Reactivity studies on a trihydride niobocene complex towards α,β-Unsaturated carboxylic acids

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A B S T R A C T

The reactions of the trihydride niobocene complex [NbCp'$_2$H$_3$] (Cp' = η^5-C$_5$H$_4$SiMe$_3$) (**1**) with different α,β-unsaturated carboxylic acids have been studied. The reactions with fumaric and maleic acids (**A** and **B**) gave a new dinuclear carboxylato-containing niobocene derivative [(NbCp'$_2$)$_2$(μ-κ^2O,O-OOC-CH$_2$-CH$_2$-COO-κ^2O,O)] (**2**), due to the occurrence of two processes, dihydrogen elimination and hydrogenation of the C=C bond of the α,β-unsaturated carboxylic acid. Likewise, the use of an α,β-unsaturated carboxylic acid derivative such as mono-methyl fumarate (ester) (**C**) gave the mononuclear [NbCp'$_2$(OOC-CH$_2$-CH$_2$-COOMe-κ^2O,O)] (**3**). When other α,β-unsaturated carboxylic acids with less activated alkenes were used, such as *trans*-cinnamic acid (**F**), (E)-2-methyl-3-phenylacrylic acid (**G**), cyclohex-1-ene-1-carboxylic acid (**H**), 3-methylbut-2-enoic acid (**I**), (E)-2-methylbut-2-enoic acid (**J**) or (E)-pent-2-enoic acid (**K**), only the complexes [NbCp'$_2$(OOCR-κ^2O,O)], (R = *trans*-CH=CHPh (**4**), *trans*-CMe = CHPh (**5**), 1-cyclohexenyl (**6**), (CH=CMe$_2$) (**7**), (*cis*-CMe = CHMe) (**8**), (*trans*-C(H) = CH-Et) (**9**)), were isolated, respectively, resulting from a process with dihydrogen elimination and the hydrogenation of the C=C bond do not takes place.

Treatment of **2**–**9** with CO (3 atm) promote that the coordination mode of the carboxylate ligand changes from (κ^2O,O-OOC-R) to (κ^1O-OOC-R) and yielding new carbonyl derivatives [(NbCp'$_2$)$_2$(μ-κ^1O-OOC-CH$_2$-CH$_2$-COO-κ^1O) (CO)$_2$] (**10**); and [NbCp'$_2$(OOCR-κ^1O) (CO)] (R = CH$_2$-CH$_2$-COOMe (**11**), *trans*-CH=CHPh (**12**), *trans*-CMe = CHPh (**13**), 1-cyclohexenyl (**14**), CH=CMe$_2$ (**15**), *cis*-CMe = CHMe (**16**) and R = *trans*-CH=CH-Et) (**17**)).

Reaction of **2** with O$_2$ afford a new diperoxo compound [{NbCp'$_2$(O$_2$-κ^2O,O)}$_2$ (μ-κ^1O-OOC-CH$_2$-CH$_2$-COO-κ^1O)](**19**), through a monoperoxo derivative [NbCp'$_2$(O$_2$-κ^2O,O) (μ-κ^1O-OOC-CH$_2$-CH$_2$-COO-κ^2O,O) NbCp'$_2$] (**18**). All the new complexes were characterized by usual IR and NMR spectroscopic methods and the crystal structure of **16** and **18** were determined by X-ray diffraction studies.

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1. Introduction

In the past years we have described several hydride-niobocene systems that have contributed to our knowledge of hydride compounds and their behavior [1]. In this area, we have reported the reactivity of some mono- and poly-hydride-niobocene complexes towards unsaturated molecules, such as CO$_2$, olefins or alkynes [1]. More recently, we have reported our results on the interaction between the trihydrideniobocene complex [NbCp'$_2$H$_3$)] (**1**) and

sterically demanding olefins such as *cis*- and *trans*-stilbene [2], Ph—CH=CH—Ph. In both cases, only one hydride-olefin-niobocene complex, i.e., [NbCp'$_2$(H) (*trans*-PhCH = CHPh-η^2C,C)], was obtained (Scheme 1) by coordination of the olefin to the niobium center and the hydrogenation product, Ph—CH$_2$—CH$_2$—Ph, was not detected in the reaction mixture.

It has also been reported that the hydridecarbonylniobocene complex [NbCp'$_2$(H) (CO)] reacts with *cis*- and *trans*-α,β-unsaturated carboxylic acids, HOOC—CH=CH—COOH, maleic or fumaric acids. In these cases, hydrogenation of the C=C bond takes place along with κ^1-O coordination of the carboxylato fragment, probably due to the use of an activated olefin with a carboxylic acid group [3] (see Scheme 2).

In contrast to the case described previously [4], an 'H···H'

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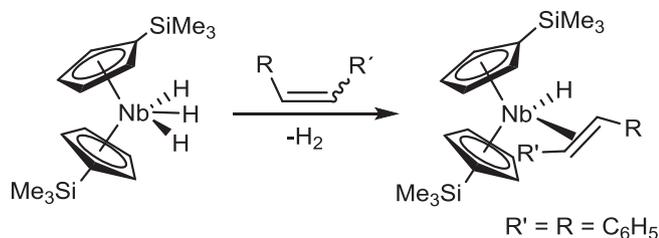
Scheme 1. Coordination of olefins to [NbCp'$_2$H$_3$] (1).

interaction was not observed between the complex fragment Nb–H and the carboxylic acid group.

In the work described here it was decided to explore the reactivity of the more hydrogen-rich niobocene derivative [NbCp'$_2$H$_3$)] (1) towards α,β-unsaturated carboxylic acids.

It is well known that the trihydride complex 1 belongs to the poly-hydride family known as a *'compressed hydride'* according to the "H···H" distances and H–Nb–H angles [5]. However, complex 1 can easily generate the coordinatively unsaturated 16-electron monohydride entity {[NbCp'$_2$H]} (1i) by thermolytic loss of H$_2$ (see Scheme 3) [6,7]. Due to the special chemical character of complex 1i, this niobocene intermediate has two-reactivity sites, see Scheme 3.

Moreover, the basic character of the hydride ligands in trihydride niobocene complex 1 has been demonstrated because, for example, in the presence of stronger organics acids, such as aromatic carboxylic acids (benzoic and terephthalic acids), compound 1 generates the corresponding (κ^2-O,O) carboxylato-containing niobocene complexes, probably due to the formation and release of dihydrogen [7] (see Scheme 3).

Therefore, the reaction of complex 1 with α,β-unsaturated carboxylic acids could provide information on which of the several rational processes occurs, namely (a) coordination of the olefin (similar to Scheme 1), (b) hydrogenation of the C=C bond [3] and κ^1-O coordination of the carboxylato fragment (similar to Scheme 2) or (c) proton transfer and H–H bond formation [6,7] between the −COOH group and the Nb–H moiety with formation of (κ^2-O,O) carboxylato-containing niobocene complexes (similar to Scheme 3).

A wide range of activated alkenes was used, such α,β-unsaturated carboxylic acids (A−K) (Fig. 1) with different electronic and steric characteristics.

2. Results and discussion

2.1. Synthesis of complexes

As a continuation of our previous studies [1−6], and taking into consideration our recent work on the reactivity of [NbCp'$_2$(H)(CO)] towards different α,β-unsaturated carboxylic acids,[3] we decided to study the reactivity of [NbCp'$_2$H$_3$] (1) towards the aforementioned carboxylic acids (see Scheme 4).

The reaction of 1 at 65 °C with maleic or fumaric acids (A or B) in a 2:1 niobocene/acid molar ratio gave rise in both cases to a new dinuclear alkylcarboxylato-niobocene complex [(NbCp'$_2$)$_2$(μ-κ^{2}O,O-OOC-CH$_2$-CH$_2$-COO-κ^{2}O,O)] (2) (see Scheme 4). Complex 2 was the same as that obtained when 1 reacted with butanedioic acid, HOOC−CH$_2$−CH$_2$−COOH, and this confirmed the hydrogenation of the C=C bond in complex 2.

The alkylcarboxylato-niobocene complex 2 was isolated as a green air-sensitive solid after the appropriate work-up (see Experimental Section).

The preparation of 2 required heating of the THF solution at 65 °C because the reaction do not take place at lower temperatures. The evolution of H$_2$ was observed during the reaction. It is noteworthy that in the reaction of 1 with maleic or fumaric acid, both carboxylic acid groups are involved in the process, regardless of whether a 1:1 or 2:1 niobocene/carboxylic acid molar ratio but when an 1:1 M ratio was used an unreacted mixture of 1 and 2 was obtained.

This result contrast with our previous study employing the [NbCp'$_2$(H)(CO)] complex [3], where only one of the COOH groups was activated and consequently, only a mononuclear niobocene derivatives was isolated [3] (see Scheme 2). However, in such process hydride-alkene or hydrogenation compounds do not were detected in the reaction mixture [1,3].

Reaction of complex 1 with the activated alkene *trans*-monomethyl fumarate (ester), MeOOC−CH=CH−COOH (C), at 65 °C in a
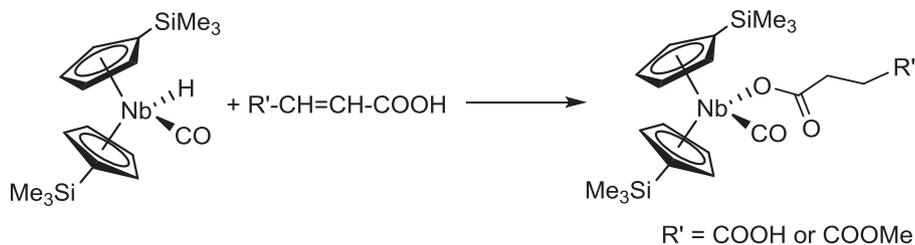
Scheme 2. Reaction of [NbCp'$_2$(H)(CO)] with unsaturated carboxylic acids.
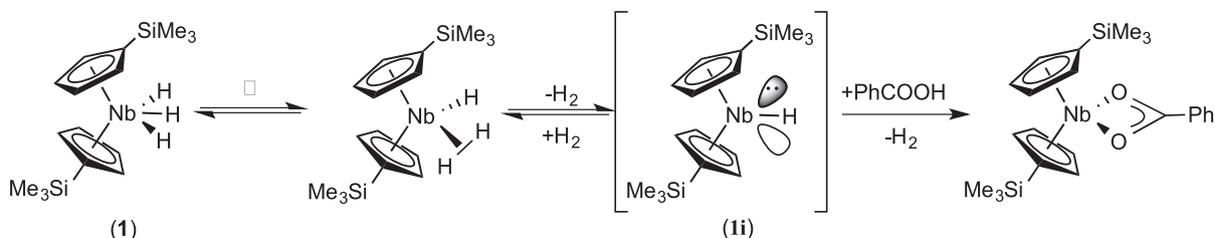
Scheme 3. Reaction of [NbCp'$_2$H$_3$] (1) with aromatic acids.

Fig. 1. α,β-Unsaturated carboxylic acids (A–K).
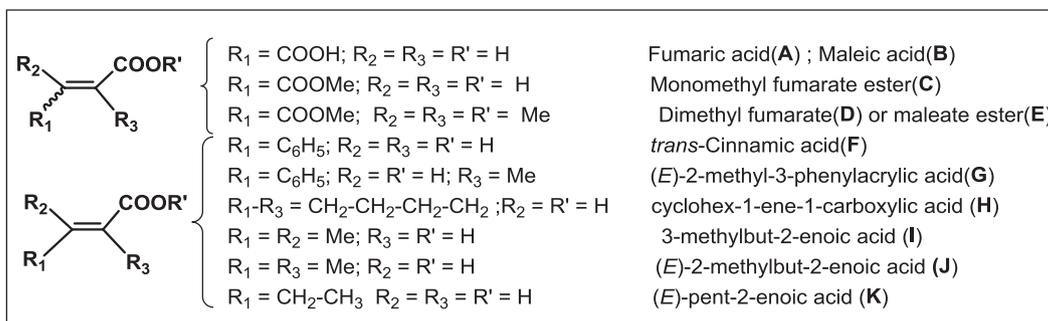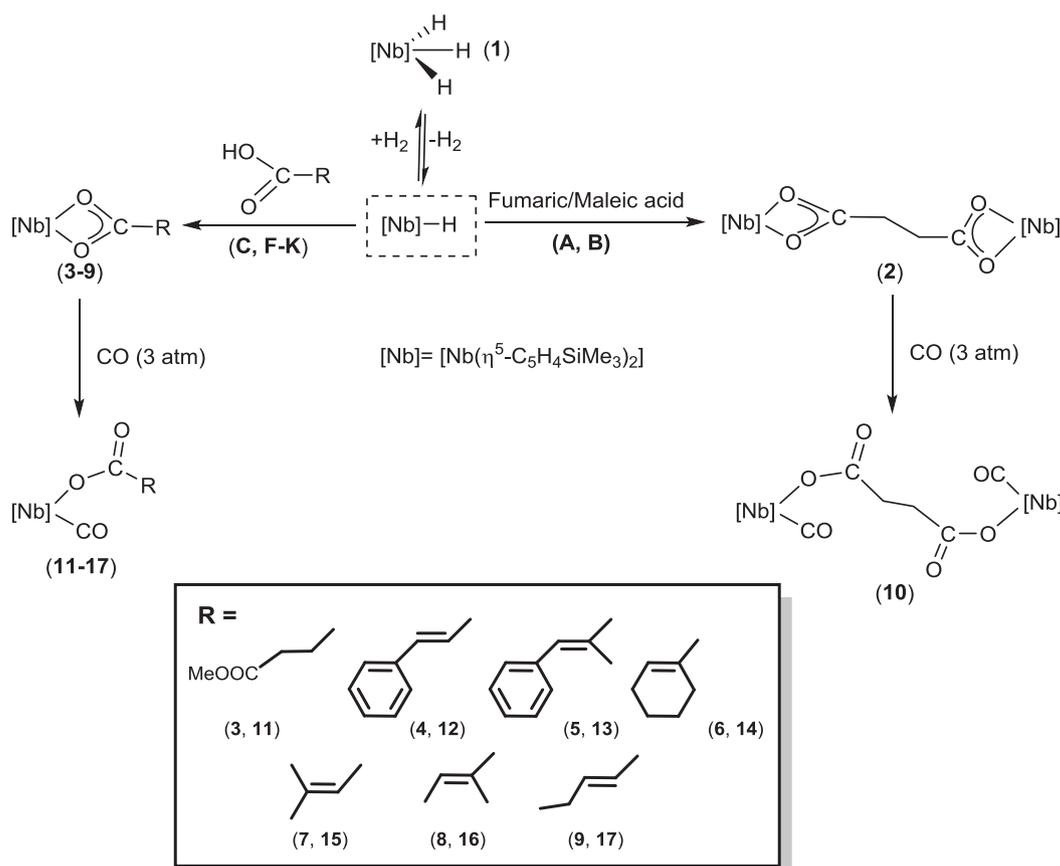

Scheme 4. Reaction of [NbCp'$_2$H$_3$] (**1**) with α,β-unsaturated carboxylic acids (**A–C**; **F–K**).

1:1 M ratio gave a green oily solid, in high yield, which was identified by NMR spectroscopy as [NbCp'$_2$(OOC-CH$_2$-CH$_2$-COOMe-κ^2O,O) (**3**) (see Scheme 4). Complex **3** could also be obtained by thermal treatment of [NbCp'$_2$(OOC-CH$_2$-CH$_2$-COOMe-κ^1O) (CO)] with CO elimination, as has been recently reported [3].

In an effort to understand this behavior, we decided to assess the reactivity of **1** with both dimethyl fumarate and dimethyl maleate (**D** and **E**, respectively). However, the result was unusual because a mixture of undefined products was obtained with total consumption of complex **1** and dimethyl succinate was not formed.

In order to ascertain whether phenyl substituents together with a −COOH functional group encourage the same behavior, α,β-unsaturated monocarboxylic acids **F** and **G**, namely *trans*-cinnamic acid **F** and (E)-2-methyl-3-phenylacrylic acid **G**, were employed

(see Fig. 2).
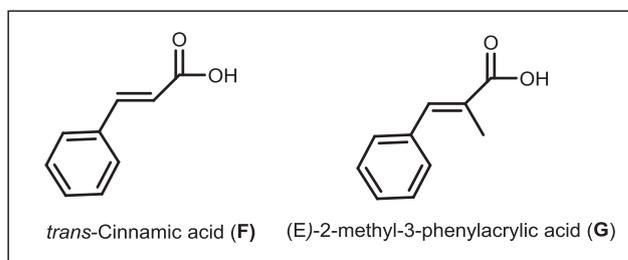
Fig. 2. α,β-Unsaturated monocarboxylic acids F and G.

The reaction of the trihydride complex **1** with these α,β-unsaturated monocarboxylic acids (**F** and **G**) is shown in Scheme 4. The reaction was carried out at 65 °C and a 1:1 M ratio was employed to give high yields of complexes [NbCp'$_2$(OOC-CR=CHPh-κ^2O,O)] R = H (**4**); CH$_3$ (**5**) with no hydrogenation of the olefin fragment.

In order to research whether alkene substituents size has some influence on the reactivity of the olefin moiety reactivity, the treatment of **1** with α,β-unsaturated monocarboxylic acids **H-K** in a 1:1 M ratio at 65 °C (see Scheme 4) was carried out. However, in this case only the carboxylato-containing niobocene complexes of the type were isolated, namely [NbCp'$_2$(OOCR-κ^2O,O], R = (1-cyclohexenyl) (**6**), CH=CMe$_2$ (**7**), *cis*-CMe=CHMe (**8**), *trans*-CH=CH-Et) (**9**) were isolated as green solids. This result indicates that the active organometallic species in the process must be the mono-hydrideniobocene intermediate **1i** [1−6] and not the trihydrideniobocene complex **1** (see Scheme 3). This was corroborated by the fact that the free di-hydrogen molecule was detected in the ^{1}H NMR spectrum of the reaction mixture and hydrogenation of the C=C bond do not take place.

In summary, regarding the diversity of α,β-unsaturated monocarboxylic acids used, three main groups can be highlighted. Firstly, when activated alkenes **A−C** were used the reaction proceeded by C=C double bond hydrogenation and coordination of the carboxylate fragment. In the second group, alkenes **F−K** only yielded carboxylic acid activation and formation of the carboxylate niobocene complexes. Finally, when the alkenes **D** and **E** were employed carboxylato niobocenes were not observed but complete consumption of the niobocene complex **1** did occur.

This reactivity differs to that previously reported [3], because the hydride carbonyl complex [NbCp'$_2$(H) (CO)] reacted only with type **A−C** activated alkenes types. However, in the case of olefins **F−K**, a protonation process in the Nb−H bond by the carboxylic acid was not observed. This behavior is consistent with the idea that strong acids must be employed to protonate the Nb−H bond in [NbCp'$_2$(H) (CO)] when compared with [NbCp'$_2$H$_3$] (**1**), probably because in this particular case the coordinately unsaturated {[NbCp'$_2$H]} (**1i**) intermediate is thermally accessible, which has the advantage of a vacant coordination site and a more accessible d^2 electron pair to react when compared to the case of the carbonyl derivative [1−6] (see Scheme 3).

Regarding the hydrogenation of the C=C double bond, it is well known that this only occurs when the alkene is previously coordinated to the metal center [8]. Nelson et al. reported a decisive study and established that the alkene addition to the metal center corresponds to a nucleophilic attack of the metal center to the C=C double bond system. In this study, it was concluded that it is possible to correlate high alkene hydrogenation relative rate values with higher alkene ionization potencials (IPs) and lower LUMO energy levels, thus confirming a nucleophilic metal center attack to the alkene. In addition, the highest alkene substitution corresponds to the highest IPs and lowest reaction rates. On the other hand, the presence of an electron-withdrawing group corresponds to a lower LUMO energy level and a higher hydrogenation rate [8].

It should be noted that when **F−K** were employed, the proton transfer final product corresponds to the favored process rather than C=C bond hydrogenation.

These results indicate the need for two **COOR** groups as alkene substituents, one of which must be a carboxylic acid group to interact with complex **1** and produce the C=C double bond hydrogenation process.

Some of us recently reported the reactivity of activated alkynes, e.g., ROOC−C≡C−COOR, with the organometallic hydridephosphiteniobocene derivative [NbCp'$_2$(H) (P(OMe)$_3$)] in an insertion process [9] that yielded the corresponding (E)-niobocene alkenyl complexes [NbCp'$_2$(C(COOR) = C(COOR)H) (P(OMe)$_3$)]. This hydride

reactivity was the first case reported in the literature in which a niobocene complex behaves as a σ-donor agent, i.e., a Lewis base, through the use of the lone electron pair at the Nb(III) metal center a situation in agreement with DFT studies.

In a similar way, the formation of complexes **2** and **3** can probably be understood only when very activated alkenes, **A−C**, interact strongly enough with intermediate **1i**, {[NbCp'$_2$H]}. The nucleophilic attack from the lone electron pair of the niobium center to the olefin-C$_\beta$ occurs due to the partial positive charge δ^+ as a consequence of the two electron-withdrawing groups present on the alkene (see Scheme 5, in which only one niobium center has been exemplified).

In the other alkenes, **F−K**, with only one carboxylic acid functional group, the higher electron density at C$_\beta$, when compared to the aforementioned compounds **A−C**, prevents nucleophilic attack of the metal center to the alkene unit. The final product corresponds to a similar carboxylate niobocene derivative, but in these cases the *proton transfer* is responsible for the final organometallic compound hindering the coordination of the C=C bond to the metal and thus hampering the hydrogenation (see Scheme 6).

All of the new complexes **2−9** described above were characterized spectroscopically. Infrared and, in particular, NMR spectroscopy proved to be useful techniques for the characterization of these carboxylato complexes [3−6]. In the IR spectra of the carboxylato-containing complexes the CO_2^- stretching frequencies were usually the most prominent feature. A commonly used approach has been to relate the $\Delta\nu$ values [the separation between $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$] with the mono- or bidentate character of the ligands [3]. The IR spectra of complexes **2−9** contain the CO_2^- bands corresponding to the $\nu_{asym}(CO_2^-)$ and ν_{sym} (CO_2^-) with $\Delta\nu$ values of *ca.* 90 cm^{-1}, which are consistent with the presence of a chelate bidentate carboxylato ligand [4−7]. Furthermore, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **2−9** confirmed the bidentate coordination of the carboxylato ligand [10]. In fact, the observation of two and three signals for each cyclopentadienyl ring in the ^{1}H and ^{13}C {^{1}H} NMR spectra, respectively, (see Experimental Section) indicates the presence of a symmetrical environment in those complexes. In addition, the ^{13}C{^{1}H} NMR spectra contain signals for the carboxylato carbon atoms at *ca.* 190 ppm. The most relevant difference between the spectra of complexes **2** and **3** and derivatives **4−9** is the absence, or presence, of a resonance in the typical region for the olefinic functional group, i.e., the CH=CH group. The spectra of complexes **2** contain one singlet at 1.53 ppm and 31,3 ppm in ^{1}H and ^{13}C{^{1}H} NMR spectra respectively and **3** two multiplets at 1.75 and 1.88 ppm and two signals at 27.8 and 31.8 ppm in ^{1}H and ^{13}C {^{1}H} NMR spectra respectively thus confirming the presence of two alkylic −CH$_2$− groups in the hydrogenated ligand (κ^2O,O-OOC-CH$_2$-CH$_2$-R). However, the spectra of derivatives **4−9** contain signals as multiplets at *ca.* 5.17 and 6.55 ppm and two singlets at *ca.* 120 and 140 ppm in the ^{1}H and ^{13}C{^{1}H} NMR spectra, respectively. These signals correspond to an olefinic group and this confirms the presence of the non-hydrogenated ligand, (κ^2-O,O-OOC-R), R = *trans*-CH=CHPh (**4**), *trans*-CMe = CHPh (**5**), 1-cyclohexenyl (**6**); CH=CMe$_2$ (**7**); *cis*-CMe = CHMe (**8**), *trans*-C) = CH-Et (**9**).

Complexes **2−9** are extremely air sensitive and even in the solid state they react with traces of residual oxygen to give a mixture of uncharacterized products.

However, a saturated hexane solution of **2** in the presence of air at −30 °C for 2 days changed from a green to a red color and a new complex **18** was isolated, alternatively, when the reaction conditions were maintained for 5 days, another new complex **19** was isolated as an air-sensitive yellow solid after the appropriate workup (see Scheme 7).

The new complexes **18** and **19** described above were characterized spectroscopically and the molecular structure of **18** was
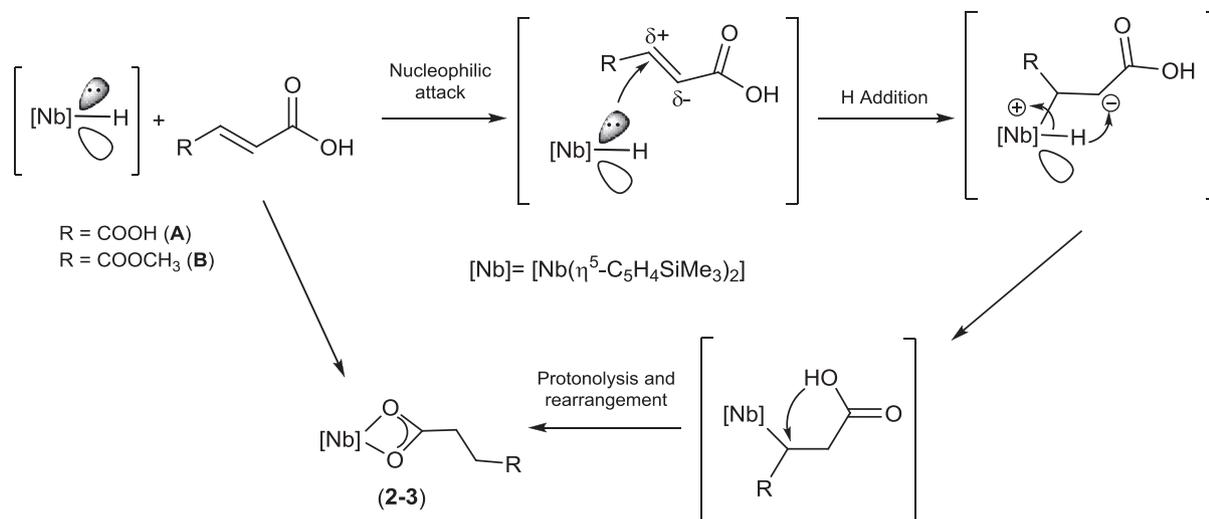
Scheme 5. Proposed mechanism for the reaction of [NbCp'$_2$H$_3$] (1) with α,β-unsaturated carboxylic acids.
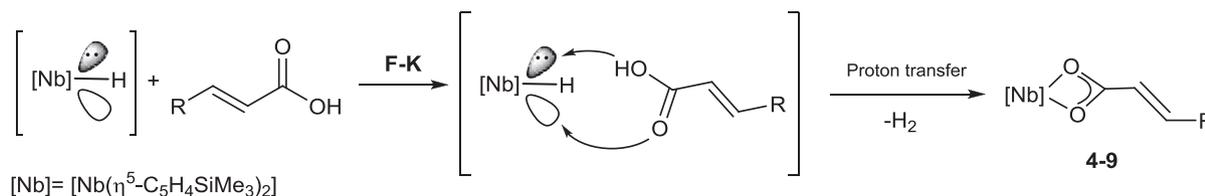
Scheme 6. Alternative proposed mechanism for the reaction of [NbCp'$_2$H$_3$] (1) with α,β-unsaturated carboxylic acids, without hydrogenation of the double bond.
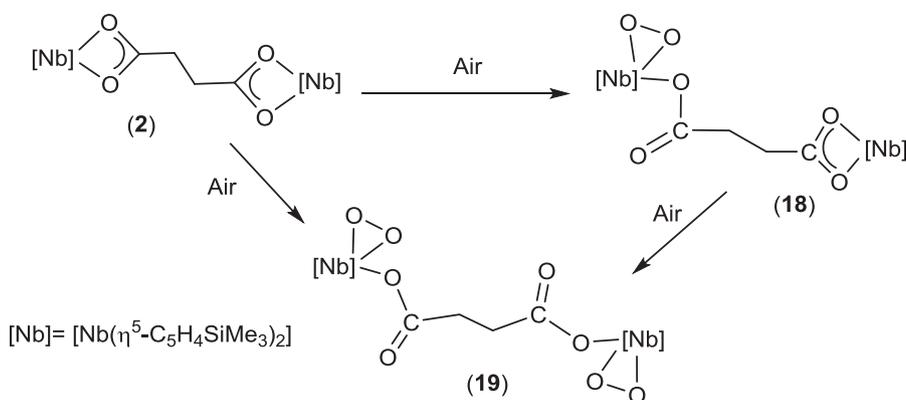
Scheme 7. Preparation of peroxo-containing complexes **18** and **19**.

determined by X-ray diffraction.

The IR spectrum of complex **18** contain broad CO_2^- bands corresponding to stretching frequencies of the $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$, with a $\Delta\nu$ value of 253 cm^{-1}, and these features are consistent with the presence of a monodentate carboxylato ligand and bands corresponding to stretching frequencies of the $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$, with a $\Delta\nu$ value of 95 cm^{-1}, and these features are consistent with the presence of a bidentate carboxylato ligand .[3] However **19** only display broad CO_2^- bands corresponding to stretching frequencies of the $\nu_{asym}(CO_2^-)$ and $\nu_{sym}(CO_2^-)$, with a $\Delta\nu$ value of 253 cm^{-1}, and these features are consistent with the presence of a monodentate carboxylato ligand Additionally, the absorption at *ca.* 876 cm^{-1} in the IR spectra must be assigned to the

ν(O−O) of a peroxo group [11,12], and the two additional absorptions at 523 and 545 cm^{-1} are probably due to ν_{asym}(Nb−O) and ν_{asym}(Nb−O), respectively. The spectra of complex **18** contain two triplets at ca. 2.02 and 2.32 ppm a and complex **19** contain one singlet at *ca.* 2.82 ppm in ^{1}H NMR spectra, confirming the presence of two −CH$_2$− groups in the hydrogenated ligand (κ^2O,O-OOC-CH$_2$-CH$_2$-R).

In complexes **2**−**9** the coordination mode of the carboxylato ligand can change from (κ^2-O,O-OOC-R) to (κ^1-O-OOC-R) upon exposure to CO (see Scheme 4). In fact, when **2**−**9** was dissolved in thf under CO (3 atm.) at room temperature a new family of carbonyl niobocene derivatives [(NbCp'$_2$)$_2$(μ−κ^1-O-OOC-CH$_2$-CH$_2$-COO-κ^1-O)(CO)$_2$] (**10**); [NbCp'$_2$(OOCR-κ^1O)(CO)] (R = CH$_2$-CH$_2$-COOMe (**11**)

trans-CH=CHPh (**12**), trans-CMe = CHPh (**13**), 1-cyclohexenyl (**14**), CH=CMe$_2$ (**15**), cis-CMe = CHMe (**16**) and R = trans-CH=CH-Et) (**17**)). were obtained as green solids (see Scheme 5). All of the new complexes **10**−**17** described above were characterized spectroscopically and the molecular structure of **16** was determined by X-ray diffraction.

The IR spectra of complexes **10**−**17** contain a strong signal corresponding to ν(CO) at ca. 1900 cm^{-1} and two CO$_2^-$ bands corresponding to ν_{asym}(CO$_2^-$) and ν_{sym} (CO$_2^-$) with $\Delta\nu$ values of ca. 250 cm^{-1}, which are consistent with the presence of a monodentate carboxylato ligand [3−6]. Furthermore, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **10**−**17** confirm the monodentate coordination of the carboxylato ligand [10]. In fact, the observation of four or five signals for each cyclopentadienyl ring in the ^{1}H and ^{13}C{^{1}H} NMR spectra, respectively, (see Experimental Section) indicates the presence of an unsymmetrical environment in those complexes. In addition, the ^{13}C{^{1}H} NMR spectra contain signals for the carboxylato carbon atoms at ca. 190 ppm and for the terminal CO at ca. 255 ppm.

2.2. X-ray crystal structure determination for complexes 16 and 18

The molecular structure of **16** was determined by X-ray diffraction. The ORTEP diagram of **16** is shown in Fig. 3. Selected bond distances and bond angles are listed in Table 1.

The structure of complex **16** consists of a mononuclear niobium metallocene linked to two cyclopentadienyl rings coordinated in a η^5 form to the niobium center, with a pseudo-tetrahedral environment adopted. The metal center is also linked to a carbonyl group and through κ^1 coordination to the carboxylate of (E)-2-methylbut-2-enoic acid. The distances and most important bond angles for complex **16** are provided in Table 3. The C3−C4 distance of 1.343(4) Å is typical for a C=C bond. The angle Cent1−Nb1−Cent2 is 139.4° and the Nb1−Cent1 and Nb1−Cent2 distances are both 2.06 Å, which is typical for a complex of Nb(III), as discussed previously. The Nb1−C1 distance of 2.058(4) Å is shorter than normal for a simple Nb−C bond (≈ 2.2 Å) [4,15]. The C1−O1 distance of 1.155(4) Å is longer than free CO (≈ 1.13 Å), as found in the other niobium(III) complexes, and this is indicative of significant back donation of the metal to the CO ligand [21,22], which is also in agreement with the Nb1−C1−O1 angle 175.9(3)°. The two cyclopentadienyl rings are eclipsed with the two groups SiMe$_3$ in a trans disposition.
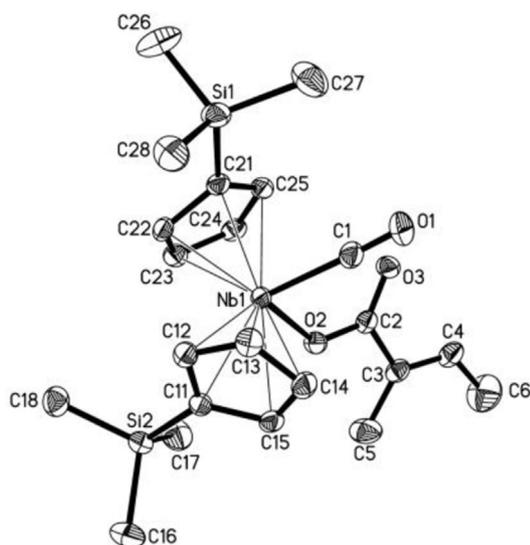
The X-ray molecular structure of complex **18** was determined from a red crystal suitable for X-ray diffraction. This X-ray crystal structure allowed us to corroborate an unexpected monoperoxoniobocene related with the dinuclear nature of complex **2**, which is bridged by a dicarboxylato moiety, and the hydrogenation of the C=C bond in the α,β-unsaturated ligand. The ORTEP diagram of **18** is shown in Fig. 4. Selected bond distances and bond angles are listed in Table 2.

The structure of **18** consists of an asymmetric binuclear niobium complex formed by two different niobocene moieties, [NbCp'$_2$(O$_2$-κ^2-O, O)] and [NbCp'$_2$], respectively, which are bridged by a dicarboxylato ligand. Each niobium atom is bound to two cyclopentadienyl rings in a η^5-mode in a distorted-tetrahedral geometry, which is characteristic of bent metallocenes. The Nb1 atom completes the coordination sphere with the carboxylato ligand in a κ^2-mode from a succinate ligand, which is bridging both niobium atoms and is bound to the Nb2 atom in a κ^1-coordination mode. A peroxo ligand in a κ^2-coordination mode completes the coordination sphere of the Nb2 atom.

The first difference between the two niobocene systems is the distance between the metal atom and the centroids of the Cp rings. For Nb1 these distances are 2.024 and 2.035 Å for centroids 1 and 2, respectively, and the angle Cent1−Nb1−Cent2 is 139.3° (Cent1 is the centroid of C11−C15 and Cent2 is the centroid of C21−C25); in Nb2 these distances are 2.135 and 2.132 Å for centroids 3 and 4, respectively, and the angle Cent3−Nb2−Cent4 is 127.8° (Cent3 is the centroid of C31−C35 and Cent4 is the centroid of C41−C45). These values are consistent with oxidation states (III) and (V) for Nb1 and Nb2, respectively [13−17], which is typical of analogous niobocene moieties described for mononuclear derivatives (see Table 3).

Complex **18** offers the opportunity to observe the structural differences arising from the addition of an oxygen molecule to a d^2 configuration in a bent niobocene system to give a d^0 configuration [12]. The enlargement of the Cent1−Nb1−Cent2 angle together with the shortening of the Nb1−centroid distances can be related to the increase in the number of d electrons. As observed previously, the distance between the metal atom and the centroid of the cyclopentadienyl ring decreases in a series of d^0-d^2 metallocene [M(η^5-C$_5$H$_5$)$_2$L$_2$] compounds, for a given ligand L, leading to stronger ring-ring and ligand-ring repulsions and, consequently, to larger ring-normal angles and narrower L−M−L angles [13−17]. The two oxygen atoms of the bidentate carboxylato ligand have similar Nb1−O bond distances (2.23(1) and 2.22(1) Å for O1 and O2, respectively) and these values are in reasonable agreement with those reported for the carboxylato ligands [7,18,19]. The other monodentate carboxylato ligand shows a κ^1 coordination mode with a Nb2−O4 bond distance of 2.10(1) Å. The κ^2-peroxo group is located in the plane that bisects the (Cp)$_2$Nb bent system with an O5−O6 bond distance of 1.40(1) Å, which is clearly longer than that in the free O$_2$ molecule. The Nb2−O5 and Nb2−O6 distances of 2.01(1) Å are consistent with a peroxo group coordinated to a Nb atom.

To the best of our knowledge, complex **18** represents the first molecular structure to be characterized by X-ray diffraction that contains a binuclear niobium entity in which each of the two niobium atoms has a different oxidation state [13−17]. At the same time, complex **18** is the first example in which two niobocene entities are bridged by a dicarboxylato ligand in κ^1 and κ^2 coordination modes simultaneously [7].

The importance of complex **18**, in addition to being one of the few peroxo-niobocenes for which an X-ray molecular structure has been reported [7,18,19], is that it adds to the chemistry of transition metal peroxo complexes.

Fig. 3. ORTEP diagram of complex **16** with thermal ellipsoids at 30% probability. H-atoms have been omitted for clarity.

Table 1
Selected bond distances and angles for compound **16**.

Bond distances (Å)		Bond angles (°)	
Nb1-O2	2.166(2)	C1-Nb1-O2	91.4(1)
Nb1-C1	2.058(4)	Nb1-C1-O1	175.9(3)
C1-O1	1.155(4)	O2-C2-O3	124.9(3)
C2-C3	1.521(4)	C2-C3-C4	117.4(3)
C3-C4	1.343(4)	C2-C3-C5	118.4(3)
Nb1-Cent1	2.06	C3-C4-C6	125.2(4)
Nb1-Cent2	2.06	Cent1-Nb1-Cent2	139.4

Cent1 and Cent2 are the centroids of C11—C15 and C21—C25, respectively.

Table 2
Selected bond distances and angles for compound **18**.

Bond distances (Å)		Bond angles (°)	
Nb1-O1	2.23(1)	O1-Nb1-O2	58.8(2)
Nb1-O2	2.22(1)	O4-Nb2-O5	75.6(3)
Nb2-O4	2.10(1)	O4-Nb2-O6	116.5(3)
Nb2-O5	2.01(1)	O5-Nb2-O6	40.9(3)
Nb2-O6	2.01(1)	O1-C1-O2	119.7(7)
O5-O6	1.40(1)	C1-C2-C3	114.0(8)
C2-C3	1.51(1)	C2-C3-C4	113.4(8)
Nb1-Cent1	2.024	O3-C4-O4	124.3(10)
Nb1-Cent2	2.035	C3-C4-O4	114.0(8)
Nb2-Cent3	2.135	Cent1-Nb1-Cent2	139.3
Nb2-Cent4	2.132	Cent3-Nb2-Cent4	127.8

Cent1, Cent2, Cent3 and Cent4 are the centroids of C11—C15, C21—C25, C31—C35 and C41—C45, respectively.
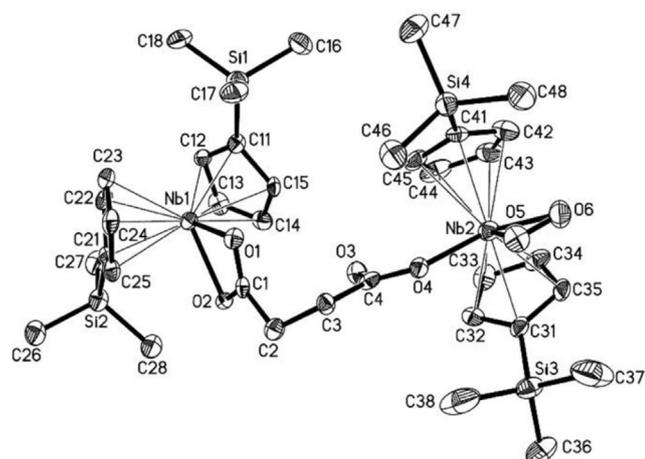
Fig. 4. ORTEP diagram of complex **18** with thermal ellipsoids at 30% probability. H-atoms have been omitted for clarity.

3. Concluding remarks

It was found that the reaction between [NbCp'$_2$H$_3$] **1** and α,β-unsaturated carboxylic acids takes place via two well-defined pathways with several steps depending of the nature of the substituents in the olefin moiety. In the case of activated alkenes, **A-C** hydrogenation of the olefin and coordination of the carboxylate group to the niobium center occur yielding **2** or **3**(see Scheme 5). Using less activated alkenes **F-K**, the mechanism is different, the hydrogenation of the C=C bond do no takes place and **4**—**9** were isolated(See Scheme 6).

The products are very air-sensitive, and this fact allowed us characterized by X-ray diffraction a new peroxo niobocene complex **18**, which is a member of an exclusive family of peroxo derivatives.

The reactions described above enable the synthesis of a new family of carboxylato niobocenes **2**—**9** with κ^2-O,O coordination and they can be easily transformed into the monodentate κ^1-O form **10**—**17** upon treatment with CO under mild conditions.

4. Experimental section

4.1. General procedures

All reactions were carried out using standard Schlenk techniques. Oxygen and water were excluded by the use of vacuum lines supplied with purified N$_2$. Hexane was distilled from Na/K alloy. THF was distilled from sodium benzophenone. All solvents were deoxygenated prior to use. Deuterated solvents were dried over 4 Å molecular sieves and degassed prior to use.

Table 3
Selected structural parameters for some niobocene complexes in oxidation states (III) or (V).

Complex		bond distances Nb—Cent (Å)	bond angles Cent1—Nb—Cent2 (°)	References
Nb(III)	[(NbCp'$_2$)$_2$\{μ−1,4-(OOC)$_2$(C$_6$H$_4$)-κ ^{2}O-O'\}]	2.019	140.3	[7]
	[NbCp'$_2$(SC(=S) PPh$_2$-κ^1S) (CO)]	2.076	137.9	[13]
	[NbCp'$_2$(P(I)Ph$_2$) (CO)]I$_3$	2.055	139.9	[13]
	[NbCp'$_2$(η^2-H$_2$BC$_8$H$_{14}$)]	2.038	140.5	[20]
Nb(V)	[Cp'$_2$Nb(O) (OOCCF$_3$-κ^1O)]	2.167	127.4	[14]
	[NbCp'$_2$(CH$_3$) (OCCPh$_2$-η^1C,κ^1O)	2.131	132.9	[15]
	[NbCp'$_2$(O)Me]	2.175	126.5	[12]
	[NbCp'$_2$Br(OCCPh$_2$-η^1C,κ^1O)]	2.110	129.0	[14]

Cp' = (η^5-C$_5$H$_4$SiMe$_3$).

[NbCp'$_2$H$_3$] (**1**) was prepared as described in the literature [23]. Fumaric acid, maleic acid, mono-methyl fumarate, *trans*-cinnamic acid, (E)-2-methyl-3-phenylacrylic acid, cyclohex-1-ene-1-carboxylic acid, 3-methylbut-2-enoic acid, (E)-2-methylbut-2-enoic acid and (E)-pent-2-enoic acid were used as supplied by Aldrich. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Innova 500 MHz spectrometer at room temperature unless stated otherwise. ^{1}H and ^{13}C{^{1}H} NMR chemical shifts (δ values) are given in ppm relative to the solvent signal (^{1}H, ^{13}C) or standard resonances. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer as Nujol/Polyethylene mulls. Microanalyses were carried out with a Perkin-Elmer 2400 microanalyzer.

4.2. Synthesis of [(nbcp'$_2$)$_2$(μ-κ^2O,O-OOC-CH$_2$-CH$_2$-COO-κ^2O,O)] (2)

4.2.1. Method 1

To a solution of **1** (0.20 g, 0.54 mmol) in anhydrous THF (50 mL) was added a stoichiometric quantity of fumaric acid (0.03 g, 0.27 mmol) (or maleic acid). The mixture was stirred at 65 °C for 3 h. During this time the solution changed color from violet to green/brown. The solvent was evaporated under vacuum to dryness. The green/brown oily residue was extracted with cold THF. After filtration, the resulting solution was evaporated under vacuum to afford a green solid, which corresponds to complex **2**. Yield: 95%. Complex **2** is soluble in polar solvents such as THF and acetone but has low solubility in solvents such as hexane and toluene.

4.2.2. Method 2

To a solution of **1** (0.20 g, 0.54 mmol) in anhydrous THF (50 mL) was added a stoichiometric quantity of succinic acid (0.03 g, 0.27 mmol). The mixture was stirred at 65 °C for 3 h. During this time the solution changed color from violet to green/brown. The solvent was evaporated under vacuum to dryness. The green/brown oily residue was extracted with cold THF. After filtration, the resulting solution was evaporated under vacuum to afford a green solid, which corresponded to complex **2**. Yield: 95%. Anal. Calcd for C$_{36}$H$_{56}$Nb$_2$O$_4$Si$_4$; C, 50.81; H, 6.63. Found: C, 50.75; H, 6.60.

IR (Nujol/Polyethylene): ν (cm^{-1}) 1641 (COO$^-$)$_{asym}$, 1554 (COO$^-$)$_{sym}$. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.01 (s, 36H, SiMe$_3$), 1.53 (s, 4H, CH$_2$), 4.14, 5.78 (m, 16H, exact assignment not possible, C$_5$H$_4$SiMe$_3$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.8 (SiMe$_3$), 31.3 (CH$_2$), 93.8 (C^1, C$_5$H$_4$SiMe$_3$), 104.7, 107.8, (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 196.4 (COO).

4.3. Synthesis of [NbCp'$_2$OOC-CH$_2$-CH$_2$-COOMe-κ^2O,O] (3)

To a solution of **1** (0.20 g, 0.54 mmol) in anhydrous THF (50 mL) was added an equimolar quantity of *trans*-mono-methyl fumarate (0.07 g, 0.54 mmol). The mixture was stirred at 65 °C for 3 h. During this time the solution changed color from violet to green/brown. The solvent was evaporated under vacuum to dryness. The green/brown oily residue was washed with cold hexane to give complex **3**. Yield: 95%.

IR (Nujol/Polyethylene): ν(cm^{-1}); 1741 (COOMe)$_{asym}$, 1682 (COOMe)$_{sym}$, 1644 (COO$^-$)$_{asym}$, 1553 (COO$^-$)$_{sym}$. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.01 (s, 18H, SiMe$_3$), 1.75 (m, 2H, CH$_2$), 1.88 (m, 2H, CH$_2$), 3.25 (s, 3H, CH$_3$), 4.22, 5.76 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.5 (SiMe$_3$), 27.8(CH$_2$), 31.8 (CH$_2$), 51.1 (CH$_3$), 93.0 (C^1, C$_5$H$_4$SiMe$_3$), 104.7, 107.4 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 172.4 (COOMe), 188.5 (COO).

4.4. Synthesis of complexes 4–9

To a solution of **1** (0.20 g, 0.54 mmol) in anhydrous THF (50 mL) was added an equimolar quantity of the corresponding acids; (*trans*-cinnamic acid (0.08 g, 0.54 mmol) to prepare **4**; (E)-2-methyl-3-phenylacrylic acid (0.08 g, 0.54 mmol) to prepare **5**; cyclohex-1-ene-1-carboxylic acid (0.07 g, 0.54 mmol) to prepare **6**; 3-methylbut-2-enoic acid (0.05 g, 0.54 mmol) to prepare **7**; (E)-2-methylbut-2-enoic acid (0.05 g, 0.54 mmol) to prepare **8** or (E)-pent-2-enoic acid (0.05 g, ρ = 0.99 g/mL, 54.60 μL, 0.54 mmol) to prepare **9**). The mixture was stirred at 65 °C for 3 h. During this time the solution changed color from violet to green/brown. The solvent was evaporated under vacuum to dryness. The green/brown oily residue was washed with cold hexane to give complexes **4**–**9**, in all cases as green solids.

[NbCp'$_2$(OOC(*trans*-CH = CHPh)-κ^2O,O)] (4). Yield: 90%. Anal. Calcd. for C$_{25}$H$_{33}$NbO$_2$Si$_2$; C, 58.12; H, 6.83. Found: C, 58.01; H, 6.93. IR (Nujol/Polyethylene): ν(cm^{-1}); 1641 (COO$^-$)$_{asym}$, 1579 (COO$^-$)$_{sym}$, 1472 (C=C). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.07 (s, 18H, SiMe$_3$), 4.26, 5.76 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 5.78 (d, 1H, $^3J_{HaHb}$ = 16.13 Hz, CH), 6.83–6.90 (m, 5H, C$_6$H$_5$), 7.33 (d, 1H, $^3J_{HaHb}$ = 16.13 Hz, CH). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.8 (SiMe$_3$), 94.0 (C^1, C$_5$H$_4$SiMe$_3$), 104.6, 107.5 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 120.4 (CH=CH−COO), 127.8–130.1 (C$_6$H$_5$), 143.6 (CH-COO),190.9 (COO).

[NbCp'$_2$(OOC(*trans*-CMe = CHPh)-κ^2O,O)] (5). Yield: 90%. Anal. Calcd. for C$_{26}$H$_{35}$NbO$_2$Si$_2$; C, 58.96; H, 6.85. Found: C, 58.94; H, 6.80. IR (Nujol/Polyethylene): ν(cm^{-1}); 1641 (COO$^-$)$_{asym}$, 1536 (COO$^-$)$_{sym}$, 1471 (C=C). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.08 (s, 18H, SiMe$_3$), 1.77 (s, 3H, CH$_3$), 4.25, 5.71 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 7.51 (s, 1H, CH), 6.93–7.03 (m, 5H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.8 (SiMe$_3$), 12.9, (CH$_3$), 94.2 (C^1, C$_5$H$_4$SiMe$_3$), 104.6, 107.3 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 129.6 (C(CH$_3$)-COO), 127.9–130.1 (C$_6$H$_5$), 137.9 (CH=C(CH$_3$)-COO) 192.6 (COO).

[NbCp'$_2$(OOC(1-cyclohexenyl)-κ^2O,O] (6). Yield: 85%. Anal. Calcd. for C$_{23}$H$_{35}$NbO$_2$Si$_2$; C, 55.96; H, 7.35. Found: C, 56.01; H, 7.22. IR (Nujol/Polyethylene): ν(cm^{-1}); 1653 (COO$^-$)$_{asym}$, 1529 (COO$^-$)$_{sym}$, 1469 (C=C). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.07 (s, 18H, SiMe$_3$), 1.12, 1.21, 1.62, 1.94 (m, 8H, CH$_2$), 4.22, 5.68 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 6.64 (m, 1H, CH). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.6 (SiMe$_3$), 21.7, 22.1, 23.3, 25.6 (CH$_2$), 94.0, (C^1, C$_5$H$_4$SiMe$_3$), 104.3, 107.1 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 132.3 (C-COO), 138.5 (CH), 192.0 (COO).

[NbCp'$_2$(OOC(CH = CMe$_2$)-κ^2O,O)] (7). Yield: 90%. Anal. Calcd. for C$_{21}$H$_{33}$NbO$_2$Si$_2$; C, 54.06; H, 7.13. Found: C, 53.93; H, 7.02. IR (Nujol/Polyethylene): ν(cm^{-1}); 1650 (COO$^-$)$_{asym}$, 1526 (COO$^-$)$_{sym}$, 1470 (C=C). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.05 (s, 18H, SiMe$_3$), 1.24 (s, 3H, CH$_3$), 1.76 (s, 3H, CH$_3$), 4.23, 5.70 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 5.03 (s, 1H, CH). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.5 (SiMe$_3$), 10.6, 13.6 (CH$_3$), 93.0, (C^1, C$_5$H$_4$SiMe$_3$), 104.3, 107.1 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 155.4 (C-COO), 119.1 (CH), 192.1 (COO).

[NbCp'$_2$(OOC(*cis*-CMe = CHMe)-κ^2O,O)] (8). Yield: 92%. Anal. Calcd. for C$_{21}$H$_{33}$NbO$_2$Si$_2$; C, 54.06; H, 7.13. Found: C, 54.01; H, 7.11. IR (Nujol/Polyethylene): ν(cm^{-1}); 1658 (COO$^-$)$_{asym}$, 1529 (COO$^-$)$_{sym}$, 1465 (C=C). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.06 (s, 18H, SiMe$_3$), 1.19 (d, 3H, $^3J_{HaHb}$ = 7.03 Hz, CH$_3$), 1.41 (s, 3H, CH$_3$), 4.21, 5.62 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 6.51 (q, 1H, $^3J_{HaHb}$ = 7.03 Hz, CH). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.6 (SiMe$_3$), 10.6, 13.6 (CH$_3$), 94.0 (C^1, C$_5$H$_4$SiMe$_3$), 104.3, 107.1 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 130.4 (C-COO), 136.1 (CH), 192.4 (COO).

[NbCp'$_2$(OOC(*trans*-C(H) = CH-Et)-κ^2O,O)] (9). Yield: 95%. Anal. Calcd. for C$_{21}$H$_{33}$NbO$_2$Si$_2$; C, 54.06; H, 7.13. Found: C, 54.00; H, 7.10. IR (Nujol/Polyethylene): ν(cm^{-1}); 1644 (COO$^-$)$_{asym}$, 1553 (COO$^-$)$_{sym}$, 1468 (C=C). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.04 (s,

18H, SiMe$_3$), 1.56 (m, 2H, CH$_2$), 0,53 (t, 3H, $^3J_{HH} = 6.55$ Hz, CH$_3$), 5.17 (dt, 1H, $^3J_{HH} = 15.67$ Hz, $^4J_{HH} = 1.65$ Hz, CH), 4.22, 5.76 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 6.55 (dt, 1H, $^3J_{HH} = 15.76$ Hz, $^3J_{HH} = 6.55$ Hz, CH). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.3 (SiMe$_3$), 11.7 (CH$_3$), 24.7 (CH$_2$), 93.6 (C^1, C$_5$H$_4$SiMe$_3$), 104.7, 107.4 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$),122.8(CH-Et), 149.3(CH-COO) 190.9 (COO).

4.5. Synthesis of complexes 10–17

After stirring the corresponding mixture, a thf solution of **2** was saturated with CO at 3 atm. in a Fisher−Porter bottle and stirred at room temperature for 1 d green solutions were formed and these were evaporated to dryness. The residues were washed with cold hexane and complex **10** was isolated as green solid.

[(NbCp'$_2$)$_2$(μ−κ^1O-OOC-CH$_2$-CH$_2$-COO-κ^1O) (CO)$_2$] (10). Yield: 95%. Anal. Calcd. for C$_{38}$H$_{56}$Nb$_2$O$_6$Si$_4$; C, 50.32H, 6.22. Found: C, 50.23; H, 6.14. IR (Nujol/Polyethylene): ν (cm^{-1}) 1914 (CO), 1627 (COO$^-$)$_{asym}$, 1302 (COO$^-$)$_{sym}$. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.17 (s, 36H, SiMe$_3$), 2.30 (s, 4H, CH$_2$), 4.87, 4.88, 5.07, 5.26 (m, 16H, exact assignment not possible, C$_5$H$_4$SiMe$_3$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.8 (SiMe$_3$), 33.8 (CH$_2$), 97.3 (C^1, C$_5$H$_4$SiMe$_3$), 94.6, 102.4, 106.2, 106.5, (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 180.0 (COO), 250 (CO).

Complexes **11** to **17** were prepared in a similar way to complex **10**. After stirring the corresponding mixtures, a thf solution of **3**−**9** saturated with CO at 3 atm. in a Fisher−Porter bottle was stirred for 1 d to give complexes **11** to **17**, respectively, with an average yield of 95%.

[NbCp'$_2$(OOCCH$_2$-CH$_2$-COOMe-κ^1O) (CO)] (11). Yield: 95%. Anal. Calcd. for C$_{22}$H$_{33}$NbO$_5$Si$_2$; C, 50.18H, 6.32. Found: C, 50.26; H, 6.28. IR (Nujol/Polyethylene): ν(cm^{-1}); 1914 (CO), 1741 (COOMe)$_{asym}$, 1683 (COOMe)$_{sym}$, 1645 (COO$^-$)$_{asym}$, 1304 (COO$^-$)$_{sym}$. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.12 (s, 18H, SiMe$_3$), 2.30, (m, 2H, CH$_2$), 2.41 (m, 2H, CH$_2$), 3.31 (s, 3H, CH$_3$), 4.78, 5.01, 5.14, 5.41 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); −0.04 (SiMe$_3$), 30.3, 32.5 (CH$_2$), 51.1 (CH$_3$), 95.0 (C^1, C$_5$H$_4$SiMe$_3$), 97.5, 102.2, 106.7, 106.9 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 173.6 (COOMe), 180.4 (COO), 254.7 (CO).

[NbCp'$_2$(OOC(trans-CH = CHPh)-κ^1O) (CO)] (12). Yield: 90%. Anal. Calcd. for C$_{26}$H$_{33}$NbO$_3$Si$_2$; C, 57.55; H, 6.13. Found: C, 58.01; H, 6.93. IR (Nujol/Polyethylene): ν(cm^{-1}); 1914 (CO), 1642 (COO$^-$)$_{asym}$, 1375 (COO$^-$)$_{sym}$, 1470 (C=C). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.10 (s, 18H, SiMe$_3$), 4.79, 5.07, 5.10, 5.31 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 6.62 (m, 1H, CH), 6.66 (m, 1H, CH), 6.94, 7.27, 7.64 (m, 5H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.1 (SiMe$_3$), 95.0 (C^1, C$_5$H$_4$SiMe$_3$), 97.8, 103.6, 105.3, 107.5 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 125.9 (CH-COO), 128.7−136.7 (C$_6$H$_5$), 139.5 (CH=CH-COO) 173.7 (COO), 255.4 (CO).

[NbCp'$_2$(OOC(trans-CMe = CHPh)-κ^1O) (CO)] (13). Yield: 90%. Anal. Calcd. for C$_{27}$H$_{35}$NbO$_3$Si$_2$; C, 58.15; H, 6.51. Found: C, 58.22; H, 6.55. IR (Nujol/Polyethylene): ν(cm^{-1}); 1911 (CO), 1641 (COO$^-$)$_{asym}$, 1470 (C=C), 1377 (COO$^-$)$_{sym}$. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.09 (s, 18H, SiMe$_3$), 2.22 (s, 3H, CH$_3$), 4.77, 5.03, 5.13, 5.31 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 7.07 (s, 1H, CH), 6.98−7.72 (m, 5H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.1 (SiMe$_3$), 15.8 (CH$_3$), 95.1 (C^1, C$_5$H$_4$SiMe$_3$), 97.4, 104.6, 105.0, 107.3 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 128.0 (CH=C(CH$_3$)-COO), 128.4−134.5 (C$_6$H$_5$), 138.4 (C(CH$_3$)-COO), 175.7 (COO), 255.6 (CO).

[NbCp'$_2$(OOC(1-cyclohexenyl)-κ^1O) (CO)] (14). Yield: 85%. Anal. Calcd. for C$_{24}$H$_{35}$NbO$_3$Si$_2$; C, 55.26; H, 6.96. Found: C, 55.01; H, 7.12. IR (Nujol/Polyethylene): ν(cm^{-1}); 1910 (CO), 1692 (COO$^-$)$_{asym}$, 1470 (C=C), 1376 (COO$^-$)$_{sym}$. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.08 (s, 18H, SiMe$_3$), 1.39 (m, 2H, CH$_2$), 1.52 (m, 2H, CH$_2$), 1.98 (m, 2H, CH$_2$),

2.44 (m, 2H, CH$_2$), 4.75, 5.00, 5.14, 5.29 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 6.82 (m, 1H, CH). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.1 (SiMe$_3$), 22.6, 23.4, 26.1, 26.4 (CH$_2$), 95.1 (C^1, C$_5$H$_4$SiMe$_3$), 22.6, 23.4, 26.1, 26.4 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 131.1 (CH), 135.8 (C-COO), 174.5 (COO), 255.2 (CO).

[NbCp'$_2$(OOCCH = CMe$_2$-κ^1O) (CO)] (15). Yield: 90%. Anal. Calcd. for C$_{22}$H$_{33}$NbO$_3$Si$_2$; C, 53.43; H, 6.73. Found: C, 53.93; H, 6.52. IR (Nujol/Polyethylene): ν(cm^{-1}); 1909 (CO), 1649 (COO$^-$)$_{asym}$, 1468 (C=C), 1377 (COO$^-$)$_{sym}$. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.09 (s, 18H, SiMe$_3$), 1.56 (s, 3H, CH$_3$), 2.25 (s, 3H, CH$_3$), 4.75, 5.06, 5.08, 5.30 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 5.82 (s, 1H, CH). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); −0.1 (SiMe$_3$), 19.7, 26.8 (CH$_3$), 94.8 (C^1, C$_5$H$_4$SiMe$_3$), 97.4, 103.1, 104.4, 105.3 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 123.4 (CH-COO), 146.3 (C=CH-COO), 174.5 (COO), 255.4 (CO).

[NbCp'$_2$(OOC(cis-CMe = CHMe)-κ^1O) (CO)] (16). Yield: 92%. Anal. Calcd. for C$_{22}$H$_{33}$NbO$_3$Si$_2$; C, 53.43 %C, 6.73 %H. Found: C, 53.50; H, 6.70. IR (Nujol/Polyethylene): ν(cm^{-1}); 1926 (CO), 1658 (COO$^-$)$_{asym}$, 1465 (C=C), 1378 (COO$^-$)$_{sym}$. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.07 (s, 18H, SiMe$_3$), 1.53 (d, 3H, $^3J_{HaHb} = 6.84$ Hz, CH$_3$), 1.92 (s, 3H, CH$_3$), 4.75, 5.01, 5.10, 5.31 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 6.70 (m, 1H, CH). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); −0.1 (SiMe$_3$), 13.6, 14.1 (CH$_3$), 95.0, (C^1, C$_5$H$_4$SiMe$_3$), 97.2, 104.3, 105.0, 105.1 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 130.4 (C-COO), 134.2 (CH), 175.0 (COO), 255.6 (CO).

[NbCp'$_2$(OOC(trans-CH = CH-Et)-κ^1O) (CO)] (17). Yield: 95%. Anal. Calcd. for C$_{22}$H$_{33}$NbO$_3$Si$_2$; C, 53.43%; H 6.73%. Found: C, 53.50; H, 7.10. IR (Nujol/Polyethylene): ν(cm^{-1}); 1910 (CO), 1654 (COO$^-$)$_{asym}$, 1465 (C=C), 1377 (COO$^-$)$_{sym}$. ^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.1 (s, 18H, SiMe$_3$), 0.81 (s, 3H, CH$_3$), 1.89 (m, 2H, CH$_2$), 4.77, 5.03, 5.08, 5.31 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$). 5.97 (m, 1H, CH-COO), 6.81 (m, 1H, CH=CH-COO). ^{13}C{^{1}H} NMR (125 MHz, C$_6$D$_6$): δ (ppm); 0.1 (SiMe$_3$), 25.3 (CH$_2$), 13.2 (CH$_3$), 95.0 (C^1, C$_5$H$_4$SiMe$_3$), 97.6, 103.0, 105.7, 106.0 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 127.1 (CH-COO), 144.2 (CH=CH-COO), 174.2 (COO), 255.9 (CO).

4.6. Synthesis of [NbCp'$_2$(O$_2$−κ^2O,O) (μ-κ^1O-OOC-CH$_2$-CH$_2$-COO-κ^2O,O)NbCp'$_2$] (18)

A saturated solution of **2** (0.20 g, 0.02 mmol) in hexane (approx. 10 mL) was kept in a Schlenk tube at −30 °C for 2 d. During this time the solution changed color from green/brown to red and an air-sensitive microcrystalline red solid precipitated. After filtration, a red solid, which corresponds to complex **18**, was isolated. Yield: 50%. Complex **18** is soluble in polar solvents such as THF and acetone.

18. Anal. Calcd. for C$_{36}$H$_{56}$Nb$_2$O$_6$Si$_4$; C, 48.97; H, 6.39. Found: C, 49.18; H, 6.31. IR (Nujol/Polyethylene): ν (cm^{-1}) 1640 (COO$^-$)$_{asym}$, 1630 (COO$^-$)$_{asym}$,1545 (COO$^-$)$_{sym}$ 1377 (COO$^-$)$_{sym}$, 875 (O−O), 524 (O−O).^{1}H NMR (500 MHz, C$_6$D$_6$): δ (ppm); 0.05 (s, 18H, SiMe$_3$), 0.21 (s, 18H, SiMe$_3$), 2.02 (t, 2H, $^3J_{HaHb} = 6.16$ Hz, CH$_2$), 2.32 (t, 2H, $^3J_{HaHb} = 6.16$ Hz, CH$_2$), 4.39, 5.93 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$), 5.50, 5.93, 6.01, 6.27 (m, 8H, exact assignment not possible, C$_5$H$_4$SiMe$_3$).

4.7. Synthesis of [{NbCp'$_2$(O$_2$-κ^2O,O)}$_2$ (μ-κ^1O-OOC-CH$_2$-CH$_2$-COO-κ^1O)] (19)

A saturated solution of **2** (0.20 g, 0.02 mmol) in hexane (approx. 10 mL) was kept in a Schlenk tube at −30 °C for 5 d. During this time the solution changed color from green/brown to brown and an air-sensitive microcrystalline yellow solid precipitated. After filtration, a yellow solid, which corresponds to complex **19**, was isolated.

Yield: 70%. Complex **19** is soluble in polar solvents such as THF and acetone but sparingly soluble in non-polar solvents such as hexane and toluene. Complex **19** was also obtained from derivative **18** using the same experimental conditions for 5 days.

19. Yield: 70%. Anal. Calcd. for $C_{36}H_{56}Nb_2O_8Si_4$; C, 47.26; H, 6.17. Found: C, 47.19; H, 6.15. IR (Nujol/Polyethylene): ν (cm^{-1}) 1630 (COO$^-$)$_{asym}$, 1377 (COO$^-$)$_{sym}$, 876 (O−O), 523 (O−O). ^{1}H NMR (500 MHz, C_6D_6): δ (ppm); 0.31 (s, 36H, SiMe_3), 2.82, (s, 4H, CH_2), 5.54, 5.98, 6.15, 6.62 (m, 16H, exact assignment not possible, C_5H_4SiMe$_3$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ (ppm); −1.1 (SiMe_3), 31.9 (CH_2), 125.3 (C^1, C_5H_4SiMe$_3$), 105.1, 112.7, 125.0, 130.2 (C$^{2-5}$, exact assignment not possible, C_5H$_4$SiMe$_3$), 180.1 (COO).

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jorganchem.2019.06.006.

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