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Synthesis and crystal structure of the oxo-bridged bimetallic organouranium complex $[(Me_3SiC_5H_4)_3U]_2[\mu-O]$

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Abstract

The compound $(Me_3SiC_5H_4)_3U$ (I) reacts with CO₂ or N₂O to give $[(Me_3SiC_5H_4)_3U]_2[\mu$ -O] (II), the crystal structure of which reveals presence of a linear U-O-U bridge with U-O distances of 2.1053 (2) Å.

Introduction

The organometallic chemistry of f-elements in low oxidation states has developed rapidly in recent years. The divalent lanthanide metallocenes $(Me_5C_5)_2Ln$ (Ln = Sm [1,2] and Yb [3,4]) and the triscyclopentadienyl uranium complexes $(RC_5H_4)_3U$ (R = H, Me, SiMe₃) [5-7] have been shown to be capable of acting as efficient electron transfer reagents towards a number of organic, inorganic, and organometallic compounds, and a variety of unusual molecular structures and reaction types have been discovered. Special attention was paid to the synthesis, structural characterization, and properties of bimetallic derivatives in which the two $(C_5Me_5)_2Ln$ or $(RC_5H_4)_3U$ fragments are linked by a group 16 element or by an inorganic or organic unsaturated unit. In particular, it has been pointed out [2] that molecular compounds with a M-O-M skeleton may serve as models for oxide supported heterogeneous organometallic catalysts or metal-oxide-containing catalysts. Here we report the preparation and the crystal structure of $[(Me_3SiC_5H_4)_3U]_2[\mu-O]$ (II), a rare example of an organouranium oxide complex.

Results and discussion

Synthesis of $[(Me_3SiC_5H_4)_3U]_2(\mu-O)$ (II)

A green solution of the tris(trimethylsilylcyclopentadienyl) uranium (Me₃SiC₅- H_4)₃U (I) in toluene immediately turned deep red on exposure to carbon dioxide (1 atm, 20 °C) and after 3 h red microcrystals of $[(Me_3SiC_5H_4)_3U]_2[\mu-O]$ (II) had

separated. The product is sparingly soluble in toluene but soluble in tetrahydrofuran (THF). It was characterized by its elemental analyses and by a single crystal X-ray diffraction study. The NMR spectrum exhibits narrow resonances characteristic of equivalent cyclopentadienyl ligands bonded to a U^{IV} centre [6]. The oxide complex II was also prepared by treatment of I with nitrous oxide, a reagent used to synthesize bridging oxo complexes of transition metals [2,8]. The metallocene I also reacted with CO₂ or N₂O in the solid state to give II as a red powder.

Organometallic oxide complexes are not common in *f*-element chemistry and are restricted to the lanthanide derivatives $[(C_5Me_5)_2Ln]_2[\mu-O]$ (Ln = Sm [2] and Yb [4]), $[(C_5H_5)_2Lu(THF)_2]_2[\mu-O]$ [9] and the uranium cationic species $[(C_9H_7)UBr-(MeCN)_4]_2[\mu-O]^{2+}$ [10]; $[(C_5H_5)_3U]_2[\mu-O]$ has been mentioned in a review [11] but without structural characterization and detailed experimental data. In these compounds the bridging oxygen atom is derived from various sources such as O_2 , H_2O , NO, N₂O, epoxybutane, or pyridine oxide, but CO₂ has never been used for their preparation. In fact, reactions of carbon dioxide with organo-*f*-element complexes are limited to some examples of insertion into metal–alkyl or metal–amide σ bonds [12]. Formation of II from I is reminiscent of the synthesis of $[Cp_2TiCI]_2[\mu-O](Cp =$ $C_5H_5)$ by treatment of the titanium(III) compound $(Cp_2TiCI)_2$ with CO₂ [13] but the latter reaction required more drastic conditions (90 ° C, 10 atm CO₂). It is noteworthy that addition of CS₂ to I gave the bridging carbon disulfide complex $[(Me_3SiC_5H_4)_3U]_2[\mu-\eta^1,\eta^2-CS_2]$ [6], and it is likely that the CO₂ deoxygenation reactions pass through an intermediate such as A (eq. 1):

$$\begin{bmatrix} M^{III} \end{bmatrix} \xrightarrow{CO_2} \begin{bmatrix} M^{IV} \end{bmatrix} \longrightarrow O \longrightarrow C \cdot \xrightarrow{(M^{III})} \begin{bmatrix} M^{IV} \end{bmatrix} \longrightarrow O \longrightarrow C \longrightarrow \begin{bmatrix} M^{IV} \end{bmatrix} \xrightarrow{(M^{IV})} O \longrightarrow O \xrightarrow{(M^{IV})} O \xrightarrow{(M^{IV$$

 $\xrightarrow{-\operatorname{CO}} [M^{\operatorname{IV}}] \longrightarrow O \longrightarrow [M^{\operatorname{IV}}] \quad (1)$

These $CO_2 \rightarrow CO$ transformations are clearly promoted by the tendency of the metal to achieve the oxidation number +4 and by the strength of the metal-oxygen bond.

Compound II was found to be inert towards NaH and $HNEt_3BPh_4$, and reacted with methyllithium to give $(Me_3SiC_5H_4)_3UMe$ (by NMR).

X-Ray crystal structure of $[(Me_3SiC_5H_4)_3U]_2[\mu-O]$ (II)

ORTEP drawings [14] of II are shown in Figs. 1 and 2; selected bond distances and angles are listed in Table 1. The molecule has S_6 symmetry with the oxygen atom lying on the inversion centre. The geometry of the $(Me_3SiC_5H_4)_3U$ fragment is unexceptional: the Cp'(centroid)-U-Cp'(centroid) angles average 117° (Cp' = $Me_3SiC_5H_4$) and the U-C bond lengths range from 2.731(6) to 2.874(6) Å (mean 2.80 Å); the average U-Cp'(centroid) distance is 2.53 Å. The cyclopentadienyl rings are planar to within ± 0.008 Å and the silicon atom of the SiMe₃ group is out of the Cp' ring plane, pointed away from the U atom, by 0.60 Å. The centroids of the three cyclopentadienyl ligands of each Cp'₃U unit form perfectly staggered equilateral triangles perpendicular to the U-O-U axis (Fig. 2); this is best geometry for minimization of steric interactions between these bulky ligands.



Fig. 1. Perspective view of molecule II. Atoms labelled with i and those unlabelled are related by an inversion centre.



Fig. 2. View of molecule II along the U-O-U axis.

U environmer	11	······································			·····	
U-C(11)	2.858(5)	U-C(21)	2.874(6)	UC(31)	2.867(6)	
U-C(12)	2.828(6)	U-C(22)	2.829(6)	U-C(32)	2.834(7)	
U-C(13)	2.760(6)	U-C(23)	2.768(6)	U-C(33)	2.777(6)	
U-C(14)	2.731(6)	U-C(24)	2.750(6)	U-C(34)	2.753(6)	
U-C(15)	2.780(7)	UC(25)	2.801(7)	U-C(35)	2.805(6)	
U-1 a	2.527(8)	U-2	2.534(8)	U-3	2.536(8)	
U-O	2.1053(2)				. ,	
O-U-1	99.4(5)	1-U-2	117.2(4)			
O-U-2	99.0(4)	1-U-3	116.9(6)			
OU-3	100.4(5)	2-U-3	117.7(5)			
Cyclopentadie	enyl ligands					
$\langle C-C \rangle$	1.41(2)	$\langle Si-C(ring) \rangle$	1.87(1)	⟨Si−C(Me)⟩	1.86(1)	
⟨C−C−C⟩	108(1)	(C-Si-C)	109(4)	,		

Sciected bond distances (A) and angles (Selected	bond	distances	(Å)	and	angles	(°
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^a 1,2,3 are the centroids of the cyclopentadienyl rings.

The most interesting structural features of II are the 180° U–O–U angle and U–O distance of 2.1053(2) Å; this distance is similar to that in the cation $[(C_9H_7)UBr(MeCN)_4]_2[\mu-O]^{2+}$ (U–O 2.057(1) Å) [10]. Linear M–O–M angles and short M–O bond lengths are characteristic of a series of oxo-bridged early transition metal and *f*-element complexes [2,9,10]. It has been pointed out previously that these structural parameters could reflect: (a) metal oxygen bond orders greater than one, resulting from π interaction between the bridging oxygen and the metal (such $O\pi \rightarrow U$ contribution to the metal oxygen bond appears to be general for uranium alkoxides [15]), and (b) minimization of electrostatic and steric interactions of the organometallic fragments. These ligand–ligand repulsions should be reduced in related chalcogenide complexes, in which the distance between the metal centres is increased, and in this case the M–E–M bridge should be bent, as it was shown to be in the sulfur compound $[(Me_3SiC_5H_4)_3U]_2[\mu-S] (U-S-U 164.9°) [7].$

Experimental

Microanalyses were carried out by the Analytical Laboratories at Engelskirchen (F.R.G.). The ¹H NMR spectra were recorded on a Bruker W60 (FT) instrument. Deuteriated solvents were dried over Na/K alloy. The chemical shifts are given as δ values relative to tetramethylsilane.

All experiments were carried out under argon, CO_2 or N_2O in Schlenk type glassware on a high vacuum line or in a glove box. Solvents were thoroughly dried and deoxygenated by standard methods and distilled immediately prior to use. CO_2 and N_2O (Air Liquide) were used without purification and $(Me_3SiC_5H_4)_3U$ was prepared as described previously [6].

$[(Me_{3}SiC_{5}H_{4})_{3}U]_{2}[\mu-O]$ (II)

(a) A 50-ml round bottom flask was charged with I (222 mg) and toluene (15 ml) was condensed in under vacuum at -78 °C. CO₂ (1 atm) was introduced, where upon the green solution immediately turned red. After 3 h stirring at 20 °C red

Table 1

microcrystals had separated; a further crop was obtained by adding pentane (10 ml). The crystals were filtered off, washed with pentane, and dried under vacuum. (120 mg, 54%). ¹H NMR (THF- d_8 , 30 °C): 0.86 (s, $w_{1/2}$ 12 Hz, 9H, CH₃), -10.04 and -20.53 (s, $w_{1/2}$ 18 Hz, 2H + 2H, CH). ¹³C NMR (THF- d_8 , 30 °C): 112 and 103 (d, J 170 Hz, CH), 5.82 (q, J 120 Hz, CH₃). Analysis. Found: C, 43.72; H, 5.79; Si, 12.45; U, 35.20. C₄₈H₇₈Si₆OU₂ calc.: C, 43.81; H, 5.97; Si, 12.80; U, 36.18%.

(b) An NMR tube was charged with I (5 mg) and benzene- d_6 (0.5 ml) was condensed under vacuum at -78 °C and N₂O (1 atm) was added at 20 °C. The green solution immediately turned red, and after 10 min the ¹H NMR spectrum showed the quantitative formation of II.

(c) An NMR tube was charged with I (5 mg) and filled with CO_2 or N_2O (1 atm). The green powder turned red and the NMR spectrum of the product was identical to that of II.

Reaction of II with MeLi

An NMR tube was charged with I (10 mg) and THF- d_8 (0.5 ml). MeLi (14.25 μ l of a 1.6 M solution in diethyl ether) was added. After 10 min, the NMR spectrum of

Table 2

Crystallographic data and experimental details for compound II

Cryst. dimensions (mm)	0.60×0.10×0.10
Color	red
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	9.690(2)
<i>b</i> (Å)	18.337(5)
c (Å)	15.881(2)
β(°)	104.43(2)
$V(Å^3)$	2733(1)
Z	2
$D_{\text{calc}} (\text{g cm}^{-3})$	1.599
$\mu(Mo-K_{\alpha})(cm^{-1})$	57.71
Radiation	Mo- <i>K_a</i> (λ 0.71073 Å)
θ limits (°)	1, 23
Scan type	$\omega/2\theta$
Scan width (°)	$0.8 + 0.35 (\tan \theta)$
Range absc. trans.	0.865, 1.102
Cryst. decay (%)	19; linearly corrected
Range h k l	-10, 10; 0, 20; 0, 17
Number of standards; freq. of observed standards	3, 100
Reflections collected	
total	4245
unique	3631
with $l > 3 \sigma(l)$	2417
Final values	
$R(F) = \sum F_{\rm o} - F_{\rm c} / \sum F_{\rm o} $	0.031
$Rw(F) = [\Sigma w[\Sigma F_{o} - F_{c}]^{2} / \Sigma w F_{o} ^{2}]^{1/2}$	0.041
Max shift/esd	0.01
Max residual e/Å ³	0.61

the red solution exhibited resonances attributed to free $Me_3SiC_5H_4Li$ (5.65 and 0.0 ppm) and $(Me_3SiC_5H_4)_3UMe$ (ca. 45%). $\delta(THF-d_8, 30^{\circ}C)$: +8.44 and -6.41 (s, 6H + 6H, CH), -5.52 (s, 27H, Me_3Si), -193.8 (s, 3H, Me). The methyl compound was also obtained in quantitative yield by treating $(Me_3SiC_5H_4)_3UCl$ [6] with 1 molar equiv. of MeLi in THF- d_8 .

X-Ray crystal structure of II

Single crystals of II were formed in an NMR tube by exposure of a toluene solution of I to 1 atm of CO_2 . A single crystal was placed in a thin walled Lindemann glass tube. X-Ray diffraction intensities were collected on an Enraf-Nonius CAD4 diffractometer equipped with a Mo X-ray tube and a graphite monochromator. The data were corrected for absorption using the program DIFABS [16], and for crystal decay and Lorentz and polarization effects. The structure was solved by the Patterson function for U and subsequent least-squares refinements and electron density maps revealed the rest of the non hydrogen atoms. Positional

Table 3

Fractional atomic coordinates, equivalent or isotropic thermal parameters and their e.s.d's for compound II

Atom	x	у	Z	$B(Å^2)^a$
υ	0.04186(5)	0.05498(3)	0.39264(3)	2.169(7)
Si(1)	0.2355(4)	-0.0292(2)	0.1887(2)	3.48(8)
Si(2)	- 0.2626(4)	0.1629(2)	0.1748(2)	3.49(8)
Si(3)	0.3094(4)	0.2469(2)	0.3801(3)	3.48(8)
0	0.000	0.000	0.500	2.3(2)
C(11)	0.103(1)	-0.0323(6)	0.2571(7)	2.2(2)
C(12)	0.107(1)	-0.0802(6)	0.3259(8)	2.8(3)
C(13)	-0.035(1)	-0.0851(7)	0.3365(8)	3.4(3)
C(14)	-0.120(1)	-0.0398(7)	0.2760(8)	3.4(3)
C(15)	-0.038(1)	-0.0070(8)	0.2278(8)	3.9(3)
C(16)	0.232(2)	0.060(1)	0.133(1)	6.2(4)
C(17)	0.178(2)	-0.100(1)	0.103(1)	6.4(4)
C(18)	0.420(1)	-0.0524(9)	0.2527(9)	4.4(3)
C(21)	-0.181(1)	0.1457(7)	0.2924(8)	3.3(3)
C(22)	-0.242(1)	0.1063(8)	0.3521(8)	3.5(3)
C(23)	-0.179(1)	0.1298(8)	0.4357(9)	4.2(3)
C(24)	-0.077(1)	0.1826(7)	0.4325(8)	3.6(3)
C(25)	-0.075(1)	0.1933(7)	0.3452(9)	3.6(3)
C(26)	-0.131(1)	0.1944(9)	0.1157(9)	4.9(4)
C(27)	-0.360(2)	0.0816(9)	0.120(1)	5.7(4)
C(28)	-0.392(2)	0.238(1)	0.173(1)	7.3(5)
C(31)	0.277(1)	0.1545(7)	0.4204(8)	2.7(3)
C(32)	0.261(1)	0.1364(8)	0.5050(8)	3.3(3)
C(33)	0.295(1)	0.0633(8)	0.5215(9)	3.8(3)
C(34)	0.331(1)	0.0325(8)	0.449(1)	4.0(3)
C(35)	0.322(1)	0.0873(7)	0.3861(8)	2.9(3)
C(36)	0.250(2)	0.2543(9)	0.2591(9)	4.7(4)
C(37)	0.507(1)	0.2617(9)	0.409(1)	5.5(4)
C(38)	0.225(2)	0.3180(8)	0.434(1)	6.5(5)

^{*a*} $B_{\rm eq} = 4/3\sum_{i}\sum_{j}\beta_{ij}\mathbf{a}_{j}\mathbf{a}_{j}$.

and anisotropic thermal parameters were refined by full matrix least squares. Hydrogen atoms, introduced at calculated positions $(C-H = 0.95 \text{ Å}, B = 6 \text{ Å}^2)$ were not refined but constrained to ride on their carbon atom. All atoms were refined anisotropically. Analytical scattering factors for neutral atoms [17] were corrected for both $\Delta f'$ and $\Delta f''$ components of anomalous dispersion. Calculations were performed on a Micro Vax II computer with the Enraf-Nonius Structure Determination Package [18]. Crystallographic data and experimental details are given in Table 2. Selected bond distances and angles are listed in Table 1 and final position parameters in Table 3. A complete table of bond lengths and angles and lists of structure factors and anisotropic thermal parameters are available from the authors.

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