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Preliminary communication

Electrochemical studies on organometallic compounds

XXVIII *. Catalysis of the electrochemical reduction of benzyl chloride by niobium(III) anionic complexes and formation of carbon–carbon bonds

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Abstract

The dicyclopentadienylniobium(III) dichloride anion has been shown to be an effective catalyst for the electrochemical reduction of benzyl chloride. Indirect cathodic reduction yields diphenylethane.

The use of Ni, Cr and Cu complexes for the catalytic activation of the halogen–carbon bond attracts much interest [1–7]. We report here an example of a C–C coupling electro-catalyzed by a niobium(III) complex.

Recently we showed [8] that the one-electron reduction of $Nb(\eta^5\text{-Cp})_2Cl_2$ (**1**) in neat tetrahydrofuran on a platinum electrode (supporting electrolyte 0.2 *M* tetrabutylammonium hexafluorophosphate) initially yields the corresponding anion $Nb(\eta^5\text{-Cp})_2Cl_2^-$ (**2**), which at low temperature is slowly converted into the dimeric species $Nb_2(\eta^5\text{-Cp})_4Cl_3^-$.

The rotating disk voltammogram of **1** is shown in Fig. 1. When benzyl chloride **3** (RCl) is added to the solution, an increase of the wave height is observed (Fig. 1); only benzyl chloride is reduced [9] at −2.25 V.

In cyclic voltammetry under the same conditions peak A (reduction of **1**) increases, whereas peak A′ (oxidation of **2**) disappears (Fig. 2).

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* For part XXVII, see ref. 13.

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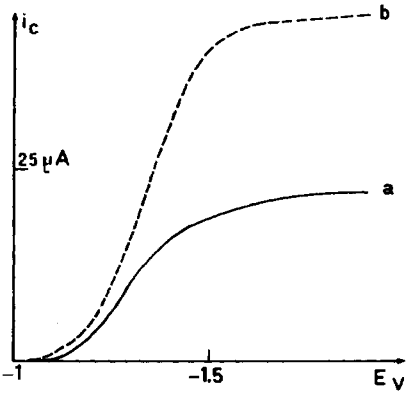

Fig. 1. Voltammograms on the rotating disk electrode in tetrahydrofuran. (a) of **1** alone (c 10^{-3} mol l^{-1}), (b) of **1** in the presence of $C_6H_5CH_2Cl$ ($c = 2\times10^{-3}$ mol l^{-1}).

We carried out electrolysis of a mixture of 0.005 g of **1** and of 0.7 g of **3** at −1.2 V (plateau of wave A). After consumption of 200 F/per mole of complex, analysis of the solution by rotating disk voltammetry showed that **3** had been completely reduced and that the concentration of **1** was unchanged. The solution was then extracted with diethyl ether. After chromatographic purification and recrystallization, diphenylethane (m.p. 51° C) was characterized by ^1H NMR and mass spectroscopy (yield: 65%).

The increase of wave A cannot be due to an outer sphere electron transfer between **2** and RCl; the difference between the reduction potentials of **1** and **3** is larger than 1 V. Formation of an intermediate complex of niobium(V) (**4**) is more

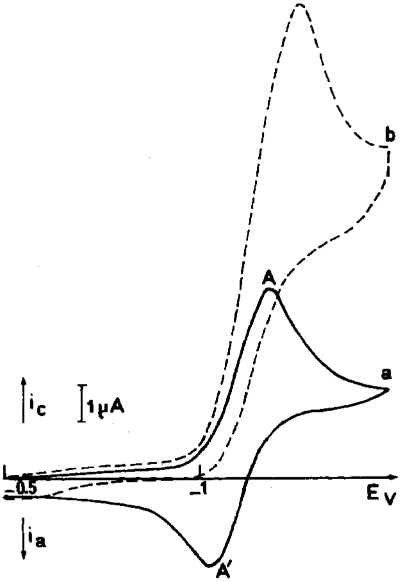

Fig. 2. Cyclic voltammograms on a platinum electrode: sweep rate 100 mV s^{-1}. (a) of **1** alone ($c = 10^{-3}$ mol l^{-1}), (b) of **1** in the presence of $C_6H_5CH_2Cl$ (c 2×10^{-3} mol l^{-1}).

probable, and three mechanisms are possible. The formation of diphenylethane can occur via radical-radical coupling [10] (Scheme a), via nucleophilic attack [3] on RCl by R^- (scheme b), or in a more complex reaction (Scheme c)

Scheme a

$$\underset{(\mathbf{1})}{Nb(\eta^5\text{-}Cp)_2Cl_2} \rightleftharpoons \underset{(\mathbf{2})}{Nb(\eta^5\text{-}Cp)_2Cl_2^-} \tag{1}$$

$$\underset{(\mathbf{2})}{Nb(\eta^5\text{-}Cp)_2Cl_2^-} + \underset{(3)}{RCl} \rightleftharpoons \underset{(\mathbf{4})}{Nb(\eta^5\text{-}Cp)_2Cl_2R} + Cl^- \tag{2}$$

$$Nb(\eta^5\text{-}Cp)_2Cl_2R \overset{+e^-}{\rightleftharpoons} Nb(\eta^5\text{-}Cp)_2Cl_2R^- \tag{3}$$

$$Nb(\eta^5\text{-}Cp)_2Cl_2R^- \rightleftharpoons Nb(\eta^5\text{-}Cp)_2Cl_2^- + R^{\cdot} \tag{4}$$

$$R^{\cdot} + R^{\cdot} \rightleftharpoons R\text{-}R \tag{5}$$

The direct electrochemical reduction of benzyl chloride occurs via a radical mechanism [10].

Scheme b

Reactions 1, 2 and 3 followed by:

$$Nb(\eta^5\text{-}Cp)_2Cl_2R^- \rightleftharpoons Nb(\eta^5\text{-}Cp)_2Cl_2 + R^- \tag{6}$$

$$R^- + RCl \rightleftharpoons R\text{-}R + Cl^- \tag{7}$$

Scheme c

Reactions 1, 2 and 3 followed by:

$$Nb(\eta^5\text{-}Cp)_2Cl_2R^- \rightleftharpoons Nb(\eta^5\text{-}Cp)_2ClR + Cl^- \tag{8}$$

$$Nb(\eta^5\text{-}Cp)_2ClR \overset{+e}{\rightleftharpoons} Nb(\eta^5\text{-}Cp)_2ClR^-$$

$$Nb(\eta^5\text{-}Cp)_2ClR^- + RCl \rightleftharpoons Nb(\eta^5\text{-}Cp)_2ClR_2 + Cl^-$$

$$Nb(\eta^5\text{-}Cp)_2ClR_2 \rightarrow R\text{-}R + Nb(\eta^5\text{-}Cp)_2Cl$$

The formation of the Nb^V derivative $Nb(\eta^5\text{-}Cp)_2Cl_2R$ as shown in eq. 2 is in keeping with the reactivity of the Lewis base **2** (d_2 configuration) towards [11] the electrophilic moiety R of RCl. At the reduction potential of **1**, this Nb^V complex should be more easily reduced than **1**, yielding $Nb(\eta^5\text{-}Cp)_2Cl_2R^-$ (eq. 3), which would decompose to give $Nb(\eta^5\text{-}Cp)_2Cl_2^-$ and $R^{\cdot}$ (eq. 4), or $Nb(\eta^5\text{-}Cp)_2Cl_2$ and R^- (reaction 6), or $Nb(\eta^5\text{-}Cp)_2ClR$ and Cl^- (eq. 8).

In the case of Scheme c, the compound $Nb(\eta^5\text{-}Cp)_2Cl$ can regenerate **1** in the presence of Cl^- ions [12], but this reaction is very slow and cannot play a role in the present system.

Scheme b, in which $Nb(\eta^5\text{-}Cp)_2Cl_2$ is regenerated, is the most probable.

We are currently investigating the reactivity of **2** towards other organic substrates.

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References

1 C. Gosden and D. Pletcher, J. Organomet. Chem., 186 (1980) 401.
2 J. Wellmann and E. Steckhan, Synthesis, (1978) 901.
3 J.M. Kern and J.P. Sauvage, J. Chem. Soc. Chem. Commun., (1987) 546.
4 J.K. Kochi, Organometallic Mechanisms and Catalysis, Academic Press, New York, 1978.
5 P.W. Jolly and G. Wilke, The Organic Chemistry of Nickel, Academic Press, New York, 1974, Vols. 1 and 2.
6 G. Schiavon, G. Bontempelli and B. Corain, J. Chem. Soc. Dalton, (1981) 1074.
7 S. Mabrouk, S. Pellegrini, J.C. Folest, Y. Rollin and J. Perichon, J. Organomet. Chem., 301 (1986) 391.
8 A. Fakhr, Y. Mugnier, R. Broussier and B. Gautheron, J. Organomet. Chem., 269 (1984) 53.
9 M.M. Baizer and J.L. Chruma, J. Org. Chem., 37 (1972) 1951.
10 J. Casanova and L. Eberson, in S. Patai (Ed.), The Chemistry of Functional Groups; the Chemistry of the Carbon-halogen Bond, John Wiley, London, 1973, p. 979.
11 W. Kaim, Coord. Chem. Rev., 76 (1987) 225.
12 A. Fakhr, Y. Mugnier, R. Broussier, B. Gautheron and E. Laviron, J. Organomet. Chem., 317 (1986) 201.
13 H. Nabaoui, A. Fakhr, Y. Mugnier, A. Antinolo, M. Fajardo, A. Otero and P. Royo, J. Organomet. Chem., 338 (1988) C17.