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Electrochemical studies on organometallic compounds

XXXII *. Pseudo-reversibility of the first reduction stage of $Nb[\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2]_2Cl_2$

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Abstract

The one-electron reduction of $Nb[\eta^5\text{-}1,3C_5H_3(SiMe_3)_2]_2Cl_2$ yields the derivative $Nb[\eta^5\text{-}1,3C_5H_3(SiMe_3)_2]_2Cl$. Pseudo-reversible behaviour is observed due to a return of Cl^- to the molecule. The effect of the disubstitution of the cyclopentadienyl ring is discussed.

We previously reported [1,2] that the uptake of an electron by the complexes $Nb(\eta^5\text{-}C_5H_5)_2Cl_2$ (**1**) and its disubstituted analogue $Nb[\eta^5\text{-}C_5H_4SiMe_3]_2Cl_2$ (**2**) leads to the corresponding anion, which can lose a Cl^- ion. This loss is much slower in the case of the anion of **2**, which is stable at −30 °C [2]. It was of interest in this respect to examine the effect of further substitution in the cyclopentadienyl ring, and we report here the behaviour of $Nb[\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2]_2Cl_2$ (**3**) ($NbCp''_2Cl_2$).

In THF with tetrabutylammonium hexafluorophosphate 0.2 M as supporting electrolyte on a platinum disc electrode, two reduction waves A and B ($E_{1/2}$ −1.28 and −1.97 V vs. the SCE electrode) are observed. The height of wave A corresponds to a 1 electron reduction, whereas that of wave B depends on the temperature (see below, cyclic voltammetry) and the rotation rate.

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* For part XXXI, see ref. 10.

** The appearance of this paper was delayed by error during the editing process.

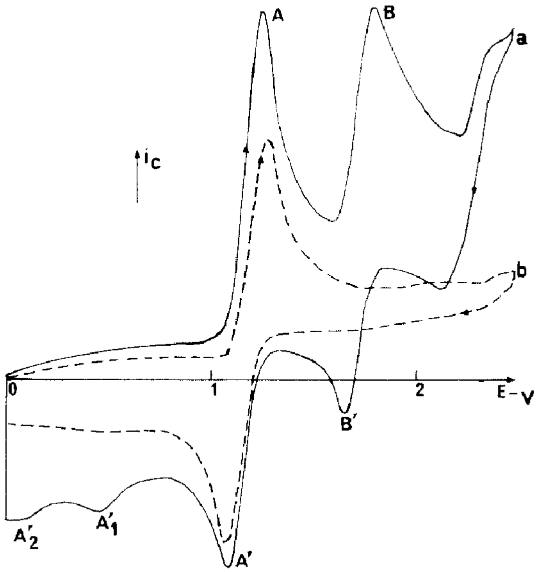

Fig. 1. Linear potential sweep voltammograms of **3** in thf on platinum electrode. Starting potential: OV, sweep rate: 0.2 V s^{-1}; (————): at room temperature; (— — —) at −30 °C.

The corresponding reduction peaks are found in linear potential sweep voltammetry. When the potential sweep is reversed after B, four anodic peaks B′, A′, A'_1 and A'_2 appear (Fig. 1a). The peaks A′, A'_1 and A'_2 are also observed when the potential sweep is reversed after A. The systems of peaks A/A′ and B/B′ are reversible. At room temperature, as the sweep rate is increased, peaks A'_1 and A'_2 increase with respect to peak A′. At low temperature (−30 °C) peak B disappears, and the only system observed is the couple A/A′ (see Fig. 1b).

After a complete electrolysis of **3** at −1.5 V (plateau of wave A), 1 F is consumed and the voltammogram of the solution shows the 1 e^- reduction wave B, the 1 e oxidation wave A′, and an ill-defined wave corresponding to peaks A'_1 and A'_2 (Fig. 2). The wave B corresponds to the reduction of the species * $Nb(Cp'')_2Cl$ (vide infra).

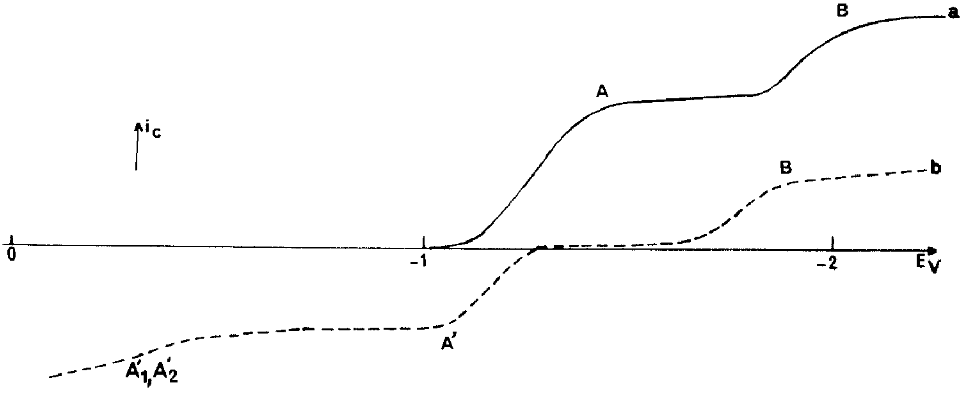

Fig. 2. Voltammograms of **3** in thf on the rotating disc electrode (a) before electrolyses (b) after reduction at −1.5 and consumption of 1 F.

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* An autoligandation as in the case of the corresponding Ti analogs [3] cannot be completely excluded.

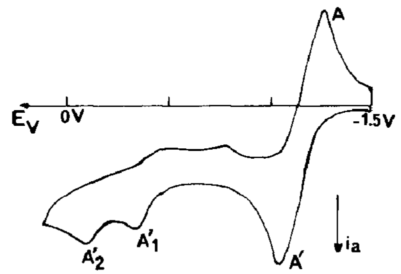


Fig. 3. Linear potential sweep voltammograms of **4** generated by reduction of **3** in thf. Starting potential: -1.5 V; sweep rate: 0.020 V s^{-1}.

Peaks A′, A'_1 and A'_2 appear in linear potential sweep voltammetry (Fig. 3). No signal is detected by ESR spectroscopy. The same results are obtained when the electrolysis is performed at $-30\,^\circ$C.

The above results can be rationalized, as in the case of the analogous complexes of titanium [3], on the basis of Scheme 1.

$$\begin{tikzcd}
\mathrm{NbCp''_2Cl_2} \arrow[r, shift left, "+e^-"] & \mathrm{NbCp''_2Cl_2}^- \arrow[l, shift left] \\
\text{(a)}\ (\mathbf{3}) \arrow[d, shift left] & (\mathbf{3'})\ \text{(b)} \arrow[d, shift left, "-\mathrm{Cl}^-"] \\
\mathrm{NbCp''_2Cl^+} \arrow[u, shift left, "+\mathrm{Cl}^-"] \arrow[r, shift left] & \mathrm{NbCp''_2Cl} \arrow[u, shift left] \arrow[l, shift left, "-e^-"] \\
\text{(d)}\ (\mathbf{4'}) & (\mathbf{4})\ \text{(c)}
\end{tikzcd}$$

Scheme 1

The uptake of one electron by complex **3** yields the anion **3′**, which is relatively stable at $-30\,^\circ$C on the time scale of voltammetry. At room temperature (voltammetry) or at low temperature (electrolysis) **3′** loses Cl^- to give **4**. Peak A′ can be interpreted as being due to the reaction c → b → a. The Cl^- anion which separates after the electron uptake now returns to the metal (pseudoreversible behaviour [3]).

For waves A'_1 and A'_2, the mechanism is probably similar to that of the oxidation of $\mathrm{TiCp_2Cl}$ [4], since the oxidation at A'_1 consumes 0.5 F and 1 F at the potential of wave A'_2.

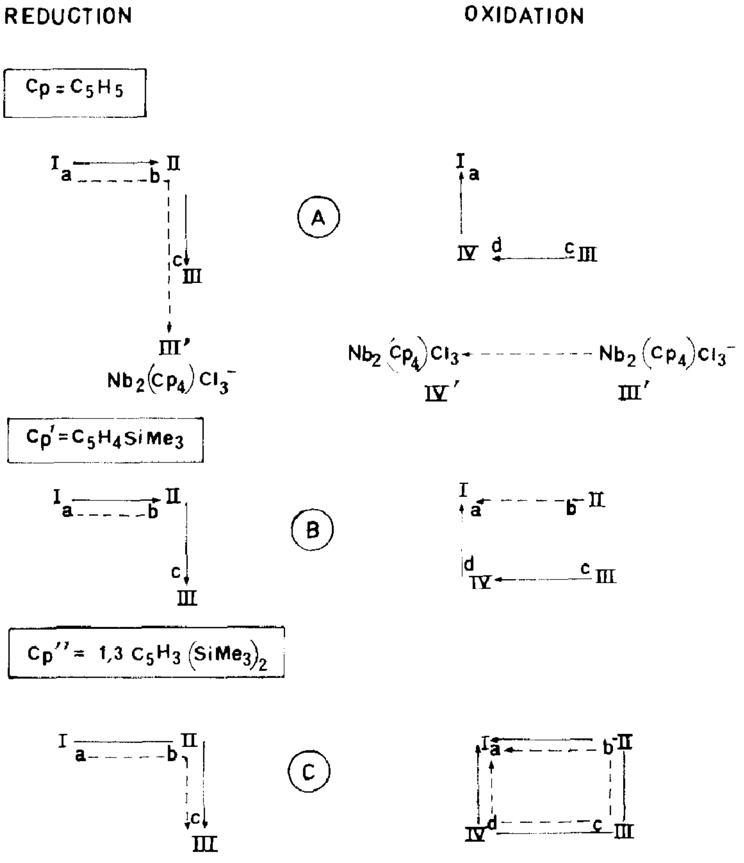
For wave A'_1 $\quad \mathrm{NbCp''_2Cl - e \longrightarrow NbCp''_2Cl^+}$

or $\quad \mathrm{(NbCp''_2Cl)_2 - e \longrightarrow (NbCp''_2Cl)_2^+}$

followed by the fast reaction

$$\left.\begin{array}{l}\mathrm{NbCp''_2Cl^+ + NbCp''_2Cl} \\ \text{or} \\ \mathrm{(NbCp''_2Cl)_2^+}\end{array}\right] \longrightarrow \mathrm{NbCp''_2Cl_2 + NbCp''_2L^+}$$

($\mathrm{NbCp''_2L^+}$ is probably coordinated with a thf molecule).



Scheme 2. - - - - - - at low temperature; ——— at room temperature.

Wave A'_2 corresponds to the process

$$NbCp''_2L^+ - e^- \longrightarrow NbCp''_2L^{2+}$$

This mechanism is confirmed by the electrochemical behaviour of the complex $Nb[\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2]_2Cl$ (**4**) which we prepared by chemical reduction (Na/Hg) of **3**. In thf, **4** exhibits the oxidation wave A'_1 and A'_2 and the reduction wave B. In the presence of Cl^-, wave A'_1 and A'_2 disappear, and only wave A' is observed by voltammetry on the rotating disc electrode.

The reduction mechanism of complex **3** is thus quite similar to that described for $Ti(\eta^5\text{-}C_5H_5)_2Cl_2$ [3]. Thus, after the reduction of one electron the Cl^- separates in both cases, but loss of Cl^- is much slower for all the Nb complexes.

On the basis of the square scheme (see Scheme 1) we can discuss the mechanism of the reduction of the derivatives of Nb^{IV} when the cyclopentadienyl group is C_5H_5, $C_5H_3SiMe_3$, or $1,3\text{-}C_5H_3(SiMe_3)_2$ (Scheme 2).

In the case of the unsubstituted complex $Nb(\eta^5\text{-}C_5H_5)_2Cl_2$ (1), the electron uptake is followed by separation of Cl^-, and the neutral complex $Nb(\eta^5\text{-}C_5H_5)_2Cl$ (III) is obtained at room temperature [1] (Scheme 2A, path abc). The oxidation of this complex occurs through path cda in cyclic voltammetry whatever the sweep rate. At low temperature, the mechanism is more complex, and the dimeric species $Nb_2(\eta^5\text{-}C_5H_5)_4Cl_3^-$ (III') is generated, and is oxidized to $Nb_2(\eta^5\text{-}C_5H_5)_4Cl_3$ (IV') [5].

In the case of complex $Nb[\eta^5\text{-}C_5H_4SiMe_3]_2Cl_2$, (I) (Scheme 2B) the anion II is very stable at low temperature [2], and a reversible system is observed in cyclic voltammetry whatever the sweep rate (path ab for the reduction and path ba for the oxidation). At room temperature the anion $Nb[\eta^5\text{-}C_5H_4SiMe_3]_2Cl_2^-$ (II) decomposes slowly into the neutral complex III, which is oxidized through path cda.

In the case of the tetrasubstituted derivative $Nb[\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2]_2Cl_2$ (I), the electrogenerated anion is unstable even at low temperature, and the neutral complex $Nb[\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2]_2Cl$ (III) is obtained (Scheme 2C, path abc). This derivative is oxidized through path cda at large sweep rates and through path cba at slow sweep rates.

The results described above show that the rate of the reaction II → III (loss of Cl^-) depends markedly on the number of Me_3Si substituents present. When two substituents are introduced into the molecule the molecule (Scheme 2B), the rate at which Cl^- separates from II, is decreased. This result is in keeping with the electron-withdrawing character of the $SiMe_3$ group, which causes a decrease in the electron density on the ring. This decrease is also apparent from the ^{13}C NMR data [6,7,8], the ring-carbon resonance being shifted to high fields by about 5.4 ppm on going from the series $Nb(\eta^5\text{-}C_5H_5)_2ClL$ to the series $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2ClL$ (where L is PhC≡CPh, PhC≡CH or HC≡CH).

Paradoxically, when two further substituents are introduced (Scheme 2C) the rate of reaction II → III increases. This can be accounted for in terms of an increase in the electron density on the metal. This is again confirmed by the ^{13}C NMR results [9]; the two carbon atoms (1 and 3) show different chemical shifts; for example for $Nb(\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2]_2Cl(CO)$. This indicates that the introduction of the second group decreases the back-donation effect from the metal towards the ligand.

Experimental

Reagents

$Nb[\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2]_2Cl_2$ was prepared by a published procedure [9].

$Nb[\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2]_2Cl$ (**4**) was prepared by Na/Hg reduction of **3**. THF (50 ml) was added to a mixture of $Nb[\eta^5\text{-}1,3\text{-}C_5H_3(SiMe_3)_2]_2Cl_2$ (1.000 g, 1.72 mmol) and sodium amalgam (1.72 mmol of Na). The mixture was vigorously stirred for 1 h at room temperature, and then filtered. The filtrate was evaporated to dryness under vacuum, the solid residue was extracted with hexane. The extract was concentrated to give brown crystals of the complex **4**.

^1H NMR complex of **4**: 0.33 (s; 18) ($SiMe_3$); 5.32 (s(broad): 3) ($C_5H_3(SiMe_3)_2$) ppm relative to TMS in C_6D_6 (analytical data: Found: C, 48.0; H, 7.5; calcd.: C, 48.3; H, 7.7%.

Tetrahydrofuran was purified by distillation from sodium benzophenone ketyl under argon.

Apparatus and procedure

The voltammetric experiments were carried out on a platinum disc electrode (ϕ 1.2 mm). For the controlled potential electrolyses, a platinum grid was used. The reference electrode was a saturated calomel electrode separated from the solution by a sintered glass disc. The auxiliary electrode was a platinum wire electrode. A Tacussel UAP 4 Unit connected to a Tektronix oscilloscope (linear potential sweep experiments), a three electrode Tacussel Tipol polarograph, an Amel 552 potentiostat, and a Tacussel IG5 integrator were used.

The supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.2 *M*) in all cases; the salt (Fluka) was twice recrystallized from ethanol, then dried and deoxygenated before use.

Carbon and hydrogen analysis was carried out with a Perkin–Elmer 240 B microanalyzer. NMR spectra were recorded on a Varian FT 80A instrument.

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