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# Synthesis and electrosynthesis of bis-silylated cyclopentadienylniobium(V) cationic complexes. Their reactions and structural characterization

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## Abstract

Chemical oxidation of complexes $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2$, X = Cl (**1**), Br (**2**), I (**3**), with ferrocenium hexafluorophosphate in dichloromethane gives the cationic complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2]^+\ PF_6^-$, X = Cl (**4**), Br (**5**), I (**6**). These species can be prepared by electrochemical oxidation of complexes **1**, **2** and **3** in dichloromethane; cationic complexes can also be prepared in THF but they are relatively unstable. In *N,N*-dimethylformamide (DMF) the complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(DMF)]^{2+}$ are electrogenerated. Complexes **4**, **5** and **6** behave as acids towards nucleophilic reagents, so that they react with alcohols and water to give adducts (which could not be isolated) and with $Me_3SiOR$ reagents to give the new niobium(V) alkoxide complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(OR)]^+\ PF_6^-$, $R = CH_3$ (**7**), $CH_2CH_3$ (**8**), $CH(CH_3)_2$ (**9**), which were isolated as crystalline solids.

## Introduction

Cationic $d^0$ complexes, such as $[M(\eta^5\text{-}C_5H_5)_2R]^+$, M = Ti, Zr have previously been studied in respect of their participation as key intermediates in Ziegler–Natta polymerization processes [1]. Recent work in this area has allowed the detection and study of the active metal sites in olefin polymerization, which in the case of the classical heterogeneous transition metal catalysts is made difficult by the complexity of the systems.

Although several bis-cyclopentadienyl niobium complexes have been reported [2] few cationic $d^0$ niobocene complexes are known, in spite of their potential interest in relation to various catalytic processes. As a part of our study of the electronic and steric influence of the trimethylsilyl-substituted cyclopentadienyl ligand on the properties of niobocene complexes [3], we describe here the preparation of some

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new halogeno bis(trimethylsilylcyclopentadienyl)niobium(V) cationic complexes by chemical and electrochemical oxidation process, and their behaviour toward some nucleophilic reagents. A preliminary account has appeared [4].

## Results and discussion

### *Chemical preparation and properties of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2]^+\ PF_6^-$, X = Cl (4), Br (5), I (6)*

The complexes $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2$ (**1**, **2** and **3**) were prepared as reported [5,6]. We previously prepared [7] several bis-cyclopentadienylniobium(V) neutral and cationic complexes by treatment of niobium(III) and niobium(IV) complexes with appropriate amounts of halogens. We have now investigated the oxidation of complexes **1**, **2** and **3** by ferrocenium hexafluorophosphate in dichloromethane, and have obtained the cationic complexes **4**, **5** and **6** in high yield, according to eq. 1:

$$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2 + [Fe(\eta^5\text{-}C_5H_5)_2]^+ PF_6^- \rightarrow$$

$$(X = Cl\ (\mathbf{4}),\ Br\ (\mathbf{5}),\ I\ (\mathbf{6}))$$

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2]^+ PF_6^- + Fe(\eta^5\text{-}C_5H_5)_2 \quad (1)$$

The complex $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]^+ PF_6^-$ was previously prepared [8] by a similar method. The new cationic $d^0$ complexes were isolated as air stable red crystals; their solutions are also stable under $N_2$ or Ar, except in the case of complex **6**, which decomposes with formation of iodine.

### *Spectroscopic characterization*

The IR spectra of the cationic complexes show the characteristic absorptions for the cyclopentadienyl [9], trimethylsilyl [10] and hexafluorophosphate [11] groups. The $^1H$ NMR spectra show the expected singlet for the $SiMe_3$ group and several broad peaks due to the non-equivalent $\eta\text{-}C_5H_4$ protons [12], shifted to downfield in according with the high oxidation state of the metal.

### *Electrooxidation processes of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2$*

We have studied the electrooxidation of complexes **1**, **2** and **3** in tetrahydrofuran (THF), dichloromethane, and *N,N*-dimethylformamide (DMF). McCullough et al. recently described the results of an exhaustive cyclic voltammetry study of $Nb(\eta^5\text{-}C_5H_5)_2X_2$, X = Cl, Br, I [13], and we present our results below.

*(i) Electrochemical studies in THF.* The rotating platinum disk electrode (rde) voltammogram of complex **1** shows an oxidation wave E′ at +0.38 V and a reduction wave A at −1.17 V (Fig. 1a). Upon electrolysis at +0.5 V and consumption of > 1 faraday three reduction waves, E, $E_1$ and A, are observed (Fig. 1b). After 1 h the height of wave E decreases and the oxidation wave E′ appears (Fig. 1c). (If chloride ion (LiCl in THF) is added to the electrolyzed solution the waves $E_1$ and E′ disappear and a new reduction wave appears at a lower cathodic potential.)

The rde voltammograms of complexes **2** and **3** also show an oxidation wave E′ and a reduction wave E (see Table 1). In cyclic voltammetry reversible systems E′/E are observed. The one-electron oxidation of **1**, **2** and **3** yields the cationic species which are reduced at the potential of E. In the case of complex **1** the

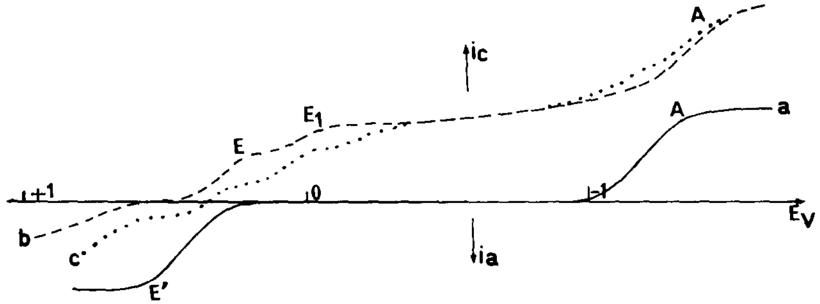


Fig. 1. Rotating disk electrode voltammogram of **1** in tetrahydrofuran: (a) before electrolysis; (b) after oxidation at +0.5 V; (c) 1 h after electrolysis.

Table 1

Half-wave oxidation of bis-(silylated cyclopentadienyl)niobium dihalides [a]

| Solvent | Complex | | |
|---|---|---|---|
| | **1** | **2** | **3** |
| THF | +0.38(−1.17) [b] | +0.47(−1.12) [b] | +0.52(−0.89) [b] |
| $CH_2Cl_2$ | +0.28 | +0.35 | +0.44 |
| DMF | +0.30 | +0.32 | +0.38 [c] |

[a] V vs aqueous SCE. [b] ( ): cathodic process ($Nb^{IV}/Nb^{III}$). [c] Value ill defined.

regeneration of the starting material after the electrolysis probably involves the decomposition of the initially formed adduct with the solvent, as shown in Scheme 1.

We previously observed [14] that the proposed [14] that the proposed reductive elimination (last process) occurs catalytically when $PPh_3$ is added to the solution. Similar electrochemical reductive eliminations of halogen [15] or trimethylsilyl [8] groups from niobium(V) complexes have been observed previously. Since > 1 F has been consumed in the electrolysis of **3** a behaviour similar to that described for **1** seems likely.

*(ii) Electrochemical studies in $CH_2Cl_2$.* The rde voltammogram of complex **1** shows an oxidation wave E′ (Fig. 2a) but the expected reduction wave does not appear because the solvent is catalytically reduced by the anion $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]^-$ [15]. After one-electron oxidation wave E is observed in the rde voltammogram (Fig. 2b). The reduction wave E is also observed in the case of a

$$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2 \underset{E}{\overset{E'}{\rightleftharpoons}} [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]^+ \overset{THF}{\rightleftharpoons}$$

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2(THF)]^+ \rightleftharpoons Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2 + THF^+$$

Scheme 1.

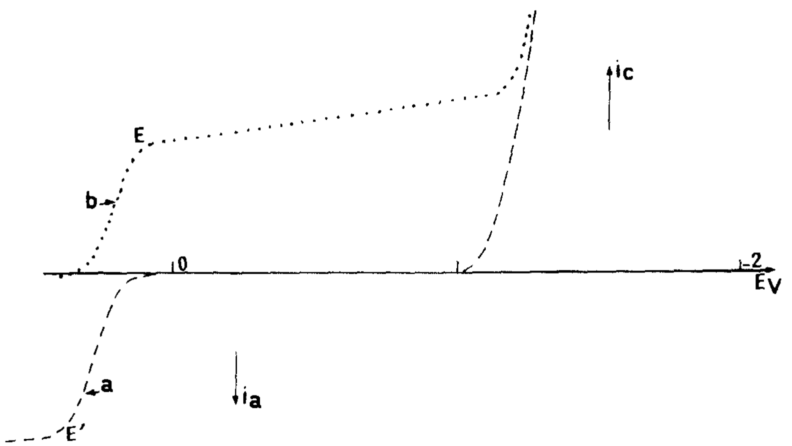


Fig. 2. Rotating disk electrode voltammogram of **1** in dichloromethane: (a) before electrolysis; (b) after one-electron oxidation.

$CH_2Cl_2$ solution of the chemically prepared complex **4**. For complexes **2** and **3** similar electrochemical behavior was observed. The results are consistent with the following electrochemical reversible process.

$$\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{X_2} \underset{E}{\overset{E'}{\rightleftharpoons}} [\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{X_2}]^+ \qquad (2)$$

*(iii) Electrochemical studies in* N,N*-dimethylformamide (DMF).* In cyclic voltammetry the complex **1** shows after oxidation along with peak E′ a reduction peak $E_1$. During the second scan another oxidation peak, $E'_1$, appears (Fig. 3). After the complete electrolysis of complex **1** at +0.6 V (plateau of wave E′) 1 F has been consumed and the rde voltammogram of the resulting solution shows a reduction wave $E_1$. The cyclic voltammogram of the same solution shows a reversible system $E_1/E_1'$ at low scan rate. We have not separated the electrogenerated product from the supporting electrolyte, but reasonable suggestions can be put forward for its stoichiometry.

The cyclic voltammogram of **2** is more complex, since in addition of peak E′, two peaks B′ and B″ are observed, and furthermore when the scan is reversed peak $E_1$

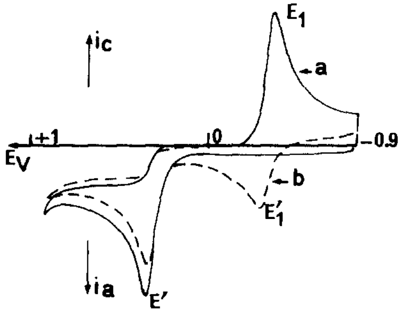


Fig. 3. Cyclic voltammogram of **1** in *N,N*-dimethylformamide on platinum electrode. Starting potential −0.9 V. Sweep rate 0.2 V $s^{-1}$: (a) first scan; (b) second scan.

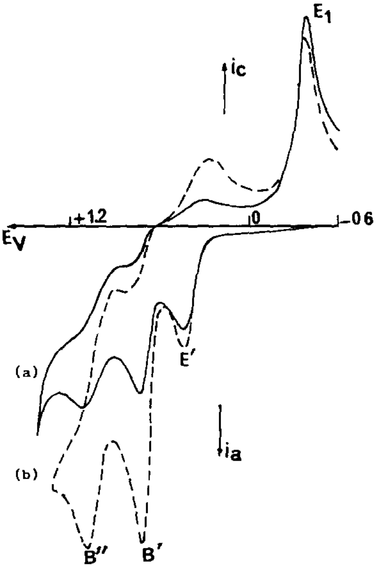


Fig. 4. Cyclic voltammogram of **2** on platinum electrode. Starting potential +0.6 V. Sweep rate 0.05 V $s^{-1}$: (a) in *N,N*-dimethylformamide; (b) in the presence of $(N^nBu_4)Br$.

appears. Moreover the oxidation peaks B′ and B″ increase (Fig. 4b) when $(N^nBu_4)Br$ is added to the solution. After electrolysis at the plateau of wave E′ 1 F is consumed, and the rde voltammogram shows the reduction and oxidation waves $E_1$ and B′. The cyclic voltammogram shows a reversible system $E_1/E'_1$.

The cyclic voltammogram of complex **3** also exhibits the peak E′, together with the additional peaks I′ and I″ that correspond to the oxidation of $I^-$.

In all cases the species $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2{}^+$ is unstable, no reduction process being observed. The initially formed cationic complex probably reacts with the solvent to give a new reducible species at the $E_1$ potential. It is probable that, upon one-electron oxidation, the 18-electron cation is initially formed, and halide dissociation may subsequently take place to give the 16-electron species, so giving rise to the reduction wave in the cyclic voltammogram (eq. 3).

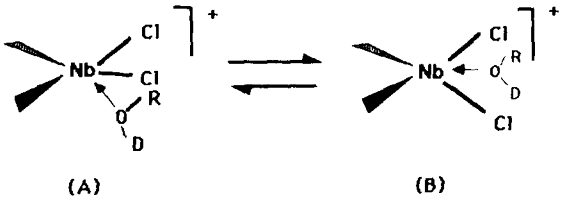
$$Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2{}^+ \xrightarrow{DMF} \left[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2(DMF)\right]^+ \rightarrow$$

$$\left[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(DMF)\right]^{2+} + X^- \qquad (3)$$

Various experimental results are in keeping with this proposal. Thus addition of DMF to solutions of complexes **4**, **5** and **6** causes release of $X^-$ anions (see, for example, Fig. 4). Furthermore, as described below, the $^1H$ NMR spectrum of the adduct of complex **4** with DMF indicates that only one DMF molecule is coordinated to the metal centre. As far as we are aware, these 16-electron species are the first reported dicationic niobium(V) complexes.

### *Reactivity of complex* $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]^+$

We have previously reported [14] that the initial coordination of the phosphine to the metal centre must be a step in the catalytic electrochemical oxidation of $PPh_3$ by



Scheme 2.

the complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2I_2]^+$. The behaviour of complex **4** towards different nucleophilic reagents was investigated. The treatment of a red solution of complex **4** in chloroform with $H_2O$ or ROH (R = Me, Et) gave after stirring a yellow solution that probably contains an adduct in which the nucleophilic agent is coordinated to the niobium atom, according to eq. 4:

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]^+ + ROH \rightarrow \text{“}[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2(OHR)]^+\text{”} \quad (4)$$

All attempts to isolate these adducts as solids were unsuccessful, since the initial red solid was isolated when the yellow solution was concentrated or evaporated to dryness. The $^1H$ NMR spectrum in deuterated methanol of a yellow solution of complex **4** shows the presence of two species, which are probably the outside (A) and inside (B) isomers present in equilibrium (Scheme 2).

On the basis of recent mechanistic studies on the carbonylation of $Zr(\eta^5\text{-}C_5H_5)_2R_2$ [16] it was suggested that the initial kinetic product, $\eta^2$-acyl O-outside, arising from the favoured lateral coordination of CO [17], subsequently isomerizes irreversibly to its thermodynamically more stable conformer $\eta^2$-acyl O-inside.

We recorded the $^1H$ NMR spectrum of a yellow solution of complex **4** in $d^1$-chloroform containing a small amount of O-deuterated methanol and only observed the signal of the inside (B) isomer ($C_{2v}$ molecular symmetry). We believe that under these operating conditions formation of the intermediate kinetic isomer A must be followed by an irreversible isomerization to give the thermodynamically more stable isomer B. The reaction of the electrochemically generated complex **4** with ethanol in dichloromethane was also studied. The rde voltammogram of the resulting solution exhibits two reduction waves $A_1$ and $A_2$ ($E_{1/2} = -0.25$ and $-0.70$ V) (Fig. 5). In cyclic voltammetry two cathodic peaks $A_1$ and $A_2$ corresponding to the waves are observed. When the scan is reversed an anodic peak E′ is obtained that corresponds to the oxidation of complex **1**. The reduction at $-0.4$ V (plateau of wave $A_1$) consumes 1 F and complex **1** is quantitatively obtained (wave E′).

Figure 6 shows the cyclic voltammogram of complex **4**. When ethanol is added to the dichloromethane solution peak E decreases, the reduction peaks $A_1$ and $A_2$ are observed, and after 1 minute the height of peak $A_2$ increases. These results suggest that, as indicated by the spectroscopic observations, the addition of ethanol produces both isomers A and B which are in equilibrium, since the reduction at $-0.4$ V (plateau of wave $A_1$) affords complex **1** and simultaneously wave $A_2$ disappears.

The reaction of complex **4** with NaOH (aq.) gives the known $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(O)Cl$ [18]. Complex **4** reacts with an excess of DMF to give an adduct

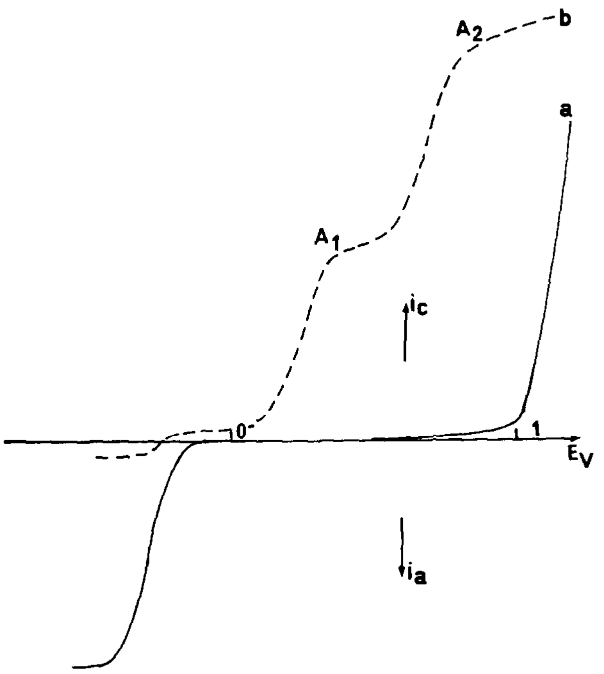


Fig. 5. Rotating disk electrode voltammogram of 1 in dichloromethane in the presence of ethanol: (a) before electrolysis; (b) after one-electron oxidation.

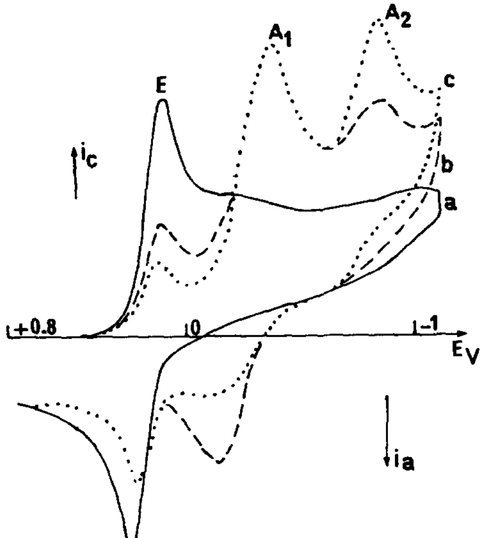


Fig. 6. Cyclic voltammogram of 4 in dichloromethane on platinum electrode. Starting potential +0.8 V. Sweep rate 0.2 V $s^{-1}$: (a) alone; (b) immediately after addition of ethanol; (c) after 1 minute.

with only one DMF molecule; the adduct can be isolated as an impure crystalline solid which was characterized by $^1H$ NMR spectroscopy.

Several new organoalkoxoniobium(V) complexes were isolated from the solution produced by reaction of complex **4** with $Me_3SiOR$ reagents, eq. 5:

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]^+ + Me_3SiOR \rightarrow [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(OR)]^+ + Me_3SiCl \quad (5)$$

$(R = CH_3$ (**7**), $CH_2CH_3$ (**8**), $CH(CH_3)_2$ (**9**))

A reasonable mechanism for this process involves the initial coordination of the alkoxylating agent to the niobium $d^0$ centre followed by the elimination of the volatile $Me_3SiCl$. We have previously described the application of $Me_3SiOR$ as a useful alkoxylating reagent for the preparation of some organoalkoxoniobium(V) complexes [19].

Complexes **7**, **8** and **9** were isolated as air-sensitive yellow crystals. The IR spectra of all the organoalkoxoniobium(V) compounds show the characteristic absorptions for the cyclopentadienyl [9], trimethylsilyl [10] and hexafluorophosphate [11] groups. The $^1H$ NMR spectra show a single signal for the $SiMe_3$ group, several peaks due to the non-equivalent $\eta\text{-}C_5H_4$ protons [12], and the signals of the alkoxo groups.

## Experimental

### *Materials and methods*

All reactions were performed by standard Schlenk techniques under dry oxygen-free nitrogen or argon. Solvents were distilled from appropriate drying agents and degassed before use.

Elemental analyses were performed with a Perkin–Elmer 240B microanalyzer. Nmr spectra were recorded on a Varian FT 80A spectrometer. IR spectra were recorded with Nujol mulls between CsI plates in the region 4000–200 $cm^{-1}$ with a Perkin–Elmer PE883 IR spectrometer. In the electrochemical experiments a calomel saturated reference electrode, separated from the solution by a sintered glass disk, was used. The auxiliary electrode was a platinum disk electrode. In all cases the supporting electrolyte was tetrabutylammonium hexafluorophosphate (0.2 *M*); the salt (Fluka) was dried and deoxygenated before use. A Tacussel UAP4 unit connected to a Tektronix oscilloscope (linear potential sweep experiments), a three-electrode Tacussel Tipol polarograph, an Amel 552 potentiostat, and a Tacussel IG 5 integrator were used.

### *Preparation of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2]^+$ $PF_6^-$ (X = Cl, **4**; Br, **5**; I, **6**)*

To a green solution of $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2$ (1.00 g, 2.28 mmol) in chloroform or dichloromethane was added $[Fe(\eta^5\text{-}C_5H_5)_2]^+PF_6^-$ (0.75 g, 2.28 mmol). The mixture was stirred for 3 h at room temperature to give a red solution. Addition of hexane precipitated the cationic complex. This was recrystallized by dissolving it in chloroform and placing a layer of hexane above it in a Schlenk tube. Red crystals began to grow within a few days; interdiffusion of the solvents was complete in 3 days. Complexes **5** and **6** were obtained similarly.

**4** (Yield 90%) (Found: C, 32.9; H, 4.4. $C_{16}H_{26}Cl_2F_6NbPSi_2$ Calc.: C, 32.7; H, 4.3). $^1$H NMR ($CDCl_3$): $\delta$ 0.33 (s, 9H, $SiMe_3$), 6.90 (m, 4H, $C_5H_4$).

**5** (Yield 87%) (Found: C, 28.6; H, 3.9. $C_{16}H_{26}Br_2F_6NbPSi_2$ Calc.: C, 27.7; H, 4.0). $^1$H NMR ($CDCl_3$): $\delta$ 0.34 (s, 9H, $SiMe_3$), 7.10 (m, 4H, $C_5H_4$)

**6** (Yield 67%) (Found: C, 25.5; H, 3.7. $C_{16}H_{26}I_2F_6NbPSi_2$ Calc.: C, 25.0; H, 3.4). $^1$H NMR ($CDCl_3$): $\delta$ 0.38 (s, 9H, $SiMe_3$), 6.90 (m, 4H, $C_5H_4$).

### *Preparation of* $Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(OR)]^+PF_6^-$ ($R = CH_3$, *7*; $CH_2CH_3$, **8**; $CH(CH_3)_2$, **9**)

A suspension of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X_2]^+$ $PF_6^-$ (0.34 g, 0.58 mmol) in $Me_3SiOCH_3$ was stirred at room temperature for 3h, during which the initially red solid was changed into a yellow solid, which was filtered off, washed with hexane, and recrystallized as described for complex **4**. Complexes **8** and **9** were obtained similarly.

**7** (Yield 87%) (Found: C, 35.3; H, 5.1. $C_{17}H_{29}ClF_6ONbPSi_2$ Calc.: C, 35.2; H, 5.2). $^1$H NMR ($CDCl_3$): $\delta$ 0.40 (s, 18H, $SiMe_3$), 7.01 (m, 6H), 7.43 (m, 2H), ($C_5H_4$), 4.61 (s, 3H, $OCH_3$).

**8** (Yield 80%) (Found: C, 36.5; H, 5.2. $C_{18}H_{31}ClF_6ONbPSi_2$ Calc.: C, 36.9; H, 5.7). $^1$H NMR ($CDCl_3$): $\delta$ 0.55 (S, 18H, $SiMe_3$), 7.11 (m, 6H), 7.45 (m, 2H), ($C_5H_4$), 1.55 (t, 3H, $J$(H–H) = 6.9 Hz, $OCH_2CH_3$), 4.96 (q, 2H, $J$(H–H) = 6.9 Hz, $OCH_2CH_3$).

**9** (Yield 80%) (Found: C, 37.6; H, 5.4. $C_{19}H_{33}ClF_6ONbPSi_2$ Calc.: C, 37.5; H, 5.9). $^1$H NMR ($CDCl_3$): $\delta$ 0.61 (s, 18H, $SiMe_3$), 7.10 (m, 4H), 7.36 (m, 2H), 7.44 (m, 2H) ($C_5H_4$), 1.60 (d, 6H, $J$(H–H) = 5.5 Hz, $OCH(CH_3)_2$, 5.26 (m, 1H, $J$(H–H) = 5.5 Hz, $OCH(CH_3)_2$).

### "$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2(ODR)]^+PF_6^-$"

$^1$H NMR ($CD_3OD$): (a) isomer (A) $\delta$ 0.53 (s, 18H, $SiMe_3$), 5.87 (m, 2H), 6.17 (m, 2H), 6.31 (m, 2H), 6.41 (m, 2H) ($C_5H_4$); (b) isomer (B) $\delta$ 0.55 (s, 18H, $SiMe_3$), 7.18 (m, 4H), 7.47 (m, 4H), ($C_5H_4$).

### $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(DMF)]^{2+}$ $2PF_6^-$

$^1$H NMR ($CDCl_3$): $\delta$ 0.28 (s, 18H, $SiMe_3$), 6.53 (m, 8H, $C_5H_4$), 2.90 (6H, $-N(CH_3)_2$), 8.00 (1H, $H$–C=O).

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