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BIS-CYCLOPENTADIENYL ALKOXIDES AND ARYL OXIDES OF URANIUM(IV). INFLUENCE OF THE STERIC HINDRANCE OF THE R GROUPS ON THE STABILITY OF THE $Cp_2U(OR)_2$, $Cp_2U(OC_6H_4R)_2$ AND $Cp_2U(OC_6H_3R_2)_2$ DERIVATIVES

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Summary

Reactions of $Cp_2U(NEt_2)_2$ with the moderately acidic agents ROH and ArOH lead to the cleavage of the $U-NEt_2$ bonds and formation of di-cyclopentadienyl dialkoxides and diaryl oxides of uranium(IV). The yields of the new derivatives are strongly dependent on the bulk of the OR or OAr groups; they can undergo disproportionation or decomposition reactions with formation of tris-cyclopentadienyl derivatives of uranium(IV). With the high-sterically crowded 2,6-$(Bu^t)_2$-C_6H_3OH ligand only one $U-NEt_2$ bond is cleaved, with formation of the stable $Cp_2U(OAr)(NEt_2)$ complex. The tris-cyclopentadienyl aryl oxides of uranium(IV) formed in the disproportionation reactions of the bis-cyclopentadienyl diaryl oxides have been also obtained by reaction of Cp_3UNEt_2 with ArOH.

Introduction

Organometallic uranium(IV) compounds have been widely investigated in recent years [1], but little information on the mixed ligand complexes $Cp_{4-n}U^{IV}(ER)_n$ (Cp and R = cyclopentadienyl and alkyl or aryl; E = Group VI donor atom, e.g. O or S, $n = 1, 2, 3$) has been reported, even though alkoxides have interesting chemical properties from both the theoretical and technological point of view [2]. The results for the few well studied complexes of these ligands with organometallic uranium(IV) moieties such as Cp_3U^{IV} [3], $Cp_2^{\star}U^{IV}$ [4] Cp_2U^{IV} [5] and $(\pi\text{-}C_3H_5)_2U^{IV}$ [6] (Cp = C_5H_5, $Cp^{\star} = C_5(CH_3)_5$ or $C_5H_3[Si(CH_3)_3]_2$) [7] suggest that the number and/or bulk of the cyclopentadienyl ligands are important factors in their stability towards disproportionation). This observation, considered along with the theoretical interpretation of the role played by the X ligands (different from C_5H_5) in determining the structure, stability and stoichiometry of the complexes $(C_5H_5)_{4-n}UX_n$ ($n = 1, 2, 3$) developed by Bagnall and Xing-fu [8a,b], prompted us to attempt the synthesis of stable bis-cyclopentadienyl dialkoxides and diaryl oxides of uranium(IV). Since for the series of ligands OR, O-2-(R)-C_6H_4 and O-2,6-$(R)_2$-C_6H_3, where R is an alkyl group of variable size interesting variations in steric hindrance can be expected, the reaction of the moderately weak parent protic acids ROH and ArOH [7a,b] with the versatile $Cp_2U(NEt_2)_2$ [9] was investigated.

Experimental

All operations involving the handling and preparation of the samples were performed inside glove boxes filled with purified nitrogen. The complexes UCl_4 [10], $UCp_2(NEt_2)_2$ [9], UCp_3NEt_2 [11] were prepared by published procedures. The solvents were dried by standard methods and deoxygenated immediately before use. Commercial grade alcohols and phenols were employed without further purification.

Proton NMR spectra were recorded with a Varian FT-80A spectrometer; Infrared spectra were recorded with a Perkin–Elmer 580B apparatus using Nujol mulls sandwiched between KBr plates in a sealed air-tight O-rings holders; Mass spectra were obtained with a VG Organic Ltd., ZAB 2F instrument (EI 70 eV, probe temperature 100°C) UV-NIR-VIS spectra were recorded with a Cary 17 D spectrometer. The abbreviations used, and the numbering of the compounds mentioned in this account, are as follows: Cp = η^5-cyclopentadienyl (C_5H_5); Et = C_2H_5;Pr = C_3H_7; $Pr^i = CH(CH_3)_2$; Bu = C_4H_9; $Bu^t = C(CH_3)_3$; Ar^I = 2,6-$(CH_3)_2$-C_6H_3; Ar^{II} = 2-(Pr^i)-C_6H_4; Ar^{III} = 2,6-$(Pr^i)_2$-C_6H_3; Ar^{IV} = 2-(Bu^t)-C_6H_4; Ar^V = 2,6-$(Bu^t)_2$-C_6H_3.

$Cp_2U(NEt_2)_2$ (**1**); Cp_3UNEt_2 (**2**); $[Cp_2U(OC_2H_5)_2]_x$ (**3**); $Cp_2U[OCH(CH_3)_2]_2$ (**4**); $Cp_2U[OC(CH_3)_3]_2$ (**5**); $Cp_2U(OAr^I)_2$ (**6**); Cp_3UOAr^I (**7**); $Cp_2U(OAr^{II})_2$ (**8**); Cp_3UOAr^{II} (**9**); $Cp_2U(OAr^{III})_2$ (**10**); Cp_3UOAr^{III} (**11**); $Cp_2U(OAr^{IV})_2$ (**12**); Cp_3UOAr^{IV} (**13**); $Cp_2U(OAr^V)(NEt_2)$ (**14**).

General procedure

The reactions between **1** and **2** with alcohols and phenols were carried out in Et_2O or n-hexane and were complete within minutes (as confirmed by the disappearance of the ^1H NMR signals of **1** and **2**). In the cases in which simple alcoholysis occurred (see preparative details) pure compounds were readily obtained by crystallization.

Syntheses in which disproportionation was significant gave a mixture of products, and separation of pure compounds was successful only in few cases, but satisfactory identification was obtained by taking the solution to dryness, dissolving the residue in C_6D_6, and recording the ^1H NMR spectrum of the solution. Generally the large isotropic shifts induced by the paramagnetic uranium(IV) ion led to the appearance of well separated signals, the shapes and intensities of which could be used for the identification of the new complexes (see Table 1).

Reactions with alcohols

1 + C_2H_5OH. 0.512 g of **1** (1 mmol) and 0.092 g of C_2H_5OH (2 mmol) were brought into reaction at room temperature in 20 ml of Et_2O. The gold-yellow colour immediately turned to brown-green, and the solution was stirred for 1 h. As shown by ^1H NMR the product was a mixture containing predominantly $Cp_3UOC_2H_5$ [3a];

other signals (10.8, s, 30H; −42.3, t, 18H; −120, q, 12H) could be ascribed to the complex $[Cp_3U]_2[U(OC_2H_5)_6]$.

A green insoluble microcristalline powder was also formed. Addition of a small excess of C_2H_5OH to the product mixture caused the signals of $Cp_3UOC_2H_5$ to disappear, and those of the presumed $[Cp_3U]_2[U(OC_2H_5)_6]$ to increase in intensity. A large excess of C_2H_5OH converted all the soluble products into the green precipitate which after isolation, gave mass-spectral data consistent with a trimeric species, such as $[U(OC_2H_5)_4]_3$. The relative intensities of the signals which can be attributed to $[Cp_3U]_2[U(OC_2H_5)_6]$ remained constant during its formation and its decomposition. When the reaction was carried out at a lower temperature (−30°C) a green mixture giving rise to a complex pattern of signals. The most intense resonances, which could be related to one another to form a set (62.2, s, 10H; −28.3, t, 6H; −60.7, q, 4H), may correspond to the species $Cp_2U(OC_2H_5)_2$. Unfortunately no pure compound could be isolated, but after stripping off the solvent, a green solid was obtained. Its mass spectrum indicated the presence of $[Cp_2U(OC_2H_5)_2]_4$ as the main component.

1 + $(CH_3)_2CHOH$. 1 mmol of **1** reacted at room temperature with 2 mmol of $(CH_3)_2CHOH$ to give a mixture containing $Cp_3UOCH(CH_3)_2$ (30%) and $Cp_2U[OCH(CH_3)_2]_2$ (70%) (as indicated by the ^1H NMR signals at 31.1, s, 10H; −5.9, d, 12H; −40.7, br.m, 2H) [12]. On standing the bis-cyclopentadienyl derivative progressively decomposed into $Cp_3UOCH(CH_3)_2$ and an unidentified insoluble green product; no useful information was obtained from its mass spectrum.

1 + $(CH_3)_3COH$. The reaction was carried out as described above, and gave a solution containing $Cp_2U[OC(CH_3)_3]_2$, slightly contamined with $Cp_3UOC(CH_3)_3$ and unidentified products. The solution was evaporated and, the residue was dissolved in 3 ml of Et_2O, and 25 ml of n-hexane were added. The $Cp_3UOC(CH_3)_3$ which separated was filtered off and the solution was concentrated in vacuum to few ml volume; pure, red-brown $Cp_2U[OC(CH_3)_3]_2$ (0.2 g) slowly separated and was filtered off.

Anal. Found: C, 41.94; H, 5.51; U, 46.22. $C_{18}H_{28}O_2U$ calcd.: C, 42.02; H, 5.45; U, 46.30%. IR (cm^{-1}): 1716w, 1656w, 1493w, 1232m, 1178s, 1022m, 941vs, 900s, 854m, 779s.

Reactions with ring-substituted phenols

The procedure used for alcohols was followed with Et_2O at room temperature as the solvent, and a 1/2 molar ratio of **1** to phenol. Again reaction was immediate, even though the bis-cyclopentadienyl derivatives could not always be isolated.

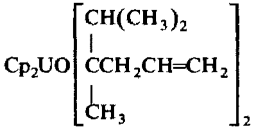
1 + HO-Ar^I. Product **6** was formed within minutes, but slowly decomposed to **7** and unidentified products. Pure **6** was obtained by dissolving the residue in n-hexane, filtering the solution to remove the insoluble **7**, pumping off the n-hexane. The oily residue became a microcrystalline red brown powder when kept for 12 h in vacuum (yield 60%).

Anal. Found: C, 51.06; H, 4.68. $C_{26}H_{28}O_2U$ calcd.: C, 51.15; H, 4.59%. IR (cm^{-1}): 1654w, 1589w, 1271m, 1212s, 1092m, 1021m, 917m, 867s, 769m, 764w, 720 m.

1 + HO-Ar^{II}. The product mixture showed a set of signals corresponding to **9** and **8** (26.2, s, 10H; and 10.2, t, 2H-*para*) along with other small unidentified signals. The **8**/**9** integration ratio of the two singlets at 26.2 and 16.4 ppm,

TABLE 1

ASSIGNMENT OF ^{1}H NMR SHIFTS (Solvent C_6D_6; T 27°C; δ in ppm relative to C_6D_5H as internal standard; negative values represent downfield shifts)

Complex	$\delta(C_5H_5)$	δ(others)
3	62.2 (10H,s)	-28.3 (6H,t,$\mathrm{CH_2}\mathit{CH}_3$); -60.7 (4H,q,$\mathit{CH}_2\mathrm{CH_3}$)
4	31.1 (10H,s)	-5.98 (12H,d,OCH($\mathit{CH}_3)_2$; -40.7 (2H,bm,O$\mathit{CH}(\mathrm{CH_3})_2$)
5	31.1 (10H,s)	-5.05 (18H,s,C($\mathit{CH}_3)_3$)
6	27.4 (10H,s)	2.8 (12H,s,*o*-CH_3); -5.5 (4H,d,*m*-H); -3.4 (2H,t,*p*-H)
7	18.1 (15H,s)	6.9 (6H,s,*o*-CH_3); [a]
8	26.2 (10H,s)	10.2 (2H,t,*p*-H) [a]
9	16.4 (15H,s)	9.5 (6H,d, *o*-CH($\mathit{CH}_3)_2$); 15.3 (1H,bm,*o*-$\mathit{CH}(\mathrm{CH_3})_2$); 0–4 [a]
10	27.2 (10H,s)	6.2 (24H,d, *o*-CH($\mathit{CH}_3)_2$); -6.2 (4H,d, *m*-H); -3.9 (2H,t, *p*-H); -3.1 (4H,bm, *o*-$\mathit{CH}(\mathrm{CH_3})_2$)
11	18.2 (15H,s)	7.2 (12H,d, *o*-CH($\mathit{CH}_3)_2$); 6.25 (2H,d, *m*-H); 5.4 (1H,t, *p*-H); 3.4 (2H,bm, *o*-$\mathit{CH}(\mathrm{CH_3})_2$)
12	26.8 (10h,s,)	8.4 (18H,s, *o*-C($\mathit{CH}_3)_3$); -5.4 (2H,m, [a]); -2.9 (2H,m, [a]); -6.3 (2H,m, [a]); -17.4 (2H,m, [a])
13	16.1 (15H,s)	13.8 (9H,s,*o*-C($\mathit{CH}_3)_3$); 2.0 (1H,dd, [a]); 0.9 (1H,t, [a]); 2.4 (1H,t, [a]); 3.5 (1H,dd, [a])
14	23.8 (10H,s)	0.3 (18H,s,C($\mathit{CH}_3)_3$); -6.6 (2H,d, *m*-H); -4.3 (1H,t, *p*-H); 4.75 (4H,q, N-($\mathit{CH}_2\mathrm{CH_3})_2$); 4.25 (6H,t,N-($\mathrm{CH_2}\mathit{CH}_3)_2$)
$[\mathrm{Cp_3U}]_2\mathrm{U(OC_2H_5)_6}$	10.8 (15H,s)	-42.3 (18H,t, *o*-$\mathrm{CH_2}\mathit{CH}_3$); -1.20 (12H,q, O$\mathit{CH}_2\mathrm{CH_3}$)
 $\mathrm{Cp_2UO}\left[\begin{array}{l}\mathrm{CH(CH_3)_2}\\ \mid\\ \mathrm{CCH_2CH{=}CH_2}\\ \mid\\ \mathrm{CH_3}\end{array}\right]_2$	31.8 (10H,s)	-8.5 (4H,m, CH_2CH=); -6.4 (2H,sept., $\mathit{CH}(\mathrm{CH_3})_2$); -5.7 (6H,s, OCCH_3); -4.6 (2H,m, $\mathrm{CH_2}\mathit{CH}{=}\mathrm{CH_2}$); -0.86 (2H,d, =CH_2-*trans*) 0.5 (2H,d, =CH_2-*cis*); 2.0 (12H,d, CH($\mathit{CH}_3)_2$)

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[a] Signals not satisfactorily identified.

respectively) corresponds to an 80/60 mixture of **8** and **9**. Unfortunately separation was not possible because of the similar solubilities and the decomposition of **8** to give **9**.

1 + HO-Ar^{III}. Complexes **10** and **11** were formed in 9/1 molar ratio. Similar solubilities again prevented isolation of pure **10**. Very slow transformation of **10** → **11** and unidentified products was also observed.

1 + HO-Ar^{IV}. **12** was the only product. It decomposed very slowly to give **13**. Pure **12** was obtained by pumping off the Et_2O soon after the reaction was complete (within a few minutes), dissolving the residue in n-hexane, filtering to separate any insoluble **13** concentrating the solution to a few ml, and cooling. The microcrystalline red brown **12** which separated was filtered off (yield 60%).

Anal. Found: C, 53.89; H, 5.49. $C_{30}H_{36}O_2U$ calcd.: C, 54.05; H, 5.40%. IR (cm^{-1}): 1592m, 1570m, 1479s, 1439vs, 1337s, 1291vs, 1246vs, 1129m, 1090m, 1052m, 1015m, 877s, 828m, 788s, 756s, 693s, 614m, 565w, 429w.

1 + HO-Ar^{V}. The reaction was carried out with 1 mmol of **1** and **2** mmol of $HOAr^V$. After 1 h stirring a good yield of the slightly insoluble red brown **14** was obtained. It was purified by washing several times with small volumes of n-hexane (3–4 ml). **14** remains unchanged when stirred for 24 h with $HOAr^V$ (1/1 molar ratio).

Anal. Found: C, 52.20; H, 6.39; N, 2.34. $C_{28}H_{41}N_2OU$ calcd.: C, 52.09; H, 6.36; N, 2.17%. IR (cm^{-1}): 1581m, 1429s, 1387vs, 1363vs, 1339s, 1317s, 1261vs, 1223vs, 1201vs, 1177vs, 1152vs, 1121vs, 1105s, 1067m, 1046m, 1015s, 1002m, 932s, 883m, 856s, 820s, 806s, 789vs, 752vs, 729m, 676m, 652m, 570m.

Synthesis of Cp_3UOAr *derivatives.* **7**, **9**, **11** and **13** were synthesized by reaction of **2** with the corresponding phenols (1/1 molar ratio) under the same conditions as above. The colour varied from brown green to red brown.

7 Anal. Found: C, 49.66; H, 4.41. $C_{23}H_{25}OU$ calcd.: C, 49.82; H, 4.36%.
9 Anal. Found: C, 50.82; H, 4.54. $C_{24}H_{26}OU$ calcd.: C, 50.70; H, 4.61%.
11 Anal. Found: C, 53.23; H, 5.22. $C_{27}H_{32}OU$ calcd.: C, 53.11; H, 5.28%.
13 Anal. Found: C, 51.69; H, 4.77. $C_{25}H_{28}OU$ calcd.: C, 51.55; H, 4.84%.
11 IR (cm^{-1}): 1712w, 1655m, 1586m, 1433s, 1333m, 1259s, 1206s, 1160w, 1098w, 1045w, 1021m, 890m, 862s, 792m, 752s, 725w, 691m, 653w, 570m, 465w, 450w.
13 IR (cm^{-1}): 1611w, 1592m, 1568w, 1433sh, 1292m, 1230s, 1203m, 1129m, 1090m, 1051m, 1018m, 870s, 827m, 791m, 759m, 727m, 691w, 607s, 564w, 504w, 424ms, 353m.

Results and discussion

Cleavage of the NEt_2 groups from **1** by the moderately acidic agents ROH and ArOH smoothly and rapidly gives the cyclopentadienyl alkoxides and aryl oxides of uranium(IV). However, the yields and the composition of the products depend strongly on the bulk of the OAr groups; the bulkier these organic groups the more complete the formation and the higher the stability of the bis-cyclopentadienyl derivatives compared with the tris-cyclopentadienyl compounds. Thus it can be assumed that the first step of the reaction is the formation of the bis-alkoxide or -aryl oxide

$$\begin{array}{l} Cp_2U(NEt_2)_2 + 2\ ROH \rightarrow Cp_2U(OR)_2 + 2\ HNEt_2 \\ Cp_2U(NEt_2)_2 + 2\ ArOH \rightarrow Cp_2U(OAr)_2 + 2\ HNEt_2 \end{array} \qquad (1)$$

This subsequently undergoes disproportionation by one of the following routes:

$$3\ Cp_2U(OR)_2 \rightarrow 2\ Cp_3UOR + U(OR)_4 \qquad (2)$$

or

$$2\ Cp_2U(OR)_2 \rightarrow Cp_3UOR + CpU(OR)_3 \qquad (3)$$

Route (2) seems to be preferred for decomposition of alkoxides as indicated by the detection of the species: $(Cp_3U)_2U(OC_2H_5)_6$

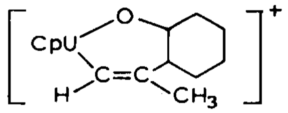
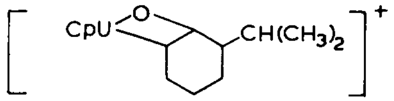
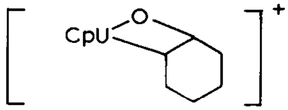
$$\left(2\ Cp_3UOC_2H_5 + U(OC_2H_5)_4 \rightarrow 2\ Cp_3U^+ + U(OC_2H_5)_6{}^{2-}\right)$$

and the precipitation of a green product identified as the trimeric species $[U(OC_2H_5)_4]_3$ [13a,b]. No hypothesis can be put forward for the decomposition of the bis-aryl oxide complexes because the by-products of the reaction could not be identified. The influence of the bulk of the phenols is shown clearly by the reaction of **1** with $ArOH^V$, which results in cleavage of one NEt_2 group but not the second even when a 1/2 molar ratio was used and a reaction period as long as 24 h. The formation of the above complexes indicates that the Cp–U bond is far more resistant than the U–N bond to the protolytic cleavage by ROH and ArOH. The complexes obtained with bulky R groups are fairly soluble in the most common organic solvents (THF, Et_2O, C_6H_6 and C_7H_8) but are sensitive to oxygen and moisture. In our hands the present method of preparing Cp_3UOR complexes has proved to be far more effective than those described previously [3a,b,14] which involve reaction of chloride compounds with alkali metal alkoxides, since it gives higher yields and is less time consuming.

Spectroscopic properties

Solutions of the complexes $Cp_2U(OR)_2$ and $Cp_2U(OAr)_2$ (**5**, **12**, **6**, **14**) in THF give rather similar absorption spectra in the range 1500–550 nm (Table 2), suggesting similar structural features. In particular the strong peaks near 1150 nm (1160 nm for **14**) and at 675 nm (this is obscured for **6**) seem indicative of low symmetry eight coordinate species [15,16]. The Cp_3UOAr derivatives (**9**, **11**, **13**) spectra in the same range strictly resemble those of other Cp_3UX species (X = Cl, R, BH_4 etc.). The vibrational spectra between 300 and 1700 cm^{-1} are characterized by the usual absorption of the π-bonded C_5H_5 group. Many additional bands are observed for **5**; those at 1360, 1178, 941 and 730 cm^{-1} are near the positions found for the complexes $U(\eta^3\text{-}C_3H_5)_2(O\text{-}Bu^t)_2$; in particular, the band at 941 cm^{-1} can be ascribed to the C–O stretching vibration. The aryl oxide complexes also give numerous bands besides those of the $\eta^5\text{-}C_5H_5$ groups; although assignments are difficult, the absorptions in the range 1090–1200 and 500–700 cm^{-1} can be ascribed to the ν(C–O), ν(U–O) or ν(U–O–U) vibrations (for oligomeric species) as suggested for other metal phenoxides [17].

The mass spectra of **7**, **9**, **11**, **13** (Table 3) show corresponding fragmentation patterns. The molecular ion peaks are quite intense, but the strongest ones correspond to the ions originating from the loss of a Cp group, with the ArO ligand still bonded to the uranium [18a,b]. This reflects the "hard" nature of the central metal, and closely resembles the behaviour of the unsubstituted complex $Cp_3UOC_6H_5$. Moreover, moderately intense peaks with *m/e* values corresponding to the formation of interesting metalated species are also observed. The more significant are:

	m/e	Starting compound
	435	9, 12 and 13
	437	11
	395	9 and 12

As can be seen, side chain substituents readily undergo partial or complete breakdown. The mass spectra of the bis-cyclopentadienyl aryl oxide derivatives (**14**, **12** and **6**) show the following features:

(a) All of them give parent molecular ion peaks.

(b) Fragments arising from the loss of one OAr group $[Cp_2MOAr]^+$ are observed in

(Continued on p. 360)

TABLE 2

THE NEAR-INFRARED SPECTRA OF SOME NEW ORGANOMETALLIC URANIUM ALKOXIDES (**5**, **6**, **9**, **11**–**14**) IN THE RANGE 1600–550 nm (Solvent THF)

5	**6**	**9** [a]	**11**	**12**	**13**	**14**
1550m,br	1475ms	1470w	1450w	1480s	1480m	1480m
1350m,br	1280br	1330m,br	1380sh	1325m	1440s	1400m
1260sh	1160s	1280m	1310m	1280m,br	1430s	1310w
1160vs	1070s	1190s	1270m	1160s	1415m	1260sh
930w,br	1020s	1150s	1190vs	1140sh	1285w	1200sh
800w	980sh	1100m	1160sh	1060s	1230s	1150vs
750m	930w	1050sh	1100m	1030s	1185vs	1120s
700sh	880w	1020s	1050sh	975sh	1100sh	1045s
675s	840w, br	990s	1020s	930w	1050m	1020s
665s	760sh	970s	910m	910w	1020m	930w
620sh		900s	780sh	880w	1000sh	880w
590s		750sh	760s	835sh	910w	860sh
		680s		750sh	800w,br	830sh
				675s	760w	760sh
				620sh	720sh	730sh
					690m	680s
					680m	650vs
					650w	
					610m	
					590m	

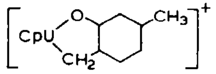
[a] In Et_2O.

TABLE 3. THE MOST SIGNIFICANT FRAGMENTS IN THE MASS SPECTRA OF SOME ORGANOMETALLIC URANIUM ALKOXIDES

$Cp_2U[OC(CH_3)_3]_2$ (**5**)

m/e	$I_{rel.}$	Fragment
514	34	$[Cp_2U(OR)_2]^+$
458	6	$[Cp_2U(OR)(OH)]^+$
449	7	$[CpU(OR)_2]^+$
441	17	$[Cp_2U(OR)]^+$
402	57	$[Cp_2U(OH)_2]^+$
385	72	$[Cp_2UOH]^+$
384	100	$[Cp_2UO]^+$
368	13	$[Cp_2U]^+$
337	24	$[CpU(OH)_2]^+$
336	19	$[CpUO(OH)]^+$
335	7	$[CpUO_2]^+$
320	11	$[CpUOH]^+$
303	4	$[CpU]^+$
270	47	$[UO_2]^+$
254	24	$[UO]^+$

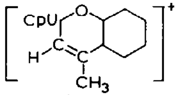
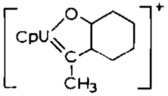
$Cp_2U[OAr^I]_2$ (**6**)

m/e	$I_{rel.}$	Fragment
610	60	$[Cp_2U(OAr^I)_2]^+$
545	100	$[CpU(OAr^I)_2]^+$
489	85	$[Cp_2UOAr^I]^+$
423	22	
368	8	
319	55	$[Cp_2U]^+$
270	65	$[CpUO]^+$
		$[UO_2]^+$

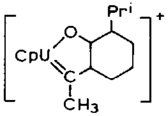
Cp_3UOAr^I (**7**)

m/e	$I_{rel.}$	Fragment
554	70	$[Cp_3UOAr^I]^+$
489	100	$[Cp_2UOAr^I]^+$
433	3	$[Cp_3U]^+$
424	32	$[CpUOAr^I]^+$
384	1	$[Cp_2UO]^+$
368	4	$[Cp_2U]^+$
319	44	$[CpUO]^+$

Cp_3UOAr^{II} (**9**)

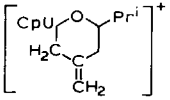
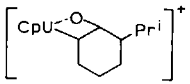
m/e	$I_{rel.}$	Fragment
568	52	$[Cp_3UOAr^{II}]^+$
503	100	$[Cp_2UOAr^{II}]^+$
435	9	
433	7	$[Cp_3U]^+$
422	9	

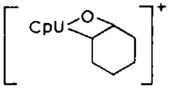
$Cp_2U(OAr^{III})_2$ (**10**)

m/e	$I_{rel.}$	Fragment
722	40	$[Cp_2U(OAr^{III})_2]^+$
657	60	$[CpU(OAr^{III})_2]^+$
545	70	$[Cp_2UOAr^{III}]^+$
503	100	$[Cp_2UOAr^{II}]^+$
464	90	

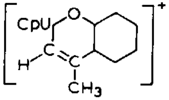
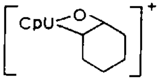
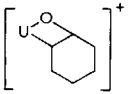
Other lighter fragments were not satisfactorily identified.

Cp_3UOAr^{III} (**11**)

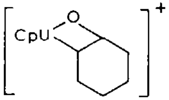
m/e	$I_{rel.}$	Fragment
610	26	$[Cp_3UOAr^{III}]^+$
545	100	$[Cp_2UOAr^{III}]^+$
477	4	
437	8	
433	15	$[Cp_3U]^+$
384	3	$[Cp_2UO]^+$

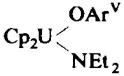
395	15					368	17	$[Cp_2U]^+$
						319	26	$[CpUO]^+$
384	4	$[Cp_2UO]^+$						
368	15	$[Cp_2U]^+$						
319	20	$[CpUO]^+$						

$Cp_2U(OAr^{IV})_2$ (**12**)

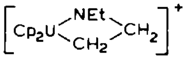
m/e	$I_{rel.}$	Fragment
666	22	$[Cp_2U(OAr^{IV})_2]^+$
601	43	$[CpU(OAr^{IV})_2]^+$
517	23	$[Cp_2UOAr^{IV}]^+$
461	4	$[Cp_2UOC_6H_5]^+$
435	11	
395	9	
368	8	$[Cp_2U]^+$
331	70	$[UOC_6H_5]^+$
330	33	
319	17	$[CpUO]^+$
270	23	$[UO_2]^+$
254	100	$[UO]^+$

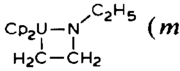
Cp_3UOAr^{IV} (**13**)

m/e	$I_{rel.}$	Fragment
582	27	$[Cp_3UOAr^{IV}]^+$
517	100	$[Cp_2UOAr^{IV}]^+$
433	13	$[Cp_3U]^+$
395	20	
384	8	$[Cp_2UO]^+$
368	40	$[Cp_2U]^+$
319	70	$[CpUO]^+$



$Cp_2U(OAr^{V})(NEt_2)$ (**14**)

m/e	$I_{rel.}$	Fragment
645	2	$[Cp_2U(OAr^{V})(NEt_2)]^+$
589	11	$[Cp_2U(OAr^{IV})(NEt_2)]^+$
587	11	$[Cp_2U(OAr^{V})N]^+$
573	50	$[Cp_2UOAr^{V}]^+$
449	30	$[Cp_3UO]^+$
447	30	$[Cp_3UN]^+$
438	20	
398	14	$[Cp_2UNO]^+$
384	44	$[Cp_2UO]^+$
382	44	$[Cp_2UN]^+$
368	55	$[Cp_2U]^+$
335	20	$[CpUO_2]^+$
333	17	$[CpUNO]^+$
319	100	$[CpUO]^+$
317	4	$[CpUN]^+$

the spectrum of **6** and **12**, while for the mixed ligand complex **14** an abundance ratio of 3/1 for the ions $[Cp_2UOAr^V]^+$ and $[Cp_2UNEt_2]^+$ is observed, indicating that the U–O bond is stronger than the U–N bond. The metalated ion  (m/e = 438) is observed.

(c) Loss of one Cp group scission and the $[M - Cp]^+$ ions is observed for **6** and **12**, but not for **14**.

(d) The compounds also suffer loss from the side chain, giving ions in which both aryl-carbons are metalated. Studies of metastable ions (B/E experiments) in the case of **6** indicate that the parent ion ($m/e = 610$) decomposes rapidly to give the ions $[CpU(Ar^1)_2]^+$ ($m/e = 545$) and $[Cp_2UOAr^1]^+$ ($m/e = 489$) directly. The ion $[Cp_2U(OCH_3)(OAr^1)]^+$, formed by loss of $C_6H_5CH_3$, appears only in this spectrum and not in the ordinary one, indicating that its formation is slow [19].

A complicated fragmentation takes place with **5**. In addition to the molecular ion, strong peaks corresponding to the rupture of O–R bonds with the formation of species containing U–O–H, U–O–R and U–O bonds appear. This is a further confirmation of the high affinity of uranium(IV) towards oxygen. The mass spectrum of the mixture obtained from the reaction of **1** with ethanol at low temperature was also studied; although not very informative because of the impurity of the sample, the spectrum shows high molecular ions corresponding to the oligonuclear organometallic species, the majority of which were tentatively identified as shown in Table 3.

The difference between ethoxide (presence of oligomeric species) and t-butoxide compounds (absence of oligomeric species) probably depends on the different steric demands of the CH_3CH_2O and $(CH_3)_3COH$ ligands.

The ^1H NMR spectra of the prepared complexes, showing large shifts, are typical of paramagnetic uranium(IV) derivatives [20]. The spectra have the expected pattern and integration ratios, and so are useful for the identification of the compounds. As far as the cyclopentadienyl protons are concerned, it should be noted that the positions of their signals depend strongly on the composition of the complex. Thus the chemical shifts on average are 31 ppm for the $Cp_2U(OR)_2$, 27 ppm for $Cp_2U(OAr)_2$, 16–18 ppm for Cp_3UOAr, and about 23.8 ppm for the mixed ligand complex $Cp_2U(OAr)(NEt_2)$. Such behaviour has been observed for other types of organometallic uranium(IV) derivatives, and seems closely related to the structure and to the ability of electron pairs to form U–O bonds from OR and OAr ligands [11,21]. The upfield shifts are larger for the $Cp_2U(OR)_2$ rather than in $Cp_2U(OAr)_2$ complexes, owing to the larger donor ability of alkyl than of aryl groups. The same feature is observed on comparing the $Cp_{4-n}U(NR_2)_n$ [9] and $Cp_{4-n}U(OR)_n$ ($n = 1, 2$) [3a] series of complexes, for which the ^1H NMR signals of the Cp groups of the alkoxy derivatives are at higher fields than those of the amido complexes; this can be accounted for in terms of the following resonance possibilities:

$$U{-}\overline{N}R_2 \leftrightarrow U^-{=}^+NR_2$$

and

$$U{-}\overline{\underline{O}}{-}R \leftrightarrow U^-{=}\underline{O}^+{-}R \leftrightarrow {}^{2-}U{\equiv}O^{2+}{-}R$$

$$U{-}\overline{\underline{O}}Ar \leftrightarrow U^-{=}O^+{-}Ar \leftrightarrow {}^{2-}U{\equiv}O^{2+}{-}Ar$$

in which nitrogen and oxygen are potential five- and three-electron donors respectively. This view is supported by the near linearity (or at least a marked opening) of the angle U–O–C found in the organometallic uranium(IV) complexes $[(\eta^3\text{-}C_3H_5)_2U(OPr^i)_2]_2$ [6], as well as in other analogous transition metal complexes [7a,13b,22a,b,c], suggesting *sp*-hybridization of the oxygen atom.

The anomalous values for compounds **3** and **15** $(Cp_3U)_2U(OC_2H_5)_6$ may reflect deviation from the normal pseudo-tetrahedral $Cp_2U(OR)_2$ structure owing to formation of oxygen bridged oligomeric species (as shown also by the mass spectrum of **3**), while in **15** the bond between Cp_3U^+ and $U(OC_2H_5)_6{}^{2-}$ may be regarded as having the same nature as in other Cp_3UX complexes (e.g. X = Cl, etc.), and therefore show analogous chemical shifts [11].

Work in this area is continuing, mainly with the aim of carrying out structural analyses in order to correlate the structural parameters with other chemico-physical properties.

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