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Preliminary communication

Electrochemical studies on organometallic compounds

XLI *. Electrogeneration and ESR characterization of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl\{P(OMe)_3\}]^+$

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Abstract

In tetrahydrofuran with 0.2 *M* $NaBPh_4$ as supporting electrolyte, the one-electron oxidation at −0.4 V relative to an aqueous saturated calomel electrode (SCE) of the electrogenerated species $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\{ClP(OMe)_3\}]$ (**3**) yields the cationic niobium(IV) complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl\{P(OMe)_3\}]^+$ (**4**), which has been characterized by ESR spectroscopy. **4** can also be obtained by chemical oxidation of **3**.

Introduction

The chemistry of metallocene derivatives of the early transition metal involving substituted cyclopentadienyl ligands has been the focus of our attention in recent years [1]. Several years ago, some of us reported an extensive family of complexes $[NbCp'_2ClL]$ ($Cp' = \eta^5\text{-}C_5H_4SiMe_3$; L = phosphine, phosphite, or acetylene [2]). Following our studies on the chemical and electrochemical behavior of disylilated niobocene complexes in different oxidation states, we report here the chemical and

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electrochemical oxidation of [$Cp'_2NbCl\{P(OMe)_3\}$] which allows us to characterize a new Nb^{IV} cationic complex, [$Cp'_2NbCl\{P(OMe)_3\}]^+$. Only a few paramagnetic cationic niobium complexes have been reported [3].

Results and discussion

In cyclic voltammetry [$NbCp'_2Cl_2$] (**1**) in tetrahydrofuran (THF) with 0.2 *M* Bu_4NPF_6 as supporting electrolyte exhibits a reversible A/A′ system (a in Fig. 1) where the peak A′ corresponds to the oxidation of [$NbCp'_2Cl_2]^-$ [4]. In the presence of an excess of $P(OMe)_3$, oxidation peak A′ disappears and a new oxidation peak A'_1 appears (b in Fig. 1). After an exhaustive controlled-potential reduction of **1** at −1.4 V/ECS in the presence of $P(OMe)_3$, one electron equivalent has been consumed; in cyclic voltammetry the electrolyzed solution exhibits a reversible system A'_1/A_1 (c in Fig. 1). The one-electron oxidation at −0.4 V (potential of peak A'_1) regenerates **1**, which has been characterized from cyclic voltammetry and ESR spectroscopy.

Figure 2 shows the cyclic voltammogram of **1** in THF with 0.2 *M* $NaBPh_4$ as supporting electrolyte; if the potential is reversed after peak A, three oxidation peaks A′, A'_2 and A'_3 are found. When an electrolysis of **1** was performed at −1.4 V at a mercury electrode, the current dropped to zero after the consumption of one electron per molecule and cyclic voltammetry of the electrolyzed solution shows two systems A'_2/A_2 and A'_3/A_3 (b in Fig. 2). The system was ESR silent. In the presence of $P(OMe)_3$, system A'_2/A_2 and A'_3/A_3 disappear and the reversible system A'_1/A_1 appears (c in Fig. 2); after one-electron oxidation at −0.4 V a red solution was obtained, which exhibits the polarographic reduction wave A_1. The

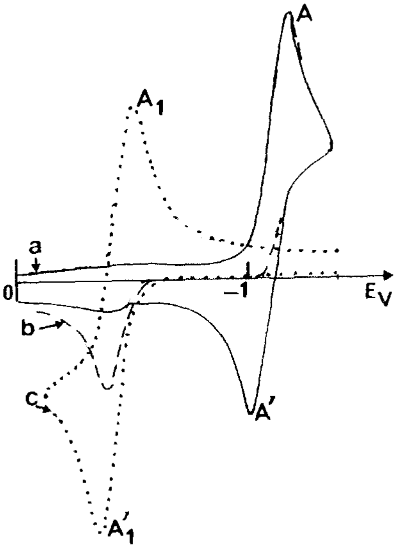


Fig. 1. Cyclic voltammogram of **1** in THF (0.2 *M* Bu_4NPF_6) at a platinum electrode. Sweep rate: 0.2 V s^{-1}. Starting potential: (a) and (b) OV, (c) −1.5 V; (a) **1** alone (b) **1** in the presence of an excess of $P(OMe)_3$, (c) after one-electron reduction at −1.4 V.

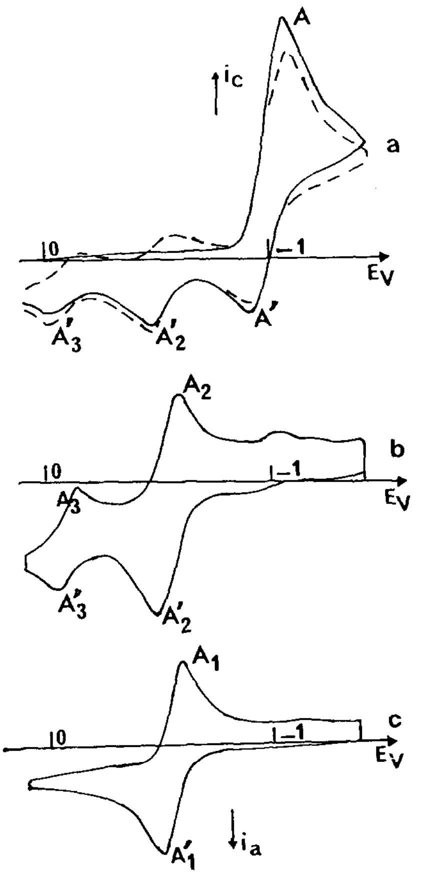


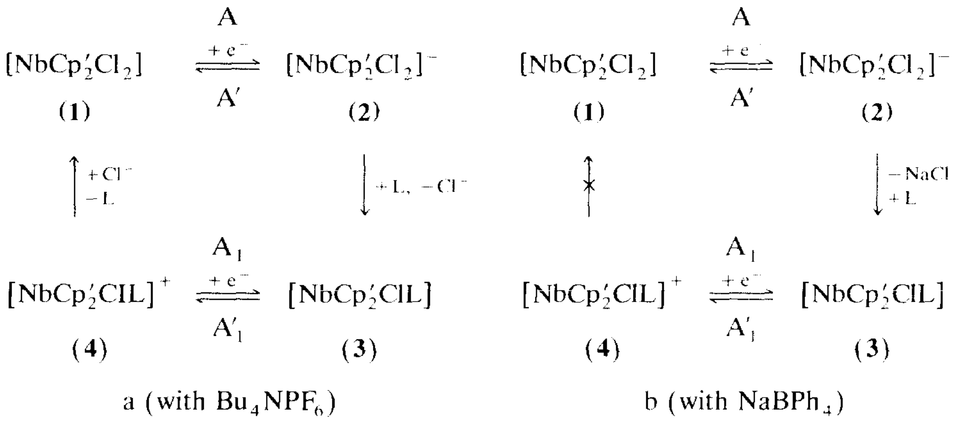
Fig. 2. Cyclic voltammogram of **1** in THF (0.2 *M* $NaBPh_4$) at a platinum electrode. Sweep rate: 0.2 V s^{-1}. Starting potential: (a) +0.1 V, (b) and (c) −1.4 V; (a) **1** alone (b) after one-electron reduction at −1.4 V, (c) after addition of an excess of $P(OMe)_3$.

ESR spectrum (centred at $g = 2.005$) of the electrolyzed solution showed coupling with both niobium ($a_{Nb} = 93.5$ G) and phosphorus nuclei ($a_P = 21.85$ G). The unpaired electron is mainly localized on the niobium. The formation of the paramagnetic cationic niobium complex **4** $[NbCp'_2Cl\{P(OMe)_3\}]^+$ is postulated from the electrochemical and spectroscopic data. Unfortunately, it was not possible to isolate **4**. However we prepared the complex $[NbCp'_2Cl\{P(OMe)_3\}]$ (**3**) in accordance with the literature method [2]. Addition of ferrocenium hexafluorophosphate to a hexane solution of **3** yields **4**.

4 was characterized by elemental analysis [5]. In THF (in the presence of Bu_4NPF_6 or $NaBPh_4$ as supporting electrolyte) the cyclic voltammogram of either chemically prepared product **4** exhibits the reversible A_1/A'_1 system. The same ESR spectrum as above was obtained.

The above results can be rationalized in terms of Scheme 1.

In THF-Bu_4NPF_6 solution (Scheme 1a) the one-electron oxidation of **3** yields **4** which is relatively stable on the cyclic voltammetric time-scale on the electrolysis



Scheme 1.

time scale a slow ligand exchange reaction between $POMe_3$ and Cl^- occurs (reaction **4** → **1**) regenerating **1**.

In THF-$NaBPh_4$ solution (Scheme 1b) a precipitation of NaCl occurs during the reaction **2** → **3**. The reoxidation of **3** in the absence of Cl^- gives **4**, which is stable in these experimental conditions.

After one-electron reduction of **1** in THF-$NaBPh_4$ solution, [$NbCp'_2Cl$] was formed. This has two oxidation steps A'_2 and A'_3 in cyclic voltammetry. A similar mechanism to that observed with [$Nb\{\eta 5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2\}_2Cl$] is postulated [6].

We have also obtained the cationic species $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(CNC_6H_{11})]^+$ after one-electron oxidation of the electrogenerated species $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2\text{-}Cl(CNC_6H_{11})$. The paramagnetic cationic niobium complex was characterized by ESR spectroscopy ($g = 1.9963$; $a_{Nb} = 98$ G)

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5 To a green solution of **3** (0.5 g; 0.95 mmol) in hexane, ferrocenylhexafluorophosphate (0.3 g; 0.75 mmol) was added and immediately the solution became orange and a brown solid was precipitated. The solid was collected by filtration and recrystallized from CH_2Cl_2/hexane to give 0.6 g (91.6% yield) of **4**. Analytical data: found (calc): C: 33.90 (33.95); H: 3.33 (3.21).

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