Inorganica Chimica Acta, 119 (1986) 107–109

Uranium–Acyl Complex Intermediate from Oxidative Addition of Uranium Triscyclopentadienyl with Acetylchloride

C. C. CHANG and N. K. SUNG-YU

National Sun Yat-Sen University, Kaohsiung, Taiwan

(Received March 18, 1986)

Abstract

The first example of uranium acyl compound $Cp_3UCl[C(O)CH_3]$, which was characterized by ^1H NMR, electrochemical data, and chemical properties is reported. It was found by the additive addition reaction of uranium triscyclopentadienyl with acetylchloride at 6 °C. The product of the oxidative addition can undergo a rearrangement to yield the substituted polycyclopentadiene.

Introduction

The search for practical new energy and organic raw materials has renewed interest in the production of fuels and chemicals from hydrogen-deficient materials. Therefore, the reduction of coal-derived carbon monoxide–hydrogen via the Fischer–Tropsch and related reactions are widely investigated [1, 2]. Collman, Casey, Gladysz and their co-workers have proposed that the metal formyl complexes may be important intermediates in the initial step of CO with hydrogen reduction [3–5]. For the past ten years there have been many reports on the reactions of transition metal formyl or metal acyl complexes. Slater and coworkers [6–8] were the first to attempt the code-position of lanthanide or actinide metal with CO in an argon matrix at 4 K to produce species that have been identified by matrix infrared spectroscopy as the compounds $M(CO)_n$, $n = 1$ to 6. There is no report on lanthanide and actinide carbonyl or acyl complexes. These areas are very attractive and wide open to explore the nature of f orbital complexes.

Our previous work studied the reaction of uranium(III) triscyclopentadienyl with ethyl halide in the presence of uranium powder, which produced ethane, ethene, n-butane and uranium(IV) triscyclopentadienyl halide [9]. If oxidative addition was expected to be one of the pathways, the decomposition of thermally unstable intermediate is reasonable. Also, Fenke reported the first oxidative addition of organoactinide with alkylhalide [10]. So, in considering the stability which was effected by the substituent groups, the metal acyl intermediate from the reaction of uranium triscyclopentadienyl with acetyl chloride was found to be in existence at the low temperature, as shown by the ^1H NMR spectra, electrochemical data and other evidence.

Experimental

Apparatus and Materials

All operations were carried out in a glove box or in an evacuated system. All organic solvents were distilled prior to use. Infrared spectra were obtained on a Perkin-Elmer 397 and Hitachi 260-30 infrared spectrophotometer. ^1H NMR spectra were recorded on a Varian Ft-80A spectrometer, and chemical shifts were measured relative to internal Me_4Si. The elemental analysis was performed by Chun-Shan Institute, Taiwan. The electro-chemical data were obtained from the PAR system. The molecular weight was determined by a gel permeation chromatograph of Waters Associates ALC 200 with a 6000A model delivery system.

I. Reaction of Uranium–Triscyclopentadienyl with Acetyl Halide

Three milliliters of acetyl chloride was added to the volume flask containing a solution of 0.30 g uranium triscyclopentadienyl (UCp_3), which was prepared according to previously described methods, in 50 ml of benzene in an evacuated system. The reaction solution changed color from bronze to red in fifteen minutes. After a 2 h reaction period, the reaction mixture turned to dark green. It was filtered and separated in silica gel column. The green residue was washed with diluted hydrochloric acid and found to be uranium chloride ($Cl/U \simeq 2$). The eluted collected fraction by benzene was pumped to dryness; the solid was characterized to be the poly-acetylcyclopentadiene. *Anal.* Calc. for $C_{21}H_{14}O$; C, 82.76, H, 8.04. Found: C, 83.19; H 7 58%. The infrared spectral data (KBr pellet) showed: 3050(m), 2940(vs), 2860(s), 1695(s), 1665(m), 1615(w), 1440(s), 1360(s), 1200(br), 950(m), 750(br) cm^{-1}. The ^1H NMR (C_6D_6) are: two fairly sharp peaks at

0020-1693/86/$3.50

$\delta = 2.3$, 5.6 ppm and three broad peaks at $\delta = 1.6$, 2.1 and 2.65 ppm. The wide range of molecular weight distribution to $M_r = 200\,000$ was determined by gel permeation chromatography.

Spectral Measurement

The excess of acetylchloride was added into the NMR tube containing the d_6-benzene solution of uranium triscyclopentadienyl **1**, which showed the chemical shift of a single peak at $\delta = -3.27$ ppm at room temperature and shifted to $\delta = -4.26$ ppm at 6 °C upper field from proton chemical shift of acetylchloride which appeared at $\delta = 1.66$ ppm. After a ten minute reaction period, the decrease of intensities of the peaks of acetyl chloride and uranium triscyclopentadienyl chloride was observed; during reaction period, a new peak gradually appeared simultaneously at $\pi = -3.86$ ppm and 1.69 ppm. The integral intensity ratio of $\delta = -3.86$ and $\delta = 1.69$ ppm was 5.2. After a 12 h reaction period, the peak at $\delta = -4.26$ ppm disappeared, while the temperature of the reaction mixture increased up to room temperature. The spectral data were listed in the previous section and showed the existence of polyacetyl-cylclopentadienyl.

Electrochemical Measurement

From cyclic voltammetric studies of the reaction at 6 °C the reductive wave at $E_{red} = -1.08$ V, which appeared when the complex was reduced at the dropping mercury electrode, disappeared at $E_{red} = -0.36$ V. The cyclic voltammetric diagram is shown in Fig. 1. Also the electrochemical data for a number of uranium complexes are shown in Table I. The reduction potentials of different valence states were studied in order to understand the valence state of the intermediate. All the parameters were kept as constant as possible.

TABLE I. Electrochemical Data of Uranium Complexes

Compound	$-E_{p,c}$ (V)	Assigned reduction	n[a]
$U(C_5H_5)_3Cl$[b]	−0.95	(IV) → (III)	1.04
$U(C_5H_5)_3Br$[b]	−0.85	(IV) → (III	1.12
$U(C_5H_5)_3I$[b]	−0.93	(IV) → (III)	0.90
$U(C_8H_8)_2$[b]	−0.98	(IV) → (III)	0.01
UCl_4[b]	−0.60		
$U(C_2H_3O_2)_4$[b]	−0.76	(IV) → (III)	1.17
$U(OCH_3)_5$[c]	−0.84	(IV) → (III)	0.90
$U(OCH_3)_6$[c]	−0.08	(VI) → (V)	1.01
	−0.70	(IV) → (III)	1.02
$U(C_5H_5)_3$[d]	−0.96	(III) → (II)	1.09

[a] Data from controlled potential at room temperature. [b] Supporting electrolytes: $C_4H_8O-(C_4H_9)_4NClO_4$ (0.1 mol). [c] Supporting electrolytes: $CH_3OH-(C_4H_9)_4NClO_4$ (0.1 mol) [d] Supporting electrolytes: $C_6H_6-(C_4H_9)_4NClO_4$ (0.1 mol).

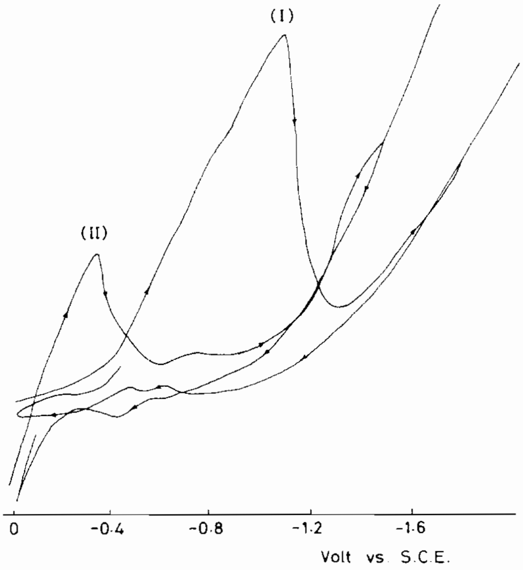

Fig. 1. Cyclic voltammograms at 6 °C of (I) benzene solution of UCp_3 and (II) after addition of acetylchloride. The scan rate is 500 mV/s.

II. Reaction of Uranium Triscyclopentadienyl with Benzoyl Chloride

Three millilitres of benzoyl chloride was added to the volume flask containing 0.30 g of uranium tricyclopentadienyl (UCp_3) in 50 ml of benzene in an evacuated system. The mixture was allowed to reflux for 2 h The reaction mixture was then filtered and separated with silica gel column. The green residue was washed with diluted hydrochloric acid and found to be uranium chloride (Cl/U = 2). The eluted benzene solution was pumped to dryness. The green solid was characterized by spectral data and elemental analysis. Calc. for $C_{17}H_{14}O$: C, 88.80; H 8.00. Found: C, 88.68; H 8.19%. The infrared spectral data (KBr pellet) showed at: 3050(m), 2935(vs), 2850(s), 1725(m), 1680(s), 1596(m). 1356(w) 1250(br), 1180(w), 1085(w). 1065(w), 1025(w), 1005(w), 750(br) 700(s).

Five broad peaks of ^1H NMR (C_6D_6) were shown at $\delta = 8.07$, 5.75, 2.77, 2.26 1.86 ppm. The wide range of molecular weight distribution to $M = 50\,000$ was determined by gel permeation chromatography.

Results and Discussion

The reaction of uranium triscyclopentadienyl with acetyl chloride or benzoyl chloride gives a green solid which is uranium tetrachloride and a polymer. ^1H NMR spectral data of the polymer from the reaction of uranium triscyclopentadienyl with acetylchloride appear at $\delta = 5.6$, 1.6 2 1, 2 3 and 2.65 ppm. Besides the peak at 2.3 ppm for the acetyl group, the data were in good agreement with polycyclopentadiene [11, 12]. Williams *et al.* had assigned the spectral data accordingly: 1.6 ppm for the non-allylic ($>CH_2$), 2.1 ppm for the allylic ($>CH_2$), 2.65 ppm for the allylic ($>CH_2$) group. The data showed the presence of 1,4-polycyclopentadiene and 1,2-polycyclopentadiene mixture. The infrared spectral data showed absorption peaks at 1695 cm^{-1} and 1665 cm^{-1} for the S-*cis* and S-*trans* C=O group, respectively. Elemental analyses were found to be in agreement with a compound having a molecular formula of $C_{12}O_{14}O$, showing the polymer to be 1,4- and 1,2-$\left(C_5H_5-C_5H_4-C(O)CH_3 \right)_n$. Other elemental analyses, ^1H NMR, and infrared spectral data of the polymer from the reaction of UCp_3 with benzoylchloride supported the presence of substitured polycyclopentadiene as well.

When the reaction was studied at low temperature, interesting data were obtained. ^1H NMR spectral data showed a single peak with a chemical shift of δ = −4.26 ppm at 6 °C, and δ = −3.27 ppm at room temperature for UCp_3, and for UCp_3Cl a single peak at δ = −3.5 ppm at room temperature. After the addition of acetylchloride to the benzene solution of uranium triscyclopentadienyl, the intensities of the two peaks changed. The chemical shifts at δ = −4.26 ppm and 1.69 ppm disappeared after ten hours of reaction and two new peaks appeared gradually with a chemical shift at −3.86 ppm and δ = 1.66 ppm; these were assigned to be from the chemical shift of the π-cyclopentadienyl group and of the methyl in acetyl group attached to the uranium atom, with the integral intensity ratio of 5.2. The chemical shift changes from δ = −4.26 ppm to −3.86 ppm which is shifted downfield. It suggested an increase in the valence state of the uranium atom, whereby the intermediate could be one of three possible compounds: UCp_3Cl (**I**) $[CH_3-C(O)UCp_3]^+Cl^-$ (**II**) or $CH_3C(O)$-UCp_3Cl (**III**). The ^1H NMR spectra showed a chemical shift at δ = −3.86 which rules out the existence of UCp_3Cl. Its solubility in benzene makes the salt $[CH_3-C(O)UCp_3]^+Cl^-$ unlikely; this suggests the presence of $CH_3C(O)UCp_3Cl$.

The existence of $CH_3C(O)UCp_3Cl$ was further investigated using electrochemical methods. The cyclic voltammetric data showed the reduction potential of uranium triscyclopentadienyl at −1.08 V. After the addition of acetylchloride, the new reductive wave appeared at E_{red} = −0.36 V which is not for acetylchloride. The data indicate that uranium metal proceeds via the oxidation of U(III) → U(V). In order to determine the valence state of uranium, many uranium complexes were used to study the electrochemical properties listed in Table I. It was found that the reduction potentials of the valence (**IV**) to U(**III**) were around −0.9 V ~0.70 V, although the parameter influencing the values was kept as constant as possible.

The E_{red} = −0.36 V confirms that the valence state is U(**V**) instead of U(**IV**). So this also supported the presence of the $CH_3C(O)UCp_3Cl$ intermediate. This is thus an oxidative type of reaction. Fenke had reported the first example of an oxidative addition of organouranium with alkyl halide.

Werner had reported a facile electrophilic substitution at the cyclopentadienyl ring in a cobalt half-sandwich complex [13]. The reaction of alkyl halides (R = CH_3, C_2H_5, i-C_3H_7 t-C_4H_9, $C(CH_3)_2$-C_2H_5) with $(Me_3P)_2(Cp)CoMe$ gave two kinds of products: (i) $C_5H_4R(Me_3P)_2CoH^+$ and (ii) $Cp(Me_3P)_2CoH^+$. They proposed that the reaction mechanism proceeded with the alkyl group attached to the cobalt metal in the first step, and then it rearranged to the cyclopentadiene ring. If the alkyl groups were bulky, an alkyl substituted cyclopentadienyl cobalt complex was formed with elimination of a proton. In the present work, a reaction mechanism is suggested in which the acetyl groups of the initially formed intermediate migrate to the cyclopentadiene ring; then the rearrangement makes it decompose to polycyclopentadiene.

Acknowledgement

Many thanks to the National Science Council for support.

References

1 C. P. Casey, M. A. Andrews and J. E. Ring, *J. Am. Chem. Soc., 101,* 741 (1979) and refs. therein.

2 G. H. Olive and S. Olive, *Angew. Chem., Int. Ed. Eng., 15,* 136 (1976).

3 J. P. Collman and S. R. Wintor, *J. Am. Chem. Soc., 95,* 4089 (1973).

4 C. P. Casey and M. S. Neumann, *J. Am. Chem. Soc., 98,* 5395 (1976).

5 J. A. Gladysz and W. Tam, *J. Am. Chem. Soc., 100,* 2545 (1978).

6 R. K. Sheline and J. L. Slater, *Angew. Chem., Int. Ed. Engl., 14,* 309 (1975).

7 J. L. Slater, T. C. Devore and V. Calder, *Inorg. Chem., 12,* 1918 (1973).

8 J. L. Slater, T. C. Devore and V. Calder, *Inorg. Chem., 13,* 1808 (1974).

9 N. K. Sung-Yu, F. F. Hsu, C. C. Chang and C. T. Chang, *Inorg. Chem., 20,* 2727 (1981).

10 R. G. Finke, Y. Hirose and G. Gaughan, *J. Chem. Soc., Chem. Commun.,* 232 (1981).

11 C. Aso, T. Kunitake, K. Ito and Y. Ishimoto, *Polymer Lett., 4,* 701 (1966).

12 M. A. Bonin, W. R. Busler and F. Willans, *J. Am. Chem. Soc., 87,* 199 (1965).

13 H. Werner and W. Hofmann, *Angew. Chem., Int. Ed. Engl., 16,* 794 (1977).