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Preliminary communication

A NEW URANIUM(IV) ORGANOMETALLIC TETRAHYDROBORATE COMPLEX. THE PREPARATION AND CHARACTERIZATION OF THE BIS(CYCLOPENTADIENYL) URANIUM (IV) BIS(TETRAHYDROBORATE): $(\eta^5\text{-}C_5H_5)_2U(BH_4)_2$

P. ZANELLA*, G. DE PAOLI and G. BOMBIERI

Laboratorio di Chimica e Tecnologia dei Radioelementi del C.N.R., Area della Ricerca, Corso Stati Uniti, 35100 - Padova - Italy.

G. ZANOTTI

Istituto di Chimica Organica, Università di Padova, 35100 - Padova - Italy.

R. ROSSI

Istituto Chimico, Università di Ferrara, 44100 - Ferrara - Italy.

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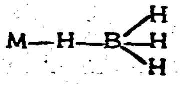
SUMMARY

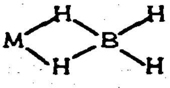
The synthesis and characterization of $(\eta^5\text{-}C_5H_5)_2U(BH_4)_2$ are reported. I.r. and room temperature Hnmr data support a tridentate ligation and the magnetic equivalence of the bridge and terminal BH_4^- hydrogen atoms. Preliminary X-ray analysis results suggest a structure consisting of the uranium atom in an approximately tetrahedral configuration surrounded by two pentahaptocyclopentadienyl rings and two tetrahydroborate groups.

The few examples of organometallic tetrahydroborate complexes of actinides reported in the literature are concerned with uranium(IV) and thorium(IV) derivatives.[1]

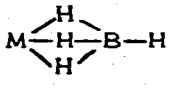
The interest in this class of compounds is chiefly due to the structural questions arising from the ligation geometry of the tetrahydroborate anion BH_4^- to the metal since it may act as a monodentate(I), bidentate(II) or tridentate (III) ligand.



(I)



(II)



(III)

In order to investigate how the number and nature of other ligands coordinated to the metal may influence the mode of the BH_4 group ligation, we prepared the complex $(\eta^5\text{-}C_5H_5)_2U(BH_4)_2$ by the following route:

$$UCl_4 + 2NaBH_4 \xrightarrow[\text{DME or THF}]{20\,^\circ C} UCl_2(BH_4)_2 + 2\,NaCl$$

$$UCl_2(BH_4)_2 + 2(\eta^5\text{-}C_5H_5)Tl \xrightarrow[\text{DME or THF}]{20\,^\circ C} (\eta^5\text{-}C_5H_5)_2U(BH_4)_2 + 2TlCl$$

On account of the sensitivity of the tetrahydroborate to oxygen and moisture, the reactions were carried out in a nitrogen atmosphere dry box (oxygen content less than 5 ppm) using very dry and oxygen-free solvents (dimethoxyethane=DME and tetrahydrofuran=THF). 0.169 g (5.2 mmoles) of purified $NaBH_4$ was added to a solution of 1 g (2.6 mmoles) of UCl_4 in 50 ml of tetrahydrofuran. After stirring for 10 hours at 20°C the NaCl was removed by filtration and to the resulting green solution 1.4 g (5.2 mmoles) of $(\eta^5\text{-}C_5H_5)Tl$ was added. The reaction mixture was stirred for 12 hours at 20°C and the TlCl filtered off. A red brown solid was obtained by vacuum evaporation of the solvent. This was purified by vacuum sublimation at 80°C (10^{-2} mmHg). By slow resublimation at 60°C (10^{-2} mmHg) red brown crystals were obtained. Anal. Calcd. for $C_{10}H_{18}B_2U$: C, 30.18; H, 4.52. Found: C, 29.93; H, 4.62.

The same product was prepared by an alternative route. This involved addition of the theoretical amount of $NaBH_4$ to a DME solution containing the product of the reaction $UCl_4 + 2(\eta^5\text{-}C_5H_5)Tl$ (the resulting TlCl being previously filtered off).

The infrared spectrum of the title compound, recorded over the range 4000-600 cm^{-1} (Nujol mulls were prepared in box with dry, degassed Nujol) shows a strong singlet (2480 cm^{-1}), a doublet (2140 and 2200 cm^{-1}; 60 cm^{-1} splitting) and a strong band (1180 cm^{-1}). According to T.J. Marks et al. [2] the observed bands may be considered to provide significant evidence for tridentate ligation by the BH_4 group. Furthermore, the modes characteristic of π-bonded cyclopentadienyl groups are present (800 cm^{-1}: C-H out-of-plane wagging and 1010 cm^{-1}: in-plane wagging).

In the room temperature 60 MHz pmr spectrum of $(\eta^5\text{-}C_5H_5)_2U(BH_4)_2$ in hexadeuterobenzene, a singlet (10 H) at +1.93 ppm and a quartet at +26.57 ppm(8H) are present (intensity ratio af the bands: 10/8). The data are relative to internal benzene (+ indicating shifts to high field) and they indicate magnetic equivalence of the bridge and terminal BH_4 hydrogen atoms as in the case of the $(\eta^5-C_5H_5)_3U(BH_4)$ complex.[3]

Crystal data. $C_{10}H_{18}B_2U$. M= 397.6, dark red prismatic crystals, monoclinic, space group $P2_{1/a}$, a= 24.636(9), b= 7.148(3), c= 14.221(6) Å and β= 92.75(9)°, U= 2501.4 Å^3, d_c=2.11 g.cm^{-3}, Z=8. Monocromated MoK_α radiation (λ=0.7107 Å). Present R value 12 % calculated on the 1250 independent observed reflexions ($I > 2.5\sigma(I)$) collected on a automatic diffractometer with the $\vartheta/2\vartheta$ scan tecniques up to ϑ=25°.

The structure has two independent $(\eta^5-C_5H_5)_2U(BH_4)_2$ molecules in the asymmetric unit. The coordination geometry around each uranium atom is tetrahedral in both cases with the boron atom positions and the centres of the two cyclopentadienyl rings as apexes. There is some disordering on the carbon atom positions that may be ascribed either to a space disorder or to a time disorder, i.e. in the latter case to a fluxional process in the crystal.

Because of the disordering we can give here only an outline description of the structure. The positions of the boron atoms and the approximate positions of the carbon atoms allow us to describe the structure as being formed by discrete molecules of $(\eta^5-C_5H_5)_2U(BH_4)_2$. The two independent units do not differ significantly (on the basis of the present e.s.d.'s viz.: 0.08 Å for distances involving the uranium atom and 12° for the angles). The two U-B distances are 2.61 and 2.58 Å for molecule 1, and 2.63 and 2.63 Å for the molecule 2. Whereas the U-C distances vary in both cases between 2.4 and 2.8 Å. The two angles involving the boron atoms and the uranium are 99.6 and 102.5°.

It appears that a satisfactory identification of the coordination geometry of the individual uranium atoms can only be achieved through neutron diffraction work; the possibility of performing this investigation is being explored. The i.r. results favour a tridentate ligation by the BH_4 group. This view is supported by the values of the U-B distances which are shorter than those reported for complexes in which a bidentate ligation is present. In fact, in the case of the $U(BH_4)_4$[4] where the BH_4 unit is either as bidentate (bridging) or tridentate, the distances are 2.52(1) Å , and 2.90(1) , 2.82(1) Å respectively. Confirmation of these hypothesis awaits the neutron diffraction studies.

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