76 for **1** and programs from the Enraf–Nonius Molen package for **2** with reflections having $I > 2\sigma(I)$ and for **1** with H atoms in riding mode with common U_{iso}(H) equal to 0.12 Å^2 or for **2** with H atoms fixed at calculated positions with U_{iso}(H) equal to $1.3U_{eq}$(C) for parent atoms. The weighting scheme was $w = \sigma^{-2}(F)$. Further details are given in Table 7. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, H atom coordinates and remaining bond lengths and angles.

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