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# Synthesis, electrosynthesis and structural studies of bis(silylcyclopentadienyl)niobium complexes with acetylene ligands

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## Abstract

The reduction of [Nb($\eta^5$-$C_5H_4SiMe_3$)$_2$$Cl_2$] (**1**) with one equivalent of sodium amalgam (10%) in the presence of acetylenes yields [Nb($\eta^5$-$C_5H_4SiMe_3$)$_2$Cl($\eta^2$-RC$_1$≡CR$_2$)], ($R_1$ = H, $R_2$ = COOMe, **3c**; $R_1$ = Me, $R_2$ = COOMe, **3d**; $R_1$ = $R_2$ = COOMe, **3e**). The structural characterization of these compounds has been carried out by NMR spectroscopy. The reduction of the (acetylene)niobium(V) complexes [Nb($\eta^5$-$C_5H_4SiMe_3$)$_2$Cl($\eta^2$-$R_1$C≡C$R_2$)] with one equivalent of sodium amalgam (10%) gives the paramagnetic niobium(IV) complexes [Nb($\eta^5$-$C_5H_4SiMe_3$)$_2$($\eta^2$-$R_1$C≡C$R_2$)] ($R_1$ = $R_2$ = Ph, **4a**; $R_1$ = H, $R_2$ = Ph, **4b**; $R_1$ = H, $R_2$ = COOMe, **4c**; $R_1$ = Me, $R_2$ = COOMe, **4d**; $R_1$ = $R_2$ = COOMe, **4e**), which have been characterized by ESR spectroscopy. However, electroreduction of **1** in the presence of the acetylenes gives the complexes **3** or **4** depending both on the nature of the acetylene and on the experimental conditions. In the electrolysis of **1** in the presence of acetylenes **c** or **d** a slow production of **4c** and **4d**, respectively, occurs to yield the alkenyl complexes [Nb($\eta^5$-$C_5H_4SiMe_3$)$_2$Cl($\eta^1$-$R_1$C = CH$R_2$)], **4'c** and **4'd**. Finally, the addition of HCl to solutions of **4a** gives a mixture of **1** and *cis*-stilbene.

*Key words:* Niobium; Cyclic voltammetry; Alkyne complexes; Polarography

## 1. Introduction

There is a rich chemistry of reactions of alkynes with transition metal compounds [1], and in several cases these are of interest in organic synthesis [2]. However, whereas $\pi$-bonded alkyne derivatives of Group 6 metals are well known, the alkyne chemistry of Group 5 metals is much less developed. In the majority of the complexes, cyclopentadienyl or aryloxide are also present [3]. Since certain niobium or tantalum complexes polymerize and cyclize alkynes [4], in order to understand the mechanism better it is necessary to study the preparation, structure and reactivity of new alkyne complexes of these metals.

In earlier communications we reported our studies of the interaction of alkynes with substituted niobocene complexes. Here we report the chemical and electrochemical preparation of a new series of chloro(alkyne) niobocene complexes and some of their chemistry, including the reduction to give paramagnetic (alkyne)niobocene derivatives.

## 2. Results and discussion

We have previously published [3a,b] a simple method to prepare 18-electron complexes of the type [Nb($\eta^5$-$C_5H_4SiMe_3$)$_2$X($\pi$-alkyne)] based on the one-electron reduction of $d^1$ precursors [Nb($\eta^5$-$C_5H_4SiMe_3$)$_2$$X_2$]

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TABLE 1. $^1$H NMR data for bis(trimethylsilylcyclopentadienyl)niobium complexes in $C_6D_6$ with $SiMe_4$ as internal standard (δ ppm (multiplicity, relative intensity))

| Complex | $SiMe_3$ | $C_5H_4$ | $R_1C\equiv$ | $\equiv CR_2$ | Relative proportion (%) |
|---|---|---|---|---|---|
| **3c** (*exo*) | 0.22 (s, 18) | 5.20 (m, 2); 5.22 (m, 2)<br>5.80 (m, 2); 6.20 (m, 2) | 7.96 (s, 1) H | 3.51 (s, 3) COOMe | 75 |
| **3c** (*endo*) | 0.18 (s, 18) | 5.26 (m, 2); 5.52 (m, 4);<br>5.59 (m, 2) | 8.42 (s, 1) H | 3.67 (s, 3) COOMe | 25 |
| **3d** (*exo*) | 0.25 (s, 18) | 5.27 (m, 2); 5.42 (m, 2);<br>5.76 (m, 2); 5.93 (m, 2) | 2.65 (s, 3) Me | 3.55 (s, 3) COOMe | 80 |
| **3d** (*endo*) | 0.30 (s, 18) | 5.15 (m, 2); 5.42 (m, 2);<br>5.63 (m, 2); 5.75 (m, 2) | 2.23 (s, 3) Me | 3.66 (s, 3) COOMe | 20 |
| **3e** | 0.27 (s, 18) | 5.59 (m, 4); 5.80 (m, 2);<br>6.11 (m, 2) | 3.46 (s, 3) COOMe | 3.56 (s, 3) COOMe | |

(**1**), so that an intermediate $d^2$, 16-electron species, $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X]$, is then trapped by an alkyne:

$$[Nb(\eta^5\text{-}C_5H_4Me_3)_2X_2] + Na/Hg + \text{alkyne (excess)} \rightarrow$$

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(\pi\text{-alkyne})] + NaX \qquad (1)$$

We have now succeeded in preparing by this method and characterizing structurally other stable (halo) (alkyne)niobocene complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}RC\equiv CR')]$ (**3**) using alkynes activated by electron-withdrawing radicals such as R = COOMe, R′ = H (**3c**), R = COOMe, R′ = Me (**3d**) and R = R′ = COOMe (**3e**).

The 18-electron neutral niobocene species were isolated as microcrystalline solids and they were characterized by analysis (see Experimental section).

The complexes have been spectroscopically characterized (Tables 1 and 2). The NMR data are consistent with the structure of analogous complexes [3a,b], established crystallographically for the related acetylene complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}PhC\equiv CPh)]$ [3a] with the acetylene C≡C bond in a plane that contains the Nb and Cl atoms. For complexes **3c** and **3d**, with an unsymmetrical acetylene, two isomers are possible due to the two possible orientations of the ligand in the Nb–Cl–(C≡C) plane (the reflection plane of the rings (Fig. 1).

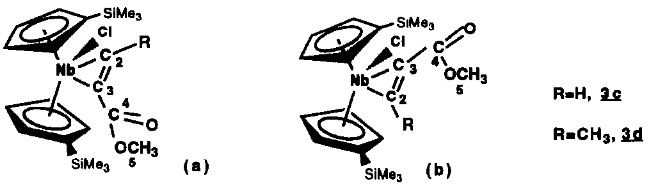


Fig. 1. Structures of isomers of complexes **3c** and **3d**.

For complexes **3c** and **3d**, $^1$H and $^{13}$C NMR data indicate the existence of a mixture of the both *endo* (b) and *exo* (a) isomers.

It has been reported [3d,k] that the sterically bulkier substituent on the alkyne will be preferentially as far as possible from the non-cyclopentadienyl ligand (in our case chloride) in a "*trans*" disposition to give the *exo* isomer (a). This is supported by $^1$H and $^{13}$C NMR evidence. For the isomeric mixtures of **3c** and **3d**, the $^1$H NMR data indicate that the major component of the mixture is the one displaying a COO*Me* resonance downfield (the smaller substituent, H in **3c** and $CH_3$ in **3d**, of the acetylene occupies preferentially the inside site and experiences an upfield shift). The $^{13}$C NMR chemical shift values agree with this. The major com-

TABLE 2. $^{13}$C NMR data for bis(trimethylsilylcyclopentadienyl)niobium complexes in $C_6D_6$ with $SiMe_4$ as internal standard (δ ppm)

| Complex | Si*Me*$_3$ | $\eta$-$C_5H_4$ | | C*Me* | $C^2$ | $C^3$ | COOMe | COO*Me* |
|---|---|---|---|---|---|---|---|---|
| | | $C^1$ | $C^2, C^3, C^4, C^5$ | | | | | |
| **3c** (*exo*) | −0.10 | 112.1 | 125.8; 119.6; 106.4; 103.1 | – | 139.5 | 148.9 | 175.0 | 51.5 |
| **3c** (*endo*) | −0.10 | 110.8 | 120.9; 117.9; 110.1; 107.8 | – | 150.5 | – | 174.1 | 50.9 |
| **3d** (*exo*) | 0.03 | 111.1 | 121.7; 119.5; 109.9; 102.3 | 14.4 | 140.1 | 137.1 | 174.2 | 51.4 |
| **3d** (*endo*) | 0.03 | 113.1 | 120.0; 119.2; 111.0; 101.0 | 20.7 | 164.0 | 135.7 | 173.7 | 50.7 |
| **3e** | 0.06 | 114.2 | 121.4; 120.9; 112.3; 103.7 | – | 150.5 | 139.3 | 171.6 | 51.0 |
| | | | | | | | 170.8 | 51.8 |

ponent of the mixture for **3c** and **3d** shows the resonance for the carbon atom $C^3$ downfield (see Table 2).

### 2.1. Chemical reduction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}R_1C{\equiv}CR_2)]$

A variety of ($\pi$-alkyne)niobocene complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}R_1C{\equiv}CR_2)]$ (**3**) were found to react cleanly with one equivalent of sodium amalgam:

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}R_1C{\equiv}CR_2)] + Na/Hg \rightarrow [Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}R_1C{\equiv}CR_2)] + NaCl \quad (2)$$

$R_1 = R_2 = Ph$ **4a**
$R_1 = H; R_2 = Ph$ **4b**
$R_1 = H; R_2 = COOMe$ **4c**
$R_1 = Me; R_2 = COOMe$ **4d**
$R_1 = R_2 = COOMe$ **4e**

Strict exclusion of air and moisture is required for these reactions. From the reaction mixtures (see Experimental section) air-sensitive solids, the novel ($\pi$-alkyne)niobium(IV) complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}R_1C{\equiv}CR_2)]$ (**4**), were isolated in > 75% yield.

The complexes have been characterized by elemental analysis and ESR spectroscopy. The ESR spectra of the complexes show a characteristic signal of ten well defined lines reflecting coupling of the unpaired electron with the nuclear spin of niobium ($I = 9/2$) [6]. The small hyperfine coupling constants (see Table 3) indicate that the complexes have a small amount of spin density on the metal [7].

### 2.2. Electrochemical preparation of complexes ($\pi$-alkyne)bis(trimethylsilylcyclopentadienyl)niobium-(V) and -(IV)

In a parallel study, we carried out the electrochemical reduction of $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ (**1**) in the presence of acetylenes $R_1C{\equiv}CR_2$ (**a**: $R_1 = R_2 = Ph$; **b**: $R_1 = H$, $R_2 = Ph$; **c**: $R_1 = H$, $R_2 = COOMe$; **d**: $R_1 = Me$, $R_2 = COOMe$; **e**: $R_1 = R_2 = COOMe$).

We have previously reported [8] that the electrogenerated anion $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl]_2^-$ (**2**) reacts slowly with acetylene **a** giving the $Nb^V$ complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}PhC{\equiv}CPh)]$ (**3a**). At the same time **3a** was reduced by **2** to give quantitatively the $Nb^{IV}$ complex $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}PhC{\equiv}CPh)]$ (**4a**), which was characterized by ESR and IR spectroscopy and mass spectrometry (see entry 1, Table 3).

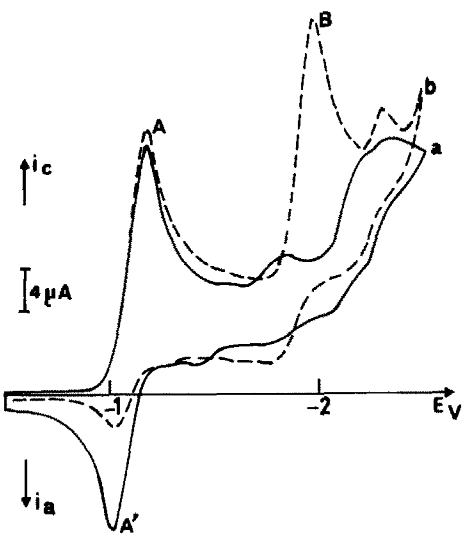


Fig. 2. Cyclic voltammogram of **1** in 0.2 M $(NBu_4)PF_6$ in THF at a platinum electrode. Starting potential, −0.5 V; sweep rate, 0.05 V $s^{-1}$; (a) **1** alone; (b) in the presence of one equivalent of **b**.

TABLE 3. Electron spin resonance data for acetylene complexes **4**

| Entry | $R_1C{\equiv}CR_2$ | $g_{iso}$ | $A_{iso}$ (G) |
|---|---|---|---|
| 1 | **a**: $R_1 = R_2 = Ph$ | 2.0140 | 16.5 |
| 2 | **b**: $R_1 = Ph$, $R_2 = H$ | 2.0092 | 12.8 |
| 3 | **c**: $R_1 = COOMe$, $R_2 = H$ | 2.0070 | 12.7 |
| 4 | **d**: $R_1 = COOMe$, $R_2 = CH_3$ | 2.0083 | 14.2 |
| 5 | **e**: $R_1 = R_2 = COOMe$ | 2.0026 | 14.2 |

The cyclic voltammetry of complex **1** at room temperature in a THF-$(Bu_4N)PF_6$ solution shows (Fig. 2) the well-known [9] reversible system A/A'. However, in the presence of one equivalent of acetylene **b**, the height of the oxidation peak A' decreases and a new reduction peak, B, appears. A similar modification on the cyclic voltammogram of **1** was observed when other acetylenes, **c**, **d** and **e**, were added, although the decrease of the oxidation peak A' and the increase of peak B were smaller than in Fig. 2. We also observed that the reduction peak B increases in size when the temperature is increased or when an excess of acetylene is added.

Controlled potential electrolysis of **1** in the presence of the acetylenes was carried out on a mercury electrode at room temperature and the results are shown in Table 4.

When the electrolysis of **1** in the presence of acetylene **b** (see entry 2, Table 4) is carried out at −1.2 V, one equivalent of electrons is consumed and a yellow-green solution is obtained. This electrolysed solution exhibits a system $B/B'_1$ in cyclic voltammetry and is ESR silent. The electrogenerated complex has been isolated and identified as complex **3b**, which has also been prepared chemically (see above). Its cyclic voltammogram is shown in Fig. 3. Two reduction peaks B and C are observed during the cathodic scan (see entry 2, Table 5), peak C being smaller than peak B.

TABLE 4. Electroreduction of **1** in the presence of acetylenes at room temperature at −1.2 V in 0.2 M $(NBu_4)PF_6$ in THF at a mercury electrode

| Entry | $R_1C{\equiv}CR_2$ | Molar ratio $R_1C{\equiv}CR_2$/ complex **1** | Coulometric data (F per mole **1**) | Products |
|---|---|---|---|---|
| 1 | **a**: $R_1 = R_2 = Ph$ | 1.10 | 1.97 | **4a** |
| 2 | **b**: $R_1 = Ph$, $R_2 = H$ | 1.05 | 1.07 | **3b** |
| 3 | **c**: $R_1 = COOMe$, $R_2 = H$ | 2.62 | 1.40 | **3c**, **4c**, **4′c** |
| 4 | **d**: $R_1 = COOMe$, $R_2 = CH_3$ | 1.92 | 1.60 | **3d**, **4′d** |
| 5 | **e**: $R_1 = R_2 = COOMe$ | 1.10 | 2.17 | **4e** |

When the scan is reversed after peak B or C, the oxidation peak $B'_1$ is obtained and when the positive-going scan is switched at −1.7 V another reduction peak $B_1$ appears, which is at a lower cathodic potential than peak B. In polarography **3b** shows an oxidation wave D′ and a reduction wave B, and the wave C does not appear (Fig. 4(a)).

After an electrolysis at −2.0 V (plateau of wave B)

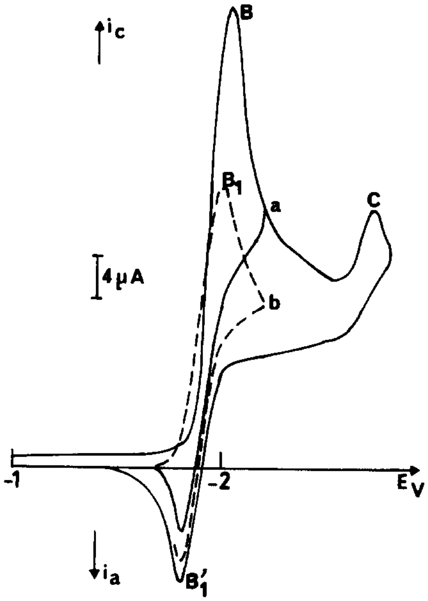


Fig. 3. Cyclic voltammogram of **3b** in 0.2 M $(NBu_4)PF_6$ in THF at a platinum electrode. Sweep rate, 0.2 V $s^{-1}$; (s) starting potential −1 V; (b) second scan after reversing the potential at −1.7 V.

TABLE 5. Electrochemical data for acetylene complexes **3** and **4**

| Entry | $R_1C{\equiv}CR_2$ | Polarography | | Cyclic voltammetry | | |
|---|---|---|---|---|---|---|
| | | $E_{1/2,c}$ (B) (V) | $E_{1/2,c}$ ($B_1$) (V) | $E_{1/2,c}$ (B) (V) | $E_{p,c}$ ($B_1$) (V) | $E_{p,a}$ ($B'_1$) (V) |
| 1 | **a**: $R_1{=}R_2{=}Ph$ | −1.87 | −1.90 | −1.92 | −1.88 | −1.73 |
| 2 | **b**: $R_1{=}Ph$, $R_2{=}H$ | −2.12 | −2.00 | −2.12 | −1.98 | −1.80 |
| 3 | **c**: $R_1{=}COOMe$, $R_2{=}H$ | −1.93 | −1.80 | −2.00 | −1.82 | −1.74 |
| 4 | **d**: $R_1{=}COOMe$, $R_2{=}CH_3$ | −1.98 | −1.83 | −2.01 | −1.86 | −1.69 |
| 5 | **e**: $R_1{=}R_2{=}COOMe$ | −1.92 | −1.58 | −1.95 | −1.57 | −1.47 |

The sweep rate was 25 and 200 mV $s^{-1}$ for polarographic and voltammetric measurements, respectively. Solute concentration was in the range 1–5 mM.

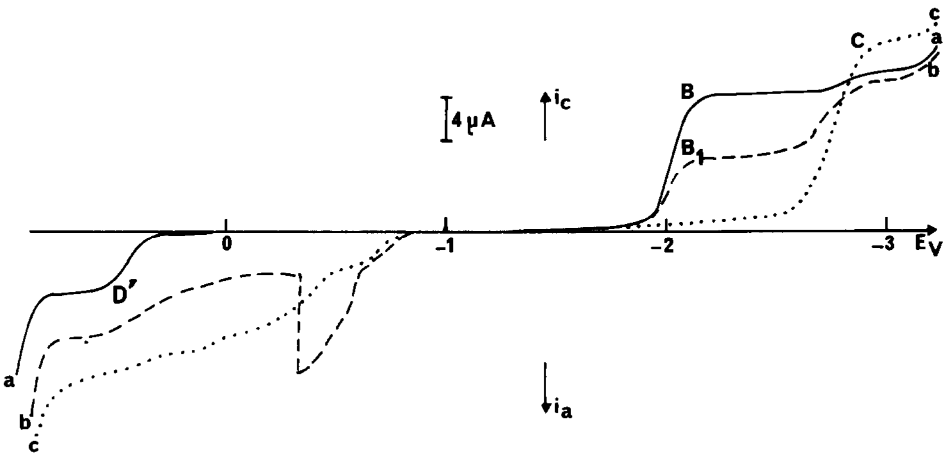


Fig. 4. Polarogram (average current) of **3b** in 0.2 M $(NBu_4)PF_6$ in THF (a) before electrolysis, (b) after one-electron reduction at −2 V and (c) after two-electron reduction at −2 V.

and consumption of one equivalent of electrons, the polarogram of the brown electrolysed solution shows the reduction waves $B_1$ and C and also ill-defined oxidation waves (Fig. 4(b)). In cyclic voltammetry the reversible system $B_1/B'_1$ appears. The solution contains the paramagnetic complex **4b**, whose ESR data have been described previously for the chemically isolated complex (see above).

If the electrolysis is carried out at −2.0 V, one equivalent of electrons is consumed and the solution changes from brown to orange. In polarography the reduction wave C appears (Fig. 4(c)) and no signal is detected by ESR spectroscopy.

The electrolysis of **1** in the presence of acetylene **c** consumes less than two equivalents of electrons (entry 3, Table 4) and a mixture of complexes, in a molar ratio which depends on the experimental conditions, is formed. One of them corresponds to the $Nb^V$–acetylene complex **3c** and the other to two paramagnetic complexes (detected by ESR spectroscopy), **4c** and **4′c**, the last resulting from protonation of **4c** (see below). The complex **4c** can be quantitatively obtained by one-electron reduction of the chemically prepared **3c**. In cyclic voltammetry **4c** exhibits a reversible $B_1/B'_1$ (see entry 3, Table 5).

However, the electrolysis of **1** in the presence of acetylene **d** consumes 1.6 equivalents of electrons (entry 4, Table 4) and a mixture of two complexes, which correspond to **3d** and a paramagnetic species **4′d**, is formed. In polarography two reduction waves, B* ($E_{1/2} = -1.36$ V) and B (entry 4, Table 5), and several oxidation waves are observed. In cyclic voltammetry the corresponding reduction peaks B* and B are found and when the scan is reversed after peak B, two oxidation peaks, $B'_1$ and B*, are obtained (Fig. 5). In the ESR spectrum there is a signal ($A_{iso} = 103.7$ G) for complex **4′d**.

When electrolysis was carried out at the potential of wave B*, the complex **4d** was formed, characterized by its ESR spectrum. Complex **4d** is relatively unstable toward protonation and a slow change occurs giving **4′d** (see below). Table 6 shows the different species electrogenerated.

Consistent with the above results, **4′d** is not obtained when the applied potential is larger than −1.2 V (see entries 2, 3 and 4, Table 6). Complex **3d** was obtained only with consumption of nearly one equivalent of electrons (entries 5 and 6, Table 6) when the electrolysis was performed at higher temperature.

We also examined the electrochemical behaviour of the chemically prepared **3d**. It exhibits a cyclic voltammogram similar to Fig. 3 (see entry 4, Table 5). The one-electron reduction of **3d** at −1.9 V at −10°C yields the complex **4d**, which was characterized by its ESR spectrum (Fig. 6(a)). Complex **4d** is relatively stable at −10°C. However, when the temperature is increased a change is observed by ESR spectroscopy. The signal of **4d** decreases as a new signal, which corresponds to **4′d**, increases (Fig. 6(b) and (c)). After 4 h the signal of **4d** disappears. Complex **4′d** was isolated after appropriate work-up and was characterized as a niobium(IV)–alkenyl complex. (see below).

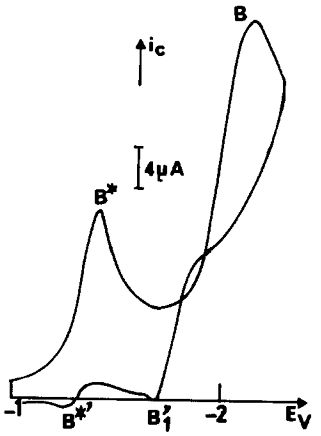


Fig. 5. Cyclic voltammogram of **1** at a platinum electrode in the presence of 1.92 equivalents of **d** in 0.2 M $(NBu_4)PF_6$ in THF after electrolysis at −1.2 V.

Finally, the electrolysis of **1** in the presence of acetylene **e** consumes nearly two equivalents of electrons (entry 5, Table 4) and the complex **4e** was formed. This complex is relatively stable under the experimental conditions and no further changes occur.

## 3. Discussion

The electrochemical results can be rationalized by Scheme 1.

The electrogenerated anion **2** reacts with several acetylenes, $R_1C{\equiv}CR_2$, to give the corresponding niobium(V) complexes **3**. At the same temperature (20°C), the reaction is faster for **b**, **c** and **d** than for **a** and **e**.

TABLE 6. Electroreduction of 1 in the presence of acetylene c in 0.2 M THF in $(NBu_4)PF_6$

| Entry | Molar ratio c/1 | T (°C) | Coulometric data (F per mole of 1) | Products | E (V/ECS) |
|---|---|---|---|---|---|
| 1 | 1.92 | Ambient | 1.60 | **3d, 4′d** | −1.2 |
| 2 | 2.06 | Ambient | 1.80 | **3d, 4d** | −1.3 |
| 3 | 1.74 | −10 | 2.05 | **3d, 4d*** | −1.4 |
| 4 | 1.79 | −10 | 2.00 | **3d, 4d*** | −1.5 |
| 5 | 2.83 | +40 | 1.20 | **3d** | −1.2 |
| 6 | 10.57 | +43 | 1.20 | **3d** | −1.2 |

Complex **3b** is quantitatively obtained after one-electron reduction of **1** in the presence of **b**. Complexes **3a** and **3e** should be more stable than **3b**, **3c** and **3d**, corresponding to the $\pi$-acid character of these alkynes [10]. However, **3a** and **3e** cannot be obtained by electroreduction of **1** in the presence of the corresponding acetylenes, since the niobium(IV) complexes **4a** and **4e** are formed. Their formation can be explained by an electron-transfer reaction between the electrogenerated species **2** and the complex **3** (see Scheme 1, reaction (5)). An inner-sphere electron-transfer reaction is postulated, since the difference between the reduction potentials of **1** and **3a** (or **3e**) is nearly 0.7 V. We have also verified that the addition of **2** to solutions of chemically prepared **3a** gives the products **1** and **4a**.

Since the complexes **3a** and **3e** are reduced at lower cathodic potentials than **3b**, **3c** and **3d** (see Table 5), reaction (5) may be favoured for the former complexes and therefore **4a** and **4e** can be quantitatively formed after a two-electron reduction of **1**, in accordance with the following overall reaction:

$$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl_2}] + \mathrm{R_1C{\equiv}CR_2} + 2e^- \rightarrow$$
$$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\eta^2\text{-}\mathrm{R_1C{\equiv}CR_2})] + 2\mathrm{Cl}^-$$

For acetylenes **c** and **d**, a mixture of complexes **3** and **4** is formed. However, it is possible to obtain quantitatively the complex **3d** when the electrolysis of **1** is performed both at higher temperature and in the presence of an excess of **d** (see entries 5 and 6, Table 6). At higher temperature reaction (2) (Scheme 1) is faster than at room temperature and the electron-transfer reaction (5) does not take place.

The two-electron reduction of **3** (peak B) (reaction (3), Scheme 1) corresponds to an ECE process involving the cleavage of the niobium–halogen bond. Anionic species **5** are formed which are oxidized at the potential of peak B$'_1$. The B$_1$/B$'_1$ system corresponds to the redox reaction (4). Species **5** is relatively unstable on the time scale of electrolysis and a protonation reaction occurs to give the hydride derivatives **6** (reaction (7)) [3b]. Only the derivative **6a** has been isolated (see Experimental section).

The formation of **4** during the electrolysis of **3** can be explained by an outer-sphere electron-transfer reaction between **5** and **3** (see reaction (6), Scheme 1), since the potential different is small (see Table 5). Complex **5**, which is generated at the electrode, diffuses towards the bulk of the solution and it comes in contact with **3**, which diffuses towards the electrode and the reaction (6) takes place.

In the electrolysis of **1** in the presence of **c** or **d**, the paramagnetic complexes **4′** are formed slowly from the corresponding complexes **4**, in accordance with the following reaction:

$$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\eta^2\text{-}\mathrm{R_1C{\equiv}CR_2})] \xrightarrow[\mathrm{H^+}\text{(from a proton source)}]{\mathrm{Cl^-}}$$
$$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl}(\eta^1\text{-}\mathrm{R_1C{=}CHR_2})]$$

**4′c**: $R_1 = H$; $R_2 = COOMe$

**4′d**: $R_1 = Me$; $R_2 = COOMe$

The spectroscopic data are consistent with the above formulation, but we have not yet been able to determine which of the two possible *cis* and *trans* alkenyl isomers is formed. The formation of alkenyl groups through the protonation of alkyne moieties is a well-known type of reaction of alkyne complexes [11a]. For example, the addition of a strong acid to the complex [(PPh$_3$)$_2$Pt(acetylene)] gives (PPh$_3$)$_2$PtX$_2$ and the corresponding olefin and alkenyl intermediate has been postulated [11b].

A similar reaction occurs when a strong acid (one

$$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl_2}] + 1e^- \rightleftharpoons [\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl_2}]^- \ \text{(system A/A')} \qquad (1)$$

$$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl_2}]^- + \mathrm{R_1C{\equiv}CR_2} \rightarrow [\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl}(\eta^2\text{-}\mathrm{R_1C{\equiv}CR_2})] + \mathrm{Cl}^- \qquad (2)$$

$$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl}(\eta^2\text{-}\mathrm{R_1{\equiv}CCR_2})] + 2e^- \rightarrow [\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\eta^2\text{-}\mathrm{R_1C{\equiv}CR_2})]^- + \mathrm{Cl}^- \ \text{(peak B)} \qquad (3)$$

$$\underset{\mathbf{5}}{[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\eta^2\text{-}\mathrm{R_1C{\equiv}CR_2})]^-} - 1e^- \rightleftharpoons \underset{\mathbf{4}}{[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\eta^2\text{-}\mathrm{R_1C{\equiv}CR_2})]} \ \text{(system B}'_1/\text{B}_1) \qquad (4)$$

$$\mathbf{3} + \mathbf{2} \rightarrow \mathbf{4} + \mathbf{1} + \mathrm{Cl}^- \qquad (5)$$

$$\mathbf{5} + \mathbf{3} \rightarrow \mathbf{24} + \mathrm{Cl}^- \qquad (6)$$

$$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\eta^2 - \mathrm{R_1C{\equiv}CR_2})]^- + \mathrm{H}^+ \ \text{(from a proton source)} \rightarrow \underset{\mathbf{6}}{[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{H}(\eta^2\text{-}\mathrm{R_1C{\equiv}CR_2})]} \qquad (7)$$

Scheme 1.

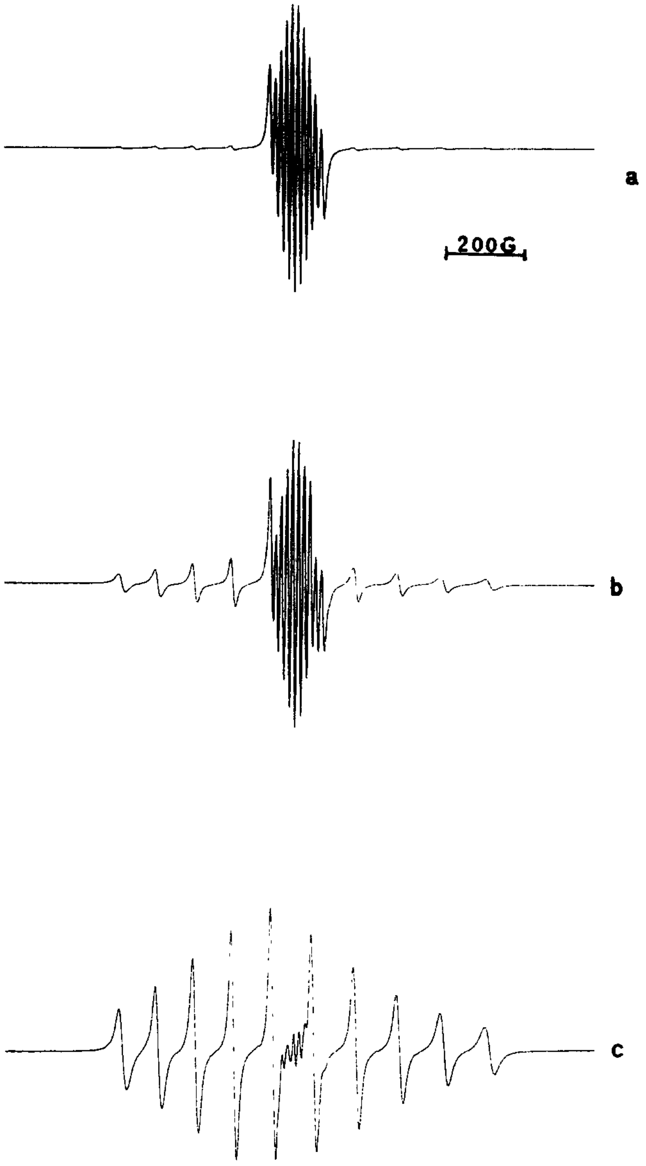
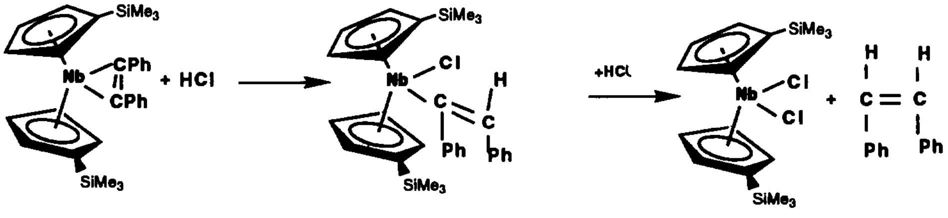


Fig. 6. (a) ESR spectrum of **4d** in 0.2 M $(NBu_4)PF_6$ in THF generated from one-electron reduction of **3d** at −1.9 V at −10°C, (b) after 1 h at ambient temperature and (c) after 3 h at ambient temperature.



**4a** **4'a'** **1**

Scheme 2.

equivalent of HCl) is added to a solution of **4a**. In cyclic voltammetry, the reduction peaks A and B* appear and the ESR spectrum indicates that the paramagnetic species **1** and **4'a** are formed. When a second equivalent of HCl is added, the characteristic ESR signal disappears and the signal of **1** increases. *cis*-Stilbene was found in the solution. The above results are consistent with Scheme 2.

It was not possible to obtain **4'a** quantitatively, probably because of the similar kinetics of the reactions (1) and (2) (Scheme 2). These processes constitute an attractive and efficient way to prepare 1,2-disubstituted olefins, as previously mentioned [12]. Further work is in progress on the scope of the reaction.

## 4. Experimental section

### 4.1. General procedures

All manipulations were performed by using standard Schlenk techniques in an atmosphere of dry, dioxygen-free dinitrogen or argon. Solvents were dried under $N_2$ and degassed before use. C,H,N analyses were carried out with a Perkin-Elmer 240 B microanalyser. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian Unity 300 instrument. IR spectra were recorded on Perkin-Elmer 881 and Nicolet 205 spectrometers, either in solution between NaCl plates or in the solid state (KBr). ESR spectra were recorded at room temperature with a Bruker Esp 300 spectrometer. $(NBu_4)PF_6$ was purchased from Fluka (puriss. p.a. for electrochemical grade) and dried and deoxygenated before use. Acetylenes **a**, **b**, **c**, **d** and **e** are commercially available; and they were used as received. Compounds **1**, **3a** and **3b** were synthesized according to published method [3a,13].

### 4.2. Electrochemical equipment and cells

Cyclic voltammetry was carried out in a standard three-electrode Tacussel UAP4 unit cell. The reference electrode was saturated calomel (SCE), separated from the solution by a sintered-glass disc. The auxiliary electrode was a platinum wire. For all voltammetric measurements the working electrode was a platinum disc electrode (surface area 3.1 $mm^2$), which was initially polished with alumina of decreasing particle size (down to 0.05 mm). For the polarograms, a three-electrode Tacussel Tipol polarograph was used. The dropping-mercury electrode characteristics were $m = 3$ mg $s^{-1}$ and $G = 0.5$ s. For controlled-potential electrolysis, a mercury pool was used as the cathode and a platinum plate as the anode, the latter being separated from the solution by sintered-glass disc. Large-scale electrolyses were carried out in a cell with three compartments separated with fritted glass of medium porosity. In all cases, the electrolyte was a 0.2 M solution of tetrabutylammonium hexafluorophosphate in tetrahydrofuran (THF). The electrolyses were performed with an Amel 552 potentiostat coupled to an Amel 721 electronic integrator.

### 4.3. $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^2\text{-}R_1C{\equiv}CR_2)]$ ($R_1 = H$, $R_2 = COOMe$, *3c*; $R_1 = Me$, $R_2 = COOMe$, *3d*; $R_1 = R_2 = COOMe$, *3d*)

The chemical procedure was similar in all cases. A solution of the acetylene (0.46 mmol) was added to a mixture of sodium amalgam (10%, 0.46 mmol of Na) and **1** (0.200 g, 0.46 mmol) in THF (100 $cm^3$). The mixture was stirred vigorously for 3 h at ambient temperature, filtered, and the filtrate evaporated to dryness under vacuum. Hexane was used to extract the solids. The resultant extracts were concentrated to give crystals of the complexes. Analyses: found (calc.) (%): **3c**, C 49.52 (49.68), H 6.18 (6.20); **3d**, C 50.66 (50.70), H 6.35 (6.43); **3e**, C 48.55 (48.75), H 5.95 (5.91).

Complex **3b** was prepared electrochemically by the following method. A mixture of **1** (0.300 g; 0.74 mmol) and **c** (0.080 g; 0.78 mmol) was added to the cathode compartment of the large-scale electrolysis cell containing 100 $cm^3$ of a 0.2 M solution of $(NBu_4)PF_6$ in THF. The potential was set at $-1.2$ V and the electron consumption was 1.07 F per mole of **1**. The THF solution was then evaporated to dryness under vacuum. Hexane was used to extract the solid. The resultant extract was concentrated and cooled to give yellow-green crystals of **3b**.

### 4.4. $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\eta^2\text{-}R_1C{\equiv}CR_2)]$ ($R_1 = R_2 = Ph$, *4a*; $R_1 = H$, $R_2 = Ph$, *4b*; $R_1 = H$, $R_2 = COOMe$, *4c*; $R_1 = Me$, $R_2 = COOMe$, *4d*; $R_1 = R_2 = COOMe$, *4e*)

To a mixture of **3e** (0.200 g 0.37 mmol) and sodium amalgam (10%, 0.37 mmol of Na) were added 60 $cm^3$ of THF. The resultant suspension was vigorously stirred for 1 h at ambient temperature, filtered, and the solution evaporated to dryness under vacuum. A 70 $cm^3$ volume of hexane was used to extract the residue. The resultant solution was evaporated to dryness to give a red solid of complex **4e**. The other complexes were isolated in a similar way. Analyses: found (calc.) (%): **4a**, C 66.38 (66.42), H 6.60 (6.64); **4b**, C 61.92 (61.80), H 6.79 (6.87); **4c**, C 53.60 (53.57), H 6.72 (6.69); **4d**, C 54.60 (54.54), H 6.91 (6.93); **4e**, C 52.15 (52.17), H 6.40 (6.32).

Complex **4a** was prepared electrochemically by the following method. Complex **1** (0.300 g, 0.74 mmol) in 60 $cm^3$ of 0.2 M $(NBu_4)PF_6$ in THF was reduced at room temperature at a potential of $-1.2$ V in the presence of **a** (0.145 g, 0.81 mmol). The electrolysis was stopped after the current had dropped to less than 1 mA for a coulometric consumption of 2.05 F per mole of **1**. The resultant brown solution was evaporated to dryness under vacuum and the residual solid was extracted with hexane. After filtration, concentration and cooling to $-10$°C, **4a** was obtained as a brown crystalline solid.

### 4.5. $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(\eta^1\text{-}R_1C{\equiv}CHR_2)]$ ($R_1 = Me$, $R_2 = COOMe$, *4'd*)

Complex **3d** (100 mg, 0.20 mmol) in 30 $cm^3$ of 0.2 M $(NBu_4)PF_6$ in THF was electrolyzed at $-10$°C at a potential of $-2.0$ V. The electrolysis was stopped after 19.3 C (1.00 F per mmole of **3d**) had passed. Once the change from **4d** to **4'd** had been completed, the solution was evaporated to dryness under vacuum and the residual solid was extracted with hexane. The resultant solution was evaporated to dryness to give a red–pink solid of complex **4'd**. Analyses: found (calc.) (%): **4'd**, C 50.50 (50.55), H 6.69 (6.62). IR ($CHCl_3$): $\nu(C=C) = 1584$ $cm^{-1}$. ESR (THF): $g = 1.9957$, $A_{Nb} = 103.76$ G.

### 4.6. $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(\eta^2\text{-}PhC{\equiv}CPh)]$ (*6a*)

The complex **3a** (0.300 g, 0.74 mmol) in 100 $cm^3$ of 0.2 M $(NBu_4)PF_6$ in THF was reduced at room temperature at $-2.1$ V in the presence of 0.5 $cm^3$ of ethanol, which had been found to enhance the reaction (7) (Scheme 1). The electrolysis was stopped after the current had dropped to less than 1 mA. The passed charge was 157.1 C (2.20 F per mmole of **3a**). The solvent was evaporated and the residual solid extracted with warm hexane. After filtration, concentration and cooling to $-30$°C, **6a** was isolated as red–brown microcrystals. It was identified by comparison with a genuine sample [3b].

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