

## ORGANOMETALLIC CHEMISTRY OF URANIUM I. DICYCLOPENTADIENYLURANIUM(IV) CHLORIDE

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### SUMMARY

Dicyclopentadienyluranium(IV) chloride ( $\text{Cp}_2\text{UCl}_2$ ) has been prepared by reaction of uranium tetrachloride with cyclopentadienylthallium in dimethoxyethane, and has been characterized by elemental analysis and UV and IR spectra.

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Studies of organometallic chemistry of uranium(IV) compounds containing both organic and halide groups have involved only the compounds  $\text{Cp}_3\text{UX}$  ( $\text{Cp} = \text{C}_5\text{H}_5$ ;  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ )<sup>1,2</sup>. This paper describes the preparation and properties of a new uranium(IV) organometallic compound,  $\text{Cp}_2\text{UCl}_2$ .

### EXPERIMENTAL

#### *Syntheses*

All the operations were carried out under nitrogen in a dry-box containing Na/K alloy. Dimethoxyethane was distilled under nitrogen from Na/K alloy, with benzophenone as indicator. Uranium tetrachloride was prepared as described in ref. 3.  $\text{CpTi}$ , prepared as in ref. 4, was purified by sublimation.

$\text{Cp}_2\text{UCl}_2$  was obtained by the reaction of  $\text{UCl}_4$  with  $\text{CpTi}$  (molar ratio 1/2) in dimethoxyethane (DME). A typical synthesis was as follows: a mixture of  $\text{UCl}_4$  (1.23 g, 3.25 mmoles) and  $\text{CpTi}$  (1.75 g, 6.50 mmoles) in DME (50 ml) was stirred for about 3 h at room temperature. The dark-green solution was filtered from  $\text{TiCl}_3$  and the solvent was removed under vacuum. The green-brown solid obtained in this way was soluble in coordinating solvents, such as THF and acetone. Attempts to recrystallize and to sublime the crude product have so far been unsuccessful.  $\text{Cp}_2\text{UCl}_2$  decomposes readily in the presence of air, both in solution and in the solid state. (Found: C, 26.6; H, 2.7; Cl, 16.0; U, 53.4.  $\text{C}_{10}\text{H}_{10}\text{Cl}_2\text{U}$  calcd.: C, 27.35; H, 2.29; Cl, 16.15; U, 54.20%.) Uranium and chloride were determined gravimetrically, as  $\text{U}_3\text{O}_8$  and  $\text{AgCl}$  respectively, after destruction of the organic matter with concentrated nitric acid.

#### *Spectra*

The UV spectrum of  $\text{Cp}_2\text{UCl}_2$  in DME, recorded on a Beckman DK2A Spectrophotometer, shows the following maxima (in the range 500–800  $m\mu$ ) 503,

539, 562, 567, 588, 606, 642, 665, 699, 713, 749, 787  $m\mu$ .

The IR spectra, measured in Nujol and hexachlorobutadiene mulls with a Perkin-Elmer 621 Spectrophotometer, show the following peaks ( $\text{cm}^{-1}$ ): 3104vw, 2927w, 1440m, 1364w, 1186vw, 1112w, 1078m, 1011s, 852m, 785s.

#### Magnetic measurements

The magnetic susceptibility was measured in the solid phase at room temperature by the Gouy method. The measured molar susceptibility value, corrected for diamagnetism ( $-133 \times 10^{-6}$  cgs u.) was  $\chi_M = 2786 \times 10^{-6}$  cgs u. Using the spin only formula, we calculate  $\mu_{\text{eff}}$  2.65 BM.

#### DISCUSSION

The new compound in DME has a spectrum very similar to that of  $\text{Cp}_3\text{UCl}$  in the region 500–800  $m\mu^{1,5}$ . Maxima associated with uranium tetrachloride in DME are not present, indicating that the reaction with  $\text{CpTi}$  is complete. The crude solid does not contain  $\text{Cp}_3\text{UCl}$ . In fact we could not obtain any sublimation product by heating under vacuum ( $\approx 10^{-4}$  mm) at about 200°.

IR spectra in the C–H stretching region show both the asymmetric band at 3104  $\text{cm}^{-1}$  and the symmetric band at 2927  $\text{cm}^{-1}$ , indicating the presence of centrally bonded cyclopentadienyl ligands. The weak bands in the 1100  $\text{cm}^{-1}$  region could indicate some degree of ionic character<sup>6</sup>.

The magnetic susceptibility of  $\text{Cp}_2\text{UCl}_2$  does not differ significantly from the values reported for  $\text{Cp}_3\text{UCl}^1$  and  $\text{Cp}_4\text{U}^7$ , and suggests the existence of two unpaired electrons.

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