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The Synthesis and X-ray Structure of a Novel Monocyclopentadienyluranium(IV) Chloride $[UCp'''Cl_2(THF)(\mu\text{-}Cl)_2Li(THF)_2]$ $[Cp''' = \eta\text{-}C_5H_2(SiMe_3)_3\text{-}1,2,4]$*

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We report the first use of the tris(1,2,4-trimethylsilyl)cyclopentadienyl ligand $\eta\text{-}\bar{C}_5H_2(SiMe_3)_3\text{-}1,2,4$ (abbreviated as $\bar{C}p'''$) in f-element chemistry. Thus we have obtained the novel crystalline complex $[UCp'''Cl_2(THF)(\mu\text{-}Cl)_2Li(THF)_2]$ from UCl_4 and $LiCp'''$ in tetrahydrofuran. The X-ray structure shows the compound to have an approximately octahedral environment about U, four equatorial Cl^- ligands, *trans*-axial $\bar{C}p'''$ and THF ligands, and with two of the Cl^- ligands bridging to Li; the approximately tetrahedral coordination geometry around Li is completed by two terminal THF ligands.

Experimental

Uranium(IV) chloride (4.49 g, 11.82 mmol) was added to a stirred solution of $LiCp'''$ (prepared in essentially quantitative yield from $Cp'''H$ [1] and $LiBu^n$ in $n\text{-}C_6H_{14}$) (3.44 g, 11.95 mmol) in tetrahydrofuran (250 cm^3) at 20 °C, producing an olive-green solution. This was stirred for 12 h at 20 °C, whereafter the volatiles were removed *in vacuo* to produce an olive-green solid. The latter was extracted into toluene (*ca.* 100 cm^3); the extract was filtered, concentrated (to *ca.* 50 cm^3), and cooled (−30 °C) to yield green needles of $[UCp'''Cl_2(THF)(\mu\text{-}Cl)_2Li(THF)_2]$ (6.26 g, 60%). *Anal.* Calc. for $C_{26}H_{53}Cl_4O_3Si_3LiU$ (M = 884.8): Cl, 16.1. Found: Cl, 16.5%. ^1H NMR chemical shifts (δ in ppm, relative to external $SiMe_4$, 360 MHz, d_8-toluene, 305 K): δ −13.62, −12.52 ($U\text{–}OC_4H_8$); −5.2, −4.1 [$(SiMe_3)_2$]; −1.78, 1.56 [$Li(OC_4H_8)_2$]; 0.82 ($SiMe_3$); 14.59, 64.79 (C_5H_2). ^7Li NMR (δ in ppm, relative to external aq. $Li[NO_3]$, 139.97 MHz, d_8-toluene): −20.9 ppm. (Spectra taken at other temperatures are not yet fully analysed, but show that kinetic processes are observable.)

Crystals (0.10 × 0.15 × 0.08 mm) suitable for an X-ray structure determination were mounted in 0.2 mm Lindemann tubes and sealed under argon.

$C_{26}H_{53}Cl_4O_3Si_3LiU$, M = 884.75, a = 11.976(5), b = 20.013(6), c = 33.411(10) Å, β = 99.66(3)°, V = 7954.19 $Å^3$, space group $C2/c$, Z = 8, D_c = 1.48 g cm^{-3}.

Diffraction intensities were collected on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (λ = 0.71069 Å) at 305 K, 2θ range 2–44°. The structure solution was based on 2087 reflections having $I > 3\sigma(I)$. The final R value was 0.033 (R' = 0.036) with GOF = 0.92.

Results and Discussion

We have used the η-1,3-bis(trimethylsilyl)cyclopentadienyl ligand $\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3$ (abbreviated as $\bar{C}p''$) quite extensively, originally in 4f element chemistry [2], but also in connection with bis-Cp''- and tris-Cp''-complexes of U(IV), U(III), Th(IV), and Th(III) [3]. The $\bar{C}p''$ ligand has provided a route to numerous hydrocarbon-soluble and volatile complexes, which have been monomers or dimers; for a brief review of such thorium and uranium chemistry, see ref. 4.

We have now turned to the even more highly substituted ligand $\eta\text{-}\bar{C}_5H_2(SiMe_3)_3\text{-}1,2,4$ ($\bar{C}p'''$), which was expected to provide lipophilic complexes even for monocyclopentadienylmetal complexes. We report herein the first such compound (**1**), prepared as shown in eqn. (1), which is clearly to be a forerunner of an extensive family of novel complexes.

$$UCl_4 + LiCp''' \xrightarrow{THF} \underset{\mathbf{1}}{[UCp'''Cl_2(THF)(\mu\text{-}Cl)_2Li(THF)_2]} \qquad (1)$$

There are three previous examples of X-ray characterized monocyclopentadienyluranium(IV) chlorides: $[U(\eta\text{-}C_5H_4Me)Cl_3(THF)_2]$ [5], $[UCpCl_3(L)_2]$, L = $OP(NMe_2)_3$ [6] or L = $OPPh_3$ [7].

Complex **1**, like the above mentioned $[UCp^xCl_3(L)_2]$ species, has a coordination geometry around U which approximates to being distorted octahedral with a $\bar{C}p^x$ and an L ligand [L = THF for **1**] occupying mutually *trans*-positions. In complex **1** the equatorial sites are occupied by four Cl^- ligands (bent away from the $\bar{C}p'''$ ligand, ⟨Cent–U–Cl⟩ 102°), one *cis*-pair being terminal and the other bridging to Li. Four-coordination about lithium is completed by two terminal THF ligands. The molecular structure and atom numbering scheme for complex **1** are

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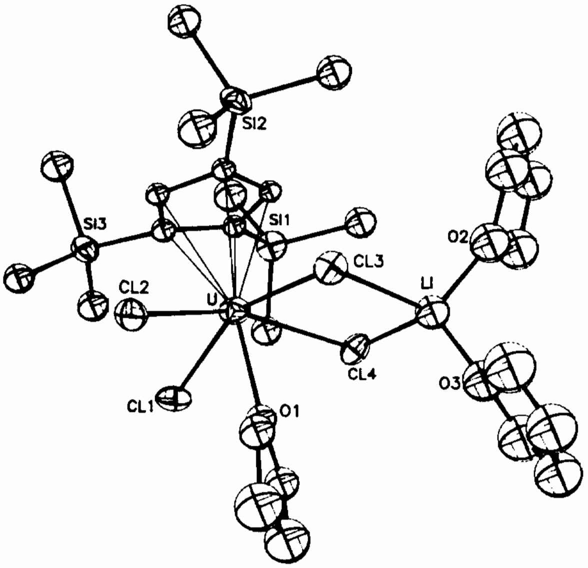

Fig. 1. The molecular structure and atom numbering scheme for [UCp‴Cl$_2$(THF)(μ-Cl)$_2$Li(THF)$_2$] [Cp‴ = η-C$_5$H$_2$(SiMe$_3$)$_3$-1,2,4] (1).

TABLE I. Some Important Bond Lengths (Å) and Angles (°) in [UCp‴Cl$_2$(THF)(μ-Cl)$_2$Li(THF)$_2$] [Cp‴ = η-C$_5$H$_2$(SiMe$_3$)$_3$-1,2,4]

Bond lengths (Å)			
U–O(1)	2.449(9)	U–C	2.69–2.76
Cl(1)–U	2.606(4)	U–Cent	2.45
Cl(2)–U	2.606(4)	Li–Cl(3)	2.39(3)
Cl(3)–U	2.734(4)	Li–Cl(4)	2.40(3)
Cl(4)–U	2.726(4)	Li–O(2)	1.90(4)
		Li–C(3)	1.84(4)
Bond angles (°) [3 Si atoms 0.36–0.41 Å out of η-C$_5$ plane]			
Cent–U–Cl(1)	104	Cl(1)–U–Cl(2)	91.4(1)
Cent–U–Cl(2)	101	Cl(1)–U–Cl(3)	154.1(1)
Cent–U–Cl(3)	102	Cl(1)–U–Cl(4)	88.8(1)
Cent–U–Cl(4)	103	Cl(3)–U–Cl(4)	79.3(1)
Cent–U–O(1)	178	Cl(2)–U–Cl(3)	90.3(1)
		Cl(2)–U–Cl(4)	155.4(2)
Cl(1)–U–O(1)	78.6(3)	O(2)–Li–O(3)	110(2)
Cl(2)–U–O(1)	78.4(3)	Cl(3)–Li–Cl(4)	93(1)
Cl(3)–U–O(1)	76.4(3)		
Cl(4)–U–O(1)	77.5(3)		

shown in Fig. 1 and selected important parameters are listed in Table I.

The THFs bonded to Li do not interact with the hydrogens of the SiMe$_3$ groups of $\bar{\text{C}}\text{p}'''$. However, there is 'gear-meshing' of (a) the H atoms of the 1- and 2-SiMe$_3$ groups, and (b) the H atoms of the 4-SiMe$_3$ group and the bridging Cl$^-$ ligands.

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