Synthesis and Characterization of New Mixed Allyl–alkoxo-complexes of Uranium(IV). The Crystal and Molecular Structure of Di-μ-isopropoxo-bis[di(η-allyl)isopropoxouranium(IV)] †

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New complexes of general formula $[U(\eta\text{-}C_3H_5)_2(OR)_2]$ [R = Et (1), Pr^i (2), or Bu^t (3)] have been prepared by reaction of $[U(\eta\text{-}C_3H_5)_4]$ with ROH. The crystal structure of (2) has been determined from single-crystal *X*-ray diffraction data (Mo-K_α radiation). The complex crystallizes in the space group $P2_1/c$ with unit-cell dimensions a = 12.324(7), b = 8.535(1), c = 17.897(9) Å, β = 126.71(3)°, Z = 4, and R 0.030 for 1 408 independent observations. In the dimeric molecular structure, with $\bar{1}$ crystallographic site symmetry, two uranium atoms are joined by two alkoxide bridges. The co-ordination polyhedron of the uranium can be regarded as a distorted pentagonal bipyramid, whose equatorial plane is defined by the terminal carbons of the η-allyl ligands and by a bridging oxygen. The axial positions of the bipyramid are occupied by the remaining bridging oxygen and by a terminal oxygen. The latter shows a linear co-ordination [U–O–C 178.0(10)°]. Other relevant bond distances are: U–O(bridging) 2.271(10) and 2.413(10); U–O(terminal) 2.056(13); and U–C(mean) 2.679(14) Å. Infrared data for (1)—(3) suggest that the uranium–allyl π bond is predominantly ionic; this is consistent with some structural peculiarities of the allyl ligands in (2). Hydrogen-1 n.m.r. results indicate monomeric structures in tetrahydrofuran [(1)—(3)] and dimeric ones in toluene solution for (1) and (2).

THE synthesis of tetra-allyluranium $[U(\eta\text{-}C_3H_5)_4]$, and its performance as a catalyst for the homogeneous polymerization of diolefins, have been previously reported.[1] Uranium alkoxides, however, more readily available and more stable than the tetra-allyluranium derivatives, in combination with AlR_3 and a Lewis acid give very active and highly stereospecific catalysts.[2] In this case, we believe that a η-allyl intermediate is formed '*in situ*' when the catalyst is prepared in the presence of the monomer. In order to verify this hypothesis, the synthesis of mixed allyl–alkoxo-complexes of uranium was attempted. Complexes of this type have never been described, either for the actinoid metals or more generally for transition metals, with the exception of the derivative $[\{Ni(\eta\text{-}C_3H_5)(OEt)\}_2]$ reported by Wilke.[3]

This paper reports the preparation and spectroscopic and *X*-ray characterization of novel complexes of general formula $[U(\eta\text{-}C_3H_5)_2(OR)_2]$. The crystal structure of $[\{U(\eta\text{-}C_3H_5)_2(OPr^i)(\mu\text{-}OPr^i)\}_2]$ reported here is the first example of an *X*-ray analysis of a mixed allyl–alkoxo-complex, and also of an η-allyl derivative of an actinoid element.

EXPERIMENTAL

All operations were carried out under dry oxygen-free nitrogen. Solvents and alcohols were dried by conventional methods and distilled immediately prior to use. Tetra-allyluranium was obtained as previously reported.[1a] Infrared spectra were recorded with Perkin-Elmer 125 and 225 spectrophotometers and calibrated with polystyrene film. Nujol mulls were prepared in a nitrogen-filled sleeve with dry degassed Nujol. Hydrogen-1 n.m.r. spectra were recorded with a Varian XL 100. Chemical shifts were measured with an internal locking signal on a Hewlett-Packard electronic counter. Chemical shifts of high-field signals were calibrated by measuring the distance to the signal from an internal standard.

Synthesis of Uranium Tetra-alkoxides.—To a solution of $[U(\eta\text{-}C_3H_5)_4]$ in diethyl ether at −30 °C was added dropwise a solution of the appropriate alcohol (1 : 5 mol ratio) in diethyl ether. The mixture was allowed to warm to room temperature, and the green precipitate was filtered off and dried *in vacuo*. In the reaction with Bu^{t}OH, the product was recovered by evaporation of the final solution to dryness, followed by recrystallization from toluene {Found: U, 56.2. $[U(OEt)_4]$ requires U, 56.9. Found: U, 50.6. $[U(OPr^i)_4]$ requires U, 50.2. Found: U, 44.5. $[U(OBu^t)_4]$ requires U, 44.9%}.‡

Syntheses.—$[U(\eta\text{-}C_3H_5)_2(OEt)_2]$ (1). Ethanol (2.33 cm^3, 0.04 mol) in hexane was added dropwise to a solution of $[U(\eta\text{-}C_3H_5)_4]$ (8.04 g, 0.02 mol) in hexane (130 cm^3) at −30 °C. The reaction mixture was stirred for 8 h at the same temperature, then the solution was allowed to warm to 0 °C and cooled again at *ca.* −78 °C. Dark brown crystals were slowly formed. The mother liquid was removed at *ca.* −78 °C and the residue recrystallized from pentane or diethyl ether (maximum temperature 0 °C), yield 6.0 g [Found: U, 57.2. (1) requires U, 58.0%].

The complex $[U(\eta\text{-}C_3H_5)_2(OPr^i)_2]$ (2) was prepared by the same procedures as light brown crystals, yield 78% [Found: U, 53.8. (2) requires U, 54.3%].

$[U(\eta\text{-}C_3H_5)_2(OBu^t)_2]$ (3). t-Butyl alcohol (3.5 cm^3, 0.037 mol) in diethyl ether (20 cm^3) was added dropwise to a stirred solution of $[U(\eta\text{-}C_3H_5)_4]$ (7.4 g, 0.018 mol) in diethyl ether (60 cm^3) at −20 °C. The red-brown solution was stirred at −10 °C for 2 d (a black residue may be formed which must be filtered off). The solution was evaporated to dryness, and the residue washed with hexane (50 cm^3) on a glass filter and dried *in vacuo*. The resulting pale green solid was purified by dissolution in diethyl ether and precipitation with hexane, yield 5.2 g [Found: U, 50.4. (3) requires U, 51.1%].

Gas-volumetric Analysis.—Hydrolyses were carried out in a gas-volumetric apparatus by decomposing the sample with diglyme–water (1 : 5). The gas was collected, measured, and analysed by g.l.c. The yields of propylene, uncorrected for the solubility of the gas in the solvent mixture, were 95 (1), 93 (2), and 92% (3).

Hydrolysis.—The alkoxide content was determined by

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‡ For all complexes, C and H analyses were constantly low by 10—15%. This feature seems to be peculiar to uranium organometallic compounds.[4]

hydrolysis of the sample with dioxan–water (5 : 1) in a sealed apparatus. The liquid was transferred *in vacuo* and analyzed by g.l.c. for the alcohol content. The yields of alcohol were 90 (1), 92 (2), and 93% (3).

Thermal Decomposition.—Thermolysis was carried out in a gas-volumetric apparatus *in vacuo*. The sample was warmed by a thermostatic bath until the gas evolution was complete. The gas was then collected, measured at room temperature, and analyzed by g.l.c. The results are in Table 1.

TABLE 1

Thermolysis data

Complex	t/h	θ_c/°C	Decomposition Products [amount/mmol (g atom U)$^{-1}$]
[U(η-C_3H_5)$_2$(OEt)$_2$]	3 [a]	115	Propylene (1.32) Propane (0.03) Ethylene (0.04) Ethane (0.08) C_5, C_6 hydrocarbons (0.01)
[U(η-C_3H_5)$_2$(OPr^i)$_2$]	3 [a]	115	Propylene (1.30) Propane (0.27) C_6 hydrocarbons (0.10)
[U(η-C_3H_5)$_2$(OBu^t)$_2$]	3 [b]	115	Propylene (0.98) Propane (0.09) 2-Methylpropene (0.30) Isobutane (0.10) C_6 hydrocarbons (0.08)
	3 [a]	115	Propylene (1.03) Propane (0.12) 2-Methylpropene (0.36) Isobutane (0.13) C_6, C_7 hydrocarbons (0.03)
	3 [a]	170	Propylene (0.85) Propane (0.17) 2-Methylpropene (0.79) Isobutane (0.20) C_6, C_7 hydrocarbons (0.06)

[a] Without solvent. [b] In dry vaseline oil.

X-*Ray Analysis.*—Crystals of (2) were sealed in thin-walled glass capillaries under an inert atmosphere. Weissenberg photographs showed monoclinic symmetry with systematic absences consistent with space group $P2_1/c$. The unit-cell parameters were refined by a least-squares fit of the setting angles of 23 reflections, measured on the diffractometer.

Crystal data. $(C_{12}H_{24}O_2U)_2$, $M = 876.8$, Monoclinic, $a = 12.324(7)$, $b = 8.535(1)$, $c = 17.897(9)$ Å, $\beta = 126.71(3)°$, $U = 1\,509.1$ Å^3, $Z = 2$, D_c (at 6 °C) $= 1.929$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu = 160.9$ cm^{-1}, space group $P2_1/c$.

Intensities were collected from a crystal of dimensions 0.15 × 0.08 × 0.35 mm, mounted with the b axis parallel to the spindle axis of a computer-operated Siemens AED diffractometer; zirconium-filtered Mo-K_α radiation was used. The crystal was bounded by the planes (100), $(10\bar{2})$, $(\bar{1}00)$, $(\bar{1}02)$, $(12\bar{2})$, (010), $(1\bar{2}\bar{2})$, and $(\bar{1}\bar{1}2)$. Because of the low stability of the complex at room temperature, the temperature of the sample was lowered to 6 °C during the collection of the intensities, by a stream of precooled dry nitrogen. The temperature, which was measured by means of a thermocouple adjacent to the crystal, fluctuated within ±2 °C during the run. A total of 2 968 reflections was measured up to $\theta = 26°$, with the θ—2θ scan method and 'five-points' technique.[5] 1 408 Reflections, having $I > 3\sigma(I)$, were classed as observed and were used in the structure determination. A standard reflection, measured every 15 reflections, showed that the intensity decay was *ca.* 5% at the end of data collection. Intensities were corrected for this effect by means of a simple linear interpolation. Absorption corrections were applied;[6] the transmission factors ranged from 0.16 to 0.33.

Structure determination and refinement. The structure was solved by the application of heavy-atom techniques. Full-matrix least-squares refinements on F were performed in which the function minimized was $\Sigma w(F_o - F_c)^2$; Cruickshank's weighting scheme[7] was used. Neutral scattering factors were from ref. 8 for non-hydrogen atoms and from ref. 9 for hydrogen. The calculations included both $\Delta f'$ and $\Delta f''$ corrections for anomalous dispersion effects on the uranium atom.[10] With the exception of ORTEP,[11] all the computer programs used were written by Immirzi.[12]

The hydrogen atoms were located from a difference-Fourier map: for some of them, slight adjustments of the positions were necessary according to the usual planar or tetrahedral geometry of the carbon atoms. The anisotropic refinement, including fixed contributions of the hydrogen atoms in the calculation of the structure factors, converged to a standard unweighted R factor of 0.033. Refinement of the positional and thermal parameters of the hydrogen atoms was subsequently performed in additional cycles with a damping factor of 0.5, which led to the final unweighted R of 0.030. The final difference-Fourier synthesis showed no peaks >0.8 e Å^{-3}, which were not due to residual peaks around the uranium atom. The final positional parameters are listed in Table 2. Thermal

TABLE 2

Atomic fractional co-ordinates for [{U(η-C_3H_5)$_2$(OPr^i)$_2$}$_2$]

Atom	x	y	z
U	0.137 27(3)	−0.006 38(4)	−0.020 13(2)
O(1)	−0.070 4(6)	0.088 8(7)	−0.075 9(4)
O(2)	0.320 7(7)	−0.119 7(8)	0.051 3(5)
C(1)	−0.140 9(10)	0.190 8(11)	−0.156 6(6)
C(2)	−0.273 8(12)	0.112 3(16)	−0.234 9(7)
C(3)	−0.163 8(11)	0.350 9(13)	−0.131 1(8)
C(4)	0.444 7(14)	−0.202 4(18)	0.100 7(13)
C(5)	0.560 6(12)	−0.092 3(18)	0.145 1(10)
C(6)	0.440 9(16)	−0.335 3(21)	0.048 8(15)
C(7)	0.025 4(13)	−0.268 6(13)	−0.120 9(9)
C(8)	0.028 4(20)	−0.168 1(20)	−0.176 2(10)
C(9)	0.094 0(16)	−0.067 1(17)	−0.181 8(9)
C(10)	0.231 6(17)	0.246 9(15)	−0.048 5(11)
C(11)	0.240 5(25)	0.286 3(16)	0.023 5(14)
C(12)	0.271 2(15)	0.237 7(14)	0.101 1(10)
H(1)	−0.104(8)	0.225(9)	−0.190(6)
H(21)	−0.236(10)	0.003(10)	−0.242(8)
H(22)	−0.331(10)	0.171(11)	−0.292(7)
H(23)	−0.347(9)	0.092(11)	−0.224(6)
H(31)	−0.095(7)	0.400(8)	−0.090(5)
H(32)	−0.216(10)	0.365(11)	−0.113(6)
H(33)	−0.208(8)	0.426(10)	−0.185(6)
H(4)	0.455(11)	−0.276(13)	0.169(8)
H(51)	0.535(16)	−0.009(14)	0.172(11)
H(52)	0.503(15)	−0.103(19)	0.071(10)
H(53)	0.628(13)	−0.160(16)	0.172(9)
H(61)	0.345(11)	−0.399(14)	0.031(7)
H(62)	0.494(13)	−0.393(17)	0.065(9)
H(63)	0.400(13)	−0.283(14)	−0.003(9)
H(71)	−0.042(10)	−0.312(11)	−0.121(7)
H(72)	0.126(8)	−0.304(9)	−0.046(5)
H(8)	−0.043(12)	−0.179(14)	−0.210(8)
H(91)	0.077(10)	−0.018(10)	−0.220(7)
H(92)	0.173(15)	−0.052(16)	−0.142(10)
H(101)	0.222(14)	0.282(16)	−0.079(10)
H(102)	0.270(11)	0.176(14)	−0.049(8)
H(11)	0.197(18)	0.338(23)	0.005(12)
H(121)	0.246(9)	0.256(10)	0.128(6)
H(122)	0.333(10)	0.169(12)	0.127(7)

parameters and structure-factor tables are available as Supplementary Publication No. SUP 22434 (14 pp.).*

RESULTS AND DISCUSSION

The title complexes are formed according to equation (1) [R = Et(1), Pr^i(2), or Bu^t(3)] in generally high yield (60—80%). Except for Bu^tOH, an excess of the alcohol

$$[U(\eta\text{-}C_3H_5)_4] + 2\ ROH \longrightarrow [U(\eta\text{-}C_3H_5)_2(OR)_2] + 2\ C_3H_6 \quad (1)$$

should be avoided in order to prevent the formation of the tetra-alkoxo-derivatives. With Bu^tOH in hexane, (3) was the only product observed, probably because of the low solubility of the desired product in the reaction medium. The fast alcoholysis of $[U(\eta\text{-}C_3H_5)_4]$ in diethyl ether is consistent with reports by Gilman [13a] concerning the reaction of uranium(IV) amides with alcohols: in both cases, tetra-alkoxo-derivatives are easily obtained. We confirm that $[U(OBu^t)_4]$, whose isolation was subsequently questioned,[13b] is the reaction product from $[U(\eta\text{-}C_3H_5)_4]$ and Bu^tOH. The new complexes (1)—(3) are extremely sensitive to air and moisture: (1) and (2) are relatively unstable thermally, decompose in a few days at room temperature, and must be stored at −20 °C; (3) however, does not decompose at room temperature under nitrogen. The three complexes are soluble in polar inert solvents; (1) and (2), but not (3), are soluble in hydrocarbon solvents. This is surprising since the solubility of the alkoxo-derivatives usually increases with the bulkiness of the R group.[13a,c] The reason for this unexpected behaviour, probably related to a dramatic structural change, could not be explored since single crystals of (3) were unobtainable and n.m.r. investigations were possible only in polar solvents, which probably promote a breakdown of the polymeric structure.

TABLE 3

Least-squares planes for $[\{U(\eta\text{-}C_3H_5)_2(OPr^i)_2\}_2]$ in the form $Ax + By + Cz - D = 0$ (x, y, and z are the crystallographic fractional co-ordinates) and deviations (Å) of the atoms from these planes in square brackets

Plane (1):
U, C(7), C(9)
$-9.438x + 3.572y + 1.187z + 1.343 = 0$

Plane (2):
C(7), C(8), C(9)
$-8.335x + 5.992y + 10.438z + 3.083 = 0$
[H(71) 0.30, H(72) −0.27, H(8) 0.18, H(91) 0.04, H(92) −0.15, U 1.69]

Plane (3):
U, C(10), C(12)
$-9.778x + 3.958y + 2.832z + 1.425 = 0$

Plane (4):
C(10), C(11), C(12)
$-10.440x - 2.420y + 2.615z + 3.142 = 0$
[H(101) −0.06, H(102) −0.23, H(11) 0.28, H(121) 0.30, H(122) −0.41, U 1.67]

Plane (5):
U, U′, O(1), O(1′)
$1.340x + 6.986y + 6.930z = 0$
[C(1) 0.06, C(2) −1.21, C(3) 1.32, O(2) −0.05, C(4) −0.12, C(5) 1.11, C(6) −1.41, C(7) −2.68, C(12) 2.72, C(8) −2.36, C(11) 2.48, C(9) −1.60, C(10) 1.70]

Angles (°) between planes:

(1)–(2)	134.6	(3)–(4)	135.9

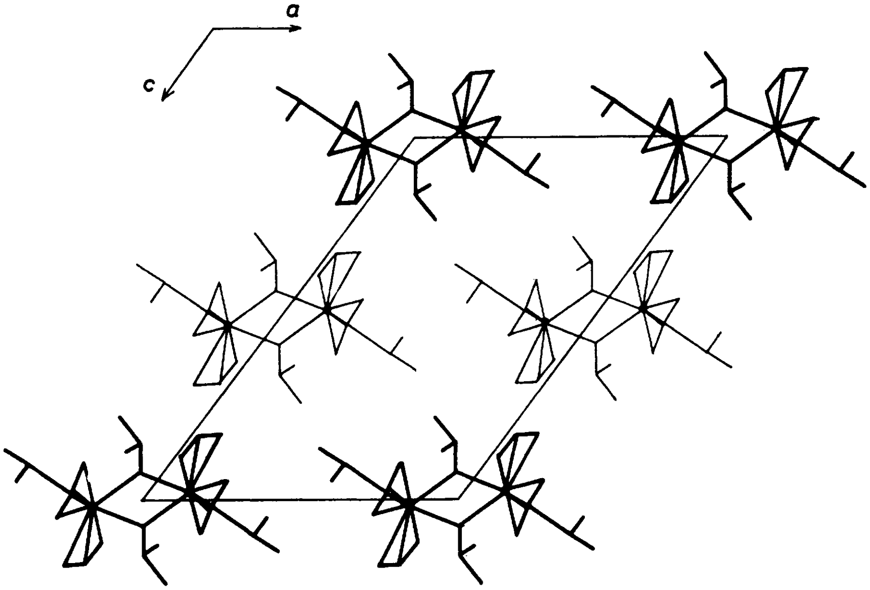

FIGURE 1 Molecular packing of $[\{U(\eta\text{-}C_3H_5)_2(OPr^i)_2\}_2]$ projected down the b axis

The crystal structure of (2) is built up of $[\{U(\mu\text{-}C_3H_5)(OPr^i)(\mu\text{-}OPr^i)\}_2]$ dimers with $\bar{1}$ crystallographic site symmetry. No critical intermolecular non-bonded interactions were observed, the minimum C · · · C distance being 3.86 Å. A schematic drawing of the crystal packing is shown in Figure 1. Within each dimeric unit the two metal atoms are bridged by the oxygen atoms of two isopropoxide-groups, forming a

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

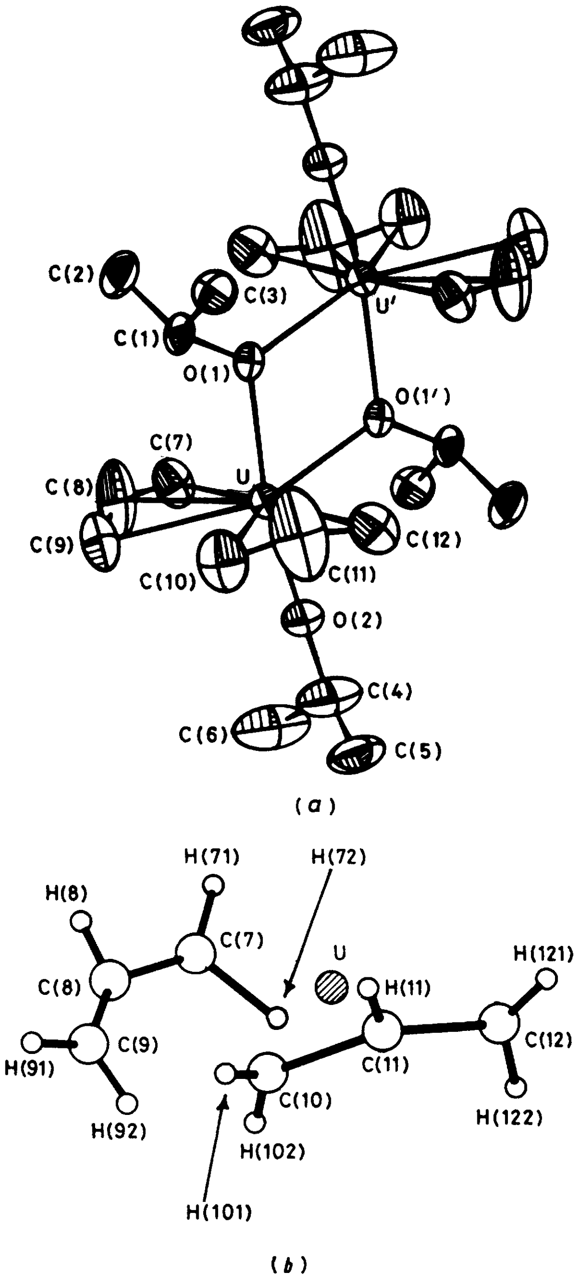


FIGURE 2 (*a*) Perspective view of the molecular structure of the $[\{U(\eta\text{-}C_3H_5)_2(OPr^i)_2\}_2]$ dimer. (*b*) View of the allyl groups around the uranium atom, including hydrogen atoms. The U–C bonds are not shown

planar four-membered ring $(UO)_2$ [see Figure 2(*a*)]. Moreover, the alkoxide and the allyl groups are so arranged that the plane of the $(UO)_2$ ring behaves practically as a pseudo-mirror plane, with the two allyl groups placed on opposite sides of it (see Table 3).

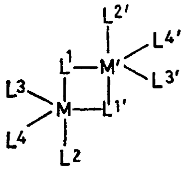
The co-ordination polyhedron around the uranium atom could be regarded as a distorted trigonal bipyramid, with O(1) and O(2) in the axial positions (considering the allyls as unidentate ligands), or as a distorted pentagonal bipyramid in which the equatorial irregular pentagon is defined by the allylic terminal carbon atoms and the oxygen O(1′). Similar structural features have been reported for $[\{TiCl_2(OPh)_2\}_2]$,[14] which contains both bridging and terminal phenoxide groups. Both terminal and bridging nitrogen atoms have also been found in the structure of $[\{U(NEt_2)_4\}_2]$.[15] In the latter complex, as well as in $[\{TiCl_2(OPh)_2\}_2]$, the axial bridge bond is lengthened with respect to the equatorial one (see Table 4); this is to be expected because of the trigonal-bipyramidal co-ordination of the metal atom. The opposite trend is observed in our complex: the axial U–O(1) bridge-bond distance [2.271(10) Å] is significantly shorter than the equatorial U–O(1′) [2.413(10) Å]. This feature fits a pentagonal-bipyramidal co-ordination [16] of the uranium atom better than a trigonal bipyramidal one.

The bridging oxygen O(1) appears to be sp^2 hybridized since it is bonded to C(1) and to the uranium with a planar co-ordination. The linear co-ordination of the terminal oxygen O(2), with the angle U–O(2)–C(4) 178.0(10)°, suggests *sp* hybridization. Values close to 180° have been reported for the Ti–O–C bond angle in $[\{TiCl_2(OPh)_2\}_2]$ [165.9(6)°] [14] and in $[\{Ti(OMe)_4\}_4]$ (161°).[17] The U–O(2) bond length [2.056(13) Å] is shorter than the U–O bridge bonds. Because of the apparent *sp* and sp^2 hybridizations of the oxygens, a π contribution of the lone pairs of the oxygen atoms to the U–O bonds can be postulated particularly for U–O(2): this is consistent with $[\{Ti(OMe)_4\}_4]$.[13c] The U–O distances are quite close to those that would be predicted from $[\{TiCl_2(OPh)_2\}_2]$,[14] if the difference between the ionic radii of U^{4+} and Ti^{4+}, *ca.* 0.3 Å, [18] and the inversion concerning the axial and the equatorial bridge bonds (see above) are taken into account (see Table 4). The i.r. absorption bands relative to the alkoxide ligands of (1)—(3) are reported in Table 5, together with those of the tetra-alkoxo-derivatives. The assignments were based on a comparison with the i.r. spectra of the corresponding tetra-alkoxouranium(IV) derivatives and the literature data of other alkoxide-bridged systems.[19a,b] The bands at 1 025—1 065 cm^{-1} in (1), at 990 cm^{-1} in (2), and at 950 cm^{-1} in (3) can be tentatively assigned to the C–O stretching vibration. No other assignments were attempted concerning the alkoxide bands; moreover, no distinction could be made between the bridging and terminal groups based on ligand vibrations.

The arrangement of the allyl groups with respect to the metal atom is symmetric. The U–C bond distances range from 2.644(16) to 2.736(18) Å (see Table 6); the mean value is 2.679(14) Å, which compares well with the U–C distances observed in η-cyclopentadienyl (2.68—2.80 Å)[20] and η-cyclo-octatetraenyl [2.647(4)[21] and 2.658(6) Å (ref. 22)] complexes of uranium. The allyl groups are not planar: in both independent ligands the *anti*-hydrogens H(72), H(92), H(102), and H(122) are considerably bent out of the three-carbon plane away from the metal, in the range of 0.15—0.41 Å. On the other hand, the other hydrogens deviate in the opposite sense (in the range 0.18—0.30 Å), with the exception of H(91) and H(101) which lie practically in the plane of the car-

TABLE 4

Comparison between geometrical parameters of [{U(η-C_3H_5)$_2$(OPr^i)$_2$}$_2$] and other complexes of similar molecular structure



Complex	L^1, L^2	M–L^1	M–$L^{1'}$	M–L^2	L^1–M–L^2	Ref.
[{(U(η-C_3H_5)$_2$(OPr^i)$_2$}$_2$]	O	2.271(10)	2.413(10)	2.056(13)	166.8(16)	This work
[{$TiCl_2$(OPh)$_2$}$_2$]	O	2.122(9)	1.910(9)	1.744(10)	167.0(3)	14
[{U(NEt_2)$_4$}$_2$]	N	2.57(1)	2.46(1)	2.24(1)	167.1(3)	15

bon atoms [see Table 3 and Figure 2 (*b*)]. It is interesting that similar trends have been observed in methyl-substituted η-allyl derivatives.[23] The allyl portions of the molecule are quite different from the η-allyl complexes of transition metals: the dihedral angle between the plane defined by the three-carbon allyl skeleton and the plane defined by the uranium and the allylic terminal carbon atoms is 134.6 and 135.9° for the two ligands.

TABLE 5

Characteristic i.r. bands (cm^{-1})

Complex		
[U(OEt)$_4$]		2 695w, 1 350w, 1 120s, 1 090vw, 1 070s, 1 030s, 905m, 880m
[U(OPr^i)$_4$]		2 620w, 1 360w, 1 330w, 1 160s, 1 130s, 995s, 980s, 950m, 835m, 825m, 805w
[U(OBu^t)$_4$]		1 355m, 1 225w, 1 180m, 980w, 955s, 910w, 775w
[U(η-C_3H_5)$_2$(OEt)$_2$]	*a*	3 060w, 1 545m, 1 235m, 1 000m, 790m, 704m, 684m, 580s
	b	2 690w, 1 350w, 1 110vs, 1 065s, 1 025s, 905m, 880m
[U(η-C_3H_5)$_2$(OPr^i)$_2$]	*a*	3 060w, 1 546m, 1 230m, 1 010m, 795s, 725m, 694m, 580s
	b	1 360w, 1 330w, 1 160vs, 1 127s, 1 100m, 990s, 935m, 840m, 820m
[U(η-C_3H_5)$_2$(OBu^t)$_2$]	*a*	3 060w, 1 546m, 1 525m, 1 230s, 1 015m, 1 000m, 780s, 684m, 580s
	b	1 375m, 1 355m, 1 180s, 950s, 755w

[a] Allyl bands. [b] Alkoxide bands.

For transition-metal complexes the values reported are usually lower, in the range 100—110°.[24,25] Therefore, the mean U–C(terminal) and U–C(central) bond distances [2.681(20) and 2.675(24) Å] are practically identical, in contrast to transition-metal derivatives where the latter distances are usually shorter than the former.[24-26] These features, in addition to the probable pentagonal-bipyramidal co-ordination of the uranium atom, suggest that the central carbon atom is less involved in the allyl-to-metal interaction. The large thermal parameters found for the central carbon atoms C(8) and C(11) [see Figure 2(*a*)] are consistent with this view. Further, the geometry of the allyl groups deviates considerably from that usually found: the C–C bond distances [mean 1.27(2) Å] are short and the C–C–C bond angle [146.0(17) and 144.1(18)° for the two ligands] is notably greater than the usual value of 120°.[24,25] The apparent geometry, however, could be affected to some extent by the large thermal parameters found for the central carbon atoms.

The i.r. absorption bands relative to the allyl ligands of complexes (1)—(3) (see Table 5) are in agreement with those previously reported for [U(η-C_3H_5)$_4$].[1a] In our complexes an η^3 (C_{2v}) geometry of the allyl group rather than the σ is suggested by the absence of bands in the 1 600—1 620 cm^{-1} region and by the presence of bands at *ca.* 1 545, 1 010, and 580 cm^{-1}, assignable to the ν_{asym}(C–C–C), ν_{sym}(C–C–C), and δ(C–C–C) vibration modes, respectively. The ν_{asym}(C–C–C) and δ(C–C–C) frequencies occur at 100—140 cm^{-1} to higher wavenumber than the corresponding vibration modes for η-bonded transition-metal allyl complexes, which are decidedly covalent in character.[27a,b] On the other hand, the observed values agree with those reported by Sourisseau and Pasquier[28] for allyl derivatives of alkali metals where a metal–ligand bond predominantly ionic in character is postulated. For these complexes, based on the values of the observed frequencies, an allylic skeletal C–C–C bond angle of 140° has been

TABLE 6

Bond distances[a] (Å) and angles (°) for [{U(η-C_3H_5)$_2$(OPr^i)$_2$}$_2$]

(*a*) Uranium inner co-ordination sphere			
U–O(1)	2.271(10)	O(1)–U–O(2)	166.8(16)
U–O(1′)	2.413(10)	O(1)–U–O(1′)	69.0(2)
U–O(2)	2.056(13)	O(1′)–U–O(2)	97.9(2)
U–C(7)	2.682(14)	O(1′)–U–C(7)	88.8(2)
U–C(8)	2.651(24)	O(1′)–U–C(12)	87.6(2)
U–C(9)	2.661(21)	C(7)–U–C(9)	54.4(5)
U–C(10)	2.644(16)	C(10)–U–C(12)	53.4(5)
U–C(11)	2.698(19)	C(9)–U–C(10)	77.0(4)
U–C(12)	2.736(18)		
Mean U–C[b]	2.679(14)		
(*b*) Bridging alkoxide			
O(1)–C(1)	1.45(2)	U–O(1)–U′	111.0(2)
C(1)–C(2)	1.53(2)	U–O(1)–C(1)	120.0(9)
C(1)–C(3)	1.52(1)	U′–O(1)–C(1)	129.0(9)
		O(1)–C(1)–C(2)	109.0(7)
		O(1)–C(1)–C(3)	110.4(6)
		C(2)–C(1)–C(3)	112.3(6)
(*c*) Terminal alkoxide			
O(2)–C(4)	1.41(3)	U–O(2)–C(4)	178.0(10)
C(4)–C(5)	1.48(3)	O(2)–C(4)–C(5)	110.7(9)
C(4)–C(6)	1.45(2)	O(2)–C(4)–C(6)	112.4(9)
		C(5)–C(4)–C(6)	119.4(9)
(*d*) Allyl			
C(7)–C(8)	1.33(3)	C(7)–C(8)–C(9)	146.0(17)
C(8)–C(9)	1.23(3)	C(10)–C(11)–C(12)	144.1(18)
C(10)–C(11)	1.27(3)		
C(11)–C(12)	1.27(4)		
Mean C–C	1.27(2)		

[a] The values of the C–H bond distances range from 0.6 to 1.3 Å, with standard deviations ranging from 0.1 to 0.3 Å. [b] Standard deviations of the mean values, *s*, were calculated as $s^2 = \Sigma_1^n(x_i - \bar{x})^2/(n - 1)n$, where $\bar{x}$ is the mean of the x_i values, *n* their number.

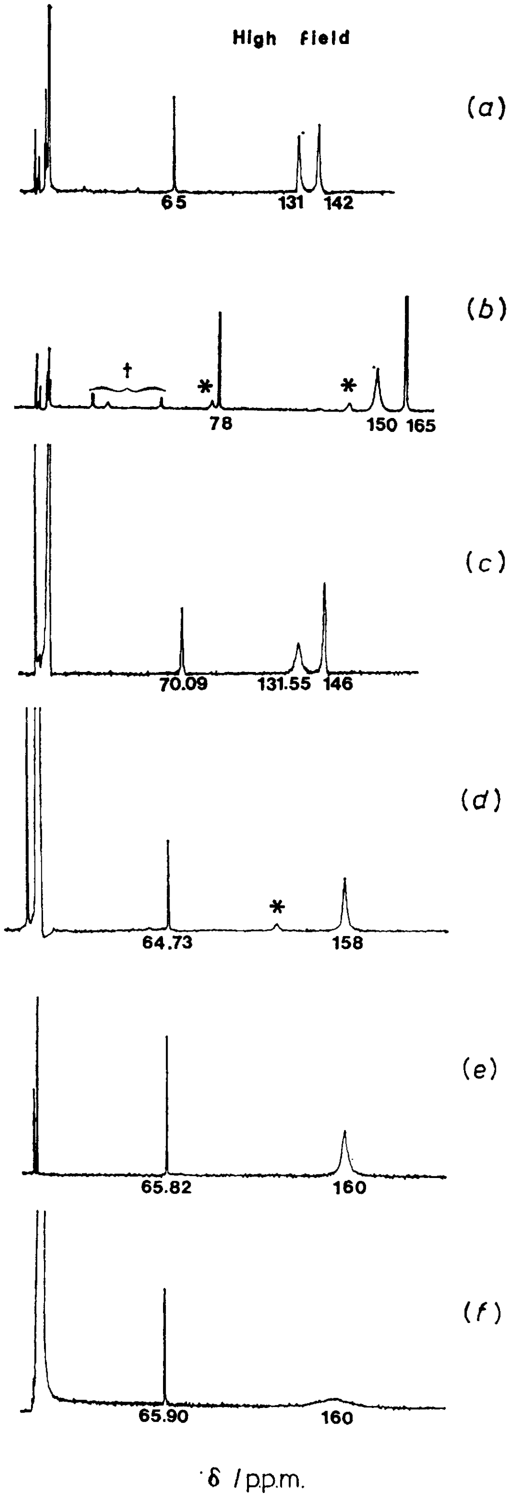


FIGURE 3 Hydrogen-1 n.m.r. spectra of the allyl portion of $[U(\eta\text{-}C_3H_5)_2(OEt)_2]$ (*a*), (*b*), (*d*); $[U(\eta\text{-}C_3H_5)_2(OPr^i)_2]$ (*c*), (*e*); $[U(\eta\text{-}C_3H_5)_2(OBu^t)_2]$ (*f*). Spectra (*a*)—(*c*) were recorded in toluene, (*d*)—(*f*) in thf at room temperature, except for (*b*) at −10 °C. The asterisks indicate unidentified species probably arising from a ligand redistribution. The mol ratio with respect to $[U(\eta\text{-}C_3H_5)_2(OEt)_2]$ ($3 \times 10^{-2} : 1$) did not change after several recrystallizations. The dagger represents $[U(\eta\text{-}C_3H_5)_4]$

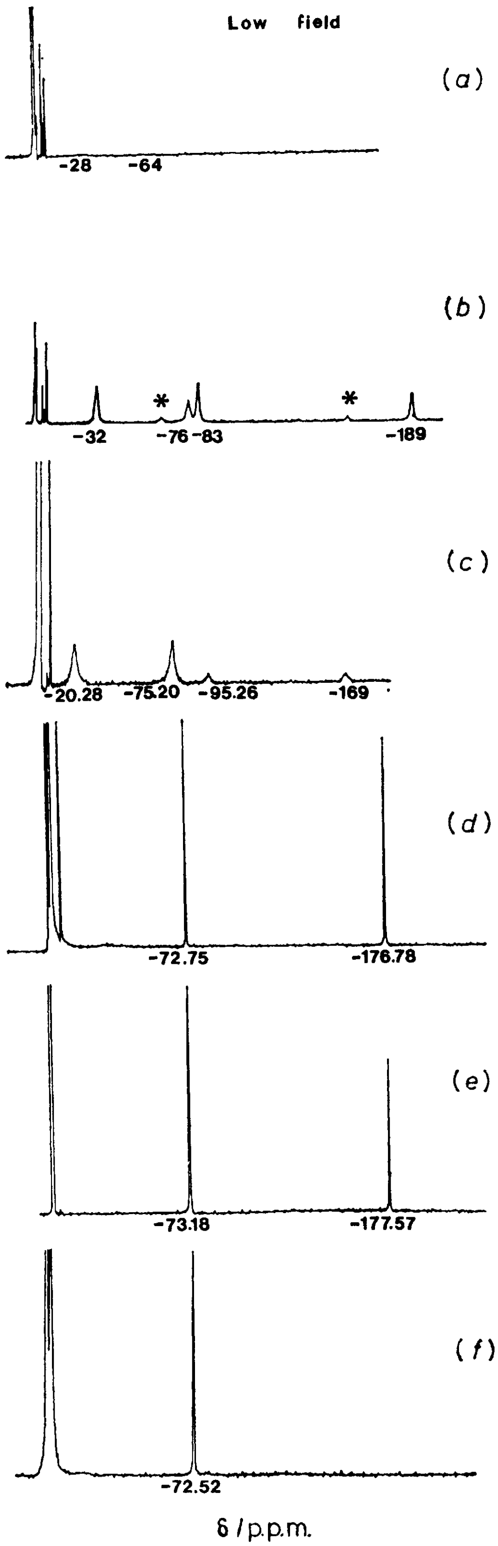


FIGURE 4 Hydrogen-1 n.m.r. spectra of the alkoxide portion of $[U(\eta\text{-}C_3H_5)_2(OEt)_2]$, $[U(\eta\text{-}C_3H_5)_2(OPr^i)_2]$, and $[U(\eta\text{-}C_3H_5)_2(OBu^t)_2]$. For details see Figure 3

calculated.[28] On the other hand, a value of 134° has been predicted for the same bond angle in allyl-lithium, on the basis of SCF studies.[29] The X-ray structural features discussed above for (2) are also consistent with a predominantly ionic uranium–allyl bond. In fact, when the allyl ligand is regarded as an anion, a negative charge located mainly on the terminal carbon atoms can be postulated; [29] the consequent repulsion between these atoms should tend to enlarge the C–C–C bond angle. Moreover, as a consequence of the different charge distribution on the ligand, stronger interaction between metal and terminal carbon atoms should be expected.

TABLE 7

Proton chemical shifts (in p.p.m. from $SiMe_4$) for (1)—(3) [a]

	Allyl		Alkoxide		
Complex	chemical shift [b]	assignment	chemical shift	assignment	Solvent
$[U(\eta\text{-}C_3H_5)_2(OEt)_2]$	65	CH(2) [c]	−28	$CH_3(3)$	$[^2H_8]$Toluene
	131	$CH_2(4)$	−64	$CH_3(3)$	
	142	$CH_2(4)$			
	78	CH(2)	−32	$CH_3(3)$ [d]	$[^2H_8]$Toluene at −10 °C
	150	$CH_2(4)$	−76	$CH_2(2)$ [d]	
	165	$CH_2(4)$	−83	$CH_3(3)$	
			−189	$CH_2(2)$	
	64.73	CH(1)	−72.75	$CH_3(3)$	$[^2H_8]$thf [e]
	142	$CH_2(4)$	−176.78	$CH_2(2)$	
$[U(\eta\text{-}C_3H_5)_2(OPr^i)_2]$	70.09	CH(2)	−20.28	$CH_3(6)$ [d]	$[^2H_8]$Toluene
	131.55	$CH_2(4)$	−75.20	$CH_3(6)$	
	146	$CH_2(4)$	−95.26	CH(1) [d]	
			−169	CH(1)	
	65.82	CH(1)	−73.18	$CH_3(6)$	$[^2H_8]$thf [e]
	160	$CH_2(4)$	−177.57	CH(1)	
$[U(\eta\text{-}C_3H_5)_2(OBu^t)_2]$	65.90	CH(1)	−72.52	$CH_3(9)$	thf [e]
	160	$CH_2(4)$			

[a] Data referred to room temperature unless otherwise indicated. [b] Integer values measured in HR mode, error ±2 p.p.m. [c] Relative peak areas on which assignments were based are given in parentheses. [d] Bridging alkoxide. [e] The peaks are broad and shifted from the values of the neat liquid: −2.58, −1.02 (1); −2.40, −0.98 (2); −2.26, 0.93 p.p.m. (3).

Thermolysis data (see Table 1) show that both allyl and alkoxide moieties of the molecule undergo thermal decomposition, although the lability of the alkoxide group depends greatly on the nature of R. The allyl ligand is recovered mainly as propylene, as reported for transition-metal allyl derivatives [30a,b] and $[U(\eta\text{-}C_3H_5)_4]$.[1a] The presence of some propane suggests that a hydrogenation mechanism is also operative. Thermolysis of the alkoxide groups gives alkene and alkane (*ca.* 3 : 1 ratio), but no significant amount of an R coupling product was observed. This product distribution suggests a β-hydrogen-abstraction mechanism rather than homolytic scission of the oxygen–carbon bond.[31]

Hydrogen-1 n.m.r. data for (1)—(3) are listed in Table 7. Very large displacements of the resonance lines from the diamagnetic position are observed for these complexes, as previously reported for other uranium(IV) derivatives.[32a–c] The proton spectra of (1) and (2) in toluene solution show three signals at high field (1 : 2 : 2 ratio) as expected for η^3-allyl complexes [Figure 3(*a*)—(*c*)]. Two very broad signals (1 : 1) at room temperature [Figure 4(*a*)], and four signals (3 : 2 : 3 : 2) at *ca.* −10 °C [Figure 4(*b*)], are observed at low field for the ethoxide protons of (1). Moreover, four signals (6 : 6 : 1 : 1) are observed at room temperature for the isopropoxide protons of (2) [Figure 4(*c*)]. These spectral features change drastically in tetrahydrofuran (thf) solution. At room temperature, the allyl protons of (1)—(3) show an AX_4 pattern [Figure 3 (*d*)—(*f*)], while the alkoxide protons display a reduced number of sharp peaks [Figure 4(*d*)—(*f*)]. Furthermore, the thf proton lines are broadened and shifted from the values for the neat liquid (see Table 7). The number of peaks attributed to the alkoxide protons is in agreement with a dimeric structure in toluene solution for (1) and (2), as established conclusively by X-ray analysis for (2). Moreover, in thf, one of the signals of the alkoxide groups disappeared, suggesting a new monomeric structure arising from a bridge-splitting reaction by thf. The assignments of the resonances to bridged and terminal alkoxide groups in Table 7 are based on the substantial invariance of the remaining resonance in thf. The bipyramidal arrangement around the uranium atom, observed in the crystal structure of (2), is probably retained in the monomeric structure, with a thf molecule replacing a bridging alkoxide group. The occurrence of dynamic processes is suggested by the large linewidths observed in both polar and non-polar solvents. These phenomena, involving thf exchange and fluxional behaviour of allyl and alkoxide ligands, will be discussed elsewhere.

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