Journal of Organometallic Chemistry, 310 (1986) C1–C4
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

SYNTHESIS AND CHARACTERIZATION OF TRICYCLOPENTADIENYLURANIUM TETRAHYDROALUMINATE

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(Received March 11th, 1986)

Summary

Cp_3UAlH_4 ($Cp = \eta^5$-cyclopentadienyl) has been synthesized by the reaction between Cp_3UBH_4 and $LiAlH_4$ in Et_2O. A polymeric structure in which trigonal planar Cp_3U units are interconnected by AlH_4 groups is proposed.

The compounds produced by the reactions of *d*-transition metal derivatives with tetrahydroaluminate salts are attracting increasing interest because they promote such reactions as hydrogenation [1,2], isomerization [3–5] and hydrometallation [3,6] of olefins. In order to extend such investigations to analogous compounds of the 5*f* series elements we have made tricyclopentadienyluranium tetrahydroaluminate Cp_3UAlH_4 which was obtained in yields of up to 90% from the exchange reaction of the corresponding tetrahydroborate Cp_3UBH_4 with $LiAlH_4$ (eq. 1):

$$Cp_3UBH_4 + LiAlH_4 \rightarrow Cp_3UAlH_4 + LiBH_4 \qquad (1)$$

Cp_3UAlH_4 separates out immediately as a green microcristalline powder * when a saturated Et_2O solution of $LiAlH_4$ is added dropwise to a Et_2O solution of Cp_3UBH_4 at room temperature **. The ^1H and ^{11}B NMR spectra of the filtered solution clearly indicate the presence of $LiBH_4$ as the co-product. Cp_3UAlH_4 is extremely air sensitive and ignites spontaneously on exposure to the atmosphere; it decomposes at 120°C with gas evolution. It is insoluble in n-hexane and in Et_2O, and reacts with the other solvents normally used in organometallic synthesis, namely benzene, toluene, DME and THF.

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* The powder was washed several times with Et_2O and dried. Found: C, 38.70; H, 4.14; Al, 5.93; U, 51.17. $C_{15}H_{19}AlU$ calcd.: C, 38.80; H, 4.12; Al, 5.81; U, 51.26%.

** The reactions of Cp_3UNEt_2, Cp_4U, Cp_3UMe, Cp_3UCl, with $LiAlH_4$ in Et_2O or THF/hexane, like those of Cp_3UBH_4, also give insoluble green compounds, whose IR spectra present some slight differences in the shape and relative intensities of the bands due to the hydride vibrations, probably because of the presence of by-products.

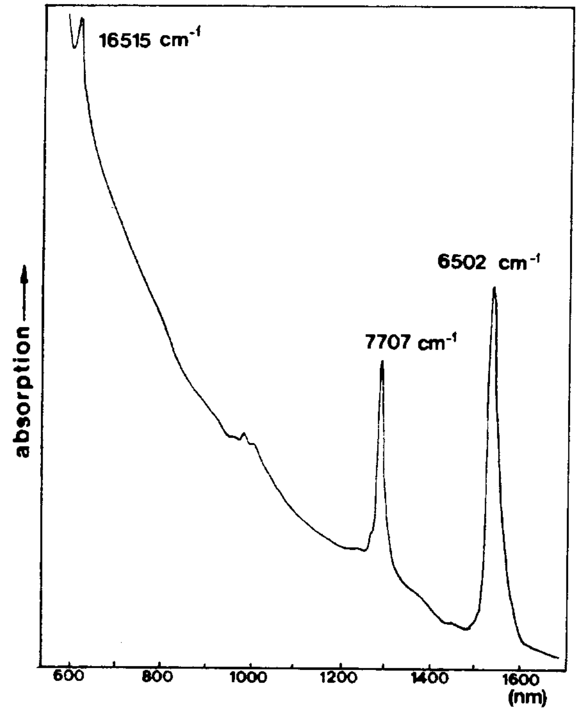

Fig. 1. Near-IR-visible spectrum of Cp_3UAlH_4 (Nujol mull sandwiched between quartz disks).

Solid Cp_3UAlH_4 in Nujol gives rise to three absorptions in the near-IR-visible spectrum (Fig. 1) at 6502, 7707 and 16515 cm^{-1}, which are characteristic of U^{IV} complexes with trigonal bipyramidal coordination around the central metal [7]. The IR spectrum of Cp_3UAlH_4 (Fig. 2) shows, in addition to the usual Cp vibrations (marked by the sign ▲), broad bands between 1800 and 1500 cm^{-1} (a, b, c, d) and at 725 cm^{-1} (e), which can be assigned to metal-hydrogen vibrations, as confirmed by the shift to lower wavenumber by a factor of about 1.37 in the spectrum of the corresponding deuterated compound Cp_3UAlD_4 (obtained by use of $LiAlD_4$ in place of $LiAlH_4$ in reaction 1). Band e is characteristic of the deformation vibrations involving the hydride hydrogens, and the bands a, b, c, d can be assigned to the terminal Al–H and to the bridging M–H–Al stretching vibrations [8–13].

Unfortunately, because of the extreme insolubility or reactivity of Cp_3UAlH_4 in the common solvents structural determination has not yet been possible; nevertheless the near-IR-visible and IR spectra, together with the insolubility and involatility, suggest a polymeric chain configuration in which trigonal planar Cp_3U-units are interconnected by AlH_4 groups (Fig. 3).

Dissolution of Cp_3UAlH_4 in THF gives rise to a gas evolution (analysis of the gas by mass spectrometry reveals the presence of H_2), while the ^1H NMR spectrum of Cp_3UAlH_4 in THF-d_8 shows initially, a sharp singlet at 16.50 ppm (upfield from benzene as internal standard) which rapidly disappears to be replaced by a signal at about 22 ppm; at this point the near-IR-visible absorption spectrum of the (now brown) solution corresponds to that of $Cp_3U^{III} \cdot (THF)$ [14].

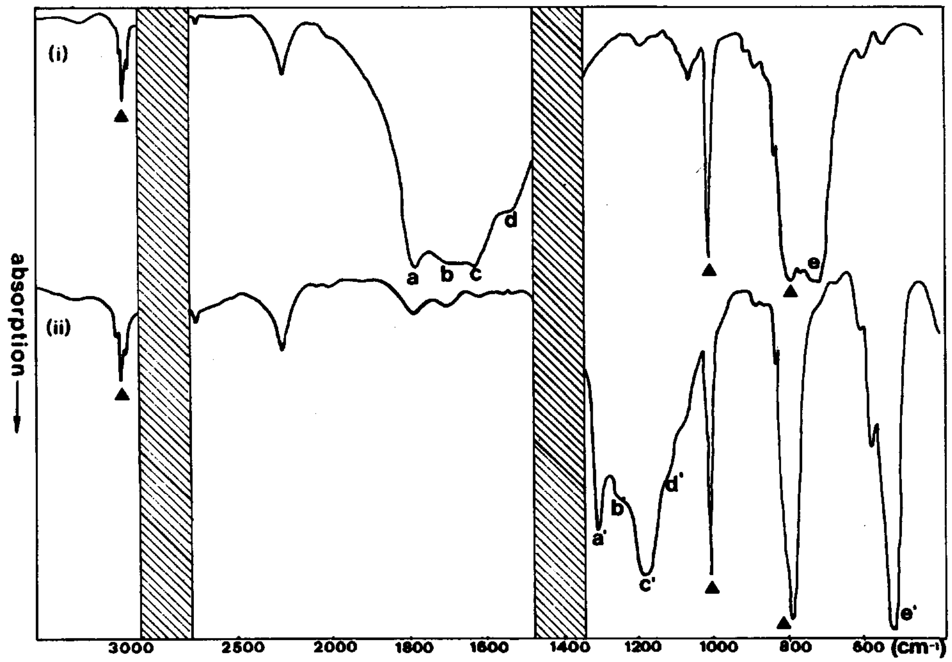

Fig. 2. IR spectra of Cp_3UAlH_4 (i) and Cp_3UAlD_4 (ii) (Nujol mulls, KBr disks) ▨ = Nujol absorption.

These observations parallel those for the reaction of Cp_3UCl with $LiAlH_4$ in THF, as reported by Marquet-Ellis and Folcher [15]. The initial signal at 16.50 ppm which we observed corresponds to their intermediate species suggested to be the hydride complex Cp_3UH, which, as in our experiment, decomposed to Cp_3U^{III} derivatives. Thus the reaction sequence in our case can be represented as follows:

$$Cp_3UAlH_4 \xrightarrow{THF} Cp_3UH + AlH_3 \cdot THF$$

$$Cp_3UH \xrightarrow{THF} Cp_3U \cdot THF + 1/2\ H_2$$

In this sequence the affinity of the acid AlH_3 towards the base THF, which

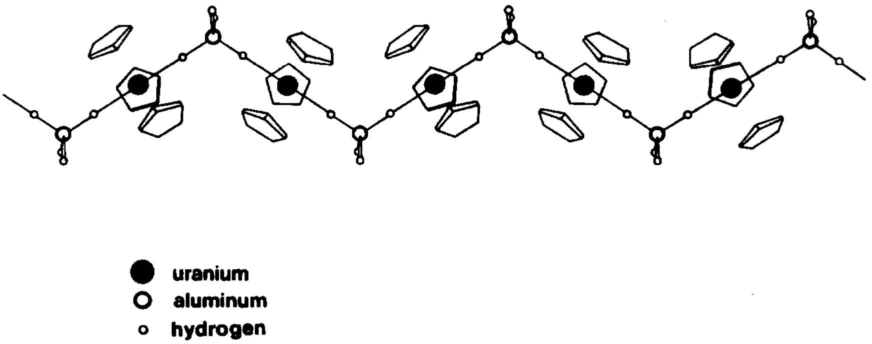

Fig. 3. Suggested structure for Cp_3UAlH_4.

causes the cleavage of the U–H–Al bonds, and the well known reducing effect of the hydride ion of U^{IV} in THF [16], have decisive influences on the reaction. Consequently the successful preparation of Cp_3UAlH_4 in Et_2O, and the impossibility of isolating it in THF, are probably due to the fact that THF is more basic than Et_2O, which is not able to abstract the acid AlH_3 from the complex Cp_3UAlH_4. Preliminary investigations have revealed the high reactivity of Cp_3UAlH_4 towards a wide range of substrates, such as alkenes, alkynes, nitriles, pyridine, ketones, alcohols, CH_3I, and BH_3.

The authors thank Prof. R.D. Fischer of the University of Hamburg for an extensive and determinant discussion, and Mr. F. Braga and Mr. A. Zaghini for the technical assistance.

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