

Syntheses and reactivity of oxo niobocene complexes $\text{Cp}_2^*\text{Nb}(=\text{O})\text{X}$ ($\text{X} = \text{H}, \text{OCH}_3$) and crystal structures of $[\text{Cp}_2^*\text{Nb}(\text{OH})\text{F}]\text{BF}_4$ and $\text{Cp}_2^*\text{Nb}(=\text{O})\text{OC}(\text{O})\text{H}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$)

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Abstract

Reaction of $\text{Cp}_2^*\text{NbCl}_2$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) with KOH or $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in THF forms the complexes $\text{Cp}_2^*\text{Nb}(=\text{O})\text{X}$ ($\text{X} = \text{Cl}$: **2**, H : **3**). The ratio of **2** and **3** depends on the stoichiometry. If NaOMe is added or MeOH in solution $\text{Cp}_2^*\text{Nb}(=\text{O})\text{OMe}$ **4** is formed in good yields. Reactivity studies with **3** and **4** show that the Nb=O as well as the Nb–X unit behave as chemically active sites. Protonation of **3** or **4** with HBF_4 is followed by an attack of fluoride (from BF_4^- anion) to give $[\text{Cp}_2^*\text{Nb}(\text{OH})\text{F}]\text{BF}_4$ **6** and $[\text{Cp}_2^*\text{NbF}_2]\text{BF}_4$ **7**. In contrast the reaction of **3** or **4** with HCO_2H results in an exchange of X^- by formate to give $\text{Cp}_2^*\text{Nb}(=\text{O})\text{OC}(\text{O})\text{H}$ **8**. The crystal structures of **6** and **8** are reported. Electrochemical investigations of **2–4** and **7**, **8** reveal reaction pathways for the transformation of **1** into **3**. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Niobocene; Oxo ligands; Formate complex; Reactivity; Structures

1. Introduction

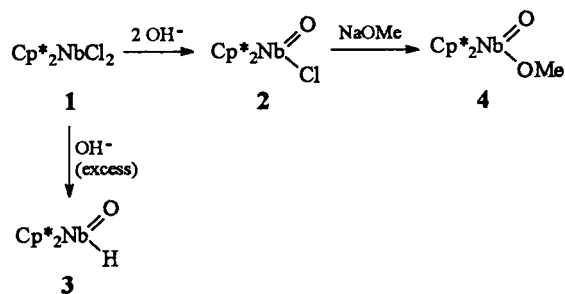
Transition metal complexes bearing terminal oxo ligands are of continuing interest because of their pronounced and manifold reactivity [1]. Among them metallocenes of the early transition metals form an own class of compounds. It is striking that reactivity studies involve only oxo metallocenes of Group 4 and 6 metals, e.g. $\text{Cp}_2^*\text{Zr}(=\text{O})\text{pyr}$ [2,3] and $\text{Cp}_2\text{M}(=\text{O})$ (Cp = any substituted cyclopentadienyl; $\text{M} = \text{Mo}, \text{W}$) [4] although there are sufficient examples of high-valent Group 5 metallocenes of the formula $\text{Cp}_2\text{M}(=\text{O})\text{L}$ ($\text{M} = \text{Nb}, \text{Ta}$; $\text{L} = 1\text{-e}$ ligand). In the latter cases, however, elimination reactions from η^2 bonded ligands like O_2 [5] or CO_2 [6] seemed to establish the M=O linkage as an obviously chemically robust unit. Structural studies on

$\text{Cp}_2^*\text{Ta}(=\text{O})\text{H}$ indicated a considerable double bond contribution of the Ta=O bond [7] which should be an essential prerequisite for reactivity [1]. Whereas a series of peralkylated oxo tantalocene compounds have been prepared [8], there is still need for a rational synthesis of peralkylated oxo niobocenes. In this paper we develop a systematic synthesis of $\text{Cp}_2^*\text{Nb}(=\text{O})\text{X}$ derivatives in which X are the one-electron donors H, Cl, and OMe. Investigations into their reactivity reveal that these complexes exhibit an interesting difunctionality involving both reaction sites.

2. Results

The reaction of $\text{Cp}_2^*\text{NbCl}_2$ **1** with KOH in THF gives a mixture of $\text{Cp}_2^*\text{Nb}(\text{O})\text{Cl}$ **2** and $\text{Cp}_2^*\text{Nb}(\text{O})\text{H}$ **3**. With two equivalents of KOH only **2** is obtained in moderate

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Scheme 1.

yield, a 5 to 10-fold excess of KOH produces **3** in strongly varying amounts (10–50%). Less decomposition products are observed if Ba(OH)₂ is employed, and the yields are reproducible at about 50%. If the reaction of **1** with KOH is carried out in methanol the formation of Cp*₂Nb(O)OMe **4** is observed along with that of **2**. Formation of the latter can be suppressed by adding one equivalent of Na to the reaction mixture after the first step has been completed (Scheme 1).

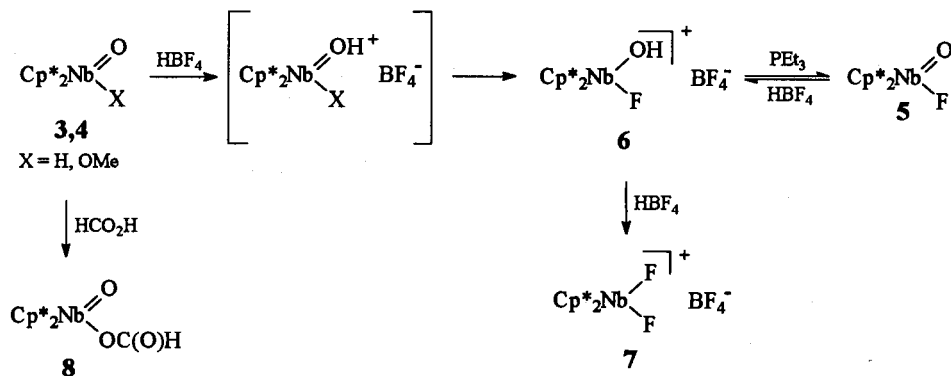
In contrast to the starting material **1** complexes **2–4** are diamagnetic Nb(V) compounds. Their IR spectra show apart from the characteristic absorptions for the Cp* ligand $\nu_{\text{Nb}=\text{O}}$ absorptions around 850 cm⁻¹. The latter are in agreement with data reported for other oxoniobocene derivatives [9,10]. Additionally, a weak $\nu_{\text{Nb}=\text{H}}$ absorption at 1740 cm⁻¹ is observed for **3**, whereas a strong absorption at 1070 cm⁻¹ (**4**) may be attributed to the $\nu_{\text{C}=\text{O}}$ frequency of the OCH₃ group. The ¹H-NMR spectra exhibit sharp signals at 1.77 (**2**), 1.82 (**4**), and 1.87 (**3**) ppm for the Cp* methyl groups and another sharp resonance (OCH₃) at 4.15 ppm for **4**. The Nb–H resonance of **3** could not be detected, probably because of the quadrupole moment of the ⁹³Nb (*I* = 9/2) nucleus [11].

For the following experiments Cp*₂Nb(=O)OMe **4** has been employed although Cp*₂Nb(=O)H **3** gives identical results. Protonation with HBF₄ in ether gives precipitates from which yellow to orange diamagnetic compounds **5–7** can be obtained (Scheme 2). It has been

proven by ¹H-NMR and mass spectra that mixtures of these complexes are formed regardless if one or two equivalents of the acid are employed. An excess of HBF₄ results in the formation of pure **7**. X-ray diffraction analyses of recrystallised and manually separated yellow needles of **6** and orange needles of **7** from such a mixture were carried out. Complex **5** was obtained in pure form by proton abstraction with PEt₃ from a mixture containing **6** and **7**.

Apart from the standard absorption patterns for the Cp* and the BF₄ groups characteristic IR absorptions appear for $\nu_{\text{Nb}=\text{O}}$ in **5** at 850 cm⁻¹ and for $\nu_{\text{O}=\text{H}}$ in **6** at 3500 cm⁻¹. Nb–F frequencies may be assigned to absorptions at 530 (**5**), 560 (**6**) and 520 and 530 (**7**) cm⁻¹. It is striking that the $\nu_{\text{O}=\text{H}}$ absorptions in crystals of **6** are very weak. The only indication of the existence of [Cp*₂Nb(OH)X]BF₄, the direct protonation product of **4**, as the first step in the reaction sequence given in Scheme 2 may be the strong absorptions in the OH region of the crude precipitate obtained from the reaction in 1:1 stoichiometry. The ¹H-NMR spectrum of complex **5** exhibits a doublet (at 1.79 ppm) with a long range H–F coupling constant of 0.7 Hz. The ¹H-NMR data of **6** was obtained from the crude material containing **6** and **7** which shows only one common broad signal for **6** and **7** at 2.13 ppm (the signal of the Nb–OH proton was not detected). After treating the mixture of **6** and **7** with PEt₃ the resulting material was found to contain unchanged [Cp*₂NbF₂]BF₄ **7** and Cp*₂Nb(O)F **5**. Complex **7** is analogous in its properties to the already well characterised [(C₅Me₄Et)₂NbF₂]PF₆ [12]. The ¹H- and ¹⁹F-NMR spectra, respectively, show a deshielded signal (2.13 ppm) for the methyl groups and a broad resonance (77 ppm) for the metal-coordinated fluoro ligands.

The crystal structure of **6** is characterised by discrete ions being well separated from each other. The cation reveals a geometry typical for pseudotetrahedral niobocene(V) oxo derivatives (Fig. 1). The H atom cannot be located but it is very likely fixed at the O atom: The found angle O–Nb–F excludes H coordina-



Scheme 2.

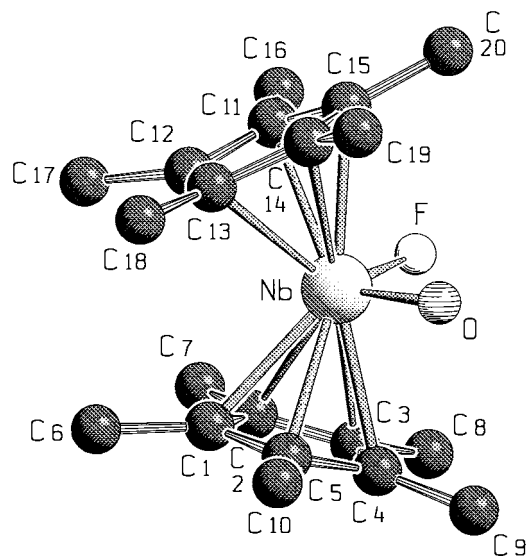


Fig. 1. Molecular structure of the $[\text{Cp}^*_2\text{Nb}(\text{OH})\text{F}]$ cation in **6**. The H atom attached to O could not be localised. Important distances (Å) and angles (°): Nb–F 1.923(8), Nb–O 1.847(8), Nb–C(1–5)_{mean} 2.439(14), Nb–C(11–15)_{mean} 2.433(12); F–Nb–O 100.9(5).

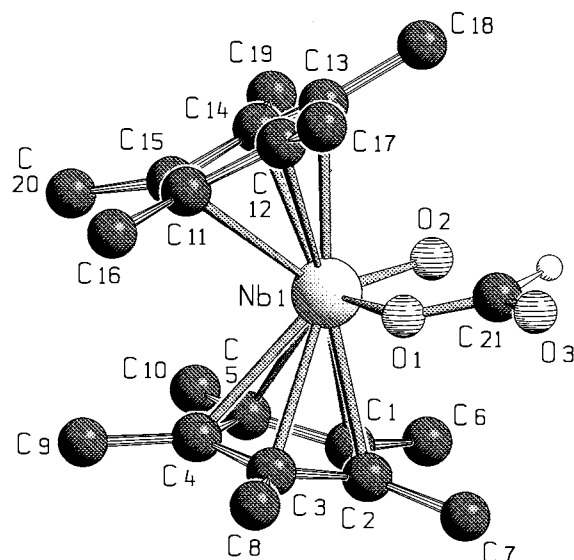


Fig. 2. Molecular structure of $\text{Cp}^*_2\text{Nb}(\text{O})\text{OC}(\text{O})\text{H}$ **8**. Important distances (Å) and angles (°): Nb(1)–O(1) 2.064(3), Nb(1)–O(2) 1.738(3), Nb(1)–C(1–5)_{mean} 2.510(4), Nb(1)–C(11–15)_{mean} 2.507(4), O(1)–C(21) 1.280(5), O(3)–C(21) 1.213(5); O(1)–Nb(1)–O(2) 97.9(1), Nb(1)–O(1)–C(21) 128.3(3), O(1)–C(21)–O(3) 123.8(5).

tion at the Nb centre (Table 1) and the Nb–O distance is significantly longer than that of Nb=O double bonds. There are no remarkable interactions between the cation and the BF_4 anion [13]. Complex **6** is unique for a metallocene in so far as the metal bears an OH group along with a halide. In this context it may be noted that $[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Nb}(\text{OH})\text{Cl}]\text{BF}_4$ has been postulated as a labile intermediate in the hydrolysis of $[(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Nb}(\text{OCH}_2\text{CPh}_3)\text{Cl}]\text{BF}_4$ which ends up with $(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Nb}(=\text{O}\cdot\text{BF}_3)\text{Cl}$ containing coordinated BF_3 at the Nb=O unit [14].

The crystal structure of **7** is identical to that of $[(\text{C}_5\text{Me}_4\text{Et})_2\text{NbF}_2]\text{PF}_6$ [12] as far as the main features are concerned.

Reaction of $\text{Cp}^*_2\text{Nb}(=\text{O})\text{OMe}$ **4** with one equivalent of formic acid gives the greenish yellow complex **8**. Its constitution as an oxo niobocene comprising a κ^1 -formate ligand is supported by analytical and spectroscopic data. X-ray diffraction analysis (Fig. 2) shows the formate ligand to form approximately a plane with the Nb=O moiety. Its hydrogen is oriented towards O(2), probably as a consequence of a weak hydrogen

Table 1
Comparison of structural data of oxo and fluoro niobocene complexes

Formula	Distances (Å)			Angles (°)		
	$d(\text{Nb}=\text{O})$	$d(\text{Nb}-\text{O})$	$d(\text{Nb}-\text{F})$	Cp–Nb–Cp ^a	O–Nb–X	ref.
$(\text{C}_5\text{H}_5)_2\text{Nb}(\text{O})\text{Cl}$	1.737(6)			128.2(1)	98.4	[10]b
$(\text{C}_5\text{H}_5)_2\text{Nb}(\text{O})\text{C}_7\text{H}_5(\text{CF}_3)_2$	1.63(3)					[24]
$(\text{MeC}_5\text{H}_4)_2\text{Nb}(\text{O})\text{Cl}$	1.732(1)				99.6	[23]
$(\text{MeC}_5\text{H}_4)_2\text{Nb}(\text{O})\text{CH}_2\text{CMe}_3$	1.741			131		[6]
$(\text{MeC}_5\text{H}_4)_2\text{Nb}(\text{O})\text{CH}_2\text{SiMe}_3$	1.741(3)					[25]
$[(\text{MeC}_5\text{H}_4)_2\text{Nb}(\text{F})\text{CH}_2\text{SiMe}_3]\text{PF}_6$			1.910(2)			[23]
$(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Nb}(\text{O})\text{Me}$	1.720(7)					[9]
$(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Nb}(\text{OBF}_3)\text{Cl}$		1.830(4)			98.8(3)	[14]
$[(\text{C}_5\text{Me}_5)_2\text{Nb}(\text{OH})\text{F}]\text{BF}_4$		1.847(8)	1.923(8)	139.9	100.9(5)	(b)
$(\text{C}_5\text{H}_4\text{SiMe}_3)_2\text{Nb}(\text{OCH}_2\text{CPh}_3)\text{Cl}$		1.879(2)			97.0(1)	[14]
$[(\text{C}_5\text{H}_5)_2\text{NbCl}]_2(\mu\text{-O})$		1.924(9)				[26]
$(\text{C}_5\text{H}_5)_2\text{Nb}(\text{Cl})(\eta^2\text{-O}_2)$		1.97(1), 2.00(1)				[27]
$(\text{C}_5\text{Me}_5)_2\text{Nb}(\text{O})\text{OC}(\text{O})\text{H}$	1.738(3)	2.064(3)		136.3	97.9(1)	(b)
$[(\text{C}_5\text{Me}_4\text{Et})_2\text{NbF}_2]\text{PF}_6$			1.906, 1.920(8)	140.7	102.3(4)	[12]

^a Centers of the cyclopentadienyl rings. ^b This work.

Table 2
 Voltammetric data for complexes **2**, **3**, **4**, **7** and **8** (THF, 0.2 M NBu₄PF₆)

	$E_{p,ox}^a$	$E_{p,red1}$	$E_{p,red2}$
2		-1.94	-2.56
3	+1.15	-2.56	
4	+1.14	-2.62	
7		-0.36	
8	+1.30	-1.96	-2.56

^a Referenced to saturated calomel electrode, collected on vitreous carbon electrode (sweep rate: 50 mV s⁻¹); all electrochemical processes are found to be irreversible except the first reduction of **7**.

bond ($d(O(2)-H(21)) = 2.67 \text{ \AA}$) [15]. Two significantly different Nb–O bonds are observed: Nb–O(2) which is within the range of known Nb–O double bonds (Table 2, [16]) and Nb–O(1) as a relatively long single bond. In contrast to the complexes (MeC₅H₄)₂M(=O)OC(O)H (M = Nb, Ta) [17] complex **8** is stable in solution and in the solid state. It is one of the few structurally characterised examples of a κ^1 -formate complex [18,19]. The bonding parameters within the ligand compare with those in (C₅H₅)(CO)₂FeOC(O)H [18].

Electrochemical studies of the new oxo niobocene derivatives **2**, **3**, **4**, **7** and **8** have been carried out. The results are listed in Table 2 where each electrochemical event is found to be irreversible. The cyclic voltammogram of **2** is depicted in Fig. 3. Two reduction peaks A and B are seen on the cathodic scan coupled with an oxidation peak B' ($E_{p,B'} = -2.10 \text{ V/SCE}$) which is observed when the potential sweep is reversed after B. No significant change takes place varying the scan rate.

Exhaustive electrolysis on a mercury pool at the potential of peak A affords the hydrido oxo complex **3** as a major product. The yield is almost quantitative when the electrolysis is performed in the presence of excess water with a coulometric consumption of nearly

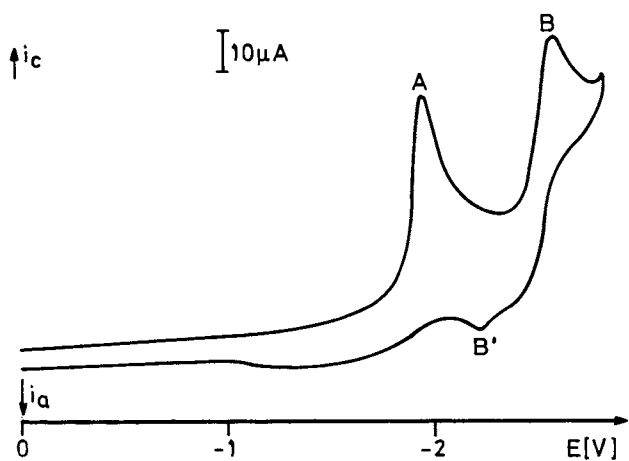


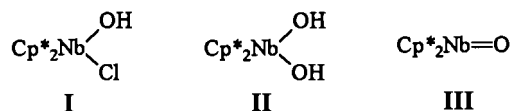
Fig. 3. Cyclic voltammogram of **2** (c ca. 2 mmol·l⁻¹) in THF (0.2 M NBu₄PF₆) on vitreous carbon electrode. Sweep rate: 50 mV s⁻¹. Initial potential: 0 V.

2 F mol⁻¹ of initial complex **2** ($n_{exp} = 1.9 \text{ F mol}^{-1}$). Complex **3** has been identified from its IR and voltammetric features. Indeed, voltammetric analysis of a chemically prepared sample of **3** shows the system B/B'. Reductive behaviour of complex **8** is similar to that of **2**. Reduction of the first stage leads to the hydrido oxo complex **3**. Peak B is seen in the initial cyclic voltammogram of **8** (second reduction stage) and complex **3** has been identified as an electrolysis product. Additionally, and in contrast to **2**, complexes **3**, **4** and **8** are oxidizable (see Table 2). The mechanism of this oxidation process is still under investigation.

The electrochemical investigation of the protonation process of **3** with HPF₆ is in agreement with the formation of [Cp₂^{*}NbF₂]PF₆. This follows from the drastic decrease of the reduction potential from -2.56 (for **3**) to -0.38 V. The reduction is found to be reversible over a wide range of potential scan rates (20–500 mV s⁻¹) like its η^3 -C₅Me₄Et analogue [12]. Exhaustive electrolysis yields the neutral paramagnetic complex Cp₂^{*}NbF₂ identified from its characteristic ESR spectrum ($g_{iso} = 1.9666$, $A_{Nb,iso} = 115.8 \text{ G}$, $A_{F,iso} = 20.4 \text{ G}$).

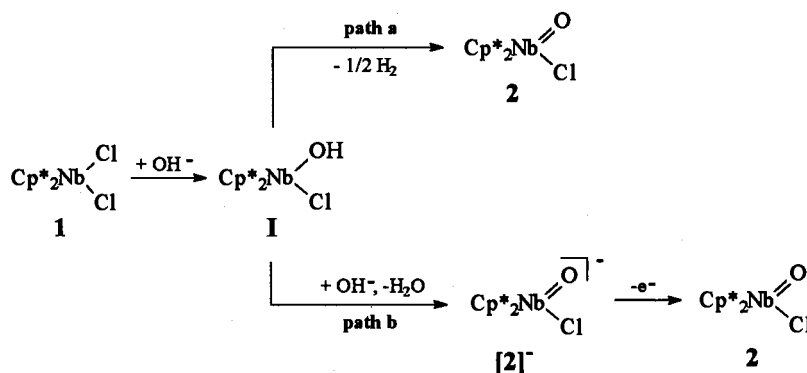
3. Discussion

The preparation of the oxo niobocenes **2–4** from Cp₂^{*}NbCl₂ includes oxidation from Nb(IV) to Nb(V). Several Nb(IV) intermediates like **I–III** may be postulated but none of them has been isolated [20]. To control the formation of **2** and **3** due to Scheme 1 appears to be difficult. It may happen that an excess of KOH gives rise to the formation of an insoluble white inorganic material, probably Nb₂O₅, along with C₅Me₅H. Reproducible and satisfactory yields are observed by employing Ba(OH)₂.



Reaction pathways for the complex formation of Cp₂^{*}Nb(O)H **3** are proposed in Schemes 3–5. The first step consists of the substitution of one chloro ligand by a hydroxide ion. α -Elimination of hydrogen from the resulting chloro–hydroxide complex **I** would give **2** (path a); a similar reaction has been demonstrated in photolysis experiments of tungstenocene complexes [21]. More likely may be deprotonation of the intermediate complex **I** by excess hydroxide ions affording another anionic intermediate [2]⁻ (path b) which is easily oxidized to **2** according to voltammetric studies (see above). Formation of Cp₂^{*}Nb(=O)OH from **2** and OH⁻ has not been observed.

As [2]⁻ may act as a reducing agent it may form with Cp₂^{*}NbCl₂ the reactive Nb(III) species



Scheme 3.

$\text{Cp}_2^*\text{Nb}(\text{OH})$. The final step would be a rearrangement to give **3** (Scheme 4). An analogous mechanism in which Na/Hg serves as reducing agent has been established by Bercaw et al. for the transformation of $\text{Cp}_2^*\text{TaCl}_2$ into $\text{Cp}_2^*\text{Ta}(\text{O})\text{H}$ [8].

Two-electron reduction of **2** or **8** in the presence of H_2O affords complex **3** probably through an ECEC process (Scheme 5) as has been demonstrated for analogous dicyclopentadienyl niobium(V) complexes [22]. The chemical steps consist of elimination of either chloro or formato anion and protonation (through residual or added water) of the negatively charged metal centre.

The protonation of **4** demonstrates the presence of a second reaction site in the complex: as a first step protonation of the $\text{Nb}=\text{O}$ group may be assumed to result in the 16-valence electron complex $[\text{Cp}_2^*\text{Nb}(\text{OH})\text{OMe}]^+$ in which the OMe group seems to be more susceptible to substitution by fluoride than the OH group. On the other hand it is known that F^- (from LiPF_6) is capable of replacing the oxo group in $(\text{MeC}_5\text{H}_4)_2\text{Nb}(\text{O})\text{CH}_2\text{SiMe}_3$ to give $[(\text{MeC}_5\text{H}_4)_2\text{Nb}(\text{F})\text{CH}_2\text{SiMe}_3]\text{PF}_6$ [23]. If HCO_2H is used the $\text{Nb}=\text{O}$ group remains unaffected and an exchange reaction of 1-e ligands is observed.

In conclusion the rational synthesis of niobocene oxo complexes of the type $\text{Cp}_2^*\text{Nb}(\text{O})\text{X}$ permits an evaluation of two different reaction sites attached to the Nb centre. It is shown that the X ligands may easily be replaced by other nucleophilic groups. These results along with those of the protonation of the $\text{Nb}=\text{O}$ group show oxo niobocenes to be more reactive than expected.

4. Experimental section

Experimental and spectroscopic techniques as well as the preparation of $\text{Cp}_2^*\text{NbCl}_2$ **1** are reported in ref. [12].

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

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 disk electrode. The controlled potential electrolysis was performed with an Amel 552 potentiostat coupled to an Amel 721 electronic integrator. In all cases the electrolyte was a 0.2 M solution of $^t\text{Bu}_4\text{NPF}_6$ in THF

4.1. Synthesis of $\text{Cp}_2^*\text{Nb}(\text{O})\text{Cl}$ **2**

4.1.1. Method a

A green suspension of 284 mg (0.65 mmol) of $\text{Cp}_2^*\text{NbCl}_2$ **1** and 74 mg (1.30 mmol) of KOH in 80 ml of MeOH was stirred for 16 h at room temperature (r.t.) giving a pale yellow solution. After evaporation of the solvent the residue was dissolved in 10 ml of toluene and chromatographed on silanised SiO_2 (column 15×3 cm). Elution with toluene gave a pale yellow band containing $\text{Cp}_2^*\text{Nb}(\text{O})\text{Cl}$ **2**. After recrystallisation from toluene at -20°C 70 mg (26% yield) of yellow crystals of **2** were obtained.

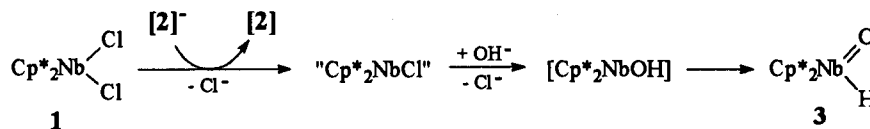
4.1.2. Method b

To a solution of 90 mg (0.22 mmol) of $\text{Cp}_2^*\text{Nb}(\text{O})\text{OMe}$ **4** in toluene one equivalent of HCl dissolved in toluene was added dropwise. After stirring for 15 min the solvent was removed in vacuo and the residue was washed with pentane to give 80 mg (88% yield) of crude material.

Complex **2**: Anal. Found: C, 57.90; H, 7.31, $\text{C}_{20}\text{H}_{30}\text{ClNbO}$ (414.36). Calc.: C, 57.89; H, 7.30%. FD-MS (from toluene): 414. $^1\text{H-NMR}$ (250 MHz, C_6D_6): 1.77 ppm. IR (KBr, cm^{-1}): 855 ($\nu_{\text{Nb}=\text{O}}$).

4.2. Synthesis of $\text{Cp}_2^*\text{Nb}(\text{O})\text{H}$ **3**

A green suspension of 1.0 g (2.3 mmol) of **1** and 1.30 g (4.6 mmol) of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ in 80 ml of THF was stirred for 20 h at 40°C until the green colour disappeared and a nearly colourless solution had formed. After evaporation of the solvent the white residue was



Scheme 4.

extracted several times with pentane (100 ml altogether). After evaporation of pentane recrystallisation from 20 ml of *n*-hexane at -20°C gave 420 mg (48% yield) of a white crystalline powder of $\text{Cp}_2^*\text{Nb}(\text{O})\text{H}$ **3**.

Complex 3: Anal. Found: C, 62.89; H, 8.11, $\text{C}_{20}\text{H}_{31}\text{NbO}$ (380.35). Calc.: C, 63.14; H, 8.23%. FD-MS (from toluene): 380. $^1\text{H-NMR}$ (250 MHz, C_6D_6): 1.87 ppm. IR (KBr, cm^{-1}): 1740 (w; $\nu_{\text{Nb-H}}$), 850 (vs; $\nu_{\text{Nb-O}}$).

4.3. Synthesis of $\text{Cp}_2^*\text{Nb}(\text{O})\text{OMe}$ **4**

A green suspension of 411 mg (0.95 mmol) of **1** and 107 mg (1.89 mmol) of KOH in 100 ml of MeOH was stirred for 3 h at 40°C . After cooling the yellow solution to r.t. 22 mg (9.5 mmol) of Na was added. Then the resulting mixture was stirred for 15 h at 40°C . After evaporation of the solvent the residue was extracted with 80 ml of pentane and then recrystallised at -20°C from *n*-hexane to give 160 mg (42% yield) of pale yellow crystals of $\text{Cp}_2^*\text{Nb}(\text{O})\text{OMe}$ **4**.

Complex 4: Anal. Found: C, 61.21; H, 8.17, $\text{C}_{21}\text{H}_{33}\text{NbO}_2$ (410.38). Calc.: C, 61.44; H, 8.12%. FD-MS (from toluene): 410. $^1\text{H-NMR}$ (250 MHz, C_6D_6): 1.82 (s, 30), 4.15 (s, 3) ppm. IR (KBr, cm^{-1}): 1070 (vs; $\nu_{\text{C-O}}$), 855 (vs; $\nu_{\text{Nb=O}}$).

4.4. Preparation of $\text{Cp}_2^*\text{Nb}(\text{O})\text{F}$ **5**

A total of one (or two) equivalents of HBF_4 dissolved in 1 ml of ether was added to a solution of 220 mg (0.53 mmol) of **4** in ether. The yellow precipitate was washed with ether (10 ml) and toluene (5 ml) and then dried in vacuo. The powder was dissolved in 10 ml of acetone before addition of one equivalent of PEt_3 . After stirring for 5 min the solvent was removed and the yellow residue was extracted with 20 ml of toluene to give 170 mg (80% yield) of crude material after solvent evaporation. Pale yellow crystals of **5** were obtained by recrystallisation from toluene/pentane.

Complex 5: Anal. Found: C, 60.21; H, 7.70, $\text{C}_{20}\text{H}_{30}\text{FNbO}$ (398.37). Calc.: C, 60.30; H, 7.59%. FD-MS (from toluene): 398.1. $^1\text{H-NMR}$ (250 MHz): 1.89 (d, $^4J_{\text{H-F}} = 1.1$ Hz; CDCl_3), 1.79 (d, $^4J_{\text{H-F}} = 0.7$ Hz; C_6D_6) ppm. $^{19}\text{F-NMR}$ (188 MHz, CDCl_3): -135 (br, NbF) ppm. IR (KBr, cm^{-1}): 850 (vs; $\nu_{\text{Nb=O}}$), 530 (vs; $\nu_{\text{Nb-F}}$).

4.5. Protonation of $\text{Cp}_2^*\text{Nb}(\text{O})\text{OMe}$ **4** with HBF_4

To a solution of 260 mg (0.63 mmol) of **4** in 10 ml of ether a solution of ten equivalents of HBF_4 in 1 ml of ether was added. After stirring for 15 min at r.t. the orange precipitate was washed with ether and dried. The powder (ca. 230 mg) was recrystallised from acetone/ether 1:1 to give a mixture of orange crystals (**7**) and a few yellow needles (**6**). Separation of crystals was carried out manually in order to perform crystallographic and IR studies on complex **6**.

Complex 6: $\text{C}_{20}\text{H}_{31}\text{BF}_5\text{NbO}$ (486.15). FD-MS (from CHCl_3): 398.1 (calc. $\text{C}_{20}\text{H}_{31}\text{FNbO}$ 399.35). $^1\text{H-NMR}$ (200 MHz, CDCl_3): 2.13 ppm. IR (KBr, cm^{-1}): 3500 (vw, $\nu_{\text{O-H}}$), 1150, 1000 (s, br, $\nu_{\text{B-F}}$), 530 (s, $\nu_{\text{Nb-F}}$).

Complex 7: Anal. Found: C, 49.07; H, 5.88, $\text{C}_{20}\text{H}_{30}\text{BF}_6\text{Nb}$ (488.17). Calc.: C, 49.21; H, 6.19%. FD-MS (from CHCl_3): 401.2 (calc. $\text{C}_{20}\text{H}_{30}\text{F}_2\text{Nb}$ 401.34). $^1\text{H-NMR}$ (200 MHz, CDCl_3): 2.13 (br) ppm. $^{19}\text{F-NMR}$ (188 MHz, CDCl_3): 77 (br, NbF_2), -153 (BF_4) ppm. IR (KBr, cm^{-1}): 1150, 1000 (s, br, $\nu_{\text{B-F}}$), 520, 530 (s, $\nu_{\text{Nb-F}}$).

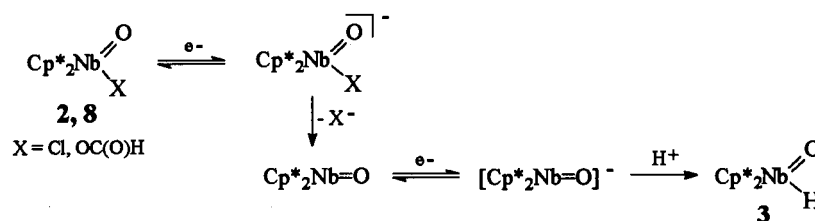
4.6. Preparation of $\text{Cp}_2^*\text{Nb}(\text{O})\text{OC}(\text{O})\text{H}$ **8**

To a solution of 140 mg (0.34 mmol) of $\text{Cp}_2^*\text{Nb}(\text{O})\text{OMe}$ **4** in 10 ml of ether a solution of one equivalent of HCO_2H in 3 ml of ether was added. After stirring for 30 min at r.t. the brown mixture was evaporated and the residue washed with pentane. The resulting powder (130 mg, 90% yield of crude **8**) was recrystallised from acetone/ether 1:1.

Complex 8: Anal. Found: C, 59.19; H, 7.22, $\text{C}_{21}\text{H}_{31}\text{NbO}_3$ (424.36). Calc.: C, 59.43; H, 7.36%. FD-MS (from toluene): 424.4. $^1\text{H-NMR}$ (250 MHz, CDCl_3): 1.88 (s, 30), 7.81 (s, 1) ppm. IR (KBr, cm^{-1}): 1660 (s; $\nu_{\text{C=O}}$), 846 (vs; $\nu_{\text{Nb=O}}$).

4.7. X-ray structure solution for **6** and **8**

X-ray diffraction data (Table 3) was collected at 20°C with a Syntex R3 diffractometer using Mo-K $_{\alpha}$ radiation ($\lambda = 0.71073$ Å) with a graphite crystal monochromator. The structures were solved using Patterson and difference Fourier methods with SHELXLS Release 4.2/800 programs [28]. The hydrogen atoms were calculated by the option HFIX of the SHELXLS program package.



Scheme 5.

Table 3
Crystallographic data for $[\text{Cp}^*_2\text{Nb}(\text{OH})\text{F}]\text{BF}_4$ **6** and $\text{Cp}^*_2\text{Nb}(\text{O})\text{OC}(\text{O})\text{H}$ **8**

Formula	$\text{C}_{20}\text{H}_{31}\text{BF}_5\text{NbO}$	$\text{C}_{21}\text{H}_{31}\text{NbO}_3$
Molecular weight	486.2	424.4
Crystal size (mm^3)	$0.15 \times 0.20 \times 0.80$	$0.50 \times 0.60 \times 0.75$
Crystal system	Monoclinic	Monoclinic
a (\AA)	12.706(8)	10.478(4)
b (\AA)	12.897(9)	9.984(5)
c (\AA)	13.33(1)	19.314(7)
β ($^\circ$)	103.48 (6)	97.05(3)
V (\AA^3)	2125(3)	2005(1)
Space group	$C2h/5, P2_1/n,$ (14)	$C2h/5, P2_1/c,$ (14)
Z	4	4
$D_{\text{calc.}}$ (g cm^{-3})	1.52	1.41
μ (mm^{-1})	0.62	0.62
Scan range	$3.0 < 2\theta < 50.0$	$3.0 < 2\theta < 57.5$
Reflections observed	1932	4303
$(I > 2.5\sigma(I))$		
No. of LS parameters	251	228
Absorption correction	Empirical (five reflections)	Empirical (eight reflections)
Transmission coefficient min/max	0.89/1.00	0.93/1.00
Residual density (e \AA^{-3}) max/min	1.00/−0.72	0.85/−0.55
R	0.079	0.041
R_w	0.066	0.040

5. Supplementary material available

Crystallographic data of **6** and **8** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101704 (**6**) and 101705 (**8**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@chemcrs.cam.ac.uk).

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