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A Contribution to the Organometallic Chemistry of Uranium: Tetra(Allyl)Uranium

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The synthesis of tetra-allyl Uranium, obtained from UCl_4 and C_3H_5 Mg Br, is reported. The isolated crystalline dark-red complex is not thermally stable above −20 °C and burns spontaneously in the air. Its infrared spectra could be reasonably in agreement with π-bonded allylic groups. Thermal decomposition and cleavage with H_2O gave the expected hydrocarbon products.

Introduction

The organometallic chemistry or low valency uranium is still an unexplored field. As far as we know, the only well characterized uranium derivatives reported in the literature are cyclopentadienyl compounds, such as $(C_5H_5)_3UCl$[1] obtained from sodium cyclopentadienide and uranium tetrachloride in tetrahydrofuran solution, and $(C_5H_5)_4U$[2] from potassium cyclopentadienide in benzene.

More recently Streitwieser[3] starting from U^{+4} and cyclooctatetraene dianion, reported the synthesis of bis(cyclooctatetraenyl) uranium, for which a sandwich-structure of the ferrocene type is postulated.

This prompted us to reporte our preliminary results on the synthesis of an allyl derivative of uranium: tetra(allyl)uranium.

Experimental Section

All operations and reactions were carried out under dry argon atmosphere or in vacuum.

Materials. Uranium tetrachloride was prepared from U_3O_8 and hexachloropropene.[4] Solvents were dehydrated by distillation over lithium aluminum hydride.

Measurements. Infrared spectra were run on P.E. 125 instrument. Magnetic susceptibility measurements in solution were carried out with a Varian 60 NMR spectrometer, by using the Evans procedure.[5] Gas analyses were carried out with an Atlas-werke CH4 spectrometer.

Analyses. Uranium was determined by precipitation with ammonium hydroxide as reported in the litterature.[6]

Preparation of $(C_3H_5)_4U$. 163 ml of a molar solution of C_3H_5MgBr in ethyl ether were added very slowly (10 h) to a suspension of 10.31 g of anhydrous UCl_4 (27.1×10^{-3} mole) in 180 ml of ethyl ether cooled at −30 °C. The mixture was stirred for a few hours while keeping the temperature in the range −20 ÷ −30°C. The green UCl_4 progressively disappeared and a deepred solution was obtained. The mixture was filtered at −30°C through a sintered glass filter and the solvent was removed under high vacuum from the clear solution.

80 ml of pentane, previously cooled at −40 °C, were added to the dry residue and the mixture was filtered again. The pentane solution was concentrated in vacuum and cooled at −78°C or lower. Bright dark-red crystals slowly set down.

The compound was purified by recrystallization in the same conditions. Yield 60% based on UCl_4.

Anal. calctd. for $C_{12}H_{20}U$: C, 35.82; H, 4.98; U, 59.20. Found: C, 35.68; H, 4.97; U. 58.40.

Decomposition reactions. Cleavage with H_2O. An ether solution containing 442 mg of $(C_3H_5)_4U$, cooled at −40 °C, was introduced in a flask and the solvent was removed in vacuum. The flask was connected to a gas-volumetric apparatus and 8 ml of H_2O were added. The flask was then slowly warmed up to room temperature and the gas evolved (90.1 Ncc) was identified by mass spectrometry as propylene (97.3%) and 1,5-hexadiene and cyclohexene (2.7%) corresponding to a total yield of 94% as C_3.

Thermal decomposition. The decomposition was carried out in an evacuated apparatus containing 450 mg (1.12 mmole) of the product cooled at −78 °C. The dry-ice acetone bath was removed and after about 30 min. a violent evolution of gas took place (61.9 Ncc).

The gas was analyzed by mass spectrometry and identified as propylene (81.5%) and propane (18.5%). The yield as C_3 product was 2.46 mmole per uranium atom.

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1) L. T. Reynolds and G. Wilkinson, *J. Inorg. Nucl. Chem.*, *2*, 246 (1956).
2) E. O. Fischer and Y. Hristidu, Z. Naturforsch., *17b*, 275 (1962).
3) A. Streitwieser and U. Muller-Westerhoff, *J. Am. Chem. Soc.*, *90*, 7364 (1968).
4) *Inorganic Sinthesis*, *5*, 143.
5) P. F. Evans, *J. Chem. Soc.*, 2003 (1959).
6) « Analytical chemistry of uranium » Akad. Sci. of the U.S.S.R., translated by Israel Programm for Scientific Translation, Jerusalem, 1963, pag. 44.

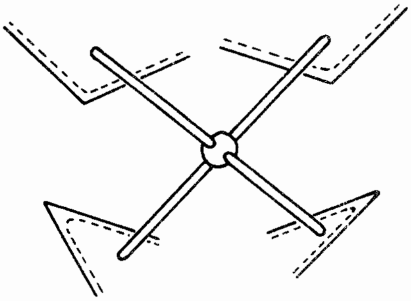
Results and Discussion

The reaction of UCl_4 with allyl Grignard, at low temperature, yields $(C_3H_5)_4U$ according to the equation:

$$4C_3H_5MgBr + UCl_4 \rightarrow (C_3H_5)_4U + 4MgClBr$$

The isolated crystalline dark-red complex quickly undergoes oxidation and burns spontaneously in the air, but it is stable under inert atmosphere. The product is thermally stable up to −20 °C, therefore it must be handled at low temperature, such as $-30 \div -40$°C, and stored at −78 °C. The compound is soluble in organic solvents and can be recrystallized from pentane or hexane solution by lowering the temperature.

Chemical analyses agree with four allyl groups per uranium atom



Preliminary characterization of the complex has been made by infrared spectroscopy and magnetic susceptibility measurements and further work is still in progress also by nuclear magnetic resonance.

Infrared spectra. The infrared spectra of the complex in the $2.5 \div 25$ μ region in C_2Cl_4 at −20°C and $(C_2H_5)_2O$ solution at −40°C show absorptions at: 3065 m, 2980 m, 2930 mw, 1550 m, 1500 vs, 1450 m, 1220 s, 1000 s, 810 vs, 750 s, 710 m, 580 s, 430 m.

In both solutions spectra there are definite evidences of olefinic CH stretching vibrations at 3065 cm^{-1}. No double stretching frequencies, which could be ascribed to a σ-allyl structure, were observed in the 1650-1600 cm^{-1} range.

Among the other absorption bands, the more defined at 1220, 1000, 810, 750 and 580 cm^{-1} could be reasonably attributed respectively to the δCH_2, $\nu C{-}C$, δCH and $\delta C\overset{C}{\diagup\,\diagdown}C$ modes of vibration of a π-allylic group in agreement with previous work.[7]

Magnetic susceptibility measurements. The compound is paramagnetic with values of χ_M (corrected for a diamagnetic contribution of -145.10^{-6}) varying from 2480.10^{-6} at 213 °K to 2180.10^{-6} at 253 °K.

Curie-Weiss law seems to be followed in this temperature interval although, given the small range of temperature investigated, a Weiss constant $\theta = \sim 100$ °K can be estimated only with some uncertainty. The magnetic moment of the compound is calculated to be 2.6 B.M., this being an upper limit which takes into account the Weiss correction.

This value of the magnetic moment is somewhat lower than the usual value of 2.8 B.M. expected[8] for U^{+4} f^2 ground state configuration in a cubic field. The result is so very similar to what is found for $(C_5H_5)_3UCl$ and $(C_5H_5)_4U$ supporting the idea of a similarity in the type of bonding.

Further measurements are in progress together with NMR studies.

Decompositions. The decomposition reaction of the product with water agrees with the proposed formula.

The thermal decomposition yields a gas phase in which propylene and propane are present according to what reported in literature[9] for similar products, such as allyl chromium.

As a matter of fact, the cleavage of an allyl radical with subsequent hydrogen shift can give propylene and allene. This last product is not present in the gas phase, probably because it can easily undergo polymerization reaction. Propane formation is not clearly interpreted on the basis of the proposed explanation.

Attempts to obtain new complexes by reaction of $(C_3H_5)_4U$ with cyclooctadiene or triphenylphosphine ligands have so far been unsuccessful; in both cases the ligands were recovered unreacted. Additional investigations on these reactions are now in progress.

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7) H. P. Fritz, *Chem. Ber.* *94*, 1217 (1961).

8) C. A. Candela et al., *J. Chem. Phys.*, *30*, 246 (1959); ibid *27*, 707 (1957).

9) W. Oberkirch, Dissertation, Technische Hochschule, Aachen, (1963).