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Synthesis of the triscyclopentadienyl(hydroxo)uranium(IV) complexes $[U(C_5H_4R)_3(OH)]$ ($R = SiMe_3$ or ^tBu) and their transformation into μ-oxo bridged derivatives. Crystal structure of the trinuclear compound $[\{U(C_5H_4SiMe_3)_2(\mu\text{-}O)\}_3]$

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Abstract

The U(IV) hydroxo-complexes $[U(C_5H_4R)_3(OH)]$ ($R = SiMe_3$ or ^tBu) have been prepared, either by hydrolysis of the corresponding hydrides $[U(C_5H_4R)_3H]$ or by treatment of the cationic compounds $[U(C_5H_4R)_3][BPh_4]$ with sodium hydroxide. Reaction of $[U(C_5H_4R)_3(OH)]$ with $[U(C_5H_4R)_3H]$ gave the μ-oxo derivative $[\{U(C_5H_4R)_3\}_2(\mu\text{-}O)]$ ($R = SiMe_3$) and thermolysis of the hydroxo-complexes afforded the trinuclear compounds $[\{U(C_5H_4R)_2(\mu\text{-}O)\}_3]$. The crystal structure of $[\{U(C_5H_4SiMe_3)_2(\mu\text{-}O)\}_3]$ has been determined.

1. Introduction

Almost all the organometallic complexes of the f elements are exceedingly sensitive to moisture, and the decomposition products are generally assumed to be hydroxide derivatives. In a few cases, new interesting organolanthanide compounds containing hydroxyl bridges have been isolated after partial hydrolysis of a given precursor, either using carefully controlled experimental conditions or, accidentally, during the work-up or crystallization in the presence of adventitious traces of water [1,2]. Such hydroxo-complexes of the 5f elements have not been characterized, although $[U(C_5H_5)_3(OH)]$ was mentioned in a review article [3], without details of its preparation and identification. Here we report synthesis of the triscyclopentadienyl(hydroxo)uranium(IV) compounds $[U(C_5H_4R)_3(OH)]$ ($R = SiMe_3$ or ^tBu) and some of their reactions which gave μ-oxo derivatives; we describe the crystal structure of the trinuclear complex $[\{U(C_5H_4SiMe_3)_2(\mu\text{-}O)\}_3]$.

2. Results and discussion

2.1. Synthesis of the hydroxo-complexes $[U(C_5H_4R)_3(OH)]$ ($R = SiMe_3$ or ^tBu)

The hydroxide complexes $[U(C_5H_4R)_3(OH)]$ (**1a**, $R = SiMe_3$; **1b**, $R = {}^tBu$) have been obtained by treatment of the corresponding hydrides $[U(C_5H_4R)_3H]$ [4] with exactly 1 mol equivalent of water in toluene; the green solution rapidly turned orange and a gas, presumably dihydrogen, was evolved (eqn. (1)).

$$[U(C_5H_4R)_3H] + H_2O \longrightarrow [U(C_5H_4R)_3(OH)] + H_2 \quad (1)$$

$$(\mathbf{1a},\ R = SiMe_3;\ \mathbf{1b},\ R = {}^tBu)$$

After extraction into pentane, the orange products were analytically pure; **1a** was isolated as an oil and **1b**

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was crystalline. The yields of these reactions were not reproducible and varied from 20% to 60%, apparently depending on the rate of addition of water, agitation, and concentration. Such difficulties in controlling the hydrolysis of organolanthanide compounds have been already noted [2].

A more reliable preparation of **1a** and **1b** consists in treating the cationic complexes $[U(C_5H_4R)_3][BPh_4]$ with 1 mol equivalent of finely powdered sodium hydroxide in tetrahydrofuran (THF); by this method (eqn. (2)), the products were isolated in much improved yields (70–95%).

$$[U(C_5H_4R)_3][BPh_4] + NaOH \longrightarrow \underset{\mathbf{1}}{[U(C_5H_4R)_3(OH)]} + NaBPh_4 \quad (2)$$

Complexes **1a** and **1b** were characterized by their elemental analyses (Table 1). In the IR spectrum, the bands centred at 3690 cm^{-1} (**1a**) and 3700 cm^{-1} (**1b**) are assigned to ν(OH). The ^1H NMR spectra exhibit a low field paramagnetic signal corresponding to the hydrogen atom of the hydroxide moiety. Osmometric measurements revealed that these compounds are monomeric in solution; this was not surprising as we had already found that in this series of $[U(C_5H_4R)_3(X)]$ complexes ($R = SiMe_3$ or ^tBu), the bulkiness of the cyclopentadienyl ligands prevents the formation of bridged dimers [4,5].

2.2. *Formation of μ-oxo derivatives from the hydroxo-complexes* $[U(C_5H_4R)_3(OH)]$

Dehydration of mononuclear [M]-OH species, leading to oxo-bridged complexes, is a classical reaction that is considered as essential in solution-gel chemistry (oxolation or condensation reactions) [6]. In some cases, such oxo compounds were obtained fortuitously during the treatment or crystallization of a metal compound, and it is often assumed that [M]-OH entities, resulting from the reaction with adventitious traces of moisture, are involved in their formation [7]. One might expect that complex **1a** should be easily transformed by elimination of H_2O into the oxo-bridged bimetallic organouranium complex $[\{U(C_5H_4SiMe_3)_3\}_2(\mu\text{-}O)]$ **2**; this was recently synthesized by treatment of $[U(C_5H_4SiMe_3)_3]$ with carbon dioxide and its crystal structure was determined [8]. In fact, complex **2** was not obtained by condensation of two molecules of **1a**; on the contrary, in the presence of one equivalent of H_2O, **2** was totally converted into **1a** (eqn. (3)) (NMR experiment).

$$\underset{\mathbf{2}}{[\{U(C_5H_4SiMe_3)_3\}_2(\mu\text{-}O)]} + H_2O \longrightarrow 2\underset{\mathbf{1a}}{[U(C_5H_4SiMe_3)_3(OH)]} \quad (3)$$

The two oxo-bridged compounds $[\{U(C_5H_4SiMe_3)_3\}_2(\mu\text{-}O)]$ **2** and $[\{U(C_5H_4SiMe_3)_2(\mu\text{-}O)\}_3]$ **3** were obtained from the hydroxide **1a**, but without elimination of water. These complexes were formed simultaneously when **1a** was heated in toluene in the presence of one equivalent of $[U(C_5H_4SiMe_3)_3H]$. The reaction, which has been monitored by NMR spectroscopy was complete after 24 h at 110°C; the spectrum showed that the ratio [**2**]:[**3**] was 65:35 but, once **1a** had totally disappeared, approximately 60% of the initial quantity of $[U(C_5H_4SiMe_3)_3H]$ was still present. Under the same conditions, thermolysis of **1a** afforded only compound **3**, with elimination of trimethylsilylcyclopentadiene (almost quantitative yield after 40 h). These results suggested that complex **2** results from the reaction de-

TABLE 1. Analytical and ^1H NMR data

Compound	Analyses ᵃ	NMR data ᵇ
1a $[U(C_5H_4SiMe_3)_3(OH)]$	C 42.97 (43.23)	35.42 (s, 1H, $w_{1/2} = 40$ Hz, OH)
	H 5.92 (6.04)	−1.14 (27H, Me)
	Si 12.90 (12.63)	−9.16 and −13.95 (6H + 6H, CH)
1b $[U(C_5H_4{}^tBu)_3(OH)]$	C 52.60 (52.42)	57.87 (s, 1H, $w_{1/2} = 80$ Hz, OH)
	H 6.42 (6.51)	0.05 (27H, Me)
	U 38.20 (38.47)	−11.76 and −16.79 (6H + 6H, CH)
3 $[\{U(C_5H_4SiMe_3)_2(\mu\text{-}O)\}_3]$	C 36.57 (36.35)	5.19 (18H, Me)
	H 5.04 (4.95)	−17.79 and −32.27 (4H + 4H, CH)
	Si 10.90 (10.62)	
$[\{U(C_5H_4{}^tBu)_2(\mu\text{-}O)\}_3]$		6.53 (18H, Me)
		−15.30 and −37.63 (4H + 4H, $w_{1/2} = 100$ Hz, CH)

[a] Analytical data: found (required) in %. [b] At 30°C in benzene-d_6. Data in the form δ (relative integral, half-height width, assignment); when not specified, the signal is a singlet with $w_{1/2} = 10–30$ Hz.

picted by eqn. (4); such formation of a μ-oxo derivative from an equimolar mixture of hydride and hydroxide complexes is, to our knowledge, unprecedented.

$$\underset{\mathbf{1a}}{[U(C_5H_4SiMe_3)_3(OH)]} + [U(C_5H_4SiMe_3)_3H] \longrightarrow \underset{\mathbf{2}}{[\{U(C_5H_4SiMe_3)_3\}_2(\mu\text{-}O)]} + H_2 \quad (4)$$

Reaction (4) was hindered by the concomitant thermal transformation of **1a** into the trinuclear compound **3** (eqn. (5)).

$$\underset{\mathbf{1a}}{[U(C_5H_4SiMe_3)_3(OH)]} \xrightarrow{110°C} 1/3\underset{\mathbf{3}}{[\{U(C_5H_4SiMe_3)_2(\mu\text{-}O)\}_3]} + C_5H_5SiMe_3 \quad (5)$$

Red needles of **3** were progressively deposited from a refluxing solution of **1a** in pentane (40% isolated yield after 5 days); these crystals were suitable for an X-ray diffraction study (*vide infra*). Complex **3** was obtained alternatively in almost quantitative yield by treating **1a** with an excess of sodium hydride in tetrahydrofuran; the reaction was complete after 10 min in the ultrasound bath, a gas was evolved and 1 mol equivalent of $NaC_5H_4SiMe_3$ was liberated (NMR experiment). Similar treatment of **1b** gave $[\{U(C_5H_4{}^tBu)_2(\mu\text{-}O)\}_3]$, which was characterized only by its NMR spectrum.

These reactions leading to the oxo-bridged compounds **2** (eqn. (4)) and **3** (Scheme 1) underscore the acidic character of the hydroxide complexes **1** and are reminiscent of the reactions of alcohols with $[U(C_5H_4R)_3H]$ [4] and $[U(C_5H_5)_3X]$ (X = Cl or OR) [9] which gave alkoxide derivatives, with elimination of dihydrogen and cyclopentadiene respectively.

It seems likely that the two routes leading to **3** (Scheme 1) involve the same intermediate $[U(C_5H_4SiMe_3)_2O]$, which undergoes rapid trimerization. Such intermediates $[M(C_5H_5)_2O]$ have been proposed to account for the synthesis of the trinuclear compounds $[\{M(C_5H_5)_2(\mu\text{-}O)\}_3]$ (M = Zr [10], Hf [11]) according to eqns. (6) and (7).

$$3[Zr(C_5H_5)_2(CO)_2] + 3CO_2 \longrightarrow [\{Zr(C_5H_5)_2(\mu\text{-}O)\}_3] + 9CO \quad (6)$$

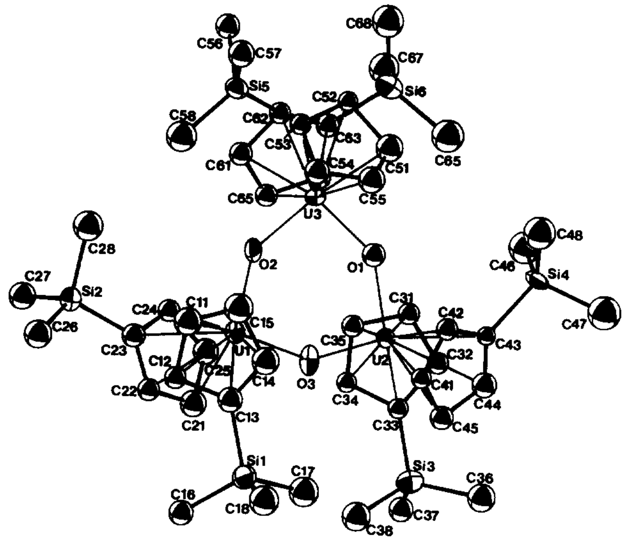


Fig. 1. Perspective view of molecule **3**.

$$3[HfCl_2O] + 6NaC_5H_5 \longrightarrow [\{Hf(C_5H_5)_2(\mu\text{-}O)\}_3] + 6NaCl \quad (7)$$

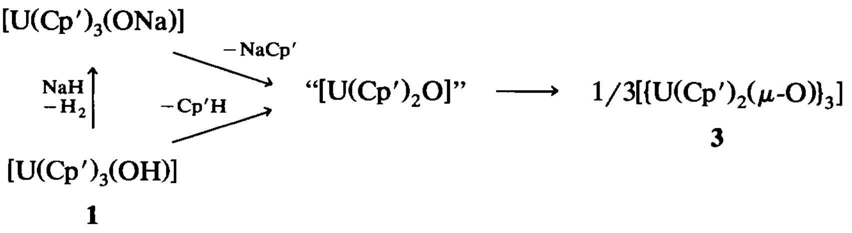
The instability of the monomeric zirconyl unit Zr=O has been compared to that of the monomeric acetaldehyde and formaldehyde, which are readily converted into paraldehyde and trioxane respectively. It is noteworthy that the species $[\{M(C_5H_4R)_2(\mu\text{-}O)\}_2]$ (M = Zr or Hf and R = H; M = U and R = $SiMe_3$), which would be formed by dimerization of the postulated intermediate, were not detected during the above reactions, whereas such a stable dinuclear compound was isolated from the hydrolysis reaction depicted by eqn. (8) [12].

$$2[U(C_5H_3R_2)_2(NMe_2)_2] + 2H_2O \longrightarrow [\{U(C_5H_3R_2)_2(\mu\text{-}O)\}_2] + 4Me_2NH \quad (8)$$

$$R = SiMe_3$$

2.3. *Crystal structure of $[\{U(C_5H_4SiMe_3)_2(\mu\text{-}O)\}_3]$*

ORTEP drawings [13] of **3** are shown in Figs. 1 and 2; selected bond distances and angles are listed in Table 2. The six-membered ring defined by the uranium and oxygen atoms is planar within ± 0.017(17) Å. The short U–O bond lengths, that range from 2.05(1) Å to



Scheme 1. Preparation of **3** (Cp' = $C_5H_4SiMe_3$)

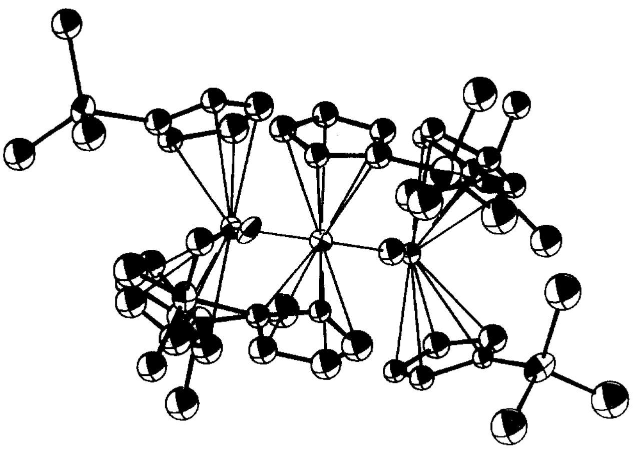


Fig. 2. View of molecule 3 in the plane of the uranium–oxygen ring.

2.12(1) Å and average 2.08(4) Å, are classical for uranium alkoxides [14], and are similar to those determined in the dinuclear complex [{U(C$_5$H$_4$SiMe$_3$)$_3$}$_2$(μ-O)] 2 (U–O = 2.1053(2) Å [8]) and the cation [{U(C$_9$H$_7$)(Br)(NCMe)$_4$}$_2$(μ-O)]$^{2+}$ (U–O = 2.057(1) Å [15]); the ring planarity and the short U–O bond distances are reflecting the strong π bonding between the metal and oxygen atoms. However, because of the ring formation, the U–O–U angles are far from linear with a mean value of 142(2)°. The geometry of the η^5-C$_5$H$_4$SiMe$_3$ is unexceptional, with U–C(ring centroid) distances ranging from 2.49(2) Å to 2.51(2) Å (⟨U–C(ring centroid)⟩ = 2.51(3) Å in [U(C$_5$H$_4$SiMe$_3$)$_3$] [16] and 2.53(1) Å in 2 [8]). The SiMe$_3$ substituents of two adjacent cyclopentadienyl rings are staggered and remote from the metal centre; this is the best geometry for minimization of steric interactions. The metal environments in the complexes [{M(C$_5$H$_4$R)$_2$(μ-O)}$_3$] (M = Zr [10], Hf [11] and R = H; M = U and R = SiMe$_3$) are quite similar since the ⟨O–M–O⟩ angles are 97.5(2), 97(2) and 97.1(4) for M = Zr, Hf, and U respectively, and the corresponding ⟨ring centroid–M–ring centroid⟩ angles are 124(1), 123 and 123(1); the ⟨M–O–M⟩ angles of the planar metal–oxygen rings are also very close: 142(1), 143(1) and 142(2) respectively.

3. Experimental details

3.1. General methods

All preparations and reactions were carried out under argon (less than 5 ppm oxygen) using standard Schlenk vessel and vacuum-line techniques, or in a dry box. Solvents were thoroughly dried and deoxygenated by the standard methods, and distilled immediately before use. Deuteriated solvents were dried over Na–K alloy.

Elemental analyses and molecular weight determinations were carried out by Analytische Laboratorien at Engelkirchen (Germany). The IR spectra were recorded on a Perkin-Elmer 782 instrument in Nujol mulls, ^{1}H NMR spectra on a Bruker W60 (FT) instrument and referenced internally using the residual proton solvent resonances relative to tetramethylsilane (δ = 0). The analytical and NMR data are presented in Table 1. Sodium hydroxide was finely divided in a grinder and dried under vacuum; a powder of NaH was obtained from a commercial suspension in mineral oil (Aldrich) after washing with toluene and drying under vacuum. The compounds [U(C$_5$H$_4$R)$_3$H], [U(C$_5$H$_4$R)$_3$][BPh$_4$] (R = SiMe$_3$ or ^{t}Bu) [4] and [{U(C$_5$H$_4$SiMe$_3$)$_3$}$_2$(μ-O)] [8] were prepared according to published methods.

TABLE 2. Selected bond distances (Å) and angles (°) with estimated standard deviations for 3

Uranium environment					
U(1)–U(2)	3.979 (1)	U(1)–U(3)	3.947 (1)	U(2)–U(3)	3.946 (1)
U(1)–O(2)	2.05 (1)	U(2)–O(1)	2.05 (1)	U(3)–O(1)	2.11 (1)
U(1)–O(3)	2.09 (1)	U(2)–O(3)	2.11 (1)	U(3)–O(2)	2.12 (1)
⟨U(1)–C⟩	2.79 (5)	⟨U(2)–C⟩	2.79 (10)	⟨U(3)–C⟩	2.77 (9)
U(1)–1 [a]	2.51 (2)	U(2)–3	2.51 (2)	U(3)–5	2.51 (2)
U(1)–2	2.50 (1)	U(2)–4	2.51 (1)	U(3)–6	2.49 (1)
U(2)–U(1)–U(3)	59.72 (2)	U(1)–U(2)–U(3)	59.74 (2)	U(1)–U(3)–U(2)	60.55 (2)
O(2)–U(1)–O(3)	97.3 (5)	O(1)–U(2)–O(3)	96.7 (5)	O(1)–U(3)–O(2)	97.4 (6)
O(2)–U(1)–1	107.1 (6)	O(1)–U(2)–3	106.8 (5)	O(1)–U(3)–5	109.9 (6)
O(2)–U(1)–2	110.7 (5)	O(1)–U(2)–4	110.4 (6)	O(1)–U(3)–6	106.8 (5)
O(3)–U(1)–1	110.1 (6)	O(3)–U(2)–3	107.5 (6)	O(2)–U(3)–5	110.4 (5)
O(3)–U(1)–2	105.3 (6)	O(3)–U(2)–4	107.4 (6)	O(2)–U(3)–6	106.6 (6)
1–U(1)–2	123.3 (5)	3–U(2)–4	124.5 (6)	5–U(3)–6	122.8 (6)
Trimethylsilylcyclopentadienyl ligand					
⟨C–C⟩$_{ring}$	1.43 (6)	⟨Si–C$_{ring}$⟩	1.86 (8)	⟨Si–C$_{Me}$⟩	1.88 (5)
⟨C–C–C⟩$_{ring}$	108 (2)	⟨C$_{ring}$–Si–C$_{Me}$⟩	109 (1)		

[a] is the centroid of the cyclopentadienyl ring 1, etc.

3.2. Synthesis of the hydroxo-complexes $[U(C_5H_4SiMe_3)_3(OH)]$ (1a) and $[U(C_5H_4{}^tBu)_3(OH)]$ (1b)

(a) A 50 ml round-bottomed flask was charged with $[U(C_5H_4SiMe_3)_3H]$ (300 mg, 0.46 mmol), and toluene (20 ml) was condensed into it under vacuum at −78°C. Water (8.3 μl, 0.46 mmol) was added *via* a microsyringe and the green solution rapidly turned orange, with gas evolution. After 10 min, the solution was evaporated to dryness and the residue was extracted into pentane (20 ml). After evaporation, an orange oil of **1a** was obtained (190 mg, 62%). A similar experiment with $[U(C_5H_4{}^tBu)_3H]$ (500 mg, 0.83 mmol) and H_2O (15 μl, 0.83 mmol) gave an ochre microcrystalline powder of **1b** (100 mg, 20%). The yields of these reactions varied from 20% to 60%.

(b) A 50 ml round-bottomed flask was charged with $[U(C_5H_4SiMe_3)_3][BPh_4]$ (202 mg, 0.21 mmol) and NaOH (8.3 mg, 0.21 mmol), and THF (15 ml) was condensed into it under vacuum at −78°C. The reaction mixture was stirred for 15 min at 20°C and the red solution turned orange, and an off-white powder of $NaBPh_4$ precipitated. The solvent was evaporated and the residue was dried overnight under vacuum. The product was extracted into pentane (20 ml) and isolated as an orange oil (136 mg, 98%). By the same procedure, $[U(C_5H_4{}^tBu)_3][BPh_4]$ (400 mg, 0.43 mmol), in the presence of NaOH (17.5 mg, 0.43 mmol), was transformed into **1b** (195 mg, 73%). Molecular weight by osmometry: 589 (theoretical 618).

(c) An NMR tube was charged with $[\{U(C_5H_4SiMe_3)_3\}_2(\mu\text{-}O)]$ (10.0 mg, 7.6 μmol) in THF-d_8 (0.4 ml) and H_2O (0.1 μl, 7.6 μmol) was added *via* a microsyringe. The tube was immersed in an ultrasound bath (60 W, 40 kHz) and after 30 min, the spectrum showed the quantitative formation of **1a**.

3.2.1. Reaction of $[U(C_5H_4SiMe_3)_3(OH)]$ (1a) with $[U(C_5H_4SiMe_3)_3H]$

An NMR tube was charged with **1a** (10.0 mg, 15.0 μmol) and $[U(C_5H_4SiMe_3)_3H]$ (9.8 mg, 15.0 μmol) in toluene-d_8 (0.4 ml). The mixture was heated at 110°C for 24 h, and the spectrum showed the signals corresponding to unreacted hydride (52%), **2** (31%) and **3** (17%).

3.2.2. Synthesis of $[\{U(C_5H_4SiMe_3)_2(\mu\text{-}O)\}_3]$ (3) and $[\{U(C_5H_4{}^tBu)_2(\mu\text{-}O)\}_3]$

(a) A 50 ml round-bottomed flask was charged with **1a** (279 mg, 0.42 mmol) and pentane (20 ml) was condensed into it under vacuum at −78°C. The solution was heated at 50°C for 5 days and progressively deposited red needles of **3**. The mixture was cooled to 20°C, filtered, and the crystals were dried under vacuum (89 mg, 40%).

(b) An NMR tube was charged with **1a** (10 mg) in toluene-d_8 (0.4 ml) and was heated at 110°C for 40 h. The spectrum showed the quantitative formation of **3** and $C_5H_5SiMe_3$; the intensities of the signals corresponding to the $SiMe_3$ groups of the cyclopentadienyl ligands of **3** and free cyclopentadiene were in the ratio 2:1. Similar results were observed with **1b**.

(c) An NMR tube was charged with **1a** (10.0 mg, 15.0 μmol) and NaH (approximately 3 mg, 125 μmol) in THF d_8 (0.4 ml). The tube was immersed in the ultrasound bath for 10 min, and a gas was evolved. The spectrum showed the exclusive formation of **3** and $NaC_5H_4SiMe_3$; integration of the signals showed that the ratio of coordinated and free cyclopentadienyl was 2:1. Similar results were obtained when $[U(C_5H_4{}^tBu)_3(OH)]$ (5.1 mg, 8.2 μmol) was treated with $KHBEt_3$ (8.2 μl of a 1M solution in THF).

3.3. X-ray crystal structure of $[\{U(C_5H_4SiMe_3)_2(\mu\text{-}O)\}_3]$

A selected single crystal was introduced into a thin-walled Lindemann glass tube in the glove box. Data

TABLE 3. Crystallographic data and experimental details for compound **3**

Crystal data	
Crystal dimensions (mm)	0.45×0.25×0.10
Colour	red
Crystal system	triclinic
Space group	$P\bar{1}$
a(Å)	12.279(2)
b(Å)	12.369(2)
c(Å)	22.766(5)
α(°)	87.33(2)
β(°)	74.33(2)
γ(°)	69.41(2)
V(Å^3)	3112(2)
Z	2
D_{calc} (g cm^{-3})	1.692
μ (Mo-Kα) (cm^{-1})	75.275
Data collection	
θ limits (°)	1, 20
Scan type	ω, 2θ
Scan width	$0.8+0.35\tan\theta$
Range abs. trans.	0.924, 1.053
Range h	−12, 12
k	0, 12
l	−22, 22
Reflections collected	
total	6513
unique	6004
with $I > 3\sigma(I)$	3332
Final values	
$R(F) = \Sigma\|\|F_0\| - \|F_c\|\|/\Sigma\|F_0\|$	0.059
$R_w(F) = [\Sigma_w\|\|F_0\| - \|F_c\|\|^2/\Sigma_w(\|F_0\|)^2]^{1/2}$	0.070
Max shift/esd	0.01

were collected at room temperature on an Enraf-Nonius CAD 4 diffractometer equipped with a graphite monochromator (λ = 0.71073 Å). The cell parameters were obtained by a least-squares refinement of the setting angles of 25 reflections with θ between 8° and 12°. Three standard reflections were measured after each hour; a decay of 38.5% in 32 h was observed and was corrected linearly. The data were corrected for Lorentz and polarization effects and absorption [17]. The structure was solved by direct method using SHELXS86 [18] and refined by full matrix least-squares on F. The U, O and Si atoms were refined anisotropically, and H atoms were not introduced in refinements. All calculations were performed on a Micro Vax II computer with the Enraf-Nonius MolEN system [19]. Analytical scattering factors for neutral atoms [20] were corrected for both Δf and $\Delta f''$ components of anomalous dispersion. Crystallographic data and experimental details are given in Table 3; final positional and thermal parameters are listed in Table 4. Full lists of atomic coordinates, bond lengths, angles, and thermal parameters are available from the Cambridge Crystallographic Data Centre.

TABLE 4. Fractional atomic coordinates, thermal parameters and their e.s.d.s. for compound **3**

Atom	x	y	z	B(Å^2)
U(1)	0.0338(1)	0.3737(1)	0.21791(5)	3.86(4) *
U(2)	−0.2998(1)	0.3881(1)	0.30393(5)	3.28(3) *
U(3)	−0.0779(1)	0.1222(1)	0.19081(5)	3.36(3) *
Si(1)	0.0727(9)	0.5542(9)	0.3560(4)	5.3(3) *
Si(2)	0.2848(9)	0.3955(9)	0.0553(4)	5.1(3) *
Si(3)	−0.5323(9)	0.735(1)	0.3436(4)	5.6(3) *
Si(4)	−0.480(1)	0.1964(9)	0.4121(4)	5.7(3) *
Si(5)	0.2456(9)	−0.1541(9)	0.1335(5)	5.2(3) *
Si(6)	−0.300(1)	−0.004(1)	0.1227(5)	6.4(4) *
O(1)	−0.232(2)	0.232(2)	0.2551(7)	3.6(6) *
O(2)	0.034(2)	0.222(2)	0.1854(8)	4.1(6) *
O(3)	−0.141(2)	0.429(2)	0.2761(8)	4.4(6) *
C(11)	0.257(3)	0.270(3)	0.238(2)	7 (1)
C(12)	0.233(3)	0.389(3)	0.251(1)	4.4(7)
C(13)	0.134(3)	0.415(3)	0.307(1)	4.2(7)
C(14)	0.113(3)	0.314(3)	0.322(1)	6.4(9)
C(15)	0.191(3)	0.216(3)	0.278(2)	7 (1)
C(16)	0.129(3)	0.662(3)	0.312(1)	5.4(9)
C(17)	−0.095(3)	0.602(3)	0.385(2)	8 (1)
C(18)	0.132(3)	0.518(3)	0.424(2)	7 (1)
C(21)	−0.040(3)	0.604(3)	0.178(1)	6.4(9)
C(22)	0.095(3)	0.551(3)	0.156(1)	4.7(8)
C(23)	0.135(3)	0.464(3)	0.109(1)	4.6(8)
C(24)	0.032(3)	0.441(3)	0.099(1)	5.2(8)
C(25)	−0.074(3)	0.527(3)	0.141(1)	5.8(9)
C(26)	0.410(3)	0.411(3)	0.085(2)	7 (1)
C(27)	0.280(3)	0.469(3)	−0.022(2)	7 (1)
C(28)	0.315(4)	0.232(4)	0.040(2)	9 (1)
C(31)	−0.473(3)	0.439(3)	0.242(1)	4.0(7)
C(32)	−0.532(3)	0.513(3)	0.296(1)	4.7(8)
C(33)	−0.480(2)	0.609(3)	0.294(1)	3.5(7)
C(34)	−0.385(3)	0.582(3)	0.236(1)	4.0(7)
C(35)	−0.386(3)	0.480(3)	0.207(1)	4.4(7)
C(36)	−0.624(3)	0.716(3)	0.421(1)	6.3(9)
C(37)	−0.627(3)	0.854(3)	0.308(1)	6.3(9)
C(38)	−0.397(3)	0.782(4)	0.349(2)	8 (1)
C(41)	−0.240(3)	0.362(3)	0.415(1)	4.0(7)
C(42)	−0.268(3)	0.262(3)	0.404(1)	5.2(8)
C(43)	−0.398(2)	0.300(3)	0.412(1)	3.4(7)
C(44)	−0.442(3)	0.412(3)	0.425(1)	4.8(8)
C(45)	−0.344(3)	0.451(3)	0.426(1)	4.7(8)
C(46)	−0.538(4)	0.210(4)	0.343(2)	10 (1)
C(47)	−0.611(4)	0.232(4)	0.482(2)	9 (1)
C(48)	−0.376(5)	0.053(5)	0.415(3)	15 (2)
C(51)	−0.093(3)	−0.067(3)	0.258(2)	7 (1)
C(52)	−0.012(2)	−0.123(3)	0.199(1)	3.4(7)
C(53)	0.096(3)	−0.096(3)	0.193(1)	4.3(7)
C(54)	0.080(3)	−0.032(3)	0.247(1)	5.9(9)
C(55)	−0.037(3)	−0.020(3)	0.285(1)	5.3(8)
C(56)	0.220(3)	−0.215(3)	0.064(1)	5.0(8)
C(57)	0.353(3)	−0.289(3)	0.160(2)	7 (1)
C(58)	0.318(4)	−0.039(4)	0.122(2)	9 (1)
C(61)	−0.028(3)	0.134(3)	0.066(1)	5.1(8)
C(62)	−0.067(3)	0.039(3)	0.080(1)	4.1(7)
C(63)	−0.191(3)	0.075(3)	0.107(1)	4.1(7)
C(64)	−0.230(3)	0.196(3)	0.115(1)	4.6(8)
C(65)	−0.132(3)	0.238(3)	0.091(1)	5.0(8)
C(66)	−0.410(5)	0.053(5)	0.197(2)	13 (2)
C(67)	−0.387(4)	0.035(4)	0.065(2)	10 (1)
C(68)	−0.215(4)	−0.156(4)	0.104(2)	11 (2)

* $B_{eq} = 4/3\Sigma_i\Sigma_j\beta_{ij}a_ia_j$

References

1 W.J. Evans, M.A. Hozbor, S.G. Bott, G.H. Robinson and J.L. Atwood, *Inorg. Chem., 27* (1988) 1990; H. Schumann, J. Loebel, J. Pickardt, C. Qian and Z. Xie, *Organometallics, 10* (1991) 215; D. Deng, F. Song, Z. Wang, C. Qian, G. Wu and P. Zheng, *Polyhedron, 11* (1992) 2883; W.A. Herrmann, R. Anwander, M. Kleine, K. Öfele, J. Riede and W. Scherer, *Chem. Ber., 125* (1992) 2391.

2 P.B. Hitchcock, M.F. Lappert and S. Prashar, *J. Organomet. Chem., 413* (1991) 79.

3 B. Kanellakopulos in T.J. Marks and R.D. Fischer (eds.), *Organometallics of the f Elements*, Reidel, Dordrecht, 1979, p. 1.

4 J.C. Berthet, J.F. Le Maréchal, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.,* (1992) 1573.

5 X. Jemine, J. Goffart, J.C. Berthet and M. Ephritikhine, *J. Chem. Soc., Dalton Trans.,* (1992) 2439; J.C. Berthet, C. Villiers, J.F. Le Maréchal, B. Delavaux-Nicot, M. Lance, M. Nierlich, J. Vigner and M. Ephritikhine, *J. Organomet. Chem., 440* (1992) 53.

6 C. Sanchez and J. Livage, *New J. Chem., 14* (1990) 513; L.G. Hubert-Pfalzgraf, *Appl. Organomet. Chem., 6* (1992) 627.

7 A. Cotton, D.O. Marler and W. Schwotzer, *Inorg. Chim. Acta, 95* (1984) 207; A. Domingos, N. Marques, A. Pires de Matos, I. Santos and M. Silva, *Polyhedron, 11* (1992) 2021.

8 J.C. Berthet, J.F. Le Maréchal, M. Nierlich, M. Lance, J. Vigner and M. Ephritikhine, *J. Organomet. Chem., 408* (1991) 335.

9 B. Delavaux-Nicot and M. Ephritikhine, *J. Organomet. Chem., 399* (1990) 77.

10 G. Fachinetti, C. Floriani, A. Chiesi Villa and G. Guastini, *J. Amer. Chem., Soc., 101* (1979) 1767.

11 R.D. Rogers, R.V. Bynum and J.L. Atwood, *J. Cryst. Spectr. Research, 12* (1982) 239.

12 P.C. Blake, M.F. Lappert, R.G. Taylor, J.L. Atwood and H. Zhang, *Inorg. Chim. Acta, 139* (1987) 13.

13 C.K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA, 1976.

14 W.G. van der Sluys and A.P. Sattelberger, *Chem. Rev., 90* (1990) 1027.

15 W. Beeckman, J. Goffart, J. Rebizant and M.R. Spirlet, *J. Organomet. Chem., 307* (1986) 23.

16 A. Zalkin, J.G. Brennan and R.A. Andersen, *Acta Crystallogr., C 44* (1988) 2104; J.G. Brennan, R.A. Andersen and J.L. Robbins, *J. Amer. Chem. Soc., 108* (1986) 335.

17 N. Walker and D. Stuart, *Acta Crystallogr., A 39* (1983) 158.

18 G.M. Sheldrick, SHELX86, *Program for the Solution of Structures,* University of Gottingen, Gottingen, 1986.

19 *MolEN, An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, 1990.

20 *International Tables for X-Ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1974. (Present distributor: Academic Publishers, Dordrecht.)