

# New reactivity of $\text{Cp}'_2\text{NbH}_3$ , $\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{SiMe}_3$ . Synthesis, electrosynthesis and reactivity of new carboxylato niobocene complexes

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## Abstract

A new family of niobium bidentate carboxylato-containing niobocene complexes, mononuclear  $\text{Cp}'_2\text{Nb}(\kappa^2\text{-O}, \text{O}'\text{-OOC}(\text{C}_6\text{H}_5))$  (**3**), binuclear  $[(\text{Cp}'_2\text{Nb})_2(1,4\text{-}(\kappa^2\text{-O}, \text{O}'\text{-OOC})_2(\text{C}_6\text{H}_4))]$  (**4**) and  $[(\text{Cp}'_2\text{Nb})_2(1,3\text{-}(\kappa^2\text{-O}, \text{O}'\text{-OOC})_2(\text{C}_6\text{H}_4))]$  (**5**) and trinuclear  $[(\text{Cp}'_2\text{Nb})_3(1,3,5\text{-}(\kappa^2\text{-O}, \text{O}'\text{-OOC})_3(\text{C}_6\text{H}_3))]$  (**6**), have been prepared by the reaction of  $\text{Cp}'_2\text{NbH}_3$  (**1**) and the corresponding carboxylic acid, namely  $(\text{C}_6\text{H}_5)\text{COOH}$ ,  $(1,4\text{-COOH})_2(\text{C}_6\text{H}_4)$ ,  $(1,3\text{-COOH})_2(\text{C}_6\text{H}_4)$  and  $(1,3,5\text{-COOH})_3(\text{C}_6\text{H}_3)$ . Complexes **3**, **4**, **5** and **6** have been prepared by an alternative route involving a two-electron reduction of  $\text{Cp}'_2\text{NbCl}_2$  (**2**) in the presence of the appropriate molar ratios of the corresponding carboxylic acids. Furthermore, the reaction of complexes **3**, **4** and **6** with 2,6- $\text{Me}_2\text{C}_6\text{H}_3\text{NC}$  (xylylNC) in the molar ratios 1:1, 1:2 and 1:3, respectively, resulted in opening of the bidentate carboxylato ligand to give the monodentate carboxylato-containing complexes  $[\text{Cp}'_2\text{Nb}(\kappa^1\text{-O}\text{-OOC}(\text{C}_6\text{H}_5))(\text{xylylNC})]$  (**7**),  $[(\text{Cp}'_2\text{Nb}(\text{xylylNC}))_2(1,4\text{-}(\kappa^1\text{-O}\text{-OOC})_2(\text{C}_6\text{H}_4))]$  (**8**) and  $[(\text{Cp}'_2\text{Nb}(\text{xylylNC}))_3(1,3,5\text{-}(\kappa^1\text{-O}\text{-OOC})_3(\text{C}_6\text{H}_3))]$  (**9**). Similarly, complex  $[(\text{Cp}'_2\text{Nb}(\eta^1\text{-C}, \kappa^1\text{-S}\text{-CS}_2))_3(1,3,5\text{-}(\kappa^1\text{-O}\text{-OOC})_3(\text{C}_6\text{H}_3))]$  (**10**) was prepared by reaction of **6** with the appropriate amount of  $\text{CS}_2$ . Complexes **7**, **8** and **9** can be prepared in an alternative way by reaction of  $[\text{Cp}'_2\text{Nb}(\text{H})(\text{xylylNC})]$  with the corresponding carboxylic acids. The structures of all complexes have been established by spectroscopic techniques. In addition, the X-ray molecular structure of **4** was determined by a single-crystal X-ray diffraction study.

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**Keywords:** Niobocene; Carboxylato; Synthesis; Electrosynthesis

## 1. Introduction

In previous studies we have investigated the chemical behaviour of the trihydride complex  $\text{Cp}'_2\text{NbH}_3$  (**1**) in

great depth. This complex constitutes an interesting example of a trihydride complex that exhibits the phenomenon of exchange coupling [1], with unusual  $^1J(\text{H},\text{H})$  couplings that vary with temperature [2]. In the last 15 years we have focused our attention on the study of the reactivity of **1**, e.g., with  $\pi$ -acid ligands to give different families of complexes  $\text{Cp}'_2\text{NbH}(\text{L})$ ,  $\text{L} = \pi$ -acid ligand [3], in  $\text{E}\text{-H}$  ( $\text{E} = \text{Si}, \text{Ge}, \text{H}$ )

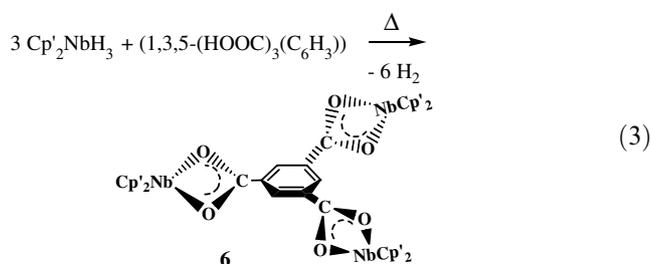
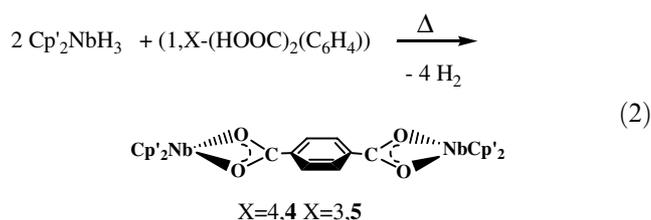
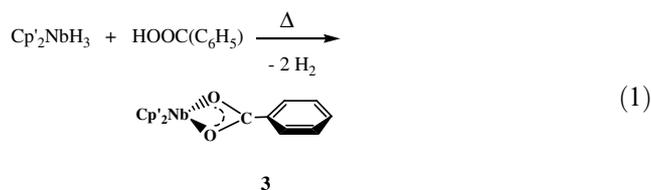
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activation processes [4] and with Lewis acids, such as  $[M(PPh_3)]PF_6$ ,  $M = Cu, Ag, Au$  to give a broad class of heterobimetallic species [5]. A few years ago, we prepared a formato niobocene complex  $Cp'_2Nb(\kappa^2-O, O'-OOCH)$  by carbon dioxide insertion into the niobium-hydrogen bond of  $Cp'_2NbH_3$ . The formato complex could also be obtained from the two-electron reduction of  $Cp'_2NbCl_2$  in the presence of formic acid [6]. In addition, an acetato-containing complex, namely  $Cp'_2Nb(\kappa^2-O, O'-OOCMe)$ , was also chemically and electrochemically prepared [6]. Other authors have prepared O-bound carboxylato complexes by the insertion of carbon dioxide into  $M-C$  bonds [7]. More recently, electrochemical and spectroscopic studies on dicarboxylato-containing niobocene complexes were carried out [8]. As a continuation of our interest in the chemistry of  $Cp'_2NbH_3$ , we report here its behaviour towards mono-, bi- and trinuclear aromatic carboxylic acids. These reactions led to the isolation of new carboxylato niobocene complexes, namely  $Cp'_2Nb(\kappa^2-O, O'-OOCR)$ ,  $[(Cp'_2Nb)_2(\kappa^2-O, O'-OOC)_2R]$ , and  $[(Cp'_2Nb)_3(\kappa^2-O, O'-OOC)_3R]$ , which can also be formed from the reduction of  $Cp'_2NbCl_2$  in the presence of the appropriate carboxylic acid. Several aspects concerning the reactivity of these systems are also discussed.

## 2. Results and discussion

We are currently interested in studying the reactivity of  $Cp'_2NbH_3$  towards different classes of carboxylic acids. With this aim in mind, four types of carboxylic acid, namely benzoic,  $(C_6H_5)COOH$ , terephthalic,  $(1,4-COOH)_2(C_6H_4)$ , isophthalic,  $(1,3-COOH)_2(C_6H_4)$  and 1,3,5-phenyltricarboxylic,  $(1,3,5-COOH)_3(C_6H_3)$ , were selected. The standard reaction procedure involved heating at ca. 60 °C a stirred THF solution of **1** with the appropriate carboxylic acid. This method allowed the isolation of the carboxylato-containing complexes after an appropriate work-up procedure (Eqs. (1)–(3)).



The different complexes were isolated as green air-sensitive solids. The evolution of  $H_2$  was detected in all of the experiments. Complexes **4**, **5** and **6** were isolated as the only carboxylato-containing species even when niobocene:carboxylic acid molar ratios lower than 2:1 or 3:1 were employed, indicating that the formation of either the corresponding binuclear or trinuclear species is thermodynamically favoured. The formation of those complexes could take place through the elimination of  $H_2$  and the formation of a very reactive sixteen-electron monohydride niobocene species, which has previously been proposed in several cases [9]. All the complexes described in this work were spectroscopically characterized. The most prominent features in the IR spectra are the  $CO_2^-$  stretching frequencies of the carboxylato group and our attention was focused upon these. The usual approach in this respect has been to relate the  $\Delta$  values (the separation between  $\nu_{asym}(CO_2^-)$  and  $\nu_{sym}(CO_2^-)$ ) with the mono- or bidentate character of the ligands [10]. The IR spectra of complexes **3**, **4**, **5** and **6** showed the  $\nu_{asym}(CO_2^-)$  and  $\nu_{sym}(CO_2^-)$  absorptions to have  $\Delta$  values of 95, 117, 121 and 74  $cm^{-1}$ , respectively, which are consistent with the presence of a bidentate carboxylato ligand [10]. Moreover, the  $^1H$  and  $^{13}C$  NMR data confirm the bidentate coordination. In fact, the observation of two and three signals for each cyclopentadienyl ring in the  $^1H$  and  $^{13}C$  NMR spectra, respectively, (see Section 4) indicate the presence of a symmetrical environment.

In addition, the  $^{13}C$  NMR spectra contain signals for the carboxylato carbon atoms at  $\delta$  190.1, 205.5, 188.9 and 187.6 for complexes **3**, **4**, **5** and **6**, respectively. In order to confirm the proposed structural disposition for these complexes, the X-ray crystal molecular structure of **4** was determined. The molecular structure and atomic numbering scheme are shown in Fig. 1. Selected bond lengths and angles for **4** are given in Table 1.

The structure of **4** consists of a symmetric binuclear niobium complex. The metal atoms are bound to two cyclopentadienyl rings in a  $\eta^5$  mode and to two oxygen atoms from the chelating carboxylato group. The six-membered aromatic ring and the two carboxylato groups are coplanar, although the niobium atom is out of the plane defined by O1, O2, C1, C2, C3 and C4 (by 0.156(6) Å). The two oxygen atoms of the bidentate carboxylato ligand have similar Nb–O bond distances (2.220(4) and 2.230(4) Å for O1 and O2, respectively) and these values are in reasonable agreement with those

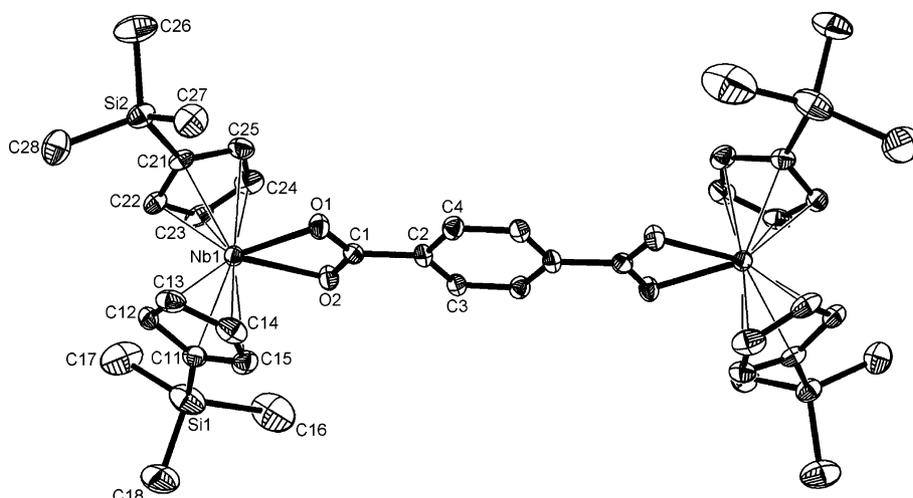


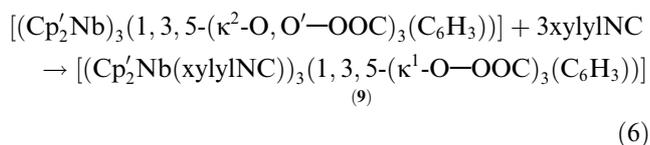
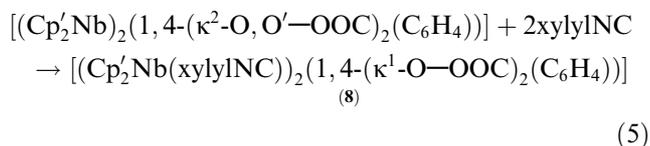
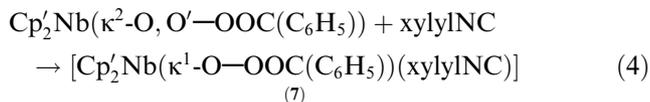
Fig. 1. Molecular structure and atom-labelling scheme for complex **4**, with thermal ellipsoids at 30% probability.

Table 1  
Selected bond lengths (Å) and angles (°) for **4**

Nb1–O1	2.220(4)
Nb1–O2	2.230(4)
O1–C1	1.262(7)
O2–C1	1.261(7)
C1–C2	1.501(8)
O1–Nb1–O2	58.9(2)
C1–O1–Nb1	90.5(4)
C1–O2–Nb1	90.1(4)
O1–C1–O2	120.3(5)
O1–C1–C2	120.0(6)
O2–C1–C2	119.7(6)

reported for the carboxylato ligands [11]. The cyclopentadienyl groups are in a typical eclipsed fashion with respect to each other and the SiMe<sub>3</sub> groups are in a *trans* disposition.

Reactions of complexes **3**, **4** and **6** with 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC (xylylNC), in the appropriate molar ratios led to a change from a bidentate to a monodentate carboxylato unit due to coordination of the incoming ligand. These reactions led to the isolation of new complexes after the appropriate work-up procedure (Eqs. (4)–(6)).



The same complexes can be prepared in an alternative way by reaction of the complex [Cp'<sub>2</sub>Nb(H)(xylylNC)] [3] with the appropriate molar ratios of the corresponding carboxylic acids. Finally, complex [Cp'<sub>2</sub>Nb((η<sup>1</sup>-C, κ<sup>1</sup>-S-CS<sub>2</sub>))<sub>3</sub>(1,3,5-(κ<sup>1</sup>-O-OOC)<sub>3</sub>(C<sub>6</sub>H<sub>3</sub>))] (**10**) was also prepared by the reaction of **6** with CS<sub>2</sub>. The different monodentate carboxylato-niobocene complexes were isolated as either air-sensitive green (for **7**, **8** and **9**) or non-air-sensitive brown (for **10**) solids. The different complexes were spectroscopically characterized. The IR spectra of complexes **7**–**10** show the ν<sub>asym</sub>(CO<sub>2</sub><sup>-</sup>) and ν<sub>sym</sub>(CO<sub>2</sub><sup>-</sup>) absorptions to have Δ values of 262, 245, 242 and 230 cm<sup>-1</sup>, respectively, which are consistent with the presence of a bidentate carboxylato ligand [10]. In accordance with the lack of symmetry in the proposed structures (see Fig. 2), the <sup>1</sup>H and <sup>13</sup>C NMR spectra of these complexes show four and five resonances for each cyclopentadienyl ring. The carbon resonances for the carboxylato ligands appear at δ 175.6, 174.2, 174.4 and 182.2, respectively, for **7**–**10**. In addition, in these spectra the carbon resonances for the ancillary ligands, namely 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC and CS<sub>2</sub>, appear at δ 208.2, 209.9, 212.5 and 250.2, respectively.

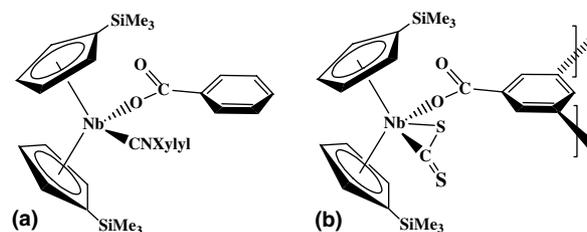


Fig. 2. (a) Proposed structure for complex **7**. An analogous structural situation may be displayed for **8** and **9**. (b) Analogous trinuclear disposition with an η<sup>1</sup>-C, κ<sup>1</sup>-S-CS<sub>2</sub> ancillary ligand proposed for complex **10**.



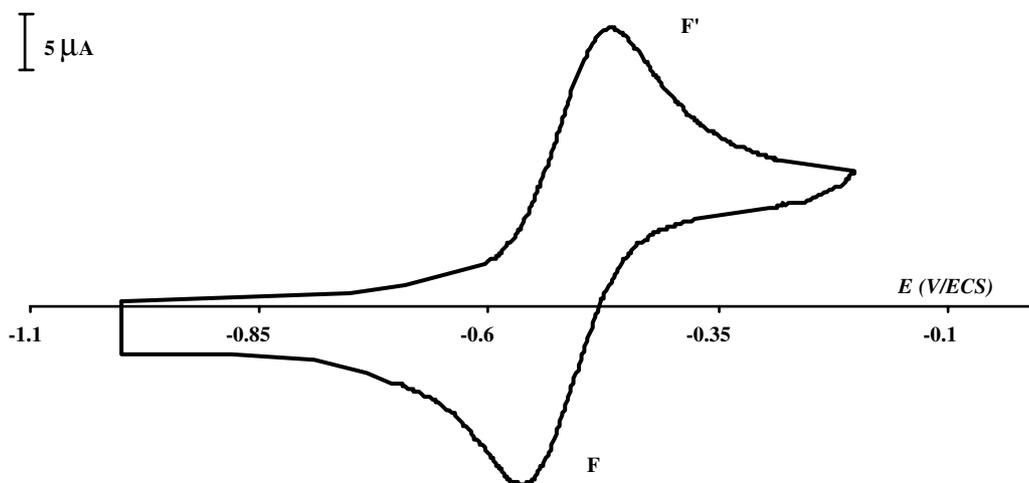


Fig. 4. Cyclic voltammogram of **3** on carbon electrode in THF containing  $0.2 \text{ mol L}^{-1}$  of  $\text{NaBPh}_4$  (scan rate:  $100 \text{ mV s}^{-1}$ ; starting potential:  $-1 \text{ V}$ ).

Table 2

Half-wave potential of the  $F/F'$  system, obtained on carbon electrode (scan rate:  $20 \text{ mV s}^{-1}$ ) in THF/ $\text{NaBPh}_4$

Complex	$E_{1/2}$ (V)
<b>4</b>	-0.482
<b>5</b>	-0.479
<b>6</b>	-0.456

voltammetry experiments, these complexes also exhibit the reversible  $F/F'$  system at the potential values indicated in Table 2.

### 3. Conclusions

The interaction of  $\text{Cp}'_2\text{NbH}_3$  with carboxylic acids was studied. The liberation of  $\text{H}_2$  and the subsequent formation of new carboxylato-containing niobocenes, which were alternatively prepared by an electrochemical method, was observed. In addition, the reactivity of these complexes towards xylylNC and  $\text{CS}_2$  was studied. It was found that a bidentate  $\rightarrow$  monodentate conversion of the coordination mode of the carboxylato ligand occurred.

### 4. Experimental

**General procedures.** All reactions were carried out using Schlenk techniques. Oxygen and water were excluded by the use of vacuum lines supplied with purified  $\text{N}_2$ . Toluene was distilled from sodium. Pentane was distilled from sodium/potassium alloy. Diethyl ether and THF were distilled from sodium benzophenone. All solvents were deoxygenated prior to use. Complexes  $\text{Cp}'_2\text{Nb}(\text{H})_3$  and  $\text{Cp}'_2\text{Nb}(\text{H})(\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3))$  were prepared as described in the literature [2,3]. Deuterated

solvents were dried over  $4 \text{ \AA}$  molecular sieves and degassed prior to use. Carboxylic acids, namely  $\text{C}_6\text{H}_5(\text{COOH})$ ,  $[1,4\text{-(HOOC)}_2(\text{C}_6\text{H}_4)]$ ,  $[1,3\text{-(HOOC)}_2(\text{C}_6\text{H}_4)]$ ,  $[1,3,5\text{-(HOOC)}_2(\text{C}_6\text{H}_3)]$ , and carbon disulphide were used as purchased from Aldrich. NMR spectra were recorded on a Varian Unity 300 (300 MHz for  $^1\text{H}$ , 75 MHz for  $^{13}\text{C}$ ) spectrometer. Chemical shifts were measured relative to partially deuterated solvent peaks and are reported relative to TMS. IR spectra were recorded on a Perkin–Elmer 883 spectrometer in Nujol mulls over CsI windows.

#### 4.1. Electrochemical experiments

All manipulations were performed using Schlenk techniques in an atmosphere of dry oxygen-free argon gas and using dry solvents. The supporting electrolyte was degassed under vacuum before use and then solubilized at a concentration of  $0.2 \text{ mol L}^{-1}$ . Voltammetric analyses were carried out in a standard three-electrode cell with a Princeton Applied Research, Model 263A. The reference electrode was a saturated calomel electrode (SCE) separated from the solution by a sintered glass disk. The auxiliary electrode was a platinum wire. For all voltammetric measurements, the working electrode was a vitreous carbon electrode ( $\phi = 3 \text{ mm}$ ). A CTV101 Speed Control unit was used to adjust the rotation speed ( $\bar{\omega} = 500 \text{ rpm}$ ) of the ED1101 electrode (Radiometer). In these conditions, when operating in THF, the formal potential for the ferrocene $^{+/-}$  couple is found to be  $+0.56 \text{ V}$  versus SCE. The controlled potential electrolysis was performed with an Amel 552 potentiostat coupled with an Amel 721 electronic integrator. High scale electrolyses were performed in a cell with three compartments separated with fritted glasses of medium porosity. A carbon gauze was used as the working electrode, a platinum plate as the counter-electrode and a saturated calomel electrode as the reference electrode.

#### 4.2. Synthesis of $Cp_2^*Nb(\kappa^2-O,O'-OOC(C_6H_5))$ (**3**)

A mixture of  $Cp_2^*NbH_3$  (**1**) (0.28 g; 0.75 mmol) and the carboxylic acid  $C_6H_5(COOH)$  (0.15 g; 0.75 mmol) was stirred with dry THF (30 mL) at 50 °C for 5 h. The solution became dark green in colour and the solvent was evaporated to dryness under vacuum. The dark green oily residue was extracted with hexane (10 mL). The resulting solution was filtered and evaporated to dryness. Complex **3** was isolated as a dark green solid (90% yield): IR (Nujol/PET  $cm^{-1}$ ) ( $\nu COO_{asym}^-$ ) 1634, ( $COO_{sym}^-$ ) 1539.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  0.06 (s, 18H,  $SiMe_3$ ), 4.18, 5.69 (4H each a complex signal,  $C_5H_4SiMe_3$ ), 6.87 (t,  $^3J_{H-H} = 7.4$  Hz, 1H,  $H_p$ ,  $C_6H_5$ ), 6.90 (t,  $^3J_{H-H} = 7.5$  Hz, 2H,  $H_m$ ,  $C_6H_5$ ), 7.78 (d,  $^3J_{H-H} = 7.5$  Hz, 2H,  $H_o$ ,  $C_6H_5$ ).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ ):  $\delta$  0.4 ( $SiMe_3$ ), 94.0 ( $C^1$ ,  $C_5H_4SiMe_3$ ), 104.3, 108.2 ( $C^{2-5}$ , exact assignment not possible,  $C_5H_4SiMe_3$ ), 127.0, 128.0, 132.7 ( $C_6H_5$ ), 190.1 ( $COO^-$ ). Anal. Calc. for  $C_{23}H_{34}NbSi_2O_2$ : C, 56.56; H, 6.35. Found: C, 56.11; H, 6.19%.

#### 4.3. Synthesis of $[(Cp_2^*Nb)_2(1,4-(\kappa^2-O,O'-OOC)_2(C_6H_4))]$ (**4**), $[(Cp_2^*Nb)_2(1,3-(\kappa^2-O,O'-OOC)_2(C_6H_4))]$ (**5**) and $[(Cp_2^*Nb)_3(1,3,5-(\kappa^2-O,O'-OOC)_3(C_6H_3))]$ (**6**)

A mixture of  $Cp_2^*NbH_3$  (**1**) (0.28 g; 0.75 mmol) and the corresponding carboxylic acid  $[1,4-(HOOC)_2(C_6H_4)]$  (0.15 g; 0.75 mmol) was stirred with dry THF (30 mL) at 50 °C for 5 h. The solution became dark green in colour and the solvent was evaporated to dryness under vacuum. The dark green oily residue was extracted with hexane (10 mL). The resulting solution was filtered and evaporated to dryness. Complex **4** was isolated as a dark green solid (90% yield). Complexes **5** and **6** were prepared in a similar way.

**4**: IR (Nujol/PET  $cm^{-1}$ ) ( $\nu COO_{asym}^-$ ) 1646, ( $COO_{sym}^-$ ) 1529.  $^1H$  NMR ( $CO(CD_3)_2$ ):  $\delta$  -0.03 (s, 36H,  $SiMe_3$ ), 4.52, 5.83 (8 H each a complex signal,  $C_5H_4SiMe_3$ ), 7.50 (s, 4H,  $H_o$ ,  $C_6H_4$ ).  $^{13}C\{^1H\}$  NMR ( $CO(CD_3)_2$ ):  $\delta$  0.4 ( $SiMe_3$ ), 96.0 ( $C^1$ ,  $C_5H_4SiMe_3$ ), 105.1, 108.1 ( $C^{2-5}$ , exact assignment not possible,  $C_5H_4SiMe_3$ ), 128.7 and 135.9 ( $C_6H_4$ ), 205.5 ( $COO^-$ ). Anal. Calc. for  $C_{40}H_{62}Nb_2Si_4O_4$ : C, 54.24; H, 5.65. Found: C, 53.97; H, 5.55%.

**5**: IR (Nujol/PET  $cm^{-1}$ ) ( $\nu COO_{asym}^-$ ) 1648, ( $COO_{sym}^-$ ) 1527.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  0.00 (s, 36H,  $SiMe_3$ ), 4.12, 5.62 (8 H each a complex signal,  $C_5H_4SiMe_3$ ), 6.72 (t,  $^3J_{H-H} = 8.0$  Hz, 1H,  $H_m$ ,  $C_6H_4$ ), 7.70 (d,  $^3J_{H-H} = 7.7$  Hz, 2H,  $H_o$ ,  $C_6H_4$ ), 8.31 (s, 1H,  $H_p$ ,  $C_6H_4$ ).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ ):  $\delta$  0.4 ( $SiMe_3$ ), 94.5 ( $C^1$ ,  $C_5H_4$ ), 104.6, 107.5 ( $C^{2-5}$ , exact assignment not possible,  $C_5H_4SiMe_3$ ), 127.0, 129.0, 132.2 and 132.5 ( $C_6H_4$ ), 188.9 ( $COO^-$ ). Anal. Calc. for  $C_{40}H_{62}Nb_2Si_4O_4$ : C, 54.24; H, 5.65. Found: C, 54.04; H, 5.55%.

**6**: IR (Nujol/PET  $cm^{-1}$ ) ( $\nu COO_{asym}^-$ ) 1605, ( $COO_{sym}^-$ ) 1531.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  -0.02 (s, 54H,  $SiMe_3$ ), 4.06, 5.58 (12 H each a complex signal,  $C_5H_4SiMe_3$ ), 8.40 (s, 3H,  $C_6H_3$ ).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ ):  $\delta$  0.3 ( $SiMe_3$ ), 94.5 ( $C^1$ ,  $C_5H_4$ ), 104.7, 107.5 ( $C^{2-5}$ , exact assignment not possible,  $C_5H_4SiMe_3$ ), 132.2 and 132.5 ( $C_6H_3$ ), 187.6 ( $COO^-$ ). Anal. Calc. for  $C_{57}H_{100}Nb_3O_6Si_6$ : C, 52.30; H, 6.19. Found: C, 52.12; H, 6.10%.

#### 4.4. Synthesis of $[Cp_2^*Nb(\kappa^1-O-OOC(C_6H_5))(xylylNC)]$ (**7**)

##### 4.4.1. Method A

A mixture of  $[Cp_2^*Nb(H)(xylylNC)]$  (0.75 g; 2.25 mmol) and the carboxylic acid  $C_6H_5(COOH)$  (0.27 g; 2.25 mmol) was stirred with dry THF (30 mL) at room temperature for 3 h. The solution became green in colour and the solvent was evaporated to dryness under vacuum. The green oily residue was extracted with hexane (10 mL). The resulting solution was filtered and evaporated to dryness. Complex **7** was isolated as a green solid (90% yield).

##### 4.4.2. Method B

A mixture of  $Cp_2^*Nb(\kappa^2-O,O'-OOC(C_6H_5))$  (**3**) (0.13 g; 0.75 mmol) and  $CN(2,6-Me_2C_6H_3)$  (0.06 g; 0.75 mmol) was stirred with dry THF (30 mL) at room temperature for 3 h. The solution became green in colour and the solvent was evaporated to dryness under vacuum. The green oily residue was extracted with hexane (10 mL). The resulting solution was filtered and evaporated to dryness. Complex **7** was isolated as a green solid (82% yield): IR (Nujol/PET  $cm^{-1}$ ) ( $\nu C\equiv N$ ) 2068, ( $COO_{asym}^-$ ) 1712, ( $COO_{sym}^-$ ) 1450.  $^1H$  NMR ( $C_6D_6$ ):  $\delta$  0.02 (s, 18H,  $SiMe_3$ ), 2.35 (s, 6H,  $CN(2,6-Me_2C_6H_3)$ ), 4.99, 5.19, 5.57, 5.86 (2 H each a complex signal,  $C_5H_4SiMe_3$ ), 6.64 (s, 3H,  $CN(2,6-Me_2C_6H_3)$ ), 7.00 (t,  $^3J_{H-H} = 7.3$  Hz, 2H,  $H_m$ ,  $C_6H_5$ ), 7.13 (t,  $^3J_{H-H} = 7.3$  Hz, 1H,  $H_p$ ,  $C_6H_5$ ), 8.14 (d,  $^3J_{H-H} = 7$  Hz, 2H,  $H_o$ ,  $C_6H_5$ ).  $^{13}C\{^1H\}$  NMR ( $C_6D_6$ ):  $\delta$  0.1 ( $SiMe_3$ ), 19.1 ( $CN(2,6-Me_2C_6H_3)$ ), 93.9 ( $C^1$ ,  $C_5H_4$ ), 96.7, 101.1, 104.2, 109.6 ( $C^{2-5}$ , exact assignment not possible,  $C_5H_4SiMe_3$ ), 126.5, 129.8, 130.3 and 130.7 ( $CN(2,6-Me_2C_6H_3)$ ), 132.9, 133.1 and 135.3 ( $C_6H_5$ ), 175.6 ( $COO^-$ ), 208.2 ( $CN(2,6-Me_2C_6H_3)$ ). Anal. Calc. for  $C_{32}H_{43}NNb_2O_2Si_4$ : C, 62.04; H, 6.46; N, 2.26. Found: C, 61.89; H, 6.32; N, 2.32%.

#### 4.5. Synthesis of $[(Cp_2^*Nb(xylylNC))_2(1,4-(\kappa^1-O-OOC)_2(C_6H_4))]$ (**8**)

A mixture of  $[(Cp_2^*Nb)_2(1,4-(\kappa^2-O,O'-OOC)_2(C_6H_4))]$  (**4**) (0.13 g; 0.75 mmol) and  $CN(2,6-Me_2C_6H_3)$  (0.19 g; 1.50 mmol) was stirred with dry THF (30 mL) at room temperature for 3 h. The solution became green in colour and the solvent was evaporated

to dryness under vacuum. The green oily residue was extracted with hexane (10 mL). The resulting solution was filtered and evaporated to dryness. Complex **8** was isolated as a green solid (82% yield): IR (Nujol/PET  $\text{cm}^{-1}$ )  $\nu(\text{CN})$  2062,  $(\text{COO}^-_{\text{asym}})$  1698,  $(\text{COO}^-_{\text{sym}})$  1453.  $^1\text{H}$  NMR ( $\text{CO}(\text{CD}_3)_2$ ):  $\delta$  0.12 (s, 36H,  $\text{SiMe}_3$ ), 2.23 (s, 12H,  $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ ), 5.21, 5.45, 5.55, 5.95 (4H, each a complex signal,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 6.80 (s, 6H,  $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ ), 8.19 (s, 4H,  $\text{C}_6\text{H}_4$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CO}(\text{CD}_3)_2$ ):  $\delta$  0.3 ( $\text{SiMe}_3$ ), 19.2 ( $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ ), 94.9, 97.2, 101.7, 110.3 ( $\text{C}^{2-5}$ , exact assignment not possible,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 104.7 ( $\text{C}^1$ ,  $\text{C}_5\text{H}_4$ ), 128.6, 128.7, 128.9 and 129.7 ( $\text{C}_6\text{H}_4$ ), 127.2, 130.2, 133.4 and 138.9 ( $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ ), 174.2 ( $\text{COO}^-$ ), 209.9 ( $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ ). Anal. Calc. for  $\text{C}_{58}\text{H}_{80}\text{N}_2\text{Nb}_2\text{O}_4\text{Si}_4$ : C, 60.00; H, 6.38; N, 2.69. Found: C, 59.56; H, 6.09; N, 2.41%.

#### 4.6. Synthesis of $[(\text{Cp}'_2\text{Nb}(\text{xylylNC}))_3(1,3,5\text{-}(\kappa^1\text{-O}, \text{O}'\text{-OOC})_3(\text{C}_6\text{H}_3))] (\mathbf{9})$

A mixture of  $[(\text{Cp}'_2\text{Nb})_3(1,3,5\text{-}(\kappa^2\text{-O}, \text{O}'\text{-OOC})_3(\text{C}_6\text{H}_3))]$  (**6**) (0.16 g; 0.75 mmol) and  $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$  (0.29 g; 2.25 mmol) was stirred with dry THF (30 mL) at room temperature for 3 h. The solution became green in colour and the solvent was evaporated to dryness under vacuum. The green oily residue was extracted with hexane (10 mL). The resulting solution was filtered and evaporated to dryness. Complex **9** was isolated as a green solid (87% yield): IR (Nujol/PET  $\text{cm}^{-1}$ )  $\nu(\text{C}\equiv\text{N})$  2046,  $(\text{COO}^-_{\text{asym}})$  1629,  $(\text{COO}^-_{\text{sym}})$  1387.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.10 (s, 54H,  $\text{SiMe}_3$ ), 2.43 (s, 18H,  $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ ), 5.05, 5.21, 5.51, 5.73 (6H, each a complex signal,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 6.80 (m, 9H,  $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ ), 8.82 (s, 3H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.3 ( $\text{SiMe}_3$ ), 19.4 ( $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ ), 93.9, 96.6, 100.8, 109.9 ( $\text{C}^{2-5}$ , exact assignment not possible,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 104.6 ( $\text{C}^1$ ,  $\text{C}_5\text{H}_4$ ), 127.5 and 129.2 ( $\text{C}_6\text{H}_3$ ), 133.1, 133.6 and 137.3 ( $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ ), 174.4 ( $\text{COO}^-$ ), 212.5 ( $\text{CN}(2,6\text{-Me}_2\text{C}_6\text{H}_3)$ ). Anal. Calc. for  $\text{C}_{84}\text{H}_{127}\text{N}_3\text{Nb}_3\text{O}_6\text{Si}_6$ : C, 59.25; H, 6.35; N, 2.82. Found: C, 59.43; H, 6.55; N, 2.71%.

#### 4.7. Synthesis of $[(\text{Cp}'_2\text{Nb}(\eta^1\text{-C}, \kappa^1\text{-S}-\text{CS}_2))_3(1,3,5\text{-}(\kappa^1\text{-O}-\text{OOC})_3(\text{C}_6\text{H}_3))] (\mathbf{10})$

A mixture of  $[(\text{Nb}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2)_3(1,3,5\text{-}(\kappa^2\text{-O}, \text{O}-\text{OOC})_3(\text{C}_6\text{H}_3))]$  (**6**) (0.16 g; 0.75 mmol) and an equimolar quantity of  $\text{CS}_2$  (0.14 mL; 2.25 mmol) was stirred with dry THF (30 mL) at room temperature for 3 h. The solution became green in colour and the solvent was evaporated to dryness under vacuum. The green oily residue was extracted with hexane (10 mL). The resulting solution was filtered and evaporated to dryness. Complex **10** was isolated as a brown solid (70% yield): IR (Nujol/PET  $\text{cm}^{-1}$ )  $\nu(\text{COO}^-_{\text{asym}})$  1638,  $(\text{COO}^-_{\text{sym}})$  1408,

$(\text{C}=\text{S})$  1151.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ): 0.06 (s, 54H,  $\text{SiMe}_3$ ), 5.91, 6.20, 6.28, 6.44 (6 H each a complex signal,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 8.83 (s, 3H,  $\text{C}_6\text{H}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ ):  $\delta$  0.2 ( $\text{SiMe}_3$ ), 94.5 ( $\text{C}^1$ ,  $\text{C}_5\text{H}_4$ ), 102.3, 104.7, 106.8, 107.5 ( $\text{C}^{2-5}$ , exact assignment not possible,  $\text{C}_5\text{H}_4\text{SiMe}_3$ ), 134.0 ( $\text{C}_6\text{H}_3$ ), 136.9 ( $\text{C}_6\text{H}_5$ ), 182.2 ( $\text{COO}^-$ ), 250.2 ( $\text{CS}_2$ ). Anal. Calc. for  $\text{C}_{60}\text{H}_{100}\text{Nb}_3\text{O}_6\text{S}_6\text{Si}_6$ : C, 48.00; H, 1.93. Found: C, 48.43; H, 2.10%.

#### 4.8. X-ray Structure determination for compound **4**

Intensity data for compound **4** were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromator (Mo  $\text{K}\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) using an  $\omega/2\theta$  scan technique. The final unit cell parameters were determined from 25 well-centered reflections and refined by least-squares method. Absorption correction was made. The crystal data and details of the data collection and structure analysis are summarized in Table 3.

The structure was solved by direct methods using SHELXS computer program [13] and refined on  $F^2$  by full-matrix least-squares (SHELXL-97) [14]. All non-hydrogen atoms were refined with anisotropic thermal parameters for all compounds. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. Weights were optimized in the final cycles.

Table 3  
Crystal data and structure refinement for **4**

Formula	$\text{C}_{40}\text{H}_{56}\text{Nb}_2\text{O}_4\text{Si}_4$
$F_w$	889.03
$T$ (K)	200(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
$a$ ( $\text{\AA}$ )	7.470(1)
$b$ ( $\text{\AA}$ )	10.763(1)
$c$ ( $\text{\AA}$ )	14.456(1)
$\alpha$ ( $^\circ$ )	103.33(1)
$\beta$ ( $^\circ$ )	96.92(1)
$\gamma$ ( $^\circ$ )	91.48(1)
$V$ ( $\text{\AA}^3$ )	1121.0(2)
$Z$	1
$D_c$ ( $\text{g cm}^{-3}$ )	1.332
$\mu$ ( $\text{mm}^{-1}$ )	0.653
$F(000)$	466
Crystal dimensions (mm)	$0.2 \times 0.2 \times 0.3$
$\theta$ Range ( $^\circ$ )	2.14 to 28.11
Index ranges	$-9 \leq h \leq 9$ , $-14 \leq k \leq 13$ , $0 \leq l \leq 19$
Number of reflections measured	5611
Number of independent reflections	5401
Number of observed reflections	3071
Goodness-of-fit on $F^2$	0.987
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0649$ , $wR_2 = 0.1287$
Largest difference peak and hole ( $\text{e \AA}^{-3}$ )	0.761/−0.765

$$R_1 = \sum \|F_o\| - |F_c| / \sum |F_o|; wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)]^{0.5}$$

C16 and C17 are in disordered positions (0.54 and 0.63 population, respectively).

Crystallographic data for the structural analysis of **4** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Number 256606. 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 <http://www.ccdc.cam.ac.uk>).

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