Electrochemical and chemical reduction of niobocene dichlorides in the presence of carbon dioxide

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Abstract

The chemical and electrochemical reduction of the niobocene dichlorides $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl_2]$ 1, $[Nb(\eta^5\text{-}C_5Me_5)_2Cl_2]$ 2 and $[Nb(\eta^5\text{-}C_5Me_4Et)_2Cl_2]$ 3, in the presence of carbon dioxide has been investigated. Formation of compounds of the type $[Cp_2Nb(CO_2)]$ and $[Cp_2^{(*)}NbCl(CO_2)]$ [1] has been established by means of IR, ESR and/or NMR spectroscopy. They contain a labile $\eta^2\text{-}CO_2$. The order of stability increases with the degree of substitution the Cp. Less stable intermediates in the reduction of the system $[Cp_2NbCl_2]/CO_2$ are discussed on the basis of cyclovoltammetric and coulometric data.

Keywords: Niobium; Electrochemistry; Carbon dioxide complexes; Reduction

1. Introduction

The transformation of carbon dioxide into organic products of practical interest is an attractive goal. Electrochemical reduction of CO_2 is an applicable method [1] although its reduction to an anion radical requires a quite negative potential [2] and dependence of the resulting products on both the nature of the electrode and the reaction medium has been observed. Considerable efforts have been made to find catalysts allowing a substantial decrease of the reduction potential of CO_2 with reaction selectivity [3]. Transition metal complexes in low oxidation states have been extensively employed

as homogeneous catalysts for the electrochemical reduction of CO_2. They may be grouped into five classes: Co and Ni tetraazamacrocycles [1a]; related phthalocyanine and porphyrin complexes [4]; metal clusters [5]; polypyridyl complexes [6]; and cyclopentadienyl complexes. In particular cases interactions between the catalyst and the substrate may lead to the formation of stable adducts [7].

Recently, some of us have shown that the electrochemical reduction of $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]$ in the presence of carbon dioxide gives the carbonyl derivative $[Nb(\eta^5\text{-}C_5H_5)_2Cl(CO)]$ as the only identified product [8]. Starting from the substituted cyclopentadienyl niobium derivatives, $[Cp_2'NbCl_2]$ 1, $[Cp_2^*NbCl_2]$ 2 and $[Cp_2^\dagger NbCl_2]$ 3, the electrochemical behaviour of which has been previously examined [9], we now report the first results of their chemical and electrochemical reduction in the presence of CO_2.

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[1] Abbreviations employed throughout the text: Cp = any substituted cyclopentadienyl, $Cp' = \eta^5\text{-}C_5H_4SiMe_3$, $Cp^* = \eta^5\text{-}C_5Me_5$, $Cp^\dagger = \eta^5\text{-}C_5Me_4Et$, $Cp^{(*)}$ = peralkylated cyclopentadienyl.
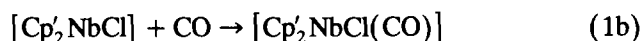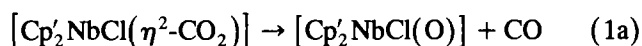
Table 1
Electrochemical and electron spin resonance data for niobocene dichloride derivatives

| Compound	$E_{1/2(Red)}$ (V)	$E_{1/2(Ox)}$ (V)	A_{iso} (G)	g_{iso}	Preparative reduction Q (F mol^{-1})	Electrogenerated product	Ref.
1	−1.19	+0.34	115.4	2.0018	1	Cp$'_2$NbCl	[9a]
2	−1.60	+0.04	109.4	2.0019	2	Cp$^*_2$Nb	[9b]
3	−1.61	+0.07	115.4	1.999	2	Cp$^\dagger_2$Nb	[9b]

2. Results and discussion

2.1. Chemical reduction of niobocene dichlorides under CO_2

Reduction of 1 with 1 equivalent of Na/Hg gives the 16-electron species [Cp$'_2$NbCl] [10], the reaction of which with CO_2 was monitored by IR spectroscopy. After 30 min a band of progressively increasing intensity at 1692 cm^{-1} was observed which gradually decreased after a further 30 min as a new band at 1917 cm^{-1} grew. This absorption may correspond to ν(CO) of [Cp$'_2$NbCl(CO)] [11]. [Cp$'_2$NbCl(O)] was identified by spectroscopic means as a further product. The formation of [Cp$'_2$NbCl(CO)] and [Cp$'_2$NbCl(O)] as the only identified products indicates the existence of a CO_2-containing intermediate which deliberates CO as in Eq. (1a). In a second step (Eq. (1b)) CO would add to the remaining starting material. A similar behaviour was reported by Nicholas et al. [12] for [Nb(η^5-C$_5$H$_4$Me)$_2$(CH$_2$SiMe$_3$)(η^2-CO$_2$)]. All attempts to isolate from the solution the species responsible for the band at 1692 cm^{-1} were unsuccessful.

$$\left[Cp'_2NbCl(\eta^2\text{-}CO_2)\right] \rightarrow \left[Cp'_2NbCl(O)\right] + CO \quad (1a)$$

$$\left[Cp'_2NbCl\right] + CO \rightarrow \left[Cp'_2NbCl(CO)\right] \quad (1b)$$

Reaction of reduced solutions of 2 or 3 in the presence of CO_2 takes place only when an excess of Na/Hg is

employed (Eq. (2)). In both cases a green solid forms which exhibits a strong band at 1730 cm^{-1} in the IR spectrum consistent with η^2-coordinated CO_2. In the crystallographically characterized complexes [Nb(η^5-C$_5$H$_4$Me)$_2$(CH$_2$SiMe$_3$)(η^2-CO$_2$)] and [Nb(η^5-C$_5$H$_4$Me)$_2$(CH$_2$Ph)(η^2-CO$_2$)] ν(CO$_2$) appears at 1695 and 1732 cm^{-1}, respectively [13]. FD–MS spectra contain only the CO_2-free fragments Cp$^{(*)}_2$NbCl indicating a weakly coordinated ligand. Unfortunately, from repeated recrystallization only well shaped crystals of 3 were obtained, as established by X-ray diffraction [14]. C and H analyses are equivocal because of the small differences of the compounds in question. Sharp ^{1}H NMR resonances exclude a paramagnetic species, e.g. 3. We believe that the very small Cl$^-$ concentrations in solution are responsible for the displacement of CO_2, forming 3 (Eq. (2))

$$\left[Cp_2^{(*)}NbCl_2\right] + CO_2$$
$$\xrightleftharpoons{Na/Hg} \left[Cp_2^{(*)}NbCl(\eta^2\text{-}CO_2)\right] + Cl^- \quad (2)$$
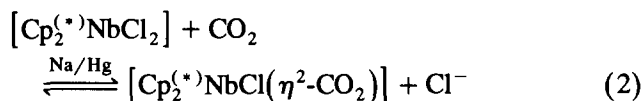
2.2. Electrochemical reduction of niobocene dichlorides

The electrochemical behaviour of 1–3 under argon is characterized by the influence of the peralkylated Cp ligands (Table 1). In 2 and 3 a drastic shift to more negative reduction potentials is observed compared to 1 [9b]. Another important difference concerns the bulk
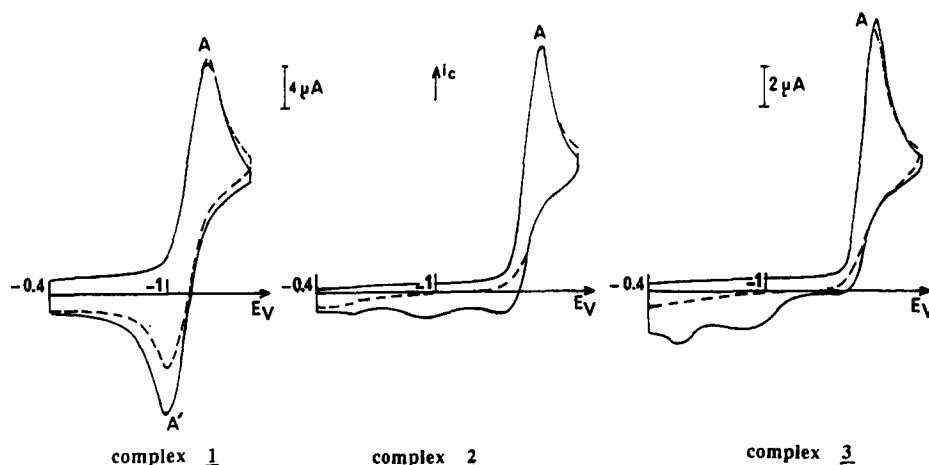

Fig. 1. Cyclic voltammograms at a vitreous carbon electrode in THF–[Bu$_4$N][PF$_6$] solution of complexes 1, 2 and 3 under argon (solid line) and in the presence of carbon dioxide (dotted line). Starting potential −0.4 V; sweep rate 0.2 V s^{-1}.
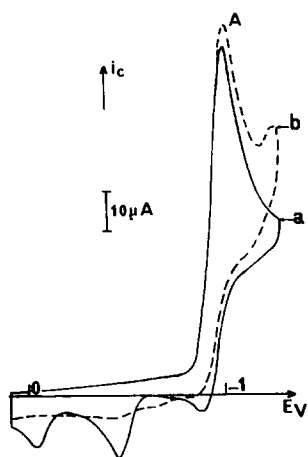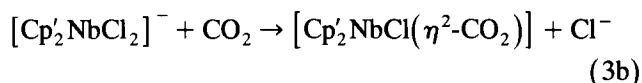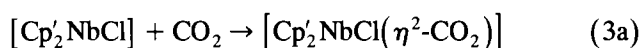
Fig. 2. Cyclic voltammograms at a vitreous carbon electrode in THF–Na[BPh$_4$] solution of **1** under argon (solid line) and in the presence of carbon dioxide (dotted line). Starting potential 0.1 V, sweep rate 0.2 V s^{-1}.

electrolysis which consumes 1 equivalent of electrons for **1** but 2 equivalents for **2** and **3**.

In the presence of CO$_2$ the oxidation peaks are influenced as shown in Fig. 1. The oxidation peak A′ of **1**, which corresponds to the oxidation of the anion [Cp$_2'$NbCl$_2$]$^-$ [15] decreases, whereas in the cyclic

voltammograms of **2** and **3** the oxidation peaks obtained during the reverse scan disappear completely, implying that in these complexes a fast reaction with CO$_2$ is taking place.

An interesting difference, which will be discussed in detail later, is observed in the behaviour of **1** when Na[BPh$_4$] is supporting electrolyte instead of [Bu$_4$N][PF$_6$]. Under argon the cyclic voltammogram exhibits three oxidation peaks in the reverse scan, which disappear in the presence of CO$_2$ (Fig. 2). In both cases the one electron reduction of **1** yields [Cp$_2'$NbCl] or [Cp$_2'$NbCl$_2$)$^-$. These Nb(III) complexes may react with CO$_2$ to give [Cp$_2'$NbCl(CO$_2$)] (Eq. (3)). Reaction (3a) is faster than reaction (3b) and the electrogenerated intermediates cannot be detected at the time scale of electrolysis (Figs. 1 and 2)

$$[Cp_2'NbCl] + CO_2 \rightarrow [Cp_2'NbCl(\eta^2\text{-}CO_2)] \qquad (3a)$$

$$[Cp_2'NbCl_2]^- + CO_2 \rightarrow [Cp_2'NbCl(\eta^2\text{-}CO_2)] + Cl^- \qquad (3b)$$

Preparative electrolysis of **1** under CO$_2$ (Table 2) gives a maroon solution, the ESR spectrum of which is silent. Its IR spectrum shows two bands at 2337 and 1917 cm^{-1}. Whereas the first absorption is typical of
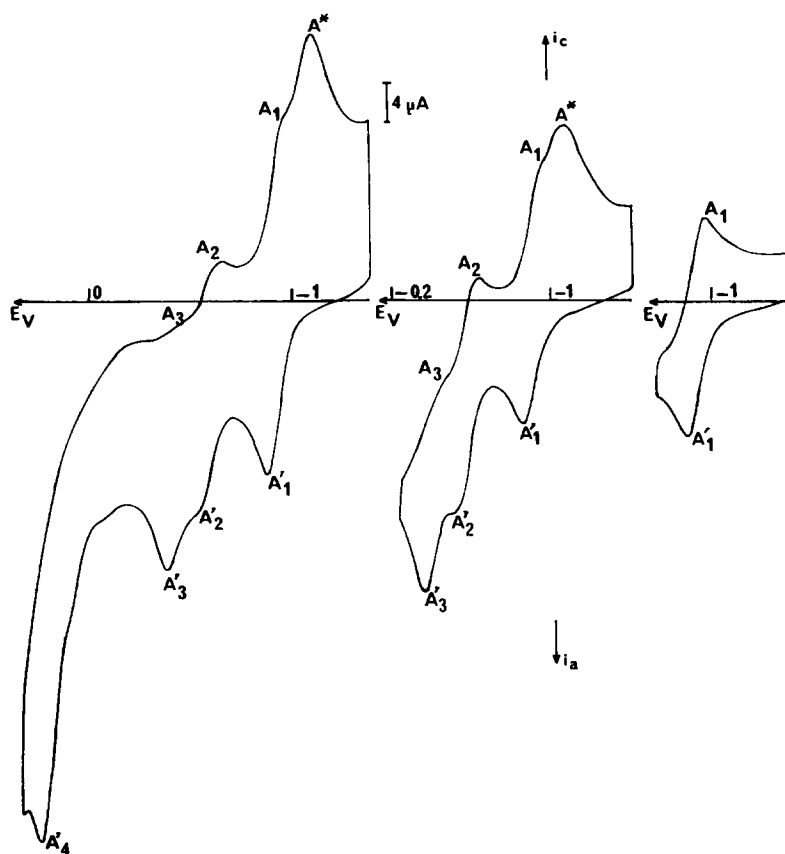

Fig. 3. Cyclic voltammograms on vitreous carbon electrode in THF–[Bu$_4$N][PF$_6$] solution of **1** after two-electron reduction in the presence of carbon dioxide. Starting potential −1.4 V; sweep rate 0.2 V s^{-1}.

free CO_2 [16] the second one corresponds to [$Cp'_2NbCl(CO)$] [11]. The polarogram of the reduced solution shows one reduction wave B and three oxidation waves A'_1, A'_2 (ill defined) and A'_4. In cyclic voltammetry at a vitreous carbon electrode, four oxidation peaks A'_1, A'_2, A'_3 and A'_4 are observed in the anodic sweep. If the potential is reversed after peak A'_4 four reduction peaks A_3, A_2, A_1 and A^* are found (Fig. 3(a)). Peaks A_1 and A^* result from the reduction of the species generated along with peak A'_1 or peak A'_2 (or A'_3), respectively (Figs. 3(b) and 3(c)). Cyclic voltammetry (THF, [Bu_4N][PF_6]) of independently prepared [$Cp'_2NbCl(CO)$] also exhibits the oxidation peak A'_4. Assignment of the other peaks in Fig. 3 is less obvious but may be discussed on the basis of CO_2 disproportionation which produces [$Cp'_2NbCl(O)$] or [$Cp'_2NbCl(O)$]$^-$ as a second intermediate product. By nucleophilic attack of the metal bound oxygen at CO_2 [17] a carbonato-complex may be formed, as expressed by Eq. (4) [18]. This assumption is supported by the observation that addition of an aqueous Na_2CO_3 solution to electrogenerated [Cp'_2NbCl] gives rise to the peaks A'_1/A_1 (Fig. 3) [19]. The addition of water alone does not give this system so that the formation of an anionic carbonato-complex seems to be likely (Eq. (4)).

$$2[Cp'_2NbCl_2] + 4e^- + 2\,CO_2$$

$$\rightarrow [Cp'_2NbClCO] + 3\,Cl^- + Cp'_2Nb(CO_3)^- \qquad (4)$$
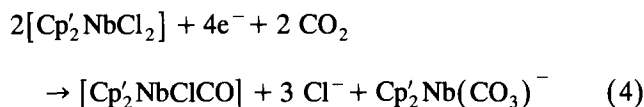
Preparative electrolysis of 1 under the same conditions as above but with Na[BPh_4] as supporting electrolyte (Table 2) gives a green solution. This exhibits a ten-line ESR spectrum ($g = 2.0228$) and a weak absorption band at 1717 cm^{-1} in the IR spectrum. The hyperfine splitting ($a_{Nb} = 54$ G) suggests appreciable delocalization of the unpaired spin density onto the ligand (Fig. 4). This is consistent with the formation of paramagnetic [$Cp'_2Nb(\eta^2$-CO_2)] which may be favoured by elimination of NaCl as in Eq. (5). The complex is reduced at -1.45 V and again the systems A'_1/A_1 and
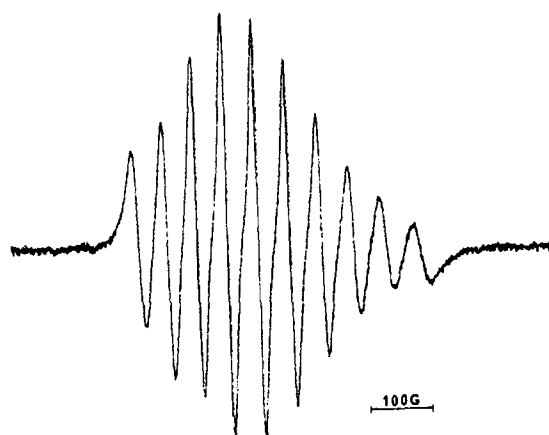
Table 2
Preparative reduction of 1–3 in the presence of carbon dioxide [a]

Complex	Potential of electrolysis	Q (F mol^{-1})	Colour
1	-1.2	1.95	Maroon
1 [b]	-1.2	1.9 [c]	Green
2	-1.7	1.0	Yellow
3	-1.5	1.1	Yellow

[a] THF, 0.2 M [Bu_4N][PF_6], mercury electrode, 20°C
[b] In the presence of Na[BPh_4] as supporting electrolyte.
[c] Coulometric data are not reproducible.

Fig. 4. ESR spectrum of electrogenerated species [$Cp'_2Nb(CO_2)$] in THF–Na[BPh_4] solution.

A'_2/A_2 are found in cyclic voltammetry, as shown in Fig. 3.

$$(5)$$
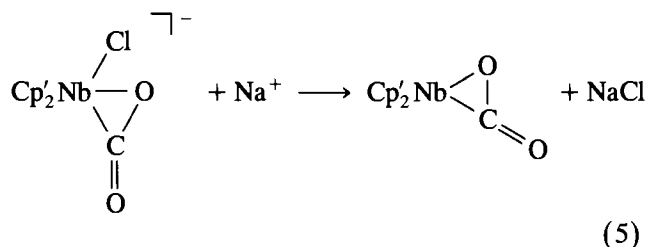
The one-electron reduction of the peralkylated compounds 2 or 3 in the presence of CO_2 gives yellow solutions which are ESR silent. Attempts to isolate the electrochemically generated products [$Cp_2^{(*)}NbCl(CO_2)$] failed because the solutions are stable only in the presence of CO_2. Under Ar a slow change into 2 and 3 is observed by ESR spectroscopy, according to the reverse of Eq. (2).

Under Ar in cyclic voltammetry at a vitreous carbon electrode [$Cp_2^*NbCl(CO_2)$] exhibits a reduction peak B. Reversing the potential scan produces an oxidation peak B'_1. In the second scan a new reduction peak B_1 situated at a lower cathodic potential is observed (Fig. 5(a)). A similar cyclic voltammogram was obtained for the electrogenerated species from 3 (Fig. 5(b)).

At low temperatures paramagnetic [$Cp_2^*Nb(CO_2)$] is sufficiently stable for spectroscopic detection. For example, electrolysis of the species generated from 2 at the plateau of wave B at -20°C [20] gives a dark yellow solution after consumption of 1 equivalent of electrons. The ESR spectrum (centred at $g = 1.9958$) of the solution shows a ten-line signal ($a_{Nb} = 46.9$ G). Its IR spectrum exhibits an absorption at 1716 cm^{-1}, again typical of coordinated CO_2. Similar behaviour was found for electrogenerated species from 3 (IR: ν(C=O); 1711 cm^{-1}; ESR: $a_{Nb} = 47.0$ G, $g = 1.9973$).

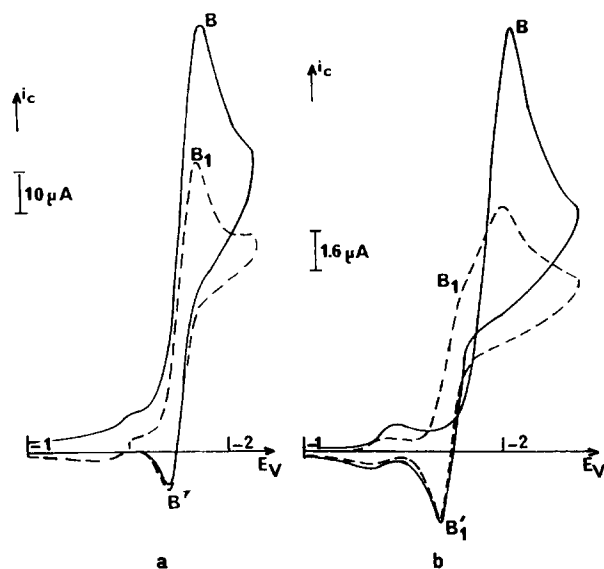The two-electron reduction of [$Cp_2^*NbCl(CO_2)$] (peak B) corresponds to an ECE process involving cleavage of

Fig. 5. Cyclic voltammograms of the electrogenerated species from 2 (a) and 3 (b) at a vitreous carbon electrode in THF–[Bu$_4$N][PF$_6$] solution under argon. Starting potential −1 V; sweep rate 0.2 V s^{-1}. First scan (solid line); second scan (dotted line).

the niobium–chloride bond. Similar behaviour has been previously reported for other Nb(V) complexes [21]. The anionic species formulated as [Cp$_2^t$Nb(CO$_2$)]$^-$ was formed, and this was oxidized at the potential of peak B$_1'$. The formation of the supposed paramagnetic species [Cp$_2^t$Nb(CO$_2$)] during the electrolysis could be explained by an outer sphere electron-transfer reaction according to the following reaction (Eq. 6).

$$\left[Cp_2^t Nb(CO_2) \right]^- + \left[Cp_2^t NbCl(CO_2) \right]$$

$$\rightarrow 2\left[Cp_2^t Nb(CO_2) \right] + Cl^- \tag{6}$$
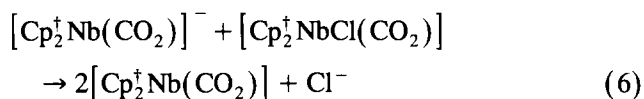
The anionic species, which is generated at the electrode diffuses towards the bulk of the solution and comes in contact with [Cp$_2^t$NbCl(CO$_2$)] which diffuses towards the electrode where above reaction takes place.

3. Experimental details

Synthesis and physical measurements for all reactions were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free, dinitrogen, argon or carbon dioxide. Solvents were distilled from appropriate drying agents and degassed before use. IR spectra were recorded at room temperature with a Nicolet 205 spectrophotomer. ESR spectra were taken at the X-band with a Bruker ESP 300 spectrometer. ^{1}H NMR spectra were recorded on a Bruker WM 250 spectrometer. Field desorption mass spectra were run on a Finnigan MAT 311A instrument from THF solution.

Voltammetric analysis was carried out in a standard three-electrode cell with a Tacussel UAP4 unit cell. The reference electrode was a saturated calomel electrode

separated from the solution by a sintered glass disk. The auxiliary electrode was a platinum wire. For voltammetric measurements the working electrode was either vitreous carbon (disk electrode) or a platinum disk electrode (surface area 3.1 mm^2) which was initially polished with silicon carbides 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 $\tau = 0.5$ s. Controlled-potential electrolysis were performed with an Amel 721 electronic integrator. Large-scale electrolysis were performed in a cell with three compartments separated with fritted glasses of medium porosity. A mercury pool or a platinum plate was used as the anode, a platinum plate as the cathode, and a saturated calomel electrode as the reference electrode.

[Nb(η^5-Me$_3$SiC$_5$H$_4$)$_2$Cl$_2$] [22] [Nb(η^5-Me$_3$Si-C$_5$H$_4$)$_2$Cl] [10], [Nb(η^5-C$_5$Me$_5$)$_2$Cl$_2$] and [Nb(η^5-C$_5$Me$_4$Et)$_2$Cl$_2$] [9b] were prepared according to published methods.

3.1. Reaction of Cp$_2'$NbCl with CO$_2$

Carbon-dioxide was bubbled for 1 h at −78°C through a solution of 650 mg (0.16 mmol) [Cp$_2'$NbCl] in 40 ml hexane. The solution was stirred and warmed to room temperature over 16 h. After this time a suspension was obtained and from the precipitate, a mixture of [Cp$_2'$NbCl(CO)] and [Cp$_2'$NbCl(O)], was isolated and identified after the appropriate separation by chromatography, by comparison of the IR and ^{1}H NMR spectra with those of genuine samples.

3.2. Preparation of [Cp$_2^t$NbCl(η^2-CO$_2$)]

Carbon dioxide was bubbled for 1 h through a mixture of 380 mg (0.82 mmol) of 3 in 50 ml of THF and Na/Hg (from 38 mg (1.64 mmol) Na in 10 ml Hg). The green solution was decanted and filtered. The solvent was then removed under vacuum and the residual solid was chromatographed on silanized SiO$_2$ (10 × 3 cm). With toluene, green 3 was eluted and with CH$_2$Cl$_2$ green [Cp$_2^t$NbCl(η^2-CO$_2$)], in 42% yield. Recrystallization of the latter from toluene gave green needles. The complex was stored and manipulated under CO$_2$. Analyses: found (calc. for C$_{23}$H$_{34}$ClNbO$_2$) (%). C 57.87 (58.70), H 7.14 (7.22); deviations were assumed to be due to the presence of some 3.

^{1}H NMR (CDCl$_3$): 2.24 (m, 4), 1.86 (s, 12), 1.84 (s, 6), 0.97 (t, 6). IR (KBr): ν(CO$_2$) = 1730 cm^{-1}.

4. Conclusion

Relatively stable CO$_2$ adducts of niobocene have been obtained from the chemical and electrochemical

reduction of various substituted niobocene dichlorides under carbon dioxide. The order of stability seems to decrease from the Nb(III) derivatives $Cp_2^{(*)}NbCl(CO_2)$ to the Nb(II) derivatives $[Cp_2^{(*)}Nb(CO_2)]$ and from peralkylated to monoalkylated niobocenes. However, cyclovoltammetric and coulometric methods show that in the reduction pathways of $[Cp_2NbCl_2]$ interesting intermediates, such as a carbonate-containing complex must be considered.

Acknowledgements

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