

## Electrogeneration of the Stable Chlorotris(cyclopentadienyl)-uranium(III) Anion

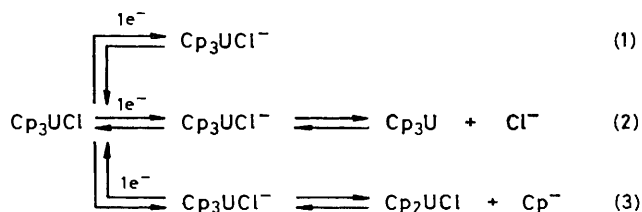
Yves Mugnier, Alain Dormond, and Etienne Laviron

Laboratoire de Synthèse et d'Electrosynthèse Organométallique associé au CNRS (LA 33), Faculté des Sciences Gabriel, 6, Boulevard Gabriel, 21100 Dijon, France

The electrochemical reduction of tris(cyclopentadienyl)uranium(IV) chloride  $\text{Cp}_3\text{UCl}$  ( $\text{Cp}$  = cyclopentadienyl) yields the anionic species  $\text{Cp}_3\text{UCl}^-$ , which remains stable for several hours.

Complexes of uranium(III), which have potentially interesting catalytic and reducing properties,<sup>1</sup> are not easy to obtain chemically in a pure state.<sup>2</sup> We examine in this note the possibility of preparing them electrochemically, with tris(cyclopentadienyl)uranium chloride ( $\text{Cp}_3\text{UCl}$ ) as an example.

In tetrahydrofuran on a platinum electrode (supporting electrolyte 0.2 M tetrabutylammonium hexafluorophosphate), a system of reversible peaks A–A' is observed by cyclic voltammetry (Figure 1) followed by an irreversible peak B at more negative potentials. The latter, which probably corresponds to the reduction of  $\text{U}^{\text{III}}$  to  $\text{U}^0$ , and an oxidation peak which appears at about +0.9 V, will be studied later.<sup>†</sup> An ex-

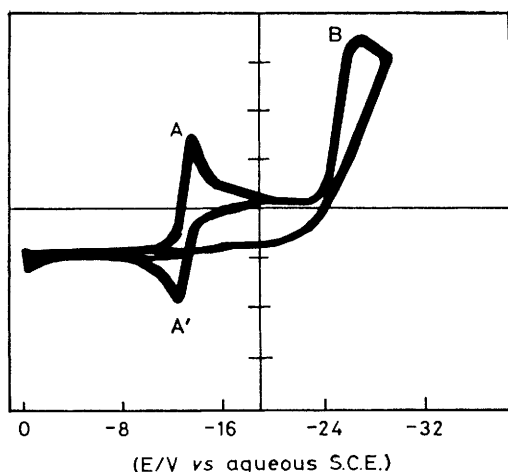


Scheme 1.

haustive controlled potential electrolysis at  $-1.8$  V consumes 1 F, and the same system A–A' is observed with the electrolysis solution.

The characteristics mentioned above are usually taken as a proof of the reversible uptake of an electron, which would

<sup>†</sup> Oxidation waves of  $\text{U}^{\text{IV}}$  complexes at positive potentials have been reported previously (cf. J. A. Butcher, R. M. Pagni, and J. Q. Chambers, *J. Organomet. Chem.*, 1980, **199**, 223).



**Figure 1.** Cyclic voltammogram of  $\text{Cp}_3\text{UCl}$  in tetrahydrofuran. Scan rate  $50 \text{ mV s}^{-1}$ ; one vertical division represents  $1.25 \mu\text{A}$ . A-A', reversible system obtained when the potential is reversed at  $-1.8 \text{ V}$ . B, irreversible peak obtained at more negative potentials. S.C.E. = standard calomel electrode.

in this case lead to the species  $\text{Cp}_3\text{UCl}^-$  [equation (1), Scheme 1]. As we have shown previously,<sup>3a</sup> however (see also refs. 3b and 3c), the same type of system is also obtained when one of the ligands rapidly separates after the electron uptake, and recombines during the backward sweep; this would correspond in the present case to equations (2) and (3), Scheme 1. The two types of mechanism are not easy to distinguish; diagnostic criteria are, for example, the influences of temperature and of sweep rate on the cyclic voltammograms, the effect of other ligands, and the analysis of the electrolytic products.<sup>3a</sup>

No modification of the cyclic voltammogram is observed within the temperature range  $-60$  to  $25^\circ\text{C}$ , at sweep rates varying from  $0.01$  to  $100 \text{ V s}^{-1}$ . No changes occur when the ligands cyclohexyl isocyanide, nicotine, or triphenylphosphine oxide, which are capable of co-ordinating uranium complexes,<sup>4</sup> are added to the solution. This is strong indication<sup>3a</sup> that no ligand separation occurs after the electron uptake, *i.e.* that the species  $\text{Cp}_3\text{UCl}^-$  is stable.

Unequivocal proof that a  $\text{Cl}^-$  ion does not separate [equation (2), Scheme 1] is obtained by examining the solution formed after the exhaustive controlled potential electrolysis at  $-1.8 \text{ V}$ . The n.m.r. spectrum of the solution shows a broad singlet, stable for several hours, at  $-13.30 \text{ p.p.m.}$  ( $\text{Me}_4\text{Si}$  as reference). In tetrahydrofuran  $\text{Cp}_3\text{U}$ , prepared<sup>2b</sup> from  $\text{Cp}_3\text{UCl}$  and  $\text{NaH}$ , gives a broad singlet at  $-21.8 \text{ p.p.m.}$

The experimental results also demonstrate that separation of  $\text{Cp}^-$  does not take place [equation (3), Scheme 1]. It is well known<sup>5</sup> that  $\text{Cp}^-$  reacts with  $\text{Cp}_3\text{UCl}$  to give  $\text{Cp}_4\text{U}$  and  $\text{Cl}^-$ . If  $\text{Cp}_4\text{U}$  was not reduced at  $-1.8 \text{ V}$ , only  $0.5 F$  would be consumed during the electrolysis. As  $1 F$  is actually involved, the only possibility would be that  $\text{Cp}_4\text{U}$  is reduced to  $\text{Cp}_3\text{U}$ , stable for several hours in the presence of  $\text{Cl}^-$  ions, but whose n.m.r. spectrum is not observed (*cf.* preceding paragraph).

It can thus be concluded from the foregoing discussion that the species  $\text{Cp}_3\text{UCl}^-$  is stable. This stability can be explained by the possibility of the electron occupying a vacant  $5f$  orbital of the metal. The stable species  $\text{Cp}_3\text{UMe}^-$  has been recently prepared by chemical<sup>6</sup> and electrochemical<sup>7</sup> reduction of  $\text{Cp}_3\text{UMe}$ .

Our results also help us to understand the behaviour observed during the reduction<sup>8</sup> of  $\text{Cp}_3\text{UCl}$  by  $\text{LiAlH}_4$ ; the n.m.r. spectrum of the solution first shows a singlet at  $-21.2 \text{ p.p.m.}$  (benzene as reference), which would correspond to the formation of  $\text{Cp}_3\text{UCl}^-$  (*cf.* above); the spectrum then slowly changes to give a singlet at  $-28.4 \text{ p.p.m.}$ § corresponding to  $\text{Cp}_3\text{U}$ . Separation of  $\text{Cl}^-$  would thus actually occur, but very slowly.

Received, 28th October 1981; Com. 1263

## References

- 1 'Organometallics of the f Elements', eds., T. J. Marks and R. D. Fischer, Reidel, Dordrecht, 1979.
- 2 P. Zanella, G. Rossetto, G. de Paoli, and O. Traverso, *Inorg. Chim. Acta*, 1980, **44**, 155; E. Klähne, G. Gianotti, H. Marquet-Ellis, G. Folcher, and R. D. Fischer, *J. Organomet. Chem.*, 1980, **201**, 399; J. M. Manriquez, P. J. Fagan, T. J. Marks, S. H. Vollmer, C. Secaur Day, and V. W. Day, *J. Am. Chem. Soc.*, 1979, **101**, 5075.
- 3 (a) Y. Mugnier, C. Moise, and E. Laviron, *J. Organomet. Chem.*, 1981, **204**, 61; (b) J. Bottomley and K. M. Kadish, *Inorg. Chem.*, 1981, **20**, 1348; (c) G. Pilloni, G. Zotti, and S. Zecchin, *J. Electroanal. Chem.*, 1981, **125**, 129.
- 4 B. Kannellakopoulos, E. O. Fischer, E. Dornberger, and F. Baumgärtner, *J. Organomet. Chem.*, 1970, **24**, 507.
- 5 E. O. Fischer and Y. Hristidu, *Z. Naturforsch., Teil B*, 1962, **17**, 275.
- 6 G. Folcher, personal communication.
- 7 G. Folcher, A. Dormond, and Y. Mugnier, to be published.
- 8 H. Marquet-Ellis and G. Folcher, *J. Organomet. Chem.*, 1977, **131**, 256.

‡ This corresponds to  $-14 \text{ p.p.m.}$  with  $\text{Me}_4\text{Si}$  as reference.

§ This corresponds to  $-21.2 \text{ p.p.m.}$  with  $\text{Me}_4\text{Si}$  as reference.