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Preliminary communication

ELECTROCHEMICAL STUDIES ON ORGANOMETALLIC COMPOUNDS

XI*. ELECTROGENERATION OF THE ZIRCONIUM(III) AND HAFNIUM(III) ANIONS OF ZIRCONOCENE AND HAFNOCENE DICHLORIDES

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Summary

The one-electron reduction of zirconocene and hafnocene dichlorides Cp_2MCl_2 (M = Zr or Hf) yields the corresponding anion $Cp_2MCl_2^-$. There is no cleavage of an M—Cl bond, in contrast to the result in the case of the analogous titanocene and vanadocene dichlorides.

Among the compounds of the type Cp_2MX_2, where Cp is a cyclopentadienyl group, X a halogen, and M a metal of Group IV or V, only those where M = titanium [1], vanadium [1c, 2] or niobium [3] have been the subject of detailed electrochemical studies. A few results for the zirconium compound have appeared [1c, 4], but the hafnium and tantalum complexes have not been examined. To the best of our knowledge, only two hafnium(III) organometallic compounds, chemically prepared, have been described [5, 6].

We report here results for the electrochemical reduction of zirconocene and hafnocene dichlorides (M = Zr or Hf, X = Cl) in tetrahydrofuran with 0.1 *M* tetrabutylammonium hexafluorophosphate as supporting electrolyte. Examples of cyclic voltammograms are shown in Fig. 1. At −35°C, Cp_2ZrCl_2 gives a reversible system of peaks BB′ (Fig. 1a) at −1.8 V vs. an aqueous calomel electrode [7]. For Cp_2HfCl_2 (Fig. 1b) a reversible system AA′ is again observed, at −2.04 V, but the peaks BB′ also appear; they are due to a small amount of Cp_2ZrCl_2 present in Cp_2HfCl_2 formed when commercial $HfCl_4$ is used in the synthesis of Cp_2HfCl_2 [8]. For Cp_2HfCl_2 the results are obtained only on a gold electrode, because on platinum the peaks are deformed and disappear after the first cycle, presumably because of fouling of the electrode by the electrolysis product. The peaks are not modified when the sweep rate or the temperature

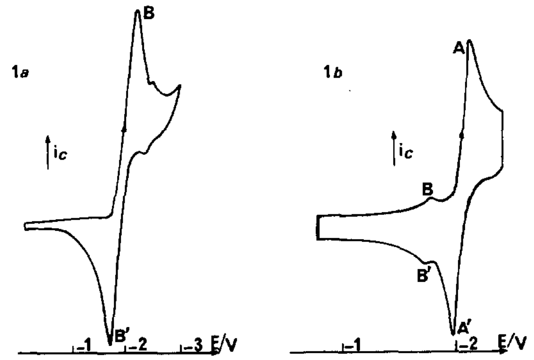

Fig. 1. Cyclic voltammograms at −35°C of a gold electrode in tetrahydrofuran with 0.1 *M* tetrabutylammonium hexafluorophosphate as supporting electrolyte: (a) of Cp_2ZrCl_2, starting potential + 0.2 V, sweep rate 50 mV s^{-1}; (b) of Cp_2HfCl_2, starting potential −0.75 V, sweep rate 100 mV s^{-1}.

(within the range of stability of the product) are changed. The rotating disk electrode (r.d.e.) voltammograms show the cathodic waves A and B corresponding to the cyclic peaks.

An exhaustive electrolysis of Cp_2ZrCl_2 at −1.75 V consumes 1F/mol. The r.d.e. voltammogram shows an anodic wave B′ at the same potential as wave B. The ESR spectrum is shown in Fig. 2a; it consists of a main signal (g = 1.9684) due to the ^{90}Zr, ^{92}Zr and ^{94}Zr isotopes (I = 0, 86%, accompanied by a smaller system of bands due to the ^{91}Zr isotope (I = 5/2, 11.2%). These results, and the fact that the cyclic voltammogram do not depend on the sweep rate or the temperature, point to the formation of the stable anion $Cp_2ZrCl_2^-$.

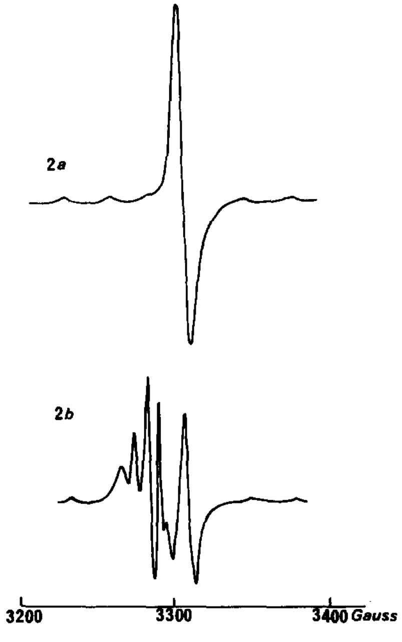

Fig. 2. ESR spectra of: (a) the anion $Cp_2ZrCl_2^-$; (b) the reduction product from Cp_2HfCl_2 (see text) at −30°C.

When Cp_2HfCl_2 is partially electrolyzed at −30°C at −2 V on a mercury electrode [9], an anodic wave A′ is obtained on the r.d.e. gold electrode, situated at the same potential as wave A; wave B′ also appears. The ESR spectrum is shown in Fig. 2b. As can be seen by comparison with Fig. 2a, it consists of the superposition of the spectrum of $Cp_2ZrCl_2^-$ with another complex spectrum, attributable to the anion $Cp_2HfCl_2^-$. The complexity of the spectrum is due to the presence of several isotopes of Hf (main isotopes: ^{177}Hf, $I = 7/2$, 18.5%; ^{178}Hf, $I = 0$, 27%; ^{179}Hf, $I = 9/2$, 13.8%; ^{180}Hf, $I = 0$, 35.2%).

The value of g for the main band is $g = 1.9839$. A value of 1.943 has been reported [5] for the complex $Hf[CH(SiMe_3)C_6H_4CH(SiMe_3)]$-$\eta$-$(C_5H_5)_2^-$.

The chemical reduction of Cp_2MCl_2 (M = Zr, Hf) at room temperature [6] gives the diamagnetic complex $(Cp_2MCl)_2$.

For the first terms of each of the IV and V columns, Cp_2TiCl_2 and Cp_2VCl_2, it has been shown that the uptake of an electron is followed by a fast cleavage (1*l*, 1*n*, 2*d*) of one of the halogens to give Cp_2MCl. For the compounds further down Groups IV and V (M = Zr, Hf, Nb [3]), in contrast, a stable anion $Cp_2MCl_2^-$ is obtained; this is also the case for the uranium derivatives [10]. We are currently examining the behavior of Cp_2TaCl_2.

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