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Synthesis and electrochemistry of niobium complexes incorporating asymmetrically substituted *ansa*-ligands

Antonio Antiñolo [a], Teresa Expósito [a], Isabel del Hierro [b], Dominique Lucas [c], Yves Mugnier [c], Irache Orive [a], Antonio Otero [a,*], Sanjiv Prashar [a,b]

[a] *Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Químicas, Campus Universitario, Universidad de Castilla-La Mancha, 13071 Ciudad Real, Spain*

[b] *Departamento de Ciencias Experimentales e Ingeniería, E.S.C.E.T., Universidad Rey Juan Carlos, 28933 Móstoles, Madrid, Spain*

[c] *Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, CNRS UMR 5632, Faculté des Sciences Gabriel, 6 bd Gabriel, 21000 Dijon, France*

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Abstract

The following asymmetric *ansa*-niobocene(IV) dichloride complexes have been prepared: [Nb{$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3R)$}$Cl_2$] (R = H (**1a**), Me (**2a**), $SiMe_3$ (**3a**), Pr^i (**4a**), PPh_2 (**5a**)). The ESR spectra of **1a**–**5a** have been recorded. Oxidation and reduction potentials have also been measured and compared with non*ansa*-niobocene complexes. The new niobocene complexes [Nb(η^5-$C_5H_4R)_2$}Cl_2] (R = Pr^i (**6a**), PPh_2 (**7a**)) have been also synthesized. In addition, reduction of **1a** in the presence of ligand (RC≡CR) (R = Me, Ph) to give [Nb{$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_4)$}Cl(RC≡CR)] (R = Me (**8a**), Ph (**9a**)) is described. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Asymmetric ansa-complexes; Niobium; Niobocene; Electrochemistry

1. Introduction

Although modifications of cyclopentadienyl ligands simultaneously change both the steric and electronic effects, a rational design of new olefin polymerization catalysts requires an approach in which the electron density at the metal and the shape of a co-ordination site can be predicted [1].

With regards to electronic effects, the use of *ansa*-cyclopentadienyl ligands has received wide attention in the chemistry of Group 4 metals in dealing with the so-called *ansa* effect [2]. Recent studies have demonstrated that the incorporation of an *ansa* bridge may have a profound influence on the chemistry of metallocene systems [3]. The electrochemical properties of Group 4 *ansa*-metallocene complexes have previously been reported [4] and indicate that a positive shift of E° occurs versus the non*ansa*-analogues. For example, the complex [Zr{$Me_2Si(\eta^5-C_5H_4)_2$}Cl_2] is more easily reduced at a lesser negative potential than [Zr(η^5-$C_5H_5)_2Cl_2$] (by 0.1 V) [4a]. Therefore, it is well established that the electron density at the metal is modified by the alkyl groups' substituents of the cyclopentadienyl ligand. In methyl-substituted zirconocene dihalide complexes [Zr(η^5-$C_5H_{5-n}Me_n)_2Cl_2$] ($n = 0$–5) such trends were observed in shifts of electrochemical reduction potentials [5].

We recently reported the first *ansa*-niobiocene complexes [6], in which both cyclopentadienyl rings are identical and bound only in a η^5 mode to niobium, and examples of novel chiral *ansa*-niobocene complexes where the *ansa* ligand contains two different cyclopentadienyl rings bearing alkyl substituents [7].

We have previously reported [8,9] the electrochemical behaviour of [Nb(η^5-$C_5H_5)_2Cl_2$] and its disubstituted analogue [Nb(η^5-$C_5H_4SiMe_3)_2Cl_2$]. It was therefore of interest to examine the effects of further substitution in the cyclopentadienyl rings and in addition the involvement of a $SiMe_2$ bridge in novel chiral *ansa*-niobocene complexes.

In this paper we report the synthesis and spectroscopic characterization of new dichloride *ansa*-niobocene complexes namely, [Nb{$Me_2Si(\eta^5-C_5Me_4)(\eta^5-C_5H_3R)$}$Cl_2$] (R = H (**1a**), Me (**2a**), $SiMe_3$ (**3a**), Pr^i

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* Corresponding author. Tel.: +34-26-295326; fax: +34-26-295318. *E-mail address:* antonio.otero@uclm.es (A. Otero).

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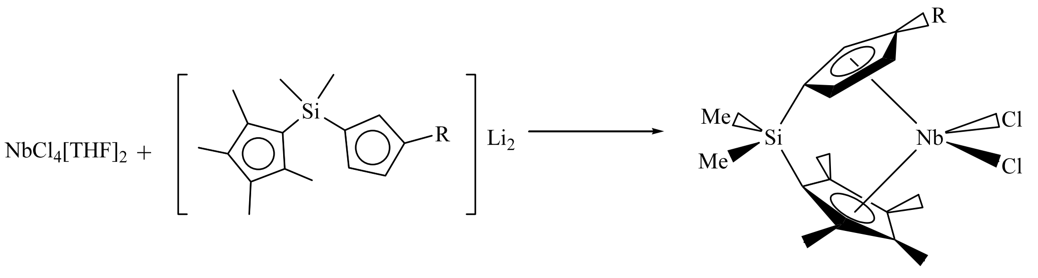
(**4a**), PPh$_2$ (**5a**)), together with two new niobocene dichloride complexes, [Nb(η^5-C$_5$H$_4$R)$_2$}Cl$_2$] (R = Pr^i (**6a**), PPh$_2$(**7a**)). Oxidation and reduction potentials for **1a**–**5a** have also been measured and compared with the theoretical non*ansa*-niobocene complexes [Nb(η^5-C$_5$Me$_5$)(η^5-C$_5$H$_4$R)}Cl$_2$] (R = H (**1b**), Me (**2b**), SiMe$_3$ (**3b**), Pr^i (**4b**), PPh$_2$ (**5b**)). Electrochemical studies of **6a**–**7a** have also been carried out in order to correlate the electronic properties of *ansa*-niobocene complexes versus non*ansa*-derivatives.

2. Results and discussion

The *ansa*-niobocene complexes [Nb{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_3$R)}Cl$_2$] (R = H (**1a**), Me (**2a**), SiMe$_3$ (**3a**), Pr^i (**4a**), PPh$_2$ (**5a**)) and the non*ansa* complexes [Nb(η^5-C$_5$H$_4$R)$_2$}Cl$_2$] (R = Pr^i (**6a**), PPh$_2$(**7a**)) were prepared by the reaction of NbCl$_4$(THF)$_2$ [10] and Li$_2${Me$_2$Si(C$_5$Me$_4$)(C$_5$H$_3$R)} [7] or Li(C$_5$H$_4$R) in THF at room temperature (Eq. (1)) in a synthesis similar to that previously used in the preparation of other dichloro-niobiocene compounds [11]. Detailed description of these and the other synthetic methods are given in Section 3. In all cases it was possible to isolate the pure compounds by fractional crystallization from different solvents.

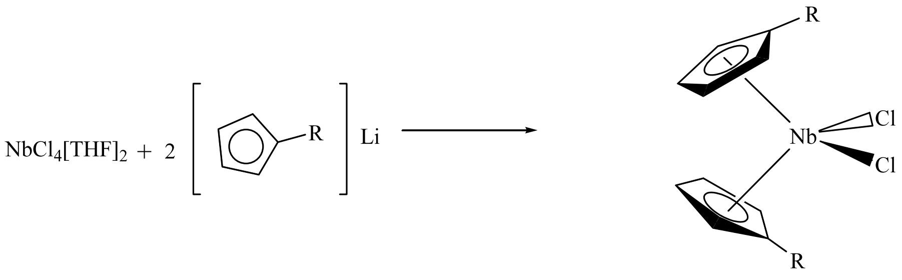
Compounds **1a**–**7a** were characterized by microanalysis and IR spectroscopy (see Table 1). EPR parameters are shown in Table 2, together with those of the previously reported symmetric *ansa*-derivatives, [Nb{Me$_2$Si(η^5-C$_5$H$_4$)$_2$}Cl$_2$] (**10a**) [6] and [Nb{Me$_2$Si(η^5-C$_5$H$_3$SiMe$_3$)$_2$}Cl$_2$] (**11a**) [12] and the non-*ansa*-derivatives [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$}Cl$_2$] (**12a**) [13] and [Nb(η^5-C$_5$R$_5$)$_2$}Cl$_2$] (R = H (**13a**) [8], Me (**14a**) [14]). Each compound exhibits the well known 10-line shape, due to hyperfine coupling with the ^{93}Nb nucleus (see Fig. 1). The g values are in agreement with those found for other dichloroniobiocene complexes [15], and are typically located between 1.97 and 2.00. For the *ansa* compounds, the $a_{iso,\mathrm{Nb}}$ values fall in the range of 99–108 G, which is nearly 10 G less than those observed for the corresponding non*ansa* derivatives (as evidenced for **10a** [6] and **11a** [12]). This difference is consistent with the reduced metal character in the HOMO orbitals for the *ansa*-derivatives [11]. The infrared spectra display in all cases the bands corresponding to the cyclopentadienyl ligands and $\nu_{\mathrm{Nb-Cl}}$ (see Table 1) [16].

The reduction of **1a** with one equivalent of Na–Hg in the presence of the alkyne ligands (RC≡CR) (R = Me, Ph) gave [Nb{Me$_2$Si(η^5-C$_5$Me$_4$)(η^5-C$_5$H$_4$)}Cl(RC≡CR)] (R = Me (**8a**), Ph (**9a**)) (Eq. (2)).



R = H (**1**a); Me (**2a**); SiMe$_3$ (**3a**); Pr^i (**4a**); PPh$_2$ (**5a**)

(1)

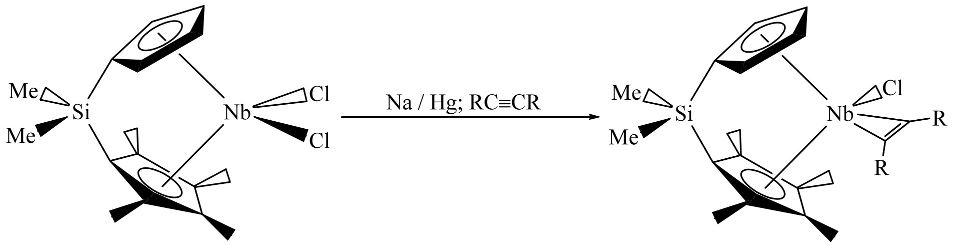


R = Pr^i (**6a**); PPh$_2$ (**7a**)

Table 1
Analytical and spectroscopic data

Compound	Analysis [a]		IR (Nujol, cm^{-1}) $\nu_{\mathrm{Nb-Cl}}$
	C	H	
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_4})\}\mathrm{Cl_2}]$ (**1a**)	47.13 (47.30)	5.40 (5.46)	269
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_3Me})\}\mathrm{Cl_2}]$ (**2a**)	48.33 (48.58)	5.77 (5.76)	254
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_3SiMe_3})\}\mathrm{Cl_2}]$ (**3a**)	47.41 (47.70)	6.21 (6.32)	307
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_3Pr}^i)\}\mathrm{Cl_2}]$ (**4a**)	50.65 (50.90)	6.21 (6.30)	305
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_3PPh_2})\}\mathrm{Cl_2}]$ (**5a**)	56.81 (56.96)	5.22 (5.29)	271
$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4Pr}^i)_2\mathrm{Cl_2}]$ (**6a**)	50.70 (50.82)	5.82 (5.86)	300
$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Cl_2}]$ (**7a**)	61.47 (61.65)	4.15 (4.26)	275
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_4})\}\mathrm{Cl}(\mathrm{MeC{\equiv}CMe})]$ (**8a**)	56.30 (56.54)	6.58 (6.64)	1720 $\nu_{\mathrm{C\equiv C}}$
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_4})\}\mathrm{Cl}(\mathrm{PhC{\equiv}CPh})]$ (**9a**)	65.46 (65.63)	5.88 (5.87)	1734 $\nu_{\mathrm{C\equiv C}}$

[a] Calculated values in parenthesis.



R = Me (**8a**); Ph (**9a**)

(2)

Table 2
Cyclovoltammetric and spectroscopic data for the dichloro niobocene complexes

Compound	Electrochemistry		ESR [a]		Reference
	$E_{1/2,\mathrm{R}}$ (V) [b,c]	$E_{1/2,\mathrm{O}}$ (V)	g_{iso}	$a_{iso,\mathrm{Nb}}$ (G)	
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_4})\}\mathrm{Cl_2}]$ (**1a**)	−1.26	+0.25	1.9932	99.2	This work
$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5Me_5})(\eta^5\text{-}\mathrm{C_5H_5})\mathrm{Cl_2}]$ (**1b**) [e]	−1.41	+0.195			
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_3Me})\}\mathrm{Cl_2}]$ (**2a**)	−1.3	+0.21	1.9872	99.3	This work
$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5Me_5})(\eta^5\text{-}\mathrm{C_5H_4Me})\mathrm{Cl_2}]$ (**2b**) [e]	−1.44	+0.195			
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_3SiMe_3})\}\mathrm{Cl_2}]$ (**3a**)	−1.3	+0.24	1.9863	100.0	This work
$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5Me_5})(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})\mathrm{Cl_2}]$ (**3b**) [e]	−1.375	+0.17			
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_3Pr}^i)\}\mathrm{Cl_2}]$ (**4a**)	−1.32	+0.21	1.9868	99.7	This work
$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5Me_5})(\eta^5\text{-}\mathrm{C_5H_4Pr}^i)\mathrm{Cl_2}]$ (**4b**) [e]	−1.40	+0.16			
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5Me_4})(\eta^5\text{-}\mathrm{C_5H_3PPh_2})\}\mathrm{Cl_2}]$ (**5a**)	−1.21	+0.26	1.9875	99.0	This work
$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5Me_5})(\eta^5\text{-}\mathrm{C_5H_4PPh_2})\mathrm{Cl_2}]$ (**5b**) [e]	−1.28	+0.225			
$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4Pr}^i)_2\mathrm{Cl_2}]$ (**6a**)	−1.20	+0.275	1.9786	113.5	This work
$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Cl_2}]$ (**7a**)	−0.96	+0.41	1.9806	112.2	This work
$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5Me_5})_2\mathrm{Cl_2}]$ (**14a**)	−1.60	+0.04	2.0000	109.4	[14]
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5H_4})_2\}\mathrm{Cl_2}]$ (**10a**)	−1.00	+0.54	1.9838	107.8	[6]
$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_5})_2\mathrm{Cl_2}]$ (**13a**)	−1.22	+0.35	1.9770 [d]	116.5 [d]	[8]
$[\mathrm{Nb}\{\mathrm{Me_2Si}(\eta^5\text{-}\mathrm{C_5H_3SiMe_3})_2\}\mathrm{Cl_2}]$ (**11a**)	−1.04	+0.41	1.9847	104.4	[12]
$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Cl_2}]$ (**12a**)	−1.15	+0.3	1.9776 [d]	115.1 [d]	[13]

[a] Hyperfine coupling constants and g factors are all corrected to second order using the Breit–Rabi equation.

[b] All potentials are referenced to the SCE.

[c] Half wave potential ($E_{1/2}$) is taken either directly on the RDE voltammogram or on the cyclic voltammogram of the complex in case of a reversible electrochemical process ($E_{1/2}$ is then defined as the half-sum of $E_{\mathrm{p,a}}$ and $E_{\mathrm{p,c}}$), A.J. Bard, L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications, Wiley, New York, 1980.

[d] Extracted from Ref. [11].

[e] Calculated electrochemical parameters.

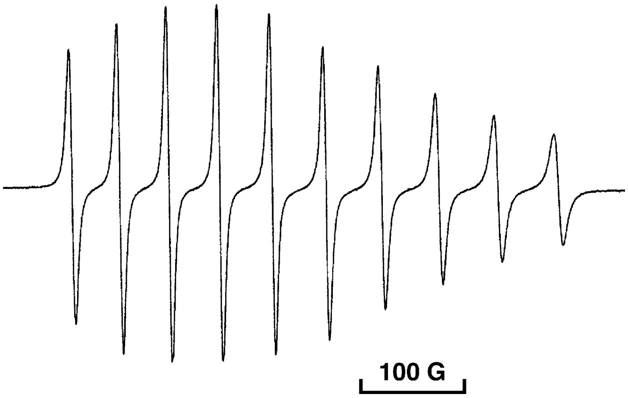


Fig. 1. ESR spectrum (X-band) of [Nb{$Me_2Si(\eta^5$-$C_5H_4)\}_2Cl_2$] (**10a**) in THF.

Compounds **8a** and **9a** were isolated as yellow crystalline solids and were characterized by ^{1}H- and ^{13}C-NMR spectroscopy (see Section 3). The unsymmetrical environment around the niobium centre produces the inequivalence in ^{1}H-NMR spectroscopy for the four protons of the cyclopentadienyl ligand and the four methyl groups of the substituted cyclopentadienyl moiety. The two methyl groups of the silylene bridge are inequivalent and display two singlets in both cases. The ^{13}C-NMR spectra are in agreement with the above comments, particularly diagnostic of the coordinated acetylene unit is the presence of the two resonances at δ 127.0 and 150.7 (**8a**) and 150.3 and 166.9 (**9a**) due to the non-equivalent acetylene carbon atoms. In the IR spectra of **8a** and **9a** in addition to the bands corresponding to the *ansa*-cyclopentadienyl ligands a band due to $\nu_{C\equiv C}$ at 1720 cm^{-1} (**8a**) and 1734 cm^{-1} (**9a**) was observed.

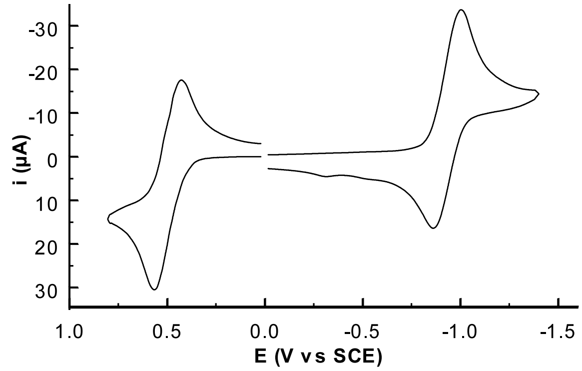


Fig. 2. Cyclic voltammogram of 5.2 mM of [Nb{$Me_2Si(\eta^5$-$C_5H_4)\}_2Cl_2$] (**10a**) in THF 0.2 M NBu_4PF_6. Scan rate: 50 mV s^{-1}.

2.1. Voltammetry of *ansa*-cyclopentadienyl substituted niobocene dichloride complexes

Table 2 shows the values of the oxidation and reduction potentials of the *ansa*-derivatives **1a**–**5a**, **10a** and **11a** together with those of other related compounds **6a**, **7a** and **12a**–**14a**. In agreement with the literature data [4], all the niobocene dichlorides are known to exhibit two voltammetry peaks, one of these is associated with an oxidation and the other with a reduction process (see Eq. (3)).

$$\{[Me_2Si(\eta^5\text{-}C_5H_{5\text{-}n}R_n)_2Nb]Cl_2\}^+ \xrightleftharpoons[-e^-]{+e^-} \{[Me_2Si(\eta^5\text{-}C_5H_{5\text{-}n}R_n)_2Nb]Cl_2\} \xrightleftharpoons[-e^-]{+e^-} \{[Me_2Si(\eta^5\text{-}C_5H_{5\text{-}n}R_n)_2Nb]Cl_2\}^- \qquad (3)$$

For each compound the charge transfer is found to be reversible so that the potentials can be directly related to the electronic effects of the ligands (Fig. 2).

As an example, the cyclic voltammogram of [Nb{$Me_2Si(\eta^5$-$C_5H_4)\}_2Cl_2$] (**10a**) is depicted in Fig. 2. Both the anodic and cathodic scans exhibit a reversible system located at +0.54 and −1.00 V, respectively. With regards to the reductive process, in the return sweep, after the anodic peak at −0.88 V, which corresponds to the oxidation of [Nb{$Me_2Si(\eta^5$-$C_5H_4)\}_2Cl_2]^-$, generated near the electrode, two peaks of very low intensity are observed at −0.32 and −0.55 V. These signals are attributed to the oxidation of Nb{$Me_2Si(\eta^5$-$C_5H_4)\}_2Cl$, which is formed from the anion by loss of Cl$^-$. This has previously been observed in the electrochemical behaviour of **12a** and **13a** [9]. This process is very slow and only affects a tiny fraction of the electrogenerated anion.

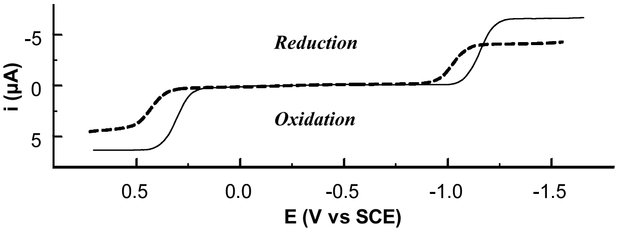


Fig. 3. RDE voltammogram of 4.1 mM [Nb(η^5-$C_5H_4SiMe_3)_2Cl_2$] (**12a**) (plain line) and 3.7 mM [Nb{$Me_2Si(\eta^5$-$C_5H_3SiMe_3)\}_2Cl_2$] (**11a**) (dashed line) in THF 0.2 M NBu_4PF_6. Sweep rate: 20 mV s^{-1}.

The *ansa* systems **1a**–**5a**, **10a** and **11a** are reduced at less negative potential than the corresponding hypothetical non*ansa*-analogues **1b**–**5b**, and the known compounds **12a** and **13a**. This is in agreement with the fact that there is less electronic density at the metal centre for *ansa* systems where the overlap between the cyclopentadienyl and the metal has less intensity than in the normal cyclopentadienyl substituted systems. In the case where the non*ansa*-derivatives are unknown the reduction potential values were calculated using the average values given by the symmetrical niobocene analogues $[Nb(\eta^5\text{-}C_5Me_5)_2Cl_2]$ (**14a**) and $[Nb(\eta^5\text{-}C_5H_4R)_2\}Cl_2]$ ((**6a**), (**7a**), (**12a**) and (**13a**)) taking into account the additive effect of the substituents in the potential values [17]. For example the reduction potential for $[Nb(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)Cl_2]$ (**1b**) (−1.41 V) was estimated from $[Nb(\eta^5\text{-}C_5Me_5)_2Cl_2]$ (**14a**) (−1.60 V) and $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]$ (**13a**) (−1.22 V). The calculated electrochemical data for the hypothetical complexes **1b**–**5b** are summarized in Table 2.

For oxidation the same effect has been observed and the oxidation potentials for complexes **1a**–**5a**, **10a** and **11a** have higher values than the corresponding non*ansa*-compounds. **1b**–**5b**, **12a** and **13a** show a bigger resistance to oxidation, which is in agreement with the higher electrophilic character at the metal centre for the *ansa*-complexes. When the non*ansa*-complexes are unknown the oxidation potential values were calculated by the average values given by the symmetrical niobocene analogues. For example the oxidation potential of $[Nb(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)Cl_2]$ (**1b**) (+0.19 V) was estimated from $[Nb(\eta^5\text{-}C_5Me_5)_2Cl_2]$ (**14a**) (+0.35 V) and $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]$ (**13a**) (+0.04 V). Fig. 3 illustrates clearly the potential shift both in the oxidation and reduction parts showing the RDE voltammograms of **11a** and its non*ansa*-analogue, **12a**.

In conclusion, we have reported the synthesis of new asymmetric *ansa*-niobocene(IV) dichloride complexes. We have studied the electrochemistry of these paramagnetic compounds. This study has allowed us to observe the influence of the *ansa*-bridge on these compounds and to predict electrochemical behaviour in unknown mixed non*ansa*-cyclopentadienyl niobium dichloride derivatives. Also the chemical properties of one of the niobocene dichlorides have been tested by chemical reduction, which allowed us to synthesize new acetylene complexes of niobium.

3. Experimental

3.1. Materials and procedures

All reactions were performed using standard Schlenk tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use.

$Li_2\{Me_2Si(C_5Me_4)(C_5H_3R)\}$ (R = H, Me, SiMe$_3$, Pr^i) [7], $[Nb\{Me_2Si(\eta^5\text{-}C_5H_4)_2\}Cl_2]$ (**10a**) [6], $[Nb\{Me_2Si(\eta^5\text{-}C_5H_3SiMe_3)_2\}Cl_2]$ (**11a**) [12] and $[NbCl_4(THF)_2]$ [10] were prepared as described earlier. $Li_2\{Me_2Si(C_5Me_4)(C_5H_3PPh_2)\}$ was prepared in a similar manner to its alkyl analogues [18]. RC≡CR (R = Me, Ph) were purchased from Aldrich and used directly. ESR spectra were taken at the X-band with a Bruker ESP 300 spectrometer. IR spectra were recorded on a Perkin–Elmer PE 883 IR spectrophotometer. ^1H and ^{13}C spectra were recorded on Varian FT-300 and Varian Gemini FT-200 spectrometers and referenced to the residual deuteriated solvent. Microanalyses were carried out with a Perkin–Elmer 2400 microanalyzer.

Voltammetric analyses were carried out in a standard three-electrode cell with a Tacussel UAP4 unit cell. The reference electrode was a saturated calomel electrode (SCE) separated from the solution by a sintered glass disk. The auxiliary electrode was a Pt wire. For all voltammetric measurements, the working electrode was a vitreous carbon electrode ($\phi = 3$ mm). Under these conditions, when operating in THF, the formal potential for the ferrocene$^{+/-}$ couple is found to be +0.56 V versus SCE.

3.2. Synthesis of $[Nb\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl_2]$ (*1a*)

Tetrahydrofuran (50 ml) was added to a solid mixture of $[NbCl_4(THF)_2]$ (1.37 g, 3.62 mmol) and $Li_2\{Me_2Si(C_5Me_4)(C_5H_4)\}$ (0.93 g, 3.62 mmol). The reaction mixture was stirred at room temperature (r.t.) for 16 h, after which the solvent was removed in vacuo. The resulting solid was extracted in CH_2Cl_2 (2 × 150 ml), solvent was removed under reduced pressure, and the oily brown solid washed with cold C_6H_{14} (−30 °C, 50 ml) and dried under vacuum (1.07 g, 73%). IR (Nujol, cm^{-1}): ν_{Nb-Cl} 269. Anal. Calc. for $C_{16}H_{22}Cl_2NbSi$: C, 47.30; H, 5.46. Found: C, 47.13; H, 5.40%.

3.3. Synthesis of $[Nb\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Me)\}Cl_2]$ (*2a*)

The synthesis of **2a** was carried out in an identical manner to **1a**. $[NbCl_4(THF)_2]$ (1.36 g, 3.59 mmol) and $Li_2\{Me_2Si(C_5Me_4)(C_5H_3Me)\}$ (0.97 g, 3.59 mmol). Yield: 1.18 g, 78%. IR (Nujol, cm^{-1}): ν_{Nb-Cl} 254. Anal. Calc. for $C_{17}H_{24}Cl_2NbSi$: C, 48.58; H, 5.76. Found: C, 48.33; H, 5.77%.

3.4. *Synthesis of* $[Nb\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3SiMe_3)\}Cl_2]$ (**3a**)

The synthesis of **3a** was carried out in an identical manner to **1a**. $[NbCl_4(THF)_2]$ (1.20 g, 3.17 mmol) and $Li_2\{Me_2Si(C_5Me_4)(C_5H_3SiMe_3)\}$ (1.04 g, 3.17 mmol). Yield: 1.25 g, 82%. IR (Nujol, cm^{-1}): ν_{Nb-Cl} 307. Anal. Calc. for $C_{19}H_{30}Cl_2NbSi_2$: C, 47.70; H, 6.32. Found: C, 47.41; H, 6.21%.

3.5. *Synthesis of* $[Nb\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3Pr^i)\}Cl_2]$ (**4a**)

The synthesis of **4a** was carried out in an identical manner to **1a**. $[NbCl_4(THF)_2]$ (1.30 g, 3.43 mmol) and $Li_2\{Me_2Si(C_5Me_4)(C_5H_3Pr^i)\}$ (1.02 g, 3.43 mmol). Yield: 1.08 g, 70%. IR (Nujol, cm^{-1}): ν_{Nb-Cl} 305. Anal. Calc. for $C_{19}H_{28}Cl_2NbSi$: C, 50.90; H, 6.30. Found: C, 50.65; H, 6.21%.

3.6. *Synthesis of* $[Nb\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_3PPh_2)\}Cl_2]$ (**5a**)

The synthesis of **5a** was carried out in an identical manner to **1a**. $[NbCl_4(THF)_2]$ (1.40 g, 3.69 mmol) and $Li_2\{Me_2Si(C_5Me_4)(C_5H_3PPh_2)\}$ (1.63 g, 3.69 mmol). Yield: 1.61 g, 74%. IR (Nujol, cm^{-1}): ν_{Nb-Cl} 271. Anal. Calc. for $C_{28}H_{31}Cl_2NbPSi$: C, 56.96; H, 5.29. Found: C, 56.81; H, 5.22%.

3.7. *Synthesis of* $[Nb(\eta^5\text{-}C_5H_4Pr^i)_2Cl_2]$ (**6a**)

The synthesis of **6a** was carried out in an identical manner to **1a**. $[NbCl_4(THF)_2]$ (1.40 g, 3.69 mmol) and $Li(C_5H_4Pr^i)$ (0.84 g, 7.38 mmol). Yield: 1.13 g, 81%. IR (Nujol, cm^{-1}): ν_{Nb-Cl} 300. Anal. Calc. for $C_{16}H_{22}Cl_2Nb$: C, 50.82; H, 5.86. Found: C, 50.70; H, 5.82%.

3.8. *Synthesis of* $[Nb(\eta^5\text{-}C_5H_4PPh_2)_2Cl_2]$ (**7a**)

The synthesis of **7a** was carried out in an identical manner to **1a**. $[NbCl_4(THF)_2]$ (1.40 g, 3.69 mmol) and $Li(C_5H_4PPh_2)$ (1.89 g, 7.38 mmol). Yield: 1.81 g, 74%. IR (Nujol, cm^{-1}): ν_{Nb-Cl} 275. Anal. Calc. for $C_{34}H_{28}Cl_2NbP_2$: C, 61.65; H, 4.26. Found: C, 61.47; H, 4.15%.

3.9. *Synthesis of* $[Nb\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl(MeC{\equiv}CMe)]$ (**8a**)

Compound **1a** (1.04 g, 2.56 mmol) was added to Na amalgam (0.058 g, 2.56 mmol of Na). To the mixture was added THF (100 ml). To this stirred solution was added via microsyringe $MeC{\equiv}CMe$ (0.20 ml, 2.56 mmol) and the reaction mixture was allowed to stir at r.t. for 16 h. The solvent was removed under reduced pressure and $C_6H_5CH_3$ (50 ml) was added. The suspension was filtered and solvent removed in vacuo from the filtrate yielding a yellow solid (0.83 g, 76%). IR (Nujol, cm^{-1}): $\nu_{C\equiv C}$ 1720. ^1H-NMR (200 MHz, C_6D_6): δ 0.25 (3H), 0.26 (3H) (s, Si*Me*$_2$), 0.82 (3H), 1.56 (3H), 1.78 (3H), 2.12 (3H) (s, C$_5$*Me*$_4$), 2.20 (3H), 2.45 (3H) (s, *Me*C≡C*Me*), 4.86 (1H), 5.10 (1H), 5.12 (1H), 5.89 (1H) (m, C$_5$*H*$_4$). $^{13}C\{^1H\}$-NMR (300 MHz, C_6D_6): δ −7.5, −5.4 (Si*Me*$_2$), 12.7, 13.4, 14.8, 16.1 (C$_5$*Me*$_4$), 11.7, 16.2 (≡C*Me*), 99.3, 100.6, 103.6 (C_{ipso}), 116.2, 124.2 (*C*$_5$H$_4$), 123.4, 126.6, 126.9, 128.4, 129.6 (*C*$_5$Me$_4$), 127.0, 150.7 (≡*C*Me). Anal. Calc. for $C_{20}H_{28}ClNbSi$: C, 56.54; H, 6.64. Found: C, 56.30; H, 6.58%.

3.10. *Synthesis of* $[Nb\{Me_2Si(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)\}Cl(PhC{\equiv}CPh)]$ (**9a**)

The synthesis of **9a** was carried out in an identical manner to **8a**. Compound **1a** (1.23 g, 3.03 mmol), Na–Hg (0.070 g, 3.03 mmol of Na) and $PhC{\equiv}CPh$ (0.54 g, 3.03 mmol). Yield: 1.33 g, 80%. IR (Nujol, cm^{-1}): $\nu_{C\equiv C}$ 1734. ^1H-NMR (200 MHz, C_6D_6): δ 0.24 (3H), 0.27 (3H) (s, Si*Me*$_2$), 1.01 (3H), 1.68 (3H), 1.77 (3H), 2.06 (3H) (s, C$_5$*Me*$_4$), 5.40 (1H), 5.45 (1H), 5.70 (1H), 5.75 (1H) (m, C$_5$*H*$_4$), 6.9–7.6 (s, 10H, *Ph*C≡C*Ph*). $^{13}C\{^1H\}$-NMR (300 MHz, C_6D_6): δ −1.3, −0.5 (Si*Me*$_2$), 11.6, 12.2, 14.6, 15.7 (C$_5$*Me*$_4$), 96.5 (C_{ipso}), 97.7, 110.6, 114.5, 121.5 (*C*$_5$H$_4$), 108.3, 111.2, 120.4, 131.8, 141.3 (*C*$_5$Me$_4$), 125.3, 127.8, 127.9, 128.5, 129.1, 129.2, 129.3, 129.4, 129.7, 130.4, 132.1, 138.6 (≡C*Ph*), 150.3, 166.9 (≡*C*Ph). Anal. Calc. for $C_{30}H_{32}ClNbSi$: C, 65.63; H, 5.87. Found: C, 65.46; H, 5.88%.

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