

Journal of Organometallic Chemistry, 408 (1991) 335–341
 Elsevier Sequoia S.A., Lausanne
 JOM 21554

Synthesis and crystal structure of the oxo-bridged bimetallic organouranium complex $[(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-O}]$

Jean-Claude Berthet, Jean-François Le Maréchal, Martine Nierlich, Monique Lance, Julien Vigner and Michel Ephritikhine *

*Service de Chimie Moléculaire, DSM/DPhG/CNRS URA 331 CEA CEN/Saclay 91191
 Gif sur Yvette Cédex (France)*

(Received October 29th, 1990)

Abstract

The compound $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ (I) reacts with CO_2 or N_2O to give $[(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-O}]$ (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 $(\text{Me}_5\text{C}_5)_2\text{Ln}$ (Ln = Sm [1,2] and Yb [3,4]) and the triscyclopentadienyl uranium complexes $(\text{RC}_5\text{H}_4)_3\text{U}$ (R = H, Me, SiMe_3) [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 $(\text{C}_5\text{Me}_5)_2\text{Ln}$ or $(\text{RC}_5\text{H}_4)_3\text{U}$ 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 $[(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-O}]$ (II), a rare example of an organouranium oxide complex.

Results and discussion

Synthesis of $[(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-O}]$ (II)

A green solution of the tris(trimethylsilylcyclopentadienyl) uranium $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}$ (I) in toluene immediately turned deep red on exposure to carbon dioxide (1 atm, 20°C) and after 3 h red microcrystals of $[(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{U}]_2[\mu\text{-O}]$ (II) had

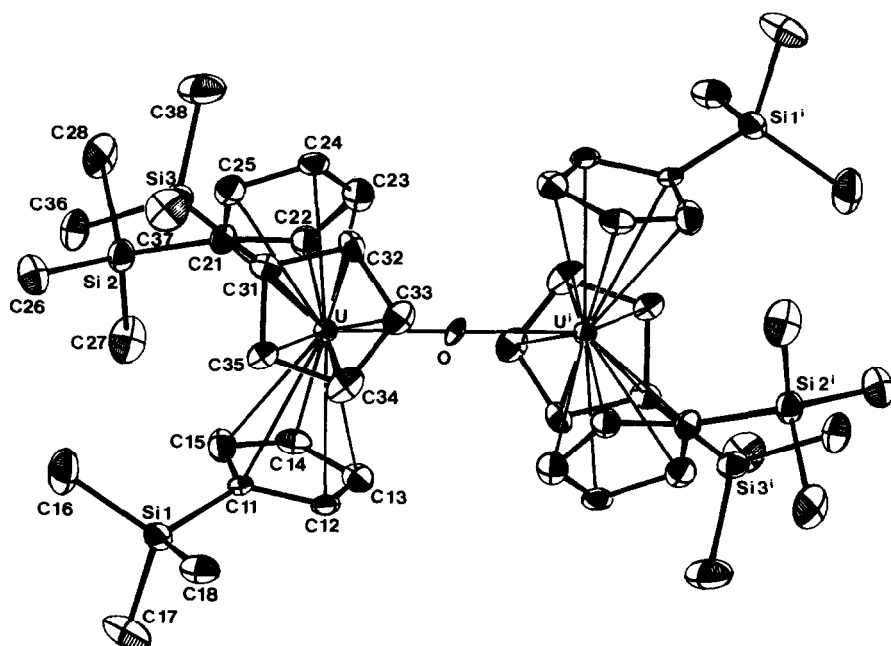


Fig. 1. Perspective view of molecule II. Atoms labelled with *i* and those unlabelled are related by an inversion centre.

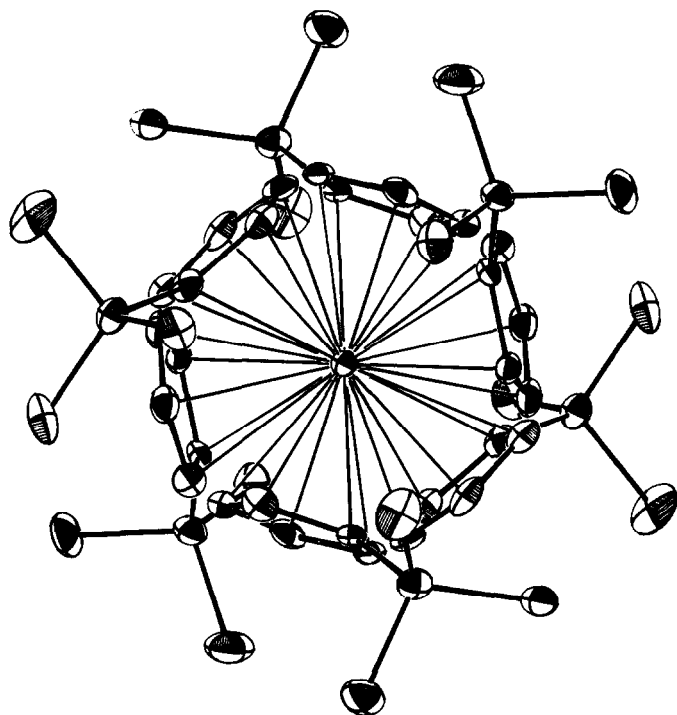


Fig. 2. View of molecule II along the U-O-U axis.

Table 1

Selected bond distances (Å) and angles (°)

<i>U environment</i>					
U-C(11)	2.858(5)	U-C(21)	2.874(6)	U-C(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)	U-C(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)		
O-U-3	100.4(5)	2-U-3	117.7(5)		
<i>Cyclopentadienyl ligands</i>					
⟨C-C⟩	1.41(2)	⟨Si-C(ring)⟩	1.87(1)	⟨Si-C(Me)⟩	1.86(1)
⟨C-C-C⟩	108(1)	⟨C-Si-C⟩	109(4)		

^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 [(C₉H₇)UBr(MeCN)₄]₂[μ-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 Oπ → 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 [(Me₃SiC₅H₄)₃U]₂[μ-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, CO₂ or N₂O 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. CO₂ and N₂O (Air Liquide) were used without purification and (Me₃SiC₅H₄)₃U was prepared as described previously [6].

[(Me₃SiC₅H₄)₃U]₂[μ-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

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, CH_3), -10.04 and -20.53 (s, $w_{1/2}$ 18 Hz, 2H + 2H, CH). ^{13}C NMR (THF- d_8 , 30°C): 112 and 103 (d, J 170 Hz, CH), 5.82 (q, J 120 Hz, CH_3). Analysis. Found: C, 43.72; H, 5.79; Si, 12.45; U, 35.20. $\text{C}_{48}\text{H}_{78}\text{Si}_6\text{OU}_2$ 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 N_2O (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 μl 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)
b (Å)	18.337(5)
c (Å)	15.881(2)
β (°)	104.43(2)
V (Å ³)	2733(1)
Z	2
D_{calc} (g cm ⁻³)	1.599
$\mu(\text{Mo-K}\alpha)$ (cm ⁻¹)	57.71
Radiation	Mo- K_α (λ 0.71073 Å)
θ limits (°)	1, 23
Scan type	$\omega/2\theta$
Scan width (°)	0.8 + 0.35 (tan θ)
Range abs. 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 $I > 3\sigma(I)$	2417
Final values	
$R(F) = \sum F_o - F_c / \sum F_o $	0.031
$Rw(F) = [\sum w[\sum F_o - F_c]^2 / \sum w F_o ^2]^{1/2}$	0.041
Max shift/esd	0.01
Max residual e/Å ³	0.61

the red solution exhibited resonances attributed to free $\text{Me}_3\text{SiC}_5\text{H}_4\text{Li}$ (5.65 and 0.0 ppm) and $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UMe}$ (ca. 45%). $\delta(\text{THF-}d_8, 30^\circ\text{C})$: +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 $(\text{Me}_3\text{SiC}_5\text{H}_4)_3\text{UCl}$ [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	y	z	$B (\text{\AA}^2)^a$
U	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)
O	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 $B_{\text{eq}} = 4/3 \sum_i \sum_j \beta_{ij} \mathbf{a}_i \mathbf{a}_j$.

and anisotropic thermal parameters were refined by full matrix least squares. Hydrogen atoms, introduced at calculated positions ($C-H = 0.95 \text{ \AA}$, $B = 6 \text{ \AA}^2$) 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.

References

- 1 W.J. Evans, T.A. Ulibarri and J.W. Ziller, *J. Am. Chem. Soc.*, 112 (1990) 219 and 2314; M.J. Evans and D.K. Drummond, *ibid.*, 111 (1989) 3329 and references therein; R.G. Finke, S.R. Keenan, D.A. Shiraldi and P.L. Watson, *Organometallics*, 6 (1987) 1356.
- 2 M.J. Evans, J.W. Grate, I. Bloom, W.E. Hunter and J.L. Atwood, *J. Am. Chem. Soc.*, 107 (1985) 405 and references cited.
- 3 D.J. Berg, R.A. Andersen and A. Zalkin, *Organometallics*, 7 (1988) 1858; R.A. Finke, S.R. Keenan and P.L. Watson, *ibid.*, 8 (1989) 263; G.B. Deacon and D.L. Wilkinson, *Inorg. Chim. Acta*, 142 (1988) 155.
- 4 D.J. Berg, C.J. Burns, R.A. Andersen and A. Zalkin, *Organometallics*, 8 (1989) 1865.
- 5 R.K. Rosen, R.A. Andersen and N.M. Edelstein, *J. Am. Chem. Soc.*, 112 (1990) 4588; S.D. Stults, R.A. Andersen and A. Zalkin, *Organometallics*, 9 (1990) 1623; C. Villiers and M. Ephritikhine, *J. Organomet. Chem.*, 393 (1990) 339; J.G. Brennan and R.A. Andersen, *J. Am. Chem. Soc.*, 107 (1985) 514.
- 6 J.G. Brennan, R.A. Andersen and A. Zalkin, *Inorg. Chem.*, 25 (1986) 1756.
- 7 J.G. Brennan, R.A. Andersen and A. Zalkin, *Inorg. Chem.*, 25 (1986) 1761.
- 8 F. Bottomley and I.J.B. Lin, *J. Chem. Soc., Dalton Trans.*, (1981) 271.
- 9 H. Schumann, E. Palamidis and J. Loebel, *J. Organomet. Chem.*, 384 (1990) C49.
- 10 W. Beeckman, J. Goffart, J. Rebizant and M.R. Spirlet, *J. Organomet. Chem.*, 307 (1986) 23.
- 11 F. Baumgartner, E.O. Fischer and B. Kanellakopoulos, in T.J. Marks and R.D. Fischer (Eds.), *Organometallics of the f-Elements*, Reidel Publ. Co., Dordrecht, The Netherlands, 1979.
- 12 D.C. Sonnenberger, E.A. Mintz and T.J. Marks, *J. Am. Chem. Soc.*, 106 (1984) 3484; A.L. Ardini, J.D. Jamerson and J. Takats, *Inorg. Chem.*, 20 (1981) 2474.
- 13 G. Fachinetti, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Am. Chem. Soc.*, 101 (1979) 1767.
- 14 C.K. Johnson (1976) ORTEP II Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, U.S.A.
- 15 F.A. Cotton, D.O. Marler and W. Schwotzer, *Inorg. Chem.*, 23 (1984) 4211.
- 16 N. Walker and D. Stuart, *Acta Cryst. A*, 39 (1983) 158.
- 17 International Tables for X-ray Crystallography, 1974, Vol. IV Kynoch Press, Birmingham (Present distributor Kluwer Academic Publishers, Dordrecht, The Netherlands).
- 18 B.A. Frenz, 1985, Structure Determination Package: SDP User's Guide, version of 17 December 1986, College Station, Texas 77840, USA, and Enraf-Nonius, Delft, The Netherlands.