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# Synthesis and reactivity of new oxo alkyl or oxo acyl niobocene complexes and crystal structure of $Cp'_2Nb(=O)(OC(O)CF_3)$ ($Cp' = \eta^5$-$C_5H_4SiMe_3$)

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**Abstract**

New alkyl and acyl oxo niobocenes $Cp'_2Nb(O)(R)$ [$Cp' = \eta^5$-$C_5H_4SiMe_3$; $R = CH_2CH_3$ (**3**), $CH_2CH_2Ph$ (**4**), $COCH_2CH_3$ (**7**), $COCH_2CH_2Ph$ (**8**)] have been synthesized. The oxo alkyl derivatives were obtained by reaction of olefin-hydride complexes $Cp'_2Nb(H)(\eta^2$-$CH_2{=}CHR)$ [R = H (**1**), Ph (**2**)] with oxygen, whereas the oxo acyl complexes were prepared by reaction of the niobium(III) carbonyl derivatives $Cp'_2Nb(CO)(COCH_2CH_2R)$ [R = H (**5**), Ph (**6**)] with oxygen. We have also studied the reaction of $Cp'_2Nb(O)(CH_2CH_2R)$ [R = H (**3**), Ph (**4**)] with $HBF_4$ and $CF_3COOH$. These reactions afforded $Cp'_2NbF(O \rightarrow BF_3)$ (**9**) and $Cp'_2Nb(O)[\eta^1$-$(O)$–$OCOCF_3)]$ (**10**), respectively. When protonation of oxo acyl niobocenes $Cp'_2Nb(O)(COCH_2CH_2R)$ [R = H (**7**), Ph (**8**)] with $CF_3COOH$ was carried out, complex **10** was obtained. Furthermore, carbon dioxide–niobocene derivatives $Cp'_2Nb(CO_2)(CH_2CH_2R)$ [R = H (**11**), Ph (**12**)] react with $BF_3{\cdot}Et_2O$ to yield the fluoro niobocene complex **9**. The structure of complex **10** was confirmed by X-ray diffraction. Complex **10** crystallizes in the monoclinic system, in the centrosymmetric $P2_1/c$ space group, with unit cell parameters: $a = 9.671(1)$ Å; $b = 12.935(2)$ Å, $c = 18.43(1)$ Å; $\beta = 99.03(2)°$; $V = 2277(1)$ Å$^3$; $\delta$(Calc.) = 1.448 mg m$^{-3}$ and $R = 0.062$. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Niobium; Alkyl and acyl oxo niobocene

## 1. Introduction

Transition metal complexes bearing oxo or imido ligands are the focus of continued interest [1]. In connection with our studies on the metal-promoted activation of unsaturated compounds such as ketenes, ketenimines, olefins and acetylenes with niobocene complexes [2], the formation of carbon dioxide–niobocene complexes was discovered. The reactivity of this late compound with the Lewis acid $B(C_6F_5)_3$ allowed us to isolate oxo alkyl niobocene adducts with $B(C_6F_5)_3$ [3]. As a continuation of our studies, in this article we report our results on the formation of new oxo alkyl or acyl niobocenes and the study of their reactivity toward protic reagents, namely $HBF_4$ or $CF_3COOH$ and the Lewis acid $BF_3$.

## 2. Results and discussion

Oxidation of olefin–hydride niobocenes $Cp'_2Nb(H)$-$(\eta^2$-$CH_2{=}CHR)$ [$Cp' = \eta^5$-$C_5H_4SiMe_3$; R = H (**1**), Ph (**2**)] with $O_2$ in hexane at room temperature (r.t.) yielded a mixture of oxo and peroxo alkyl niobocenes $Cp'_2Nb(O)(CH_2CH_2R)$ [R = H (**3**), Ph (**4**)], respectively, and $Cp'_2Nb(O_2)(CH_2CH_2R)$ (R = H, Ph). When this mixture was stirred at 40°C for 4 h, the peroxo alkyl complexes evolved to the corresponding oxo alkyl niobocenes, which were isolated as single products (Eq. (1)).

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$$Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CHR)_{R=H\ (1),\ Ph\ (2)} + O_2 \rightarrow Cp'_2Nb(O)(CH_2CH_2R)_{R=H\ (3),\ Ph\ (4)} \quad (1)$$

Nicholas et al. [4] have previously reported the isolation of several alkyl carbon dioxide–niobocene complexes by reaction of $Cp_2^{Me}Nb(CO)$(alkyl) with $O_2$. By contrast, when the reaction was carried out using carbonyl acyl niobocene derivatives $Cp'_2Nb(CO)(COCH_2CH_2R)$ [R = H (**5**), Ph (**6**)] with $O_2$ in hexane at r.t., the oxo acyl niobocene complexes $Cp'_2Nb(O)(COCH_2CH_2R)$ [R = H (**7**), Ph (**8**)] were isolated as pure compounds (Eq. (2)). The different behavior could be assigned to the higher electrophilic character of the acyl group compared with the corresponding alkyl group, which probably prevents the stabilization of the corresponding $CO_2$-containing species [3,5,6].

$$Cp'_2Nb(CO)(COCH_2CH_2R)_{R=H\ (5),\ Ph\ (6)} + O_2 \rightarrow Cp'_2Nb(O)(COCH_2CH_2R)_{R=H\ (7),\ Ph\ (8)} + CO \quad (2)$$

Protonation reactions of $Cp'_2Nb(O)(CH_2CH_2R)$ [R = H (**3**), Ph (**4**)] with an excess of $HBF_4{\cdot}Et_2O$ take place at −78°C in ether. The solution was stirred at r.t. for 4 h. In all cases the same complex, $Cp'_2NbF(O \rightarrow BF_3)$ (**9**), was obtained, in which the $BF_3$ moiety is coordinated to the oxygen atom and the R group has been replaced by the fluoride to give the alkane and alkene (Eq. (3)). The IR spectrum for compound **9** shows, in addition to the characteristic bands for Cp at 841 $cm^{-1}$ and $SiMe_3$ at 1250 $cm^{-1}$, a broad absorption at 1053 $cm^{-1}$ corresponding to the $BF_3$ and the $\nu$(Nb–F) vibration at 520 $cm^{-1}$. The $^1$H-NMR spectrum shows signals at 6.82 (2H), 6.99 (2H), 7.11 (2H) and 7.31 (2H) ppm for the Cp′ groups and a signal at 0.29 ppm for the $SiMe_3$ group. The $^{19}$F-NMR spectrum shows two signals at −144.44 and −145.46 ppm, corresponding to (Nb–F) and $BF_3$, respectively. These data confirm the proposed structure.

$$Cp'_2Nb(O)(CH_2CH_2R)_{R=H\ (3),\ Ph\ (4)} + HBF_4 \rightarrow Cp'_2Nb(F)_{(9)}(O \rightarrow BF_3) \quad (3)$$

The substitution of chloride by fluoride by abstraction from $BF_4^-$ [6] or $PF_6^-$ [7] has been observed previously. When the protonation reaction of the oxo-alkyl niobocenes with $HBF_4{\cdot}OEt_2$ was monitored by $^1$H-NMR spectroscopy in an NMR tube in acetone-$d_6$ at low temperature, the loss of the alkyl group as the corresponding alkane and alkene was detected.

The rapid protonation of these complexes prevents the isolation of any reaction intermediate. Initially, we could distinguish two groups of signals, those corresponding to complex **9** and the signals corresponding to other complexes (**3a** and **4a**, respectively), where the alkyl group is still coordinated to the niobium atom [8]. This intermediate rapidly affords the final complex **9**, with loss of the alkyl group [9].

Taking into account the splitting of $HBF_4$ by oxo niobocene complexes observed by Bruno et al. [10], we proposed that these reactions proceed by initial interaction of the Lewis acid $BF_3$ with the oxo group to give the oxo alkyl niobocene $Cp'_2Nb(CH_2CH_2R)(O \rightarrow BF_3)$ [R = H (**3a**), Ph (**4a**)], which has been observed previously [3,11]. A possible reaction pathway is shown in Scheme 1 (see below). There are two possible paths to explain the presence of the alkane and alkene as reaction byproducts: (a) the usual protonation of the alkyl group, followed by nucleophilic attack by fluoride; and (b) β-elimination of the alkyl group to yield the oxo-hydride derivative, which could not be detected (probably due to its high reactivity), followed by substitution of the hydride by the fluoride ligand.

$BF_3{\cdot}OEt_2$ has been used to provide evidence that the first step of this reaction is not the initial protonation of the oxo group in the time scale of our experiment, as has been proposed for complexes $Cp_2^*Nb(O)(R)$ (R = H, OMe) [12]. The reaction of $Cp'_2Nb(O)(CH_2CH_2R)$ [R = H (**3**), Ph (**4**)] with $BF_3{\cdot}OEt_2$ afforded the same intermediates **3a** and **4a**, which rapidly evolved to the final complex **9** and the corresponding alkene (Eq. (4)).

$$Cp'_2Nb(O)(CH_2CH_2R)_{R=H\ (3),\ Ph\ (4)} + BF_3{\cdot}OEt_2 \rightarrow Cp'_2Nb(O \rightarrow BF_3)(CH_2CH_2R)_{R=H\ (3a),\ Ph\ (4a)} \rightarrow Cp'_2Nb(O \rightarrow BF_3)(F)_{(9)} + CH_2{=}CHR \quad (4)$$

The same intermediates can be detected by treatment of $Cp'_2Nb(CO_2)(CH_2CH_2R)$ [R = H (**11**), Ph (**12**)] with $BF_3{\cdot}OEt_2$ (Scheme 2) (see below), probably due to the rapid decarbonylation reaction of the adducts $Cp'_2Nb(\eta^2\text{-}CO_2\text{–}BF_3)(CH_2CH_2R)$ to afford the oxo-alkyl complexes [3].

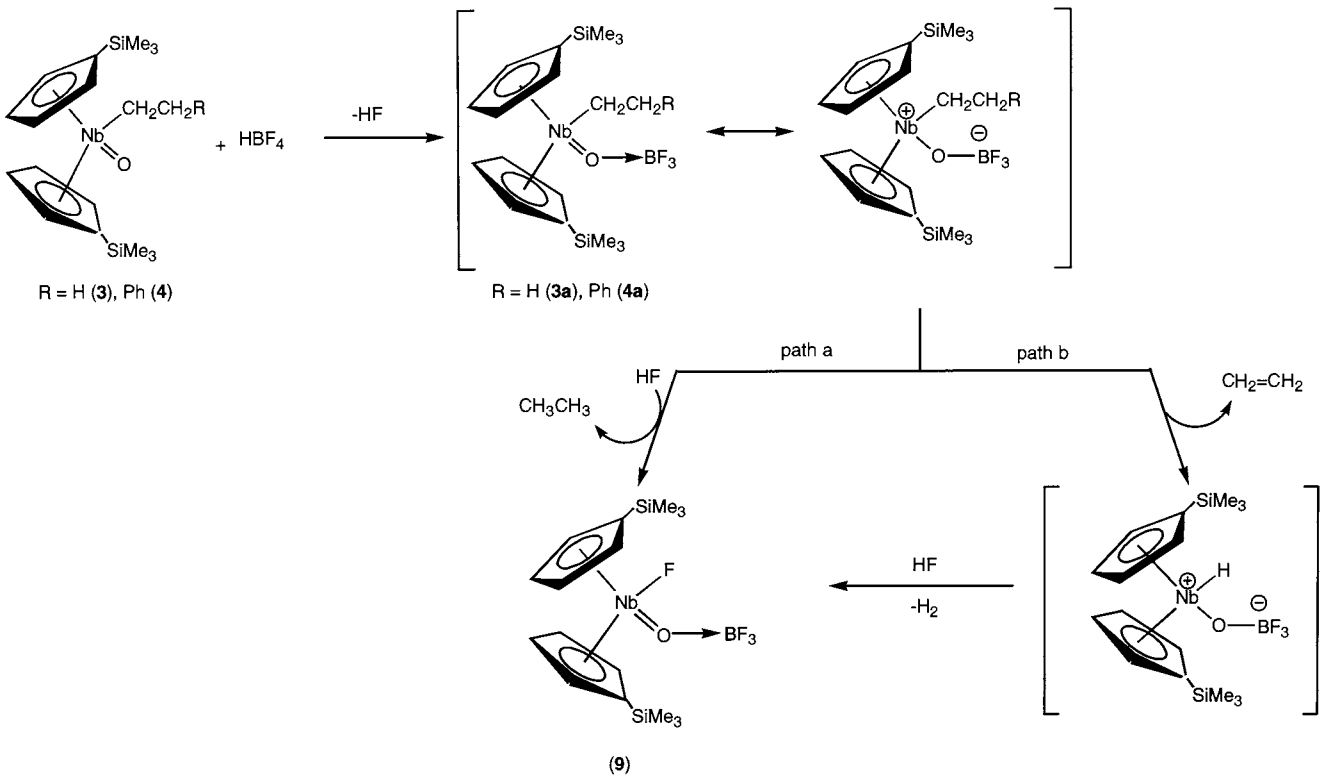
The reaction of alkyl and acyl derivatives $[Nb(Cp')_2R(O)]$ [R = Et (**3**), $CH_2CH_2Ph$ (**4**), $COCH_2CH_3$ (**7**), $COCH_2CH_2Ph$ (**8**)] with an excess of $CF_3COOH$ at −78°C in ether yielded $[Nb(Cp')(O)(\eta^1\text{-}(O)\text{–}OCOCF_3)]$ (**10**) with loss of the R group as either the alkane or aldehyde in alkyl or acyl derivatives, respectively (Eq. (5)). The IR spectrum for compound **10** shows the characteristic bands for Cp at 839 $cm^{-1}$, $\nu$(Nb=O) at 900 $cm^{-1}$ and $SiMe_3$ at 1253 $cm^{-1}$ and two absorptions at 1717 and 1407 $cm^{-1}$, corresponding to the asymmetric and symmetric vibrations, respectively, that are typical for the carboxylate group as a unidentate ligand [13]. The $^1$H-NMR spectrum shows signals at 6.24 (2H), 6.66 (2H) and 6.87 (4H) ppm for the Cp′ group and a signal at 0.24 ppm for the $SiMe_3$ group. The $^{13}$C-NMR spectrum confirmed the presence of the $CF_3COO^-$ group, with chemical shifts of 158.80 ppm [$^2J(^{19}F-^{13}C) = 40.9$ Hz] and 116.19 ppm [$^1J(^{19}F-^{13}C) = 285.4$ Hz]. The $^{19}$F-NMR spectrum shows a unique signal at −75.79 ppm. Similar complexes have been obtained in our group, namely $[Nb(Cp')L(\eta^1\text{-}(O)\text{–}OCOCF_3)]$ (L = CN–xylyl, CO) [14].

$$\underset{R = CH_2CH_3\ (\mathbf{3}),\ CH_2CH_2Ph\ (\mathbf{4}),\ COCH_2CH_3\ (\mathbf{7}),\ COCH_2CH_2Ph\ (\mathbf{8})}{Cp'_2Nb(O)(R)} + CF_3OOH \rightarrow \underset{(\mathbf{10})}{Cp'_2Nb(O)(\eta^1\text{-}(O)\text{-}OCOCF_3)} \quad (5)$$

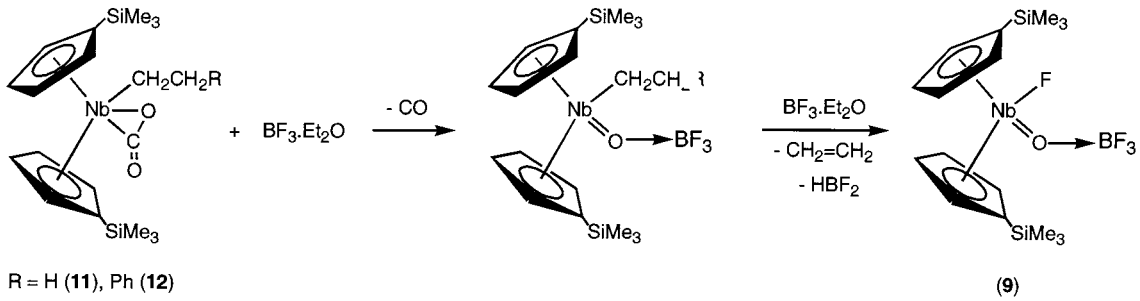
The reactions of alkyl derivatives $[Nb(Cp')_2(O)(CH_2CH_2R)]$ [R = H (**3**), Ph (**4**)] with $CF_3COOH$ were followed by $^1$H-NMR spectroscopy in an NMR tube in acetone-$d_6$. We proposed that these reactions proceed by initial protonation of the oxo group to afford cationic intermediates **3b** and **4b** [15], followed by the elimination of alkane and the nucleophilic attack of the $CF_3COO^-$ ligand to yield complex **10**, which has been previously observed [14] (Scheme 3). The same intermediate could be obtained by protonation of $[Nb(Cp')_2(CO_2)(CH_2CH_2R)]$ [R = H (**11**), Ph (**12**)] with $CF_3COOH$. Another pathway, where the initial protonation takes place at the Nb–C bond, cannot be excluded.

An X-ray crystal structure determination of complex $[Nb(Cp')(O)(\eta^1\text{-}(O)\text{–}OCOCF_3)]$ (**10**) confirmed the proposed structure. The crystal structure is depicted in Fig. 1 together with the atomic numbering scheme. Selected bond distances and angles are given in Table 1.

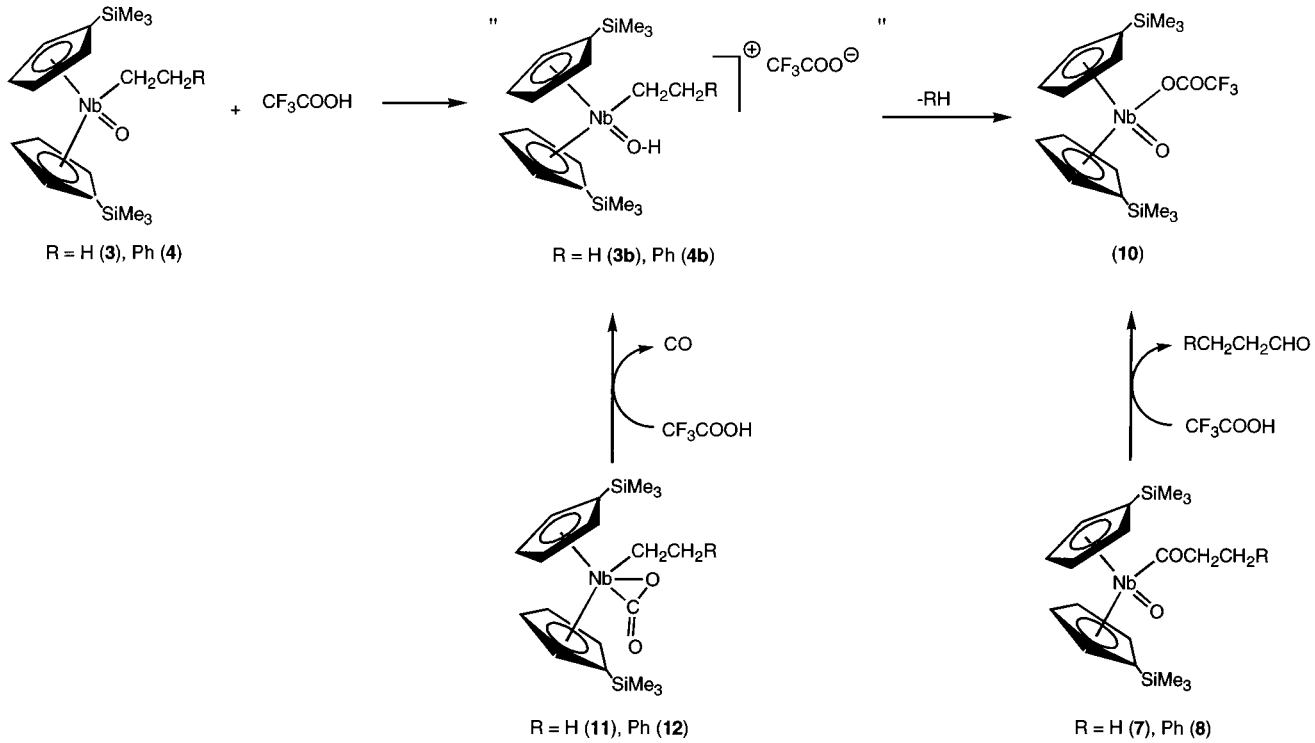
The structure consists of discrete molecules separated by van der Waals distances. The niobium atom shows a geometry that is typical for pseudo-tetrahedral niobocene(V) oxo derivatives. The angle between the two cyclopentadienyl rings is 127.35(3)°. The environment of the niobium atom is completed by an oxygen and a trifluoroacetate group bonded through the oxy-




Scheme 1.




Scheme 2.




Scheme 3.

gen atom to the niobium as a monodentate ligand. Bond distances are within the normal range found for these complexes [16], with Nb–O1 and Nb–O2 bond lengths of 1.718(4) and 2.097(5) Å, respectively.

## 3. Experimental

All reactions were performed using standard Schlenk-tube techniques under a nitrogen atmosphere. Solvents were distilled from appropriate drying agents. The complexes $Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CHR)$ [R = H (**1**), Ph (**2**)], and $Cp'_2Nb(CO)(COCH_2CH_2R)$ [R = H (**5**), Ph (**6**)] were synthesized using previously reported methods [3]. The C and H analyses were carried out using a Perkin–Elmer 2400B microanalyzer. The infrared spectra were recorded as Nujol mulls in the range 4000–200 $cm^{-1}$ using a Perkin–Elmer 883 spectrophotometer. NMR spectra were recorded on Varian-Unity FT-300 and Gemini FT-200 spectrometers, and the chemical shifts were determined by reference to the residual deuterated solvent peaks for $^1$H- and $^{13}$C-NMR and externally with $CFCl_3$ for $^{19}$F-NMR. When protonations were observed by NMR spectroscopy, $CF_3COOH$ (10%) or $HBF_4$ (10%) was added to an acetone-$d_6$ solution of niobocene complexes in an NMR tube at −78°C.

### 3.1. Preparation of $Cp'_2Nb(O)(CH_2CH_2R)$] [R = H (3), Ph (4)]

A solution of $Cp'_2Nb(H)(\eta^2\text{-}CH_2{=}CHR)$] [R = H (**1**), Ph (**2**)] (1 mmol) in hexane (30 ml) was stirred for 4 h at 40°C under dry $O_2$. The solvent was removed under vacuum and the yellow solid was recrystallized from hexane (5 ml) at −40°C. The yellow crystals were filtered off and identified as complexes **3** or **4**, respectively.

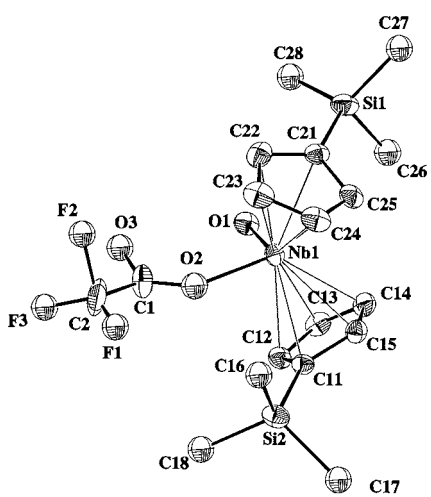



Fig. 1. Molecular structure of compound $Cp'_2Nb(O)(\eta^1\text{-}(O)\text{–}OC(O)CF_3)$ (**10**). ORTEP, 50% ellipsoids. Disorder and H atoms were omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for $Cp'_2Nb(=O)(OC(O)CF_3)$ (**10**)

| | |
|---|---|
| *Bond lengths* | |
| Nb1–O1 | 1.718(4) |
| Nb1–O2 | 2.097(5) |
| C1–O2 | 1.199(9) |
| C1–O3 | 1.30(2) |
| C1–C2 | 1.56(1) |
| *Bond angles* | |
| O1–Nb1–O2 | 99.7(2) |
| Nb1–O2–C1 | 133.2(5) |
| O2–C1–O3 | 127.4(9) |
| O2–C1–C2 | 114.8(8) |
| O3–C1–C2 | 113.7(10) |

Complex **3**. Yield: 87%. Anal. Calc. for $C_{18}H_{31}Si_2ONb$: C, 52.41; H, 7.58. Found: C, 52.45; H, 7.50. IR (Nujol): $\nu$ ($cm^{-1}$) 1245 ($SiMe_3$), 907 (Nb=O), 834 ($C_5H_4SiMe_3$). $^1$H-NMR (acetone-$d_6$): $\delta$ (ppm) 0.26 (s, 18H, $SiMe_3$), 5.80(2), 5.94(2), 6.16(2) 6.58(2) (m, $C_5H_4SiMe_3$), 2.01 [q, $J(^1H-^1H) = 7.36$ Hz $CH_2CH_3$], 1.66 [t, $J(^1H-^1H) = 7.36$ Hz $CH_2CH_3$]. $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ (ppm) −0.53 ($SiMe_3$), 20.54 ($CH_2CH_3$), 25.00 ($CH_2CH_3$), 111.01, 111.27, 114.47, 120.32 ($C_5H_4SiMe_3$), 120.21 ($C_{ipso}$).

Complex **4**. Yield: 76%. Anal. Calc. for $C_{24}H_{35}Si_2ONb$: C, 59.00; H, 7.23. Found: C, 58.99; H, 7.15. IR (Nujol): $\nu$ ($cm^{-1}$) 1595 (Ph), 1244 ($SiMe_3$), 906 (Nb=O), 834 ($C_5H_4SiMe_3$). $^1$H-NMR (acetone-$d_6$): $\delta$ (ppm) 0.24 (s, 18H, $SiMe_3$), 5.87(2), 6.05(2), 6.26(2) 6.62(2) (m, $C_5H_4SiMe_3$), 3.08 (m, $CH_2CH_2Ph$), 2.19 (m, $CH_2CH_2Ph$), 6.95–7.40 (m, $CH_2CH_2Ph$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta$ (ppm) −0.52 ($SiMe_3$), 34.14 ($CH_2CH_2Ph$), 42.84 ($CH_2CH_2Ph$), 111.27, 111.73, 114.49, 120.01 ($C_5H_4SiMe_3$), 120.36 ($C_{ipso}$–$C_5H_4SiMe_3$), 125.20, 127.68, 128.32 ($CH_2CH_2Ph$), 147.97 ($C_{ipso}$–Ph).

### 3.1.1. Preparation of $Cp'_2Nb(O)(\eta^1\text{-}C(O)CH_2CH_2R)$ [R = H (7), Ph (8)]

A solution of $Cp'_2Nb(CO)(\eta^1\text{-}C(O)CH_2CH_2R)$ [R = H (**5**), Ph (**6**)] (0.75 mmol) in hexane (30 ml) was stirred for 30 min at r.t. under dry $O_2$. The solvent was removed under vacuum and the yellow solid was recrystallized from hexane (5 ml) at −40°C. The yellow crystals were filtered off and identified as **7** or **8**, respectively.

Complex **7**. Yield: 92%. Anal. Calc. for $C_{19}H_{31}Si_2O_2Nb$: C, 51.81; H, 7.10. Found: C, 51.45; H, 7.00. IR (Nujol) $\nu$ ($cm^{-1}$) 1641 (C=O), 1247 ($SiMe_3$), 906 (Nb=O), 835 ($C_5H_4SiMe_3$). $^1$H-NMR ($C_6D_6$): $\delta$ (ppm) 0.19 (s, 18H, $SiMe_3$), 5.16(2), 5.49(2), 5.50(2), 5.65(2) (m, $C_5H_4SiMe_3$), 3.33 [q, $J(^1H-^1H) = 7.20$ Hz, $CH_2CH_3$], 1.20 [t, $J(^1H-^1H) = 7.20$ Hz, $CH_2CH_3$]; $^{13}C\{^1H\}$-NMR ($C_6D_6$): $\delta$ (ppm) −0.86 ($SiMe_3$), 9.63 ($CH_2CH_3$), 43.57 ($CH_2CH_3$), 107.25, 110.30, 111.62, 119.16 ($C_5H_4SiMe_3$), 113.89 ($C_{ipso}$), 273.22 ($\eta^1$-C(O)R).

Complex **8**. Yield: 89%. Anal. Calc. for $C_{25}H_{35}Si_2O_2Nb$: C, 58.13; H, 6.83. Found: C, 57.99; H, 6.45. IR (Nujol) $\nu$ ($cm^{-1}$) 1635 (C=O), 1597 (Ph), 1245 ($SiMe_3$), 905 (Nb=O), 838 ($C_5H_4SiMe_3$). $^1$H-NMR ($C_6D_6$): $\delta$ (ppm) 0.20 (s, 18H, $SiMe_3$), 5.50 (2), 5.52 (2), 5.70 (2) 6.12 (2) (m, $C_5H_4SiMe_3$), 2.91 ($A_2B_2$ system, $J_{AB} = 6.88$ Hz, $CH_2CH_2Ph$), 3.55 ($A_2B_2$ system, $J_{AB} = 6.88$ Hz, $CH_2CH_2Ph$), 7.20–7.30 (m, $CH_2CH_2Ph$). $^{13}C\{^1H\}$-NMR ($C_6D_6$): $\delta$ (ppm) −0.85 ($SiMe_3$), 31.23 ($CH_2CH_2Ph$), 51.80 ($CH_2CH_2Ph$), 107.48, 110.95, 111.10, 119.29 ($C_5H_4SiMe_3$), 125.99, 128.67, 129.30 ($CH_2CH_2Ph$), 143.07 ($C_{ipso}$–Ph), 272.99 ($\eta^1$-C(O)R).

### 3.1.2. Preparation of $[Cp'_2Nb(F)(O \rightarrow BF_3)]$ (9)

To a solution of $Cp'_2Nb(O)(CH_2CH_2R)$ [R = H (**3**), Ph (**4**)] (0.4 mmol) in (20 ml) $Et_2O$ at −78°C was added $HBF_4 \cdot OEt_2$ (10% excess). Immediately a brown precipitate is formed. The mixture was stirred at r.t. for 4 h. The solid was filtered off, washed with $Et_2O$ and dried under vacuum. Yield 56%. Anal. Calc. for $C_{16}H_{26}Si_2BF_4ONb$: C, 40.85; H, 5.57. Found: C, 40.77; H, 5.54. IR (Nujol): $\nu$ ($cm^{-1}$) 1053 ($BF_3$), 1250 ($SiMe_3$), 841 ($C_5H_4SiMe_3$), 520 (Nb–F); $^1$H-NMR (acetone-$d_6$): $\delta$ (ppm) 0.29 (s, 18H, $SiMe_3$), 6.82(2), 6.99(2), 7.11(2), 7.31(2) (m, $C_5H_4SiMe_3$). $^{13}C\{^1H\}$-NMR (acetone-$d_6$): $\delta$ (ppm) −0.57 ($SiMe_3$), 113.75, 116.05, 131.42, 132.99 ($C_5H_4SiMe_3$), 127.71 ($C_{ipso}$). $^{19}$F-NMR (acetone-$d_6$) $\delta$ (ppm) −144.44 (Nb–F), −145.46 ($BF_3$).

### 3.1.3. Preparation of $[Cp'_2Nb(O)(\eta^1\text{-}(O)\text{–}OCOCF_3)]$ (10)

#### 3.1.3.1. Method A.

To a solution of $Cp'_2Nb(O)(CH_2CH_2R)$ [R = H (**3**), Ph (**4**)] (0.4 mmol) in $Et_2O$ (20 ml) at −78°C was added trifluoroacetic acid (10% excess). Immediately a red precipitate was formed. The mixture was stirred at r.t. for 3 h, then the solid was filtered off, washed with $Et_2O$ and dried under vacuum. Yield 71%.

#### 3.1.3.2. Method B.

To a solution of $Cp'_2Nb(O)(\eta^1\text{-}C(O)CH_2CH_2R)$ [R = H (**5**), Ph (**6**)] (0.4 mmol) in $Et_2O$ (20 ml) at −78°C, trifluoroacetic acid (10% excess) was added. Immediately a red precipitate was formed. The mixture was stirred at r.t. for 3 h. The solid was filtered off, washed with $Et_2O$ and dried under vacuum. Yield 83%. Anal. Calc. for $C_{18}H_{26}Si_2F_3O_3Nb$: C, 43.54; H, 5.28. Found: C, 43.10; H, 5.30. IR (Nujol): $\nu$ ($cm^{-1}$) 1717, 1407 (COO), 1253 ($SiMe_3$), 900 (Nb=O), 839 ($C_5H_4SiMe_3$). $^1$H-NMR (acetone-$d_6$): $\delta$ (ppm) 0.24 (s, 18H, $SiMe_3$), 6.24(2), 6.66(2), 6.87(4) (m, $C_5H_4SiMe_3$). $^{13}C\{^1H\}$-NMR (acetone-$d_6$): $\delta$ (ppm) −0.60 ($SiMe_3$), 115.62, 118.19, 120.23, 127.76 ($C_5H_4SiMe_3$), 131.29 ($C_{ipso}$), 116.19 [q, $^1J(^{19}F-^{13}C) = 285.4$ Hz, $CF_3COO$], 158.80 [q, $^2J(^{19}F-^{13}C) = 40.9$ Hz, $CF_3COO$]. $^{19}$F-NMR (acetone-$d_6$): $\delta$ (ppm) −75.79 ($CF_3COO$).

### 3.2. Crystal structure determination and refinement of complex $Cp'_2Nb(O)(\eta^1\text{-}(O)\text{–}OCOCF_3)$ (**10**)

Diffraction data were obtained at 298 K on a Nonius-Mach3 four-circle diffractometer equipped with a graphite monochromated Mo–$K_\alpha$ radiation source ($\lambda = 0.7107$ Å) using an $\omega/2\theta$ scan technique to a maximum value of 56°. The compound crystallizes in the monoclinic group $P2_1/c$ with $Z = 4$. There is one molecule of $Cp'_2Nb(O)(\eta^1\text{-}(O)\text{–}OCOCF_3)$ per asymmetric unit. Parameters for the collection and refinement of diffraction data are contained in Table 2. Data were corrected for Lorentz and polarization effects and absorption correction was not necessary ($\mu = 6.72$ cm$^{-1}$).

The structure was solved using direct methods [17] and refinements on $F^2$ was carried out by full-matrix least-squares analysis (SHELXL-93) [18]. For the disordered atoms in the acetate ligand, occupancies were refined initially and then fixed at 0.5. The hydrogen atoms were included in calculated positions and refined 'riding' on their parent carbon atoms.

## 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 130274 for compound **10**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Table 2
Crystal analysis parameters of complex **10**

| | |
|---|---|
| Formula | $C_{18}H_{26}F_3NbO_3Si_2$ |
| Formula weight | 496.48 |
| Crystal size (mm) | $0.3 \times 0.2 \times 0.2$ |
| Habit | Prismatic |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | |
| $a$ (Å) | 9.671(1) |
| $b$ (Å) | 12.935(2) |
| $c$ (Å) | 18.43(1) |
| $\beta$ (°) | 99.03(2) |
| $V$ (Å$^3$) | 2276.9(13) |
| $Z$ | 4 |
| $\mu$ (cm$^{-1}$) | 6.72 |
| Reflections collected | 5492 |
| Observed reflections | 3090 |
| Independent reflections | 5492 |
| Index range | $0 \le h \le 12$, $0 \le k \le 17$, $-24 \le l \le 24$ |
| Largest diff. peak and hole (e Å$^{-3}$) | 0.778 and −0.591 |
| $R$, $R_w$ | 0.062, 0.152 |

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[8] **3a**. $^1$H-NMR (acetone-$d_6$): $\delta$ (ppm) 0.32 (s, 18H, $SiMe_3$), 6.36(2), 6.63(2), 6.72(2), 6.80(2) (m, $C_5H_4SiMe_3$), 2.40 [q, $J(^1H-^1H) = 6.80$ Hz, $CH_2CH_3$], 1.69 [t, $J(^1H-^1H) = 6.80$ Hz, $CH_2CH_3$]. **4a**: 0.31 (s, 18H, $SiMe_3$), 6.47 (2), 6.81 (4), 7.15 (2) (m, $C_5H_4SiMe_3$), 2.55 (m, $CH_2CH_2Ph$), 3.15 (m, $CH_2CH_2Ph$), 7.30 (m, $CH_2CH_2Ph$).

[9] $CH_3CH_3$. $^1$H-NMR (acetone-$d_6$): $\delta$ (ppm) 0.83, s. $CH_2{=}CH_2$: 5.37, s. $PhCH_2CH_3$: 1.23 [t, 3H, $J(^1H-^1H) = 7.60$ Hz, $PhCH_2\mathit{CH_3}$]; 2.65 [q, 2H, $J(^1H-^1H) = 7.60$ Hz, $Ph\mathit{CH_2}CH_3$]; 7.20–7.50 (m, 5H, $\mathit{Ph}CH_2CH_3$). $PhCH{=}CH_2$: 5.20 (d, 1H, $PhCH{=}\mathit{CH_2}$); 5.80 (d, 1H, $PhCH{=}\mathit{CH_2}$); 6.70 (dd, 1H, $Ph\mathit{CH}{=}CH_2$); 7.20–7.50 (m, 5H, $\mathit{Ph}CH{=}CH_2$).

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[15] **3b**. $^1$H-NMR (acetone-$d_6$): $\delta$ (ppm) 0.26 (s, 18H, $SiMe_3$), 6.15(2), 6.34(2), 6.54(2), 6.74(2) (m, $C_5H_4SiMe_3$), 2.21 [q, $J(^1H-^1H) = 7.22$ Hz, $CH_2CH_3$], 1.69 [t, $J(^1H-^1H) = 7.22$ Hz, $CH_2CH_3$]. **4b**:

0.26 (s, 18H, $SiMe_3$), 5.87(2), 6.20(2), 6.37(2), 6.46(2) (m, $C_5H_4SiMe_3$), 2.40 (m, $CH_2CH_2Ph$), 3.03 (m, $CH_2CH_2Ph$), 7.20 (m, $CH_2CH_2Ph$).

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