Synthesis, Spectroscopic Properties and Crystal Structures of $[ML_2Cl_2]$ [M = Th or U; L = η-$C_5H_3(SiMe_3)_2$-1,3] and $[UL_2X_2]$ (X = Br, I or BH_4)†

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1,3-Bis(trimethylsilyl)cyclopentadienyl has been employed in the preparation of some actinocene(IV) halides and tetrahydridoborates. Crystal structure determinations of $[M\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$ (M = Th or U) and $[U\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$ (X = Br or BH_4) showed that these four complexes are isostructural, crystallising in the space group *C*2/*c*. The iodo derivative $[U\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2I_2]$ crystallises in the chiral space group $P2_12_12_1$ in which the two cyclopentadienyl groups within the molecule are crystallographically distinct. Variable-temperature ^1H and ^{11}B NMR spectroscopic data for $[U\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2(BH_4)_2]$ and its thorium analogue revealed the presence of fluxional processes.

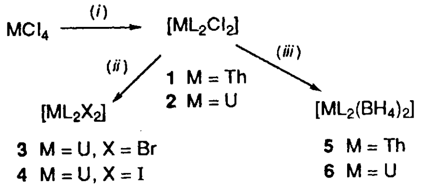
Substituted bis(η-cyclopentadienyl)actinoid(IV) halides are of interest due in part to the difficulty in preparing '$U(C_5H_5)_2Cl_2$'.[1,2] Hence, stable peralkylated complexes such as $[M(C_5Me_5)_2Cl_2]$[3] (M = Th or U) and $[U(C_5Me_4Et)_2Cl_2]$[4] have been synthesised. We had previously used the 1,3-bis(trimethylsilyl)cyclopentadienyl ligand to stabilise a series of low-co-ordination number lanthanoid[5-7] and paramagnetic zirconocene(III) halogeno complexes.[8]

We have already briefly reported the synthesis of complexes $[M\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$ (M = Th **1** or U **2**)[9] and their use as precursors to a range of new complexes including the unusual uranocene(IV) tetrafluoroborato complex $[\{U[C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}BF_4)(\mu\text{-}F)\}_2]$,[10] the uranocene(III) compounds $[\{U[C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}X)\}_2]$ (X = Cl or Br),[11] $[\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2U(\mu\text{-}Cl)_2Li(thf)_2]$[12a] (thf = tetrahydrofuran), $[\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2U(\mu\text{-}Cl)_2Li(pmdeta)]$[12b] [pmdeta = $MeN(CH_2CH_2NMe_2)_2$] and $[PPh_4][U\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cl_2]$,[12b] and the first crystallographically authenticated thorium(III) compound $[Th\{C_5H_3(SiMe_3)_2\text{-}1,3\}_3]$[13a] which was shown to have a $6d^1$ rather than a $5f^1$ electronic ground state.[13b]

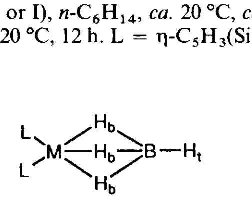
In this paper we report (*i*) the synthesis of new bromo **3** and iodo **4** derivatives of uranium(IV) and bis(tetrahydridoborato) derivatives of thorium(IV) **5** and uranium(IV) **6**, $[M\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$, (*ii*) the dynamic solution behaviour of **6**, using ^1H and ^{11}B NMR spectroscopy and (*iii*) the molecular structures of the crystalline complexes **1**–**4** and **6**. Complex **4** is isostructural with the zirconium analogue.[14] The uranocene(IV) and thorocene(IV) dihalides **1**–**3** and **5** are useful precursors for other uranocene(IV) or thorocene(IV) derivatives, as well as the metallocene(III) compounds, as will be described in later parts of this series.

Results and Discussion

Complexes **1**–**6** were prepared by the routes shown in Scheme 1. Yields, colours, melting points and analytical data are listed in Table 1. The complexes were readily soluble in hydrocarbon solvents, yielding highly crystalline, air- and moisture-sensitive solids. The thermal stability of the halides decreased in the order Cl < Br < I with **3** and **4** being sublimable at 95–98 °C (10^{-2} Torr, 1.33 Pa).



Scheme 1 Routes to metallocene halides or tetrahydridoborates of thorium(IV) and uranium(IV): (*i*) 2LiL, thf (OEt_2 for Th), *ca.* 20 °C, *ca.* 15 h; (*ii*) BX_3 (X = Br or I), *n*-C_6H_{14}, *ca.* 20 °C, *ca.* 3 h; (*iii*) excess of $NaBH_4$, OEt_2–thf, *ca.* 20 °C, 12 h. L = η-$C_5H_3(SiMe_3)_2$-1,3



A

L = η–$C_5H_3(SiMe_3)_2$–1,3

Complexes **5** and **6** were assigned to have the tridentate $[BH_4]^-$ ligation mode (**A**) on the basis of IR spectroscopy. This was subsequently verified by X-ray crystallography for **6**. Both complexes possess sharp IR singlets at *ca.* 2490 cm^{-1} and doublets at *ca.* 2210 cm^{-1} (separation 78 cm^{-1}) assigned as $\nu(B\text{–}H_t)$ and $\nu(B\text{–}H_b)$, respectively. The only other non-cyclopentadienyl stretching mode, at 1201 **5** and 1185 cm^{-1} **6**, was assigned to BH_4 bridge deformation. The unsubstituted cyclopentadienyl derivative, $[U(C_5H_5)_2(BH_4)_2]$,[15] also had tridentate $[BH_4]^-$ ligation. The U–X stretching modes of **3** and **4** were presumably too low (below 200 cm^{-1}) to be observed using CsI plates. Some IR spectroscopic data are in Table 1.

The ^1H NMR spectra of complexes **2**–**4** and **6** each exhibited paramagnetic shifts relative to their diamagnetic thorium(IV) analogues. These shifts were particularly pronounced for the cyclopentadienyl ring and tetrahydridoborate protons (Table

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† Organometallic Chemistry of the Actinides. Part 1. No reprints available.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

2). The ^{11}B NMR spectrum of **5** (Table 3) exhibited the usual 1:4:6:4:1 quintet structure [$^1J(^{11}B-^1H)$ = 90 Hz] for an ^{11}B nucleus coupled to four equivalent protons. A similar quintet structure was only observed in the ^{11}B NMR spectrum of complex **6** on warming to 95 °C (Fig. 1); upon proton decoupling, these quintets collapsed to sharp singlets as is also shown in Fig. 1. Such variable-temperature behaviour had previously been observed for an analogous lanthanoid complex [Sc{$C_5H_3(SiMe_3)_2$-1,3}$_2$(BH_4)][7] and was explained in terms of a rapid $H_b \rightleftharpoons H_t$ exchange at high temperatures.

A variable-temperature ^1H NMR spectroscopic study was undertaken on complex **6** and the results are shown in Fig. 2. The 1:1:1:1 quartet, which was not completely resolved at 100 °C, collapsed on cooling and became progressively broader as the temperature was lowered. Similar results were found for [Zr(BH_4)$_4$][16] and were attributed to rapid spin–lattice relaxation effects of the ^{11}B nucleus.

Table 1 Analytical and infrared data for complexes **1**–**6**

Compound[a]	M.p.[b] (θ_c/°C)	Analysis (%)[c] C	Analysis (%)[c] H
1 [ThL_2Cl_2]	150–152	36.6 (36.6)	6.0 (5.9)
2 [UL_2Cl_2]	140–147 (decomp.)	36.0 (36.3)	5.6 (5.8)
3 [UL_2Br_2]	160–163	32.3 (32.4)	5.2 (5.0)
4 [UL_2I_2]	180–183	29.1 (29.0)	4.8 (4.6)
5 [$ThL_2(BH_4)_2$]	—	39.6 (39.8)	7.7 (7.4)
6 [$UL_2(BH_4)_2$]	145–148	38.9 (38.5)	7.6 (7.5)

Compound[a]	IR[d]/cm^{-1} ν(M–X)	IR[d]/cm^{-1} ν(B–H)
1 [ThL_2Cl_2]	290s	—
2 [UL_2Cl_2]	282s	—
3 [UL_2Br_2]	*e*	—
4 [UL_2I_2]	*e*	—
5 [$ThL_2(BH_4)_2$]	—	2483s, 2228s 2150s, 1201s
6 [$UL_2(BH_4)_2$]	—	2498s, 2198s 2120m, 1185s

[a] L = η-$C_5H_3(SiMe_3)_2$-1,3. [b] Argon atmosphere in sealed capillaries and uncorrected. [c] Calculated values are given in parentheses. [d] Excluding stretches assigned to L ligands; m = medium, s = strong. As Nujol mulls calibrated against polystyrene at 1601 cm^{-1}. [e] Not observed.

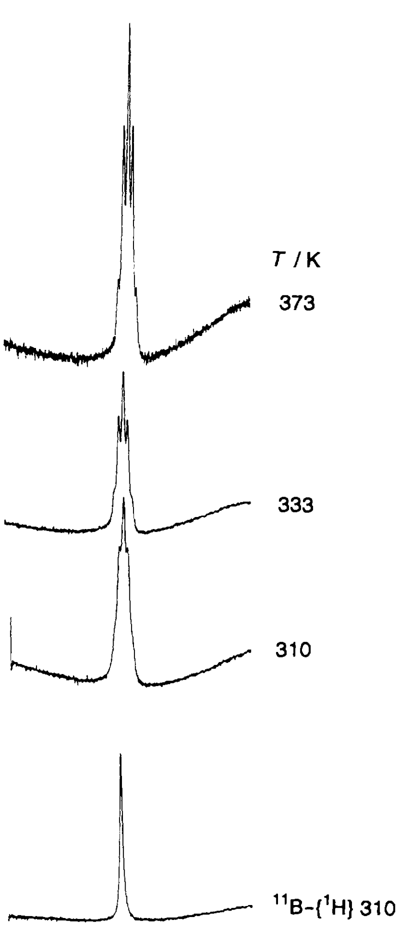


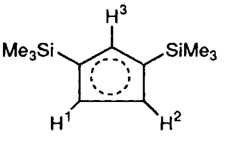
Fig. 1 Variable-temperature ^{11}B NMR spectra for complex **6** in [$^2H_8$]toluene

Table 3 Boron-11 NMR data for complexes **5** and **6** at 305 K in toluene solution

Compound[a]	$\delta(^{11}B)$ for BH_4[b]	$^1J(^{11}B-^1H)$/Hz
5	−9.78	90.3 (qnt)[c]
6	+99.71	77 (br qnt)[d]

[a] qnt = quintet, br = broad. [b] Broad-band decoupled, line positions relative to $BF_3(OEt_2)$. [c] Average coupling (quintet). [d] Quintet structure only observed at high temperature (*ca.* 95 °C; broad at 305 K).

Table 2 Hydrogen-1 chemical shifts[a] (δ relative to internal solvent [$^2H_8$]toluene, resonances)[b]



Compound	$SiMe_3$	Cyclopentadienyl ring $H^1 = H^2$	Cyclopentadienyl ring H^3	Tetrahydridoborate
1	+0.35 (s)	+6.93 (d)	+7.32 (t)	—
2	−2.55 (s)	−33.39 (s)	+87.26 (s)	—
3	−1.784 (s)	−37.06 (s)	+99.5 (s)	—
4	+0.744 (s)	−36.21 (s)	+99.7 (s)	—
5	+0.24 (s)	+6.96 (s)	+7.08 (s)	+3.4 (vbq)[c]
6	−1.25 (s)	−31.65 (s)	+68.21 (s)	−19.57 (vbq)[d]

[a] s = Singlet, d = doublet, t = triplet, vbq = very broad quartet. [b] Internal resonance for $C_6D_4HCD_3$ at δ 7.0. [c] Peak width at half peak height = 267 Hz. [d] Peak width at half peak height = 380 Hz.

Table 4 Selected bond lengths (Å) and angles (°) for complexes $[M\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$ **1**–**4** and **6**

	1 (M = Th, X = Cl)	**2** (M = U, X = Cl)	**3** (M = U, X = Br)	**6** (M = U, X = BH_4)
M–X	2.632(2)	2.579(2)	2.734(1)	2.56(1)
M–C(1)	2.771(7)	2.712(6)	2.719(9)	2.711(8)
M–C(2)	2.769(6)	2.696(6)	2.70(1)	2.687(8)
M–C(3)	2.804(6)	2.732(6)	2.72(1)	2.740(7)
M–C(4)	2.789(6)	2.712(6)	2.70(1)	2.713(7)
M–C(5)	2.786(6)	2.733(6)	2.70(1)	2.727(8)
M–C (average)	2.78(1)	2.72(1)	2.71(2)	2.72(2)
X–M–X′	95.93(6)	95.3(1)	94.60(4)	97.4(3)

4

U–I(1)	2.953(2)	U–Cp(1)	2.70(3)	U–Cp(6)	2.74(2)	U–Cp(1–5) (av.)	2.70(3)
U–I(2)	2.954(2)	U–Cp(2)	2.67(2)	U–Cp(7)	2.74(2)	U–Cp(6–10) (av.)	2.72(2)
		U–Cp(3)	2.70(3)	U–Cp(8)	2.74(3)		
		U–Cp(4)	2.72(3)	U–Cp(9)	2.70(2)		
I(1)–U–I(2)	105.40(8)	U–Cp(5)	2.71(2)	U–Cp(10)	2.68(2)		

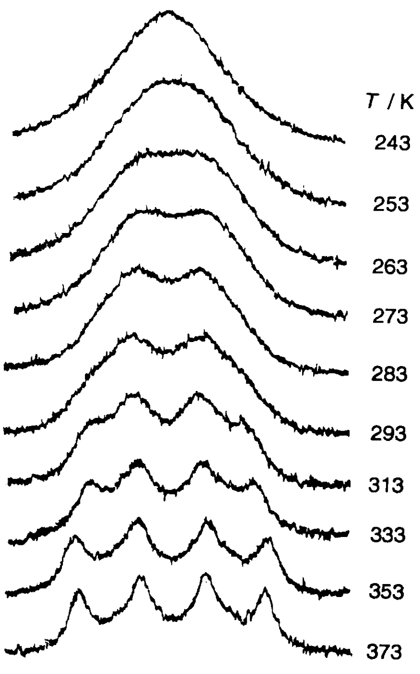


Fig. 2 Variable-temperature ^1H NMR spectra for complex **6** in $[^2H_8]$toluene

The structures of complexes **1**–**4** and **6** have been determined by X-ray crystallography and important bond lengths and angles are compared in Table 4; details for individual complexes are in Tables 5(**1**), 6(**2**), 7(**3**), 8(**4**) and 9(**6**), while atomic coordinates are in Tables 10–14, respectively. All five are monomeric and **1**–**3** and **6** are isostructural (space group *C*2/*c*) with two equivalent $C_5H_3(SiMe_3)_2$ groups and two equivalent X groups per molecule (the metal atoms lie on a crystallographic two-fold axis in each case, Fig. 3). By contrast, $[U\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2I_2]$ **4** crystallises in the space group $P2_12_12_1$ and has non-equivalent cyclopentadienyl and I^- ligands, Fig. 4. In **1**–**3** and **6** the $SiMe_3$ groups in the two cyclopentadienyl groups are in a roughly eclipsed configuration, while in **4** they are staggered. The latter configuration opens up more space around the molecule and produces a much greater X–U–X′ angle of 105.40(8)° relative to *ca.* 95° for the other complexes. Similar distortions have been reported in zirconium chemistry,[14] but in this case both $[ZrL_2X_2]$ [L = $C_5H_3(SiMe_3)_2$-1,3, X = I or Br] crystallised in the space group $P2_12_12_1$. The difference is attributed to lesser steric effects for the larger uranium atom which is able to accommodate two

Table 5 Bond lengths (Å) and angles (°) for complex **1**

Th–Cl(1)	2.632(2)	Th–C(1)	2.771(7)
Th–C(2)	2.769(6)	Th–C(3)	2.804(6)
Th–C(4)	2.789(6)	Th–C(5)	2.786(6)
Th–Cp	2.506	Th–C(1–5) (av.)	2.78(1)
Si(1)–C(3)	1.856(7)	Si(1)–C(6)	1.85(1)
Si(1)–C(7)	1.844(8)	Si(1)–C(8)	1.861(8)
Si(2)–C(5)	1.884(7)	Si(2)–C(9)	1.858(8)
Si(2)–C(10)	1.84(1)	Si(2)–C(11)	1.860(9)
C(1)–C(2)	1.404(9)	C(1)–C(5)	1.44(1)
C(2)–C(3)	1.46(1)	C(3)–C(4)	1.406(9)
C(4)–C(5)	1.417(9)		
Cl(1)–Th–Cl(1′)	95.93(6)	Cl(1)–Th–Cp′	110.44
Cl(1)–Th–Cp	106.01	Cp–Th–Cp′	124.36
C(3)–Si(1)–C(6)	109.7(4)	C(3)–Si(1)–C(7)	111.8(4)
C(6)–Si(1)–C(7)	111.0(5)	C(3)–Si(1)–C(8)	107.0(4)
C(6)–Si(1)–C(8)	109.0(5)	C(7)–Si(1)–C(8)	108.2(4)
C(5)–Si(2)–C(9)	112.3(3)	C(5)–Si(2)–C(10)	108.3(4)
C(9)–Si(2)–C(10)	109.7(5)	C(5)–Si(2)–C(11)	106.9(4)
C(9)–Si(2)–C(11)	108.2(5)	C(10)–Si(2)–C(11)	111.5(4)
C(2)–C(1)–C(5)	108.1(6)	C(1)–C(2)–C(3)	109.8(6)
Si(1)–C(3)–C(2)	127.3(5)	Si(1)–C(3)–C(4)	126.5(5)
C(2)–C(3)–C(4)	104.0(6)	C(3)–C(4)–C(5)	112.4(6)
Si(2)–C(5)–C(1)	126.2(5)	Si(2)–C(5)–C(4)	127.0(6)

Cp and Cp′ are centroids of cyclopentadienyl rings C(1)–C(5) and its symmetry equivalent.

Table 6 Bond lengths (Å) and angles (°) for complex **2**

U–Cl(1)	2.579(2)	U–C(1)	2.712(6)
U–C(2)	2.696(6)	U–C(3)	2.732(6)
U–C(4)	2.718(6)	U–C(5)	2.732(6)
U–Cp	2.435	U–C(1–5) (av.)	2.72(1)
Si(1)–C(3)	1.879(6)	Si(1)–C(6)	1.854(9)
Si(1)–C(7)	1.827(8)	Si(1)–C(8)	1.864(7)
Si(2)–C(5)	1.873(6)	Si(2)–C(9)	1.848(8)
Si(2)–C(10)	1.855(9)	Si(2)–C(11)	1.861(8)
C(1)–C(2)	1.421(9)	C(1)–C(5)	1.421(9)
C(2)–C(3)	1.426(9)	C(3)–C(4)	1.419(8)
C(4)–C(5)	1.418(9)		
Cl(1)–U–Cl(1′)	95.3(1)	Cl(1)–U–Cp′	110.91
Cl(1)–U–Cp	105.47	Cp–U–Cp′	124.85
C(3)–Si(1)–C(6)	110.4(3)	C(3)–Si(1)–C(7)	111.8(3)
C(6)–Si(1)–C(7)	111.5(5)	C(3)–Si(1)–C(8)	106.0(3)
C(6)–Si(1)–C(8)	108.3(4)	C(7)–Si(1)–C(8)	108.6(4)
C(5)–Si(2)–C(9)	112.3(3)	C(5)–Si(2)–C(10)	108.5(3)
C(9)–Si(2)–C(10)	110.2(4)	C(5)–Si(2)–C(11)	106.9(4)
C(9)–Si(2)–C(11)	108.8(4)	C(10)–Si(2)–C(11)	110.1(4)
C(2)–C(1)–C(5)	109.2(6)	C(1)–C(2)–C(3)	108.4(6)
Si(1)–C(3)–C(2)	127.3(5)	Si(1)–C(3)–C(4)	125.2(5)
C(2)–C(3)–C(4)	105.8(6)	C(3)–C(4)–C(5)	111.0(6)
Si(2)–C(5)–C(1)	126.5(5)	Si(2)–C(5)–C(4)	126.7(5)

bromide ligands without interligand repulsions becoming so great that distortion is necessary.

Bis(cyclopentadienyl)actinoid(IV) halides have previously been poorly structurally characterised although some data have been reported for $[M(C_5Me_5)_2Cl_2]$ (M = Th or U).[17] Few structural determinations have been reported for actinoid bromide or iodide derivatives. A bromide complex to have been structurally authenticated is $[U(C_9H_7)Br_3]\cdot 2thf$,[18] in which the U–Br bond lengths range from 2.76 to 2.79 Å. The U–Br distance in $[U\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2Br_2]$ **3** of 2.734(1) Å is comparable. For UBr_4 the U–Br terminal bond lengths are 2.78(3) Å.[19] The U···B separation in **6** is similar to that in $[U(C_5H_5)_2(BH_4)_2]$.[15] Complex **6** has two independent molecules in the unit cell with average U···B separations of 2.60(8) and 2.63(8) Å. The U–H bond lengths, 2.37, 2.37 and 2.42 Å, are longer than the expected *ca.* 2.25 Å. However, given the limited accuracy in the placement of the hydrogen atoms, the distances are reasonable.

Experimental

General Procedures.—All experiments were performed under an atmosphere of argon using conventional vacuum-line and Schlenk techniques. Uranium(IV) chloride was prepared from uranyl(VI) nitrate, *via* UO_3, by a literature procedure.[20] Solvents were rigorously dried and freeze degassed prior to use. Microanalyses were carried out within this School or by Elemental Microanalysis Ltd., Devon. Infrared spectra were recorded between CsI plates as Nujol mulls using a Perkin-

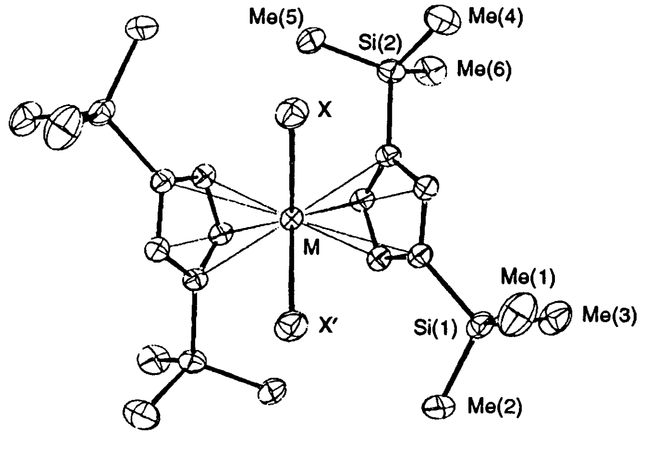


Fig. 3 Molecular structure of $[M\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2X_2]$ (M = Th and X = Cl **1**; M = U and X = Cl **2**, Br **3** or BH_4 **6**) and atom labelling; the figure is based on data for **1**

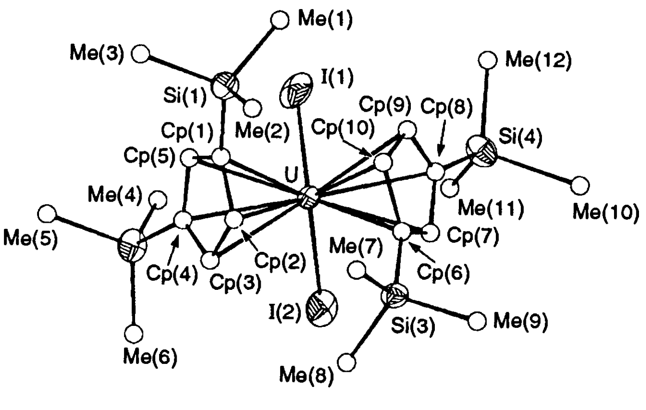


Fig. 4 Molecular structure of $[U\{C_5H_3(SiMe_3)_2\text{-}1,3\}_2I_2]$ **4** and atom labelling

Table 7 Bond lengths (Å) and angles (°) for complex **3**

U–Br	2.734(1)	U–C(1)	2.719(9)
U–C(2)	2.70(1)	U–C(3)	2.72(1)
U–C(4)	2.70(1)	U–C(5)	2.70(1)
Si(1)–C(1)	1.89(1)	Si(1)–Me(1)	1.89(1)
Si(1)–Me(2)	1.87(1)	Si(1)–Me(3)	1.91(1)
Si(2)–C(3)	1.88(1)	Si(2)–Me(4)	1.86(1)
Si(2)–Me(5)	1.88(1)	Si(2)–Me(6)	1.89(1)
C(1)–C(2)	1.45(1)	C(1)–C(5)	1.43(2)
C(2)–C(3)	1.42(1)	C(3)–C(4)	1.44(2)
C(4)–C(5)	1.42(2)		
Br–U–Br′	94.60(4)	C(1)–Si(1)–Me(1)	110.9(6)
C(1)–Si(1)–Me(2)	105.5(5)	Me(1)–Si(1)–Me(2)	108.9(7)
C(1)–Si(1)–Me(3)	109.4(6)	Me(1)–Si(1)–Me(3)	112.8(7)
Me(2)–Si(1)–Me(3)	109.1(6)	C(3)–Si(2)–Me(4)	112.5(6)
C(3)–Si(2)–Me(3)	108.4(6)	Me(4)–Si(2)–Me(5)	110.1(7)
C(3)–Si(2)–Me(6)	108.6(6)	Me(4)–Si(2)–Me(6)	108.4(7)
Me(5)–Si(2)–Me(6)	110.8(7)	Si(1)–C(1)–C(2)	123.6(8)
Si(1)–C(1)–C(5)	128.0(9)	C(2)–C(1)–C(5)	106(1)
C(1)–C(2)–C(3)	109(1)	Si(2)–C(3)–C(2)	125.4(9)
Si(2)–C(3)–C(4)	126.8(9)	C(2)–C(3)–C(4)	106.8(9)
C(3)–C(4)–C(5)	108(1)	C(1)–C(5)–C(4)	109(1)

Table 8 Bond lengths (Å) and angles (°) for complex **4**

U–I(1)	2.953(2)	U–I(2)	2.954(2)	Si(3)–Cp(6)	1.87(3)	Si(3)–Me(7)	1.98(3)
U–Cp(1)	2.70(3)	U–Cp(2)	2.67(2)	Si(3)–Me(8)	1.91(3)	Si(3)–Me(9)	1.88(3)
U–Cp(3)	2.70(3)	U–Cp(4)	2.72(3)	Si(4)–Cp(8)	1.87(3)	Si(4)–Me(10)	2.23(2)
U–Cp(5)	2.71(2)	U–Cp(6)	2.74(2)	Si(4)–Me(11)	1.90(4)	Si(4)–Me(12)	1.96(4)
U–Cp(7)	2.74(2)	U–Cp(8)	2.74(3)	Cp(1)–Cp(2)	1.41(4)	Cp(1)–Cp(5)	1.48(3)
U–Cp(9)	2.70(2)	U–Cp(10)	2.68(2)	Cp(2)–Cp(3)	1.46(3)	Cp(3)–Cp(4)	1.47(3)
Si(1)–Cp(1)	1.88(2)	Si(1)–Me(1)	1.99(3)	Cp(4)–Cp(5)	1.39(3)	Cp(6)–Cp(7)	1.39(3)
Si(1)–Me(2)	1.87(3)	Si(1)–Me(3)	1.92(3)	Cp(6)–Cp(10)	1.55(3)	Cp(7)–Cp(8)	1.43(3)
Si(2)–Cp(4)	1.88(3)	Si(2)–Me(4)	2.01(5)	Cp(8)–Cp(9)	1.45(4)	Cp(9)–Cp(10)	1.42(3)
Si(2)–Me(5)	1.96(4)	Si(2)–Me(6)	1.91(4)				
I(1)–U–I(2)	105.40(8)	Cp(1)–Si(1)–Me(1)	112(1)	Cp(8)–Si(4)–Me(12)	110(2)	Me(10)–Si(4)–Me(12)	106(1)
Cp(1)–Si(1)–Me(2)	109(1)	Me(1)–Si(1)–Me(2)	111(1)	Me(11)–Si(4)–Me(12)	112(2)	Si(1)–Cp(1)–Cp(2)	129(2)
Cp(1)–Si(1)–Me(3)	108(1)	Me(1)–Si(1)–Me(3)	109(1)	Si(1)–Cp(1)–Cp(5)	124(2)	Cp(2)–Cp(1)–Cp(5)	106(2)
Me(2)–Si(1)–Me(3)	109(1)	Cp(4)–Si(2)–Me(4)	109(2)	Cp(1)–Cp(2)–Cp(3)	110(2)	Cp(2)–Cp(3)–Cp(4)	107(2)
Cp(4)–Si(2)–Me(5)	108(2)	Me(4)–Si(2)–Me(5)	103(2)	Si(2)–Cp(4)–Cp(3)	126(2)	Si(2)–Cp(4)–Cp(5)	125(2)
Cp(4)–Si(2)–Me(6)	110(2)	Me(4)–Si(2)–Me(6)	114(2)	Cp(3)–Cp(4)–Cp(5)	107(2)	Cp(1)–Cp(5)–Cp(4)	111(2)
Me(5)–Si(2)–Me(6)	112(2)	Cp(6)–Si(3)–Me(7)	114(1)	Si(3)–Cp(6)–Cp(7)	128(2)	Si(3)–Cp(6)–Cp(10)	125(2)
Cp(6)–Si(3)–Me(8)	109(1)	Me(7)–Si(3)–Me(8)	110(1)	Cp(7)–Cp(6)–Cp(10)	107(2)	Cp(6)–Cp(7)–Cp(8)	112(2)
Cp(6)–Si(3)–Me(9)	107(1)	Me(7)–Si(3)–Me(9)	105(1)	Si(4)–Cp(8)–Cp(7)	126(2)	Si(4)–Cp(8)–Cp(9)	127(2)
Me(8)–Si(3)–Me(9)	111(1)	Cp(8)–Si(4)–Me(10)	107(1)	Cp(7)–Cp(8)–Cp(9)	106(2)	Cp(8)–Cp(9)–Cp(10)	111(2)
Cp(8)–Si(4)–Me(11)	114(2)	Me(10)–Si(4)–Me(11)	108(1)	Cp(6)–Cp(10)–Cp(9)	104(2)		

Table 9 Bond lengths (Å) and angles (°) for complex **6**

U–C(1)	2.711(8)	U–C(2)	2.687(8)
U–C(3)	2.740(7)	U–C(4)	2.713(7)
U–C(5)	2.727(8)	U–Cp	2.434
U–C(1–5) (av.)	2.72(2)	U–B	2.56(1)
U–H(22)	2.4221(4)	U–H(23)	2.3655(4)
U–H(24)	2.3713(1)	Si(1)–C(3)	1.870(8)
Si(1)–C(6)	1.85(1)	Si(1)–C(7)	1.845(9)
Si(1)–C(8)	1.86(1)	Si(2)–C(5)	1.871(8)
Si(2)–C(9)	1.816(9)	Si(2)–C(10)	1.83(1)
Si(2)–C(11)	1.88(1)	C(1)–C(2)	1.43(1)
C(1)–C(5)	1.41(1)	C(2)–C(3)	1.41(1)
C(3)–C(4)	1.42(1)	C(4)–C(5)	1.42(1)
B–H(22)	1.13(1)	B–H(23)	1.20(1)
B–H(24)	1.11(1)	B–H(25)	1.23(1)
Cp–U–Cp′	121.201	B–U–B′	97.4(3)
Cp′–U–B	109.98(8)	Cp–U–B	107.8(1)
C(3)–Si(1)–C(6)	110.0(4)	C(3)–Si(1)–C(7)	112.4(4)
C(6)–Si(1)–C(7)	110.8(6)	C(3)–Si(1)–C(8)	106.7(4)
C(6)–Si(1)–C(8)	108.2(5)	C(7)–Si(1)–C(8)	108.5(5)
C(5)–Si(2)–C(9)	113.4(4)	C(5)–Si(2)–C(10)	108.9(4)
C(9)–Si(2)–C(10)	109.4(5)	C(5)–Si(2)–C(11)	106.3(5)
C(9)–Si(2)–C(11)	108.5(6)	C(10)–Si(2)–C(11)	110.2(6)
C(2)–C(1)–C(5)	108.2(8)	C(1)–C(2)–C(3)	109.5(8)
Si(1)–C(3)–C(2)	127.4(7)	Si(1)–C(3)–C(4)	125.4(7)
C(2)–C(3)–C(4)	105.2(7)	C(3)–C(4)–C(5)	111.4(8)
Si(2)–C(5)–C(1)	126.4(7)	Si(2)–C(5)–C(4)	126.0(7)
C(1)–C(5)–C(4)	105.6(7)	H(22)–B–H(25)	116(1)
H(23)–B–H(25)	111.6(8)	H(24)–B–H(25)	107.2(8)
U–H(22)–B	84.0(6)	U–H(23)–B	85.4(5)
U–H(24)–B	87.0(5)		

Table 10 Non-hydrogen atom coordinates for complex **1**

Atom	*X/a*	*Y/b*	*Z/c*
Th	0.50	0.398 64(5)	0.75
Si(1)	0.320 3(1)	0.341 0(3)	0.698 2(1)
Si(2)	0.585 0(1)	0.609 0(4)	0.974 6(1)
Cl(1)	0.584 3(1)	0.151 1(3)	0.861 8(1)
C(1)	0.476 4(3)	0.708(1)	0.802 4(4)
C(2)	0.413 2(3)	0.642(1)	0.735 5(4)
C(3)	0.401 1(3)	0.462(1)	0.754 6(4)
C(4)	0.459 2(3)	0.429(1)	0.835 0(4)
C(5)	0.506 7(3)	0.574(1)	0.866 3(4)
C(6)	0.334 3(4)	0.090(1)	0.725 5(6)
C(7)	0.266 4(4)	0.371(2)	0.588 5(4)
C(8)	0.278 6(4)	0.451(2)	0.729 4(6)
C(9)	0.658 3(4)	0.649(1)	0.986 0(5)
C(10)	0.598 5(4)	0.399(2)	1.032 2(5)
C(11)	0.572 4(5)	0.823(1)	1.010 7(6)

All non-hydrogen atoms were refined with anisotropic thermal parameters.

Table 11 Non-hydrogen atom coordinates for complex **2**

Atom	*X/a*	*Y/b*	*Z/c*
U	0.50	0.402 65(5)	0.75
Si(1)	0.321 70(9)	0.335 4(3)	0.698 9(1)
Si(2)	0.585 5(1)	0.611 9(3)	0.973 4(1)
Cl(1)	0.581 80(9)	0.157 4(3)	0.859 0(1)
C(1)	0.477 3(3)	0.707 2(9)	0.802 4(4)
C(2)	0.413 7(3)	0.638 8(9)	0.734 1(4)
C(3)	0.402 8(3)	0.462 6(9)	0.754 7(4)
C(4)	0.461 5(3)	0.426 0(9)	0.835 3(4)
C(5)	0.508 1(3)	0.574 1(9)	0.865 9(4)
C(6)	0.336 3(4)	0.083(1)	0.728 1(6)
C(7)	0.267 8(3)	0.364(1)	0.590 2(4)
C(8)	0.280 5(4)	0.447(1)	0.731 5(5)
C(9)	0.658 7(4)	0.656(1)	0.984 9(5)
C(10)	0.599 4(4)	0.401(1)	1.032 1(5)
C(11)	0.570 8(5)	0.823(1)	1.009 5(5)

All non-hydrogen atoms were refined with anisotropic thermal parameters.

Table 12 Non-hydrogen atom coordinates for complex **3**

Atom	*X/a*	*Y/b*	*Z/c*
U	0	0.094 56(9)	0.75
Br	0.086 20(6)	0.352 8(2)	0.865 01(7)
Si(1)	−0.179 5(2)	0.161 9(5)	0.698 8(2)
Si(2)	0.084 9(2)	−0.108 5(5)	0.973 3(2)
C(1)	−0.098 1(5)	0.037(2)	0.752 6(6)
C(2)	−0.038 1(5)	0.077(2)	0.834 7(6)
C(3)	0.007 6(5)	−0.073(2)	0.865 0(7)
C(4)	−0.023 2(6)	−0.207(2)	0.800 6(7)
C(5)	−0.087 2(6)	−0.138(2)	0.732 7(8)
Me(1)	−0.165 1(7)	0.416(2)	0.728 2(9)
Me(2)	−0.218 7(7)	0.047(2)	0.733 3(9)
Me(3)	−0.235 2(6)	0.126(2)	0.585 6(7)
Me(4)	0.160 2(6)	−0.145(2)	0.987 0(8)
Me(5)	0.096 6(7)	0.101(2)	1.031 9(7)
Me(6)	0.070 7(8)	−0.324(2)	1.008 2(9)

All non-hydrogen atoms were refined with anisotropic thermal parameters.

Elmer 597 spectrometer, hydrogen-1 and ^{11}B NMR spectra using a Bruker WM360 or WP80 instrument, respectively.

Syntheses.—*Bis*[1,3-*bis*(*trimethylsilyl*)*cyclopentadienyl*]*dichlorothorium*(IV) **1**. A precipitate of Li[$C_5H_3(SiMe_3)_2$-1,3] in diethyl ether (*ca.* 250 cm^3) was prepared by adding a hexane solution of *n*-butyllithium (21 cm^3, 33.6 mmol) dropwise to a stirred, cooled (0 °C) solution of 1,3-bis(trimethylsilyl)cyclopentadiene (7.08 g, 33.6 mmol) in diethyl ether (*ca.* 250 cm^3). The mixture was stirred at *ca.* 20 °C for *ca.* 12 h. This was then slowly added dropwise, *via* a wide-bore (*ca.* 3 mm) stainless-steel tube, to a stirred, cooled (0 °C) slurry of thorium(IV) chloride (6.27 g, 16.8 mmol) in diethyl ether (*ca.* 250 cm^3). The mixture was warmed to *ca.* 20 °C and stirred for *ca.* 15 h. The solvent was removed and the resultant foamy off-white solid extracted into warm (*ca.* 50 °C) hexane (*ca.* 150 cm^3) and filtered to remove lithium chloride. Concentration (to 75 cm^3) and cooling to −30 °C afforded colourless *crystals* of compound **1** (4.45 g, 40%). A further crop was obtained from the mother-liquor giving a total yield of 60%.

Bis[1,3-*bis*(*trimethylsilyl*)*cyclopentadienyl*]*dichlorouranium*(IV) **2**. A solution of 1,3-bis(trimethylsilyl)cyclopentadienyllithium in tetrahydrofuran was prepared by adding *n*-butyllithium (18 cm^3, 29 mmol) dropwise to a stirred, cooled (0 °C) solution of 1,3-bis(trimethylsilyl)cyclopentadiene (5.89 g, 28 mmol) in tetrahydrofuran (*ca.* 100 cm^3). The mixture was warmed to *ca.* 20 °C and stirred for *ca.* 12 h. The resultant pale yellow solution was added dropwise to a stirred, cooled (0 °C) solution of uranium(IV) chloride (5.45 g, 14 mmol) in tetrahydrofuran (*ca.* 100 cm^3) followed by warming to *ca.* 20 °C and stirring for *ca.* 12 h. The solvent was removed *in vacuo* to give a sticky brown residue which was warmed to *ca.* 60 °C *in vacuo* for *ca.* 30 min to remove residual tetrahydrofuran. The brown solid was extracted into warm (*ca.* 60 °C) toluene (*ca.* 100 cm^3) and filtered to remove lithium chloride. The brown filtrate was concentrated (*ca.* 50 cm^3) and allowed to crystallise at −30 °C affording large orange-brown *crystals* of compound **2** (6.1 g, 60%). Two further crops were obtained from the mother-liquor giving a total yield of *ca.* 90%.

Bis[1,3-*bis*(*trimethylsilyl*)*cyclopentadienyl*]*dibromouranium*(IV) **3**. Boron tribromide (0.4 cm^3, five-fold excess) was added dropwise to a stirred solution of complex **2** (2.73 g, 3.8 mmol) in C_6H_{14} (*ca.* 100 cm^3) at *ca.* 20 °C. The mixture was stirred for 2 h, filtered and concentrated (*ca.* 25 cm^3). On cooling to −30 °C, red-brown *needles* of compound **3**

(2.67 g, 87%) were formed which were washed with cold (*ca.* –78 °C) C_5H_{12} and dried *in vacuo*.

Table 13 Non-hydrogen atom coordinates for complex **4**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
U	0.660 06(8)	0.249 42(8)	0.241 13(4)
I(1)	0.623 9(2)	0.122 7(1)	0.353 1(1)
I(2)	0.511 6(2)	0.389 0(2)	0.289 3(2)
Si(1)	0.856 9(9)	0.413 0(5)	0.119 2(4)
Si(2)	0.871(1)	0.305 8(6)	0.421 8(4)
Si(3)	0.758 1(8)	0.069 5(5)	0.098 0(4)
Si(4)	0.298 8(8)	0.208 3(6)	0.197 1(5)
Cp(1)	0.852(3)	0.339(2)	0.197(1)
Cp(2)	0.891(2)	0.258(2)	0.199(1)
Cp(3)	0.897(2)	0.230(1)	0.275(1)
Cp(4)	0.856(3)	0.298(2)	0.320(1)
Cp(5)	0.830(2)	0.363(1)	0.273(1)
Cp(6)	0.641(2)	0.146(1)	0.124(1)
Cp(7)	0.536(2)	0.134(1)	0.164(1)
Cp(8)	0.459(3)	0.204(2)	0.163(1)
Cp(9)	0.522(2)	0.264(2)	0.120(1)
Cp(10)	0.637(2)	0.235(1)	0.096(1)
Me(1)	0.694(3)	0.460(2)	0.098(2)
Me(2)	0.922(3)	0.362(2)	0.037(1)
Me(3)	0.964(3)	0.499(2)	0.149(2)
Me(4)	0.717(4)	0.352(3)	0.464(2)
Me(5)	0.989(4)	0.391(3)	0.443(2)
Me(6)	0.918(4)	0.204(3)	0.462(2)
Me(7)	0.886(2)	0.113(2)	0.033(1)
Me(8)	0.831(3)	0.025(2)	0.184(1)
Me(9)	0.679(3)	–0.011(2)	0.043(2)
Me(10)	0.197(1)	0.108 9(9)	0.141 8(8)
Me(11)	0.285(4)	0.193(3)	0.300(2)
Me(12)	0.223(4)	0.310(2)	0.165(2)

The U, I and Si atoms were refined with anisotropic thermal parameters. No attempt was made to determine the absolute configuration.

Bis[1,3-*bis*(*trimethylsilyl*)*cyclopentadienyl*]*diiodouranium*(IV) **4**. Boron triiodide (1.13 g, 2.9 mmol) was added portionwise to a stirred solution of complex **2** (2.10 g, 2.9 mmol) in C_6H_{14} (*ca.* 100 cm^3) at *ca.* 20 °C. The mixture was stirred for 4 h, filtered and concentrated (*ca.* 20 cm^3). On cooling to –30 °C, red *cubes* of compound **4** (2.17 g, 82%) were formed which were washed with cold (–78 °C) C_5H_{12} and dried *in vacuo*.

Bis[1,3-*bis*(*trimethylsilyl*)*cyclopentadienyl*]*bis*(*tetrahydridoborato*)*thorium*(IV) **5**. To a solution of complex **1** (1.44 g, 2.0 mmol) in tetrahydrofuran (*ca.* 50 cm^3) at *ca.* 20 °C was added $NaBH_4$ (0.8 g, five-fold excess) and the resultant mixture was

Table 14 Non-hydrogen atom coordinates for complex **6**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
U	0.50	0.382 95(7)	0.75
Si(1)	0.325 0(1)	0.357 9(5)	0.701 5(1)
Si(2)	0.588 8(1)	0.578 8(4)	0.977 2(1)
C(1)	0.486 4(4)	0.690(1)	0.808 5(5)
C(2)	0.422 0(4)	0.632(2)	0.740 0(5)
C(3)	0.407 3(4)	0.463(1)	0.757 1(5)
C(4)	0.464 6(4)	0.416(1)	0.836 1(4)
C(5)	0.513 7(4)	0.552(1)	0.868 9(5)
C(6)	0.333 1(5)	0.110(2)	0.731 6(7)
C(7)	0.272 0(4)	0.378(2)	0.591 9(5)
C(8)	0.286 9(5)	0.491(2)	0.731 9(7)
C(9)	0.660 8(4)	0.638(2)	0.993 9(5)
C(10)	0.603 2(5)	0.360(2)	1.029 4(5)
C(11)	0.571 9(6)	0.774(2)	1.016 6(6)
B	0.585 0(5)	0.146(2)	0.856 4(6)
H(22)	0.573 5	0.120 4	0.798 4
H(23)	0.537 6	0.152 2	0.848 1
H(24)	0.599 1	0.292 7	0.877 7
H(25)	0.627 5	0.044 1	0.912 9

All non-hydrogen atoms were refined with anisotropic thermal parameters. The BH_4 hydrogens were located from a difference electron-density map.

Table 15 Crystal data,[a] structure solution[b] and refinement for complexes **1**–**4** and **6**

	1	**2**	**3**	**4**	**6**
Empirical formula	$C_{22}H_{42}Cl_2Si_4Th$	$C_{22}H_{42}Cl_2Si_4U$	$C_{22}H_{42}Br_2Si_4U$	$C_{22}H_{42}I_2Si_4U$	$C_{22}H_{50}B_2Si_4U$
M	721.8	727.8	816.8	910.8	680.6
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	*C*/2*c*	*C*/2*c*	*C*/2*c*	$P2_12_12_1$	*C*/2*c*
a/Å	27.263(9)	27.037(9)	27.005(6)	11.026(5)	27.731(8)
b/Å	7.118(4)	7.084(3)	7.179(2)	16.448(4)	7.138(3)
c/Å	22.441(8)	22.327(9)	22.367(4)	18.340(4)	22.561(8)
β/°	132.24(5)	131.93(4)	131.91(2)	—	132.24(4)
U/Å^3	3224	3186	3227	3326	3306
Z	4	4	4	4	4
D_c/g cm^{-3}	1.50	1.52	1.68	1.82	1.42
Crystal size/mm	0.24 × 0.18 × 0.15	0.22 × 0.15 × 0.12	0.15 × 0.20 × 0.16	0.23 × 0.10 × 0.15	0.21 × 0.14 × 0.12
μ(Mo-Kα)	60.6	65.6	89.3	80.1	58.9
Standard reflections	400, 020, 004	400, 020, 004	400, 040, 004	400, 020, 006	200, 040, 002
Variation (%)	±1	±2	±2	±2	±1
Reflections					
measured	2594	2554	1701	2620	1878
observed	1891	1701	1347	1789	1199
2θ Range/°	2–46	2–46	2–40	2–46	2–40
No. of parameters refined	132	132	132	152	132
S[c]	0.96	1.05	0.95	0.96	1.02
R	0.026	0.020	0.027	0.042	0.026
R′	0.030	0.026	0.035	0.051	0.028

[a] From least-squares refinement of the angular settings of 25 high-angle reflections. Data common to all compounds: instrument, Enraf-Nonius CAD-4; radiation, Mo-Kα (λ = 0.710 69 Å); scan mode, θ–2θ; scan rate, 0.50–20° min^{-1}; scan length, 0.80 + 0.20 tan θ; observed reflections, $I > 3\sigma(I)$. All calculations performed on a UNIVAC 1100/10 computer using SHELX 76.[21a] Data were corrected for Lorentz and polarisation effects and for absorption (empirical, based on ψ scans). [b] Structure solution: Th or U atom located by Patterson synthesis and all other non-hydrogen atoms located by Fourier-difference synthesis (for the isostructural compounds the coordinates of the atoms in the first structure were used as a starting set). Neutral atom scattering factors were used.[21b] Anomalous dispersion corrections were applied to all non-hydrogen atoms. Unit weights. All H atoms in geometry-fixed sites were placed in calculated positions and not refined. Methyl hydrogens could not be located. [c] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{\frac{1}{2}}$, $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$ where N_o is the number of observed reflections and N_v the number of variables.

stirred for 15 h. The solvent was removed *in vacuo* and the white solid extracted into C_6H_{14} (*ca.* 50 cm^3). After filtration to remove sodium chloride and excess of $NaBH_4$, the filtrate was concentrated (*ca.* 10 cm^3) and cooled to −30 °C. White *needles* of compound **5** (0.55 g, 40%) were collected, washed with cold (*ca.* −78 °C) C_5H_{12}, and dried *in vacuo*.

Bis[1,3-*bis*(*trimethylsilyl*)*cyclopentadienyl*]*bis*(*tetrahydridoborato*)*uranium*(IV), **6**. To a solution of complex **2** (1.93 g, 2.7 mmol) in tetrahydrofuran (*ca.* 100 cm^3) at *ca.* 20 °C was added $NaBH_4$ (0.3 g, 1.5-fold excess) and the resultant mixture was stirred for *ca.* 12 h. The solvent was removed *in vacuo* and the orange residue extracted into C_6H_{14} (*ca.* 100 cm^3) and filtered. The filtrate was concentrated to *ca.* 10 cm^3 and cooled to −30 °C. Large orange *crystals* of compound **6** (1.2 g, 70%) were formed which were washed with cold (*ca.* −78 °C) C_6H_{14} (*ca.* 5 cm^3) and dried *in vacuo*.

X-Ray Crystallography.—Suitable crystals of each of the complexes **1**–**4** and **6** were mounted in Lindemann capillaries and sealed under argon for data collection on the diffractometer. Table 15 shows details of the crystal data, structure solution and refinement.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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