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Reduction of $(\eta^5\text{-}C_5H_5)_3UCl$ with Sodium Hydride: the Preparation and Spectral Studies of $(\eta^5\text{-}C_5H_5)_3U$ and $(\eta^5\text{-}C_5H_5)_3U\cdot OC_4H_8$

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The organometallic chemistry of the actinide elements, especially uranium(IV), has recently received renewed attention. Important contributions have been devoted to π-bonded complexes of uranium(IV), while little work has been done in the organometallic chemistry of uranium(III) [1]. The main reason of the lack of information concerning the uranium atom in this unusual oxidation state has to be ascribed to the experimental difficulties in handling UCl_3, which could be considered the most simple precursor, and in preparing $(\eta^5\text{-}C_5H_5)_3U$. So far, the methods used in the synthesis of the tris-(cyclopentadienyl)uranium(III) complex involve the reaction of UCl_3 with ionic cyclopentadienide in non-aqueous media such as benzene or tetrahydrofuran, and the reduction of the uranium(IV) complex $(\eta^5\text{-}C_5H_5)_4U$ with potassium in benzene. According to the latter method, the reduction to uranium(III) is promoted by the highly reactive uranium metal produced, in turn, by reacting potassium and $(\eta^5\text{-}C_5H_5)_4U$ in benzene [2]. The mentioned methods generally need prolonged reaction times and complicated procedures in isolating the reaction products whose yields are often very low.

This paper describes a new, rapid and efficient route for obtaining $(\eta^5\text{-}C_5H_5)_3U$.

Experimental

All operations and reactions were carried out in glove-boxes with controlled atmosphere (Oxygen content less than 10 ppm).

Materials

$(\eta^5\text{-}C_5H_5)_3UCl$ was prepared according to the reported methods [3]. The solvents were purified by distillation from $LiAlH_4$ and potassium under nitrogen, using benzophenone as an indicator. NaH was a commercially available product of analytical grade.

Spectral Measurement

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer, using Nujol mulls and KBr plates. Absorption spectra in the visible and near i.r. regions were recorded on a Varian Cary 17D spectrophotometer.

Preparation of $(\eta^5\text{-}C_5H_5)_3U$

In a 50 ml reaction vessel, 0.5 g of $(\eta^5\text{-}C_5H_5)_3UCl$ and 0.13 g of NaH in 30 ml of benzene were reacted by stirring for three days at room temperature. During this time the color of the solution changed from red-brown to pale pink and a dark residue separated. The product was Soxhlet extracted with benzene for ten days in a rigorously controlled atmosphere. By evaporation of the benzene solution a brown solid (0.2 g) was isolated. The compound was identified as $(\eta^5\text{-}C_5H_5)_3U$ by comparing its electronic spectrum with the corresponding one reported in literature [2]. The same product was obtained following similar procedure using diethyl ether as a solvent.

Preparation of $(\eta^5\text{-}C_5H_5)_3U\cdot OC_4H_8$

The product was obtained following the above reported procedure, using tetrahydrofuran (THF) as a solvent. The product was precipitated from THF with n-pentane and identified by ir and electronic spectra [2].

I.R. Spectra

The ir spectrum of $(\eta^5\text{-}C_5H_5)_3U\cdot OC_4H_8$ exhibits the typical pattern of the $(\eta^5\text{-}C_5H_5)$ group in tris-(cyclopentadienyl)actinide derivatives [4] and the stretching frequencies of the coordinated THF [2]. Furthermore, in the Nujol i.r. spectra of both compounds no evidence of metal–hydride bond nor cyclopentadienyl ring bonding unlike *pentahapto* has been observed.

Electronic spectra

The electronic spectra in the range 5000–18000 cm^{-1} have been investigated in the following media: benzene, diethyl ether and tetrahydrofuran at 298 K and 315 K (Fig. 1 and Table I).

At least fourteen bands occur in each spectrum carried out at room temperature and at 315 K, with relatively small deviations in energies. The largest band maxima deviations, amounting only to five or six hundred wavenumbers, occur with the solvent having the best donating properties, *viz.*, tetrahydrofuran. The $(\eta^5\text{-}C_5H_5)_3U$ complex presents a strong Lewis acid character [5] and forms 1:1 adducts with

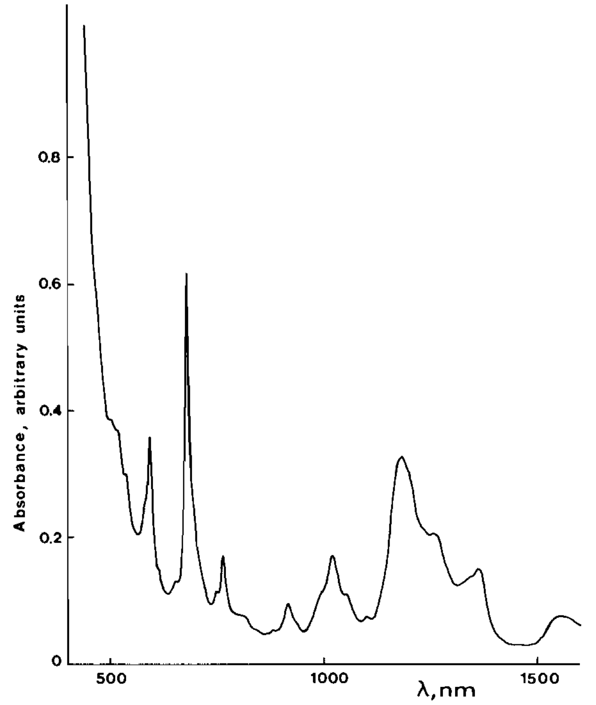

Fig. 1. Absorption spectrum of $(\eta^5\text{-}C_5H_5)_3U$ in Et_2O.

neutral basic molecules such as tetrahydrofuran. The $(\eta^5\text{-}C_5H_5)_3U\cdot THF$ adduct is more deeply coloured than the parent $(\eta^5\text{-}C_5H_5)_3U$, probably due to the bathochromic shift through the metal oxygen bonding.

Table I compares the position of the bands observed for $(\eta^5\text{-}C_5H_5)_3U$ with the energy levels calculated by Jørgensen [6]. The agreement between the observed and predicted transitions is reasonable. The bands between 5000–18000 cm^{-1} are Laporte-forbidden, internal f–f transitions. Although these transitions seem to be typical of uranium(III), some changes in their separation occur. The comparison of the position (Table I) among the bands shows that all the f–f transitions in $(\eta^5\text{-}C_5H_5)_3U$ move towards lower frequency. This is consistent with the fact that cyclopentadienyl anion as a ligand is stronger than others in actinide complexes and tends to shift the f–f transitions to lower energies. On the basis of the observed spectra one may infer that the 5f electrons seem more sensitive to the variation of the ligands than 4f electrons in analogous lanthanide complexes.

TABLE I. Comparison of Observed and Calculated Levels in U^{III}.

Obsd. in soln. (cm^{-1})[a,b,c]	Calcd. (cm^{-1})[d]
20000	26500
(18692)	26300
16949	25100
14925	23200
(13333)	22200
13178	20900
10929	19700
(10309)	18800
9804	18100
(9524)	17300
8475	16600
(8000)	15000
7353	12600
6452	11700
	7800
	4100

[a] in Et_2O. [b] Allowed transitions found in the u.v. region in solution are not included in this table. [c] Figures in parentheses indicate shoulders. [d] See Ref. 6.

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