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Electrochemical studies on organometallic compounds

XLII *. Electrogeneration and spectroscopic characterization of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PhC\equiv CPh\text{-}C,C)]$

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Abstract

The two-electron reduction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ in the presence of PhC≡CPh yields the first acetylene niobium(IV) complex, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PhC\equiv CPh\text{-}C,C)]$.

Several studies of the chemical behaviour of bis(silylated cyclopentadienyl)niobium(III) complexes in the presence of π-acid ligands and cumulenes have been reported [1]. Acetylene complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2XL]$ (X = Cl or Br; L=PhC≡CPh) were obtained when PhC≡CPh was added to the coordinatively unsaturated species $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X]$ [2]. We describe here the electrochemical behaviour of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ (**1**) in the presence of PhC≡CPh. This allowed us to isolate the first niobium(IV) complex containing acetylene.

The cyclic voltammogram of **1** in tetrahydrofuran (THF) in the presence of 0.2 *M* tetrabutylammonium hexafluorophosphate as supporting electrolyte shows a

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[*] For Part XLI, see ref. 7.

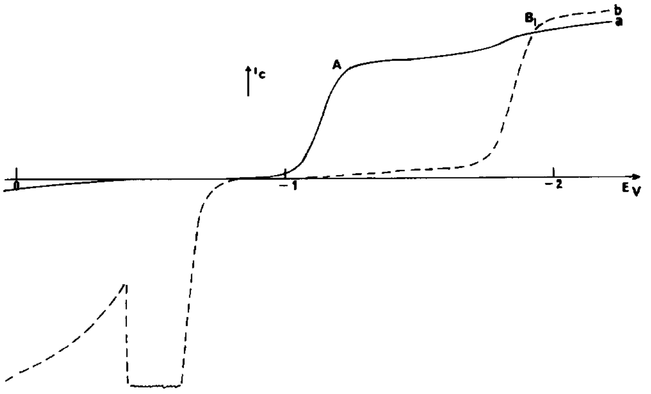

Fig. 1. Polarogram (average current) of **1** in THF in the presence of 1 equiv of PhC≡CPh: (a) before electrolysis; (b) after two electron reduction at −1 15 V.

reversible A/A′ system, where A′ corresponds to the oxidation of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]^-$ [3]. In the presence of 1 equiv. or an excess of PhC≡CPh, no important modifications are observed at 0.2 V s^{-1}.

The electrolysis of **1** in the presence of 1 equiv. of PhC≡CPh at −1.15 V (plateau of wave A) and consumption of 2 equiv. of electrons, yields a brown solution which exhibits polarographic reduction wave B_1 for the electrogenerated species **4** ($E_{1/2} = -1.85$, *versus* SCE electrode) and several ill-defined oxidation waves [4*] (Fig. 1).

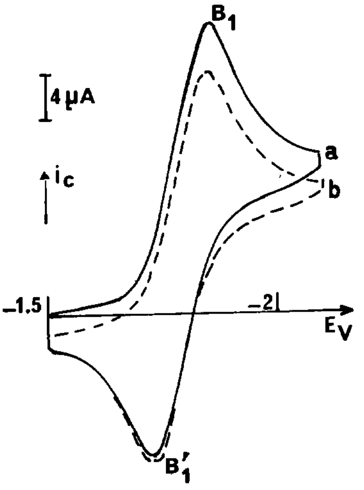

Fig. 2. Cyclic voltammogram of **4** in THF on a platinum electrode. Starting potential, −1.5 V; sweep rate, 0.2 V s^{-1}

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* Reference with asterisk indicates a note in the list of references.

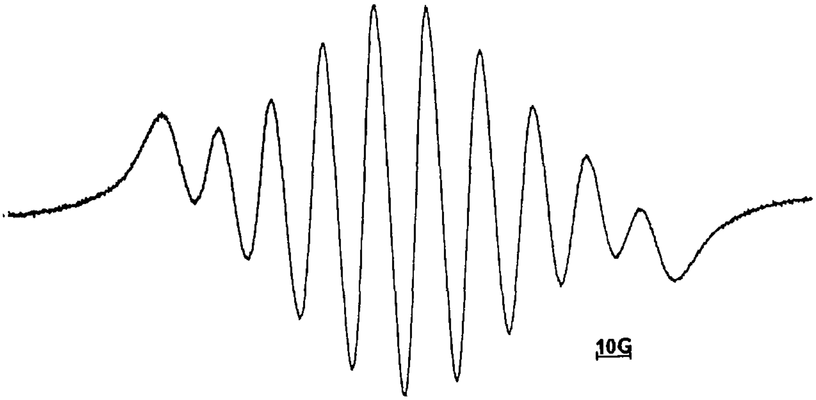

Fig. 3. ESR spectrum of **4** in THF at room temperature.

In cyclic voltammetry, a reversible B_1/B_1' system was observed (Fig. 2). The ESR spectrum ($g = 2.011$) of **4** in THF is shown in Fig. 3. It consists of ten well-defined lines with $a_{Nb} = 16.37$ G reflecting coupling of the unpaired electron with the nuclear spin of niobium and extensive delocalization of the spin. Similar behaviour has been previously reported for other Nb^{IV} complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PhN{=}C{=}CPh_2\text{-}N,C)]$ [1b], $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Ph_2C{=}C{=}O,C,O)]$ [5] and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(Ph_2CHCHO\text{-}C,O)]$[6].

We can formulate that the electrogenerated species **4** is $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PhC{\equiv}CPh\text{-}C,C)]$. The height of wave B_1 indicates that **4** was formed quantitatively. The IR spectrum of **4** in THF shows a band at 1710 cm^{-1} which corresponds to $\nu(C{\equiv}C)$ of the η^2 coordinated diphenylacetylene. Complex **4** was isolated from the THF solution as a very air-sensitive brown crystalline solid after appropriate work-up [8*].

The formation of complex **4** agrees with the following global reaction:

$$\underset{(1)}{\left[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2\right]} + PhC{\equiv}CPh \xrightarrow{+2e^-} \underset{(4)}{\left[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(PhC{\equiv}CPh)\right]} + 2Cl^- \qquad (1)$$

We have also studied the electrochemical behaviour of the known Nb^V derivative $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(PhC{\equiv}CPh\text{-}C,C)]$ (**3**) [2]. The cyclic voltammogram of **3** exhibits a reduction peak B and an oxidation peak B_1'; during the second scan, a reduction peak B_1 appears at lower cathodic potential than B (Fig. 4). The B_1/B_1' system is similar to that of Fig. 2.

When the electrolysis of **3** was performed at −2.1 V (plateau of wave B) and after consumption of 1 equiv. of electrons, the reduction wave B_1 and the same ESR spectrum (Fig. 3) were obtained. This ESR spectrum was also obtained after one-electron reduction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(PhC{\equiv}CPh)]$ (X = Br or I). This indicates that halide (choride, bromide, or iodide) is not present in complex **4**.

The two-electron transfer (see reaction 1) can be explained by the following reactions. One-electron reduction of **1** generates the anion $[Nb(C_5H_4SiMe_3)_2Cl_2]^-$

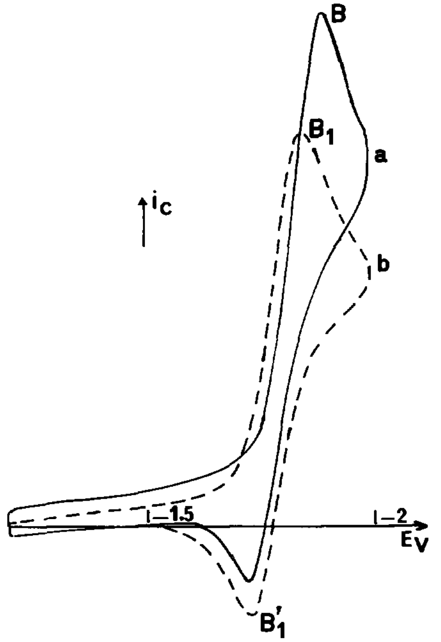

Fig. 4. Cyclic voltammogram of 3 in THF on a platinum electrode. Starting potential, −1.2 V; sweep rate, 0.2 V s^{-1}. (a) First scan; (b) second scan.

(2) which is oxidized at the potential of peak A′. The addition of PhC≡CPh leads slowly to the partial regeneration of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)Cl_2]$ and the formation of **4** which is reducible at the potential of B_1. On the other hand, when complex **3** is added to the anionic species **2**, the reaction is faster and the formation of **1** and **4** was observed by polarography and by ESR spectroscopy (the characteristic signal of $Nb(\eta^5\text{-}C_5H_4SiMe_3)Cl_2$ is superimposed on the spectrum of Fig. 3).

The above results can be rationalized by the following scheme:

$$\underset{(1)}{[\mathrm{NbCp'_2Cl_2}]} \xrightarrow{e^-} \underset{(2)}{[\mathrm{NbCp'_2Cl_2}]^-} \quad \text{(system A/A')} \qquad \text{(a)}$$

$$\underset{(2)}{[\mathrm{NbCp'_2Cl_2}]^-} + \mathrm{PhC{\equiv}CPh} \xrightarrow{\text{slow}} \underset{(3)}{[\mathrm{NbCp'_2Cl(Ph{\equiv}CPh)}]} + \mathrm{Cl^-} \qquad \text{(b)}$$

$$\mathbf{2} + \mathbf{3} \xrightarrow{\text{fast}} \mathbf{1} + \underset{(4)}{[\mathrm{NbCp'_2(PhC{\equiv}CPh)}]} + \mathrm{Cl^-} \qquad \text{(c)}$$

$$\mathbf{3} \xrightarrow{2e^-} \underset{(5)}{[\mathrm{NbCp'_2(Ph{\equiv}CPh)}]^-} + \mathrm{Cl^-} \quad \text{(peak B)} \qquad \text{(d)}$$

$$\mathbf{5} + \mathbf{3} \longrightarrow 2\underset{(4)}{[\mathrm{NbCp'_2(PhC{\equiv}CPh)}]} + \mathrm{Cl^-} \qquad \text{(e)}$$

$$\underset{(4)}{[\mathrm{NbCp'_2(PhC{\equiv}CPh)}]} \xrightarrow{e^-} \underset{(5)}{[\mathrm{NbCp'_2(Ph{\equiv}CPh)}]^-} \quad \text{(system } B_1/B'_1) \qquad \text{(f)}$$

$(\mathrm{Cp'} = \eta^5\text{-}C_5H_4SiMe_3)$

The anion **2** reacts slowly with PhC≡CPh to give the Nb^V derivative **3** (reaction b). Electrogenerated derivative **3** is reducible by the anion **2** yielding complexes **4** and **1** (reaction c); an inner-sphere electron-transfer reaction is postulated because the difference between the reduction potentials of **1** and **3** is nearly 0.9 V.

The two-electron reduction of complex **3** (peak B) corresponds to an ECE process involving cleavage of the niobium–halogen bond. The anionic species formulated as $[Nb(C_5H_4SiMe_3)_2(PhC{\equiv}CPh)]^-$ (**5**) was formed, and is oxidized at the potential of peak B_1'. The formation of **4** during the electrolysis of **3** can be explained by an outer-sphere electron-transfer reaction between **3** and **5** (reaction e) since the potential difference is 0.18 V; complex **5**, which is generated at the electrode, diffuses towards the bulk of the solution and comes in contact with **3**, which diffuses towards the electrode and reaction e takes place. The B_1/B_1' system corresponds to the redox reaction (f).

A full paper concerning the chemical synthesis of acetylenic niobium(V) derivatives and the electrochemical synthesis of acetylene niobium(IV) complexes will be published later.

Acknowledgements

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4 Oxidation waves of chloride ions were observed.

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8 The THF solution, obtained from the two-electron reduction of **1** at −1 15 V was evaporated to dryness, **4** was extracted with hexane and then the solution was concentrated and cooled to −10°C to give a brown crystalline precipitate which was identified as complex **4**. Mass spectrum (*m/e*)· 545 (molecular ion).