Studies on the Insertion Reactions of Activated Alkynes into Nb−H Bonds in Hydride−Niobocene Complexes. X-ray Crystal Structures of $Nb(\eta^5-C_5H_4SiMe_3)_2(H)[\eta^2-RO_2C(H)=C(H)CO_2R]$ ($R = Me$ or ${}^tBu$)

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The hydride isocyanide complexes, $Nb(\eta^5-C_5H_4SiMe_3)_2(H)(CNR)$, R = xylyl = 2,6-dimethylphenyl; Cy (cyclohexyl); ${}^tBu$; as well as the hydride carbonyl complex $Nb(\eta^5-C_5H_4SiMe_3)_2(H)(CO)$ react with several activated alkynes to afford the corresponding alkenyl isocyanide complexes $Nb(\eta^5-C_5H_4SiMe_3)_2(CNR)(C(R')=CH(R''))$, R = xylyl, $R' = R'' = CO_2Me$ **1**; R = Xylyl, $R' = R'' = CO_2{}^tBu$ **2**; R = Xylyl, $R' = CO_2Me$, $R'' = H$ **3**; R = Xylyl, $R' = CO_2Me$, $R'' = Me$ **4**; R = Cy, $R' = R'' = CO_2Me$ **5**; R = Cy, $R' = R'' = CO_2{}^tBu$ **6**; R = Cy, $R' = CO_2Me$, $R'' = Me$ **7**; $R = {}^tBu$, $R' = R'' = CO_2Me$ **8**; ${}^tBu$, $R' = R'' = CO_2{}^tBu$ **9** and alkenyl-carbonyl complexes, $Nb(\eta^5-C_5H_4SiMe_3)_2(CO)(C(R')=CH(R''))$, $R' = R'' = CO_2Me$ **10**; $R' = R'' = CO_2{}^tBu$ **11**; $R' = CO_2Me$, $R'' = H$ **12**. The reaction of hydride isocyanide complexes with activated alkynes gives *cis*-insertion resulting in the formation of (*E*)-alkenyl products. However, the hydride carbonyl derivative undergoes insertion to give, under kinetic control, a mixture of (*E*)- and (*Z*)-alkenyl isomers. Finally, the trihydride niobocene complex $Nb(\eta^5-C_5H_4SiMe_3)_2(H)_3$, reacts with esters $RO_2CC\equiv CCO_2R'$ or $MeO_2CC\equiv CH$ to give the hydride olefin derivatives, $Nb(\eta^5-C_5H_4SiMe_3)_2(H)[\eta^2-RO_2C(H)=C(H)CO_2R']$, $R = R' = Me$ **13**; $R = R' = {}^tBu$ **14**; and $Nb(\eta^5-C_5H_4SiMe_3)_2(H)[\eta^2-MeO_2C(H)=CH_2]$ **15**, probably as the result of a stereospecific *trans*-insertion. The different complexes have been characterized by spectroscopic methods. In addition, the structure of **13** and **14** were determined by single crystal X-ray diffraction.

Introduction

Insertion of unsaturated molecules into metal−hydride bonds are considerered as fundamental chemical steps in several catalytic cycles and frequently leads to reactive intermediates. In particular the insertion of alkynes into transition metal−hydrogen bonds is a key elementary step in catalytic polymerization and hydrogenation processes.[1] In the last few years, the stereochemistry and mechanism involved in the insertion process have received considerable attention.[2] Insertion results in the formation of alkenyl products show that *cis*- and *trans*-insertions yield the (*E*)-alkenyl and (*Z*)-alkenyl products, respectively, and that the importance of the *cis*/*trans* stereochemistry depends on several factors, such as the nature of the metal center, ancillary ligands, and substituents on the alkyne. Electron-rich, coordinatively saturated, metallocene−hydride complexes of early transition metals react readily with activated alkynes bearing electron-withdrawing groups to give alkenyl complexes, and thus in earlier work the behavior of niobocene−hydrides, especially $Nb(\eta^5-C_5H_5)_2(H)(CO)$ was extensively studied.[2h,3] In connection with our studies on the use of unsaturated molecules in the synthesis of new families of niobium organometallics, the insertions of CO_2 and CS_2 into Nb−H bonds to produce formate and dithioformate derivatives were

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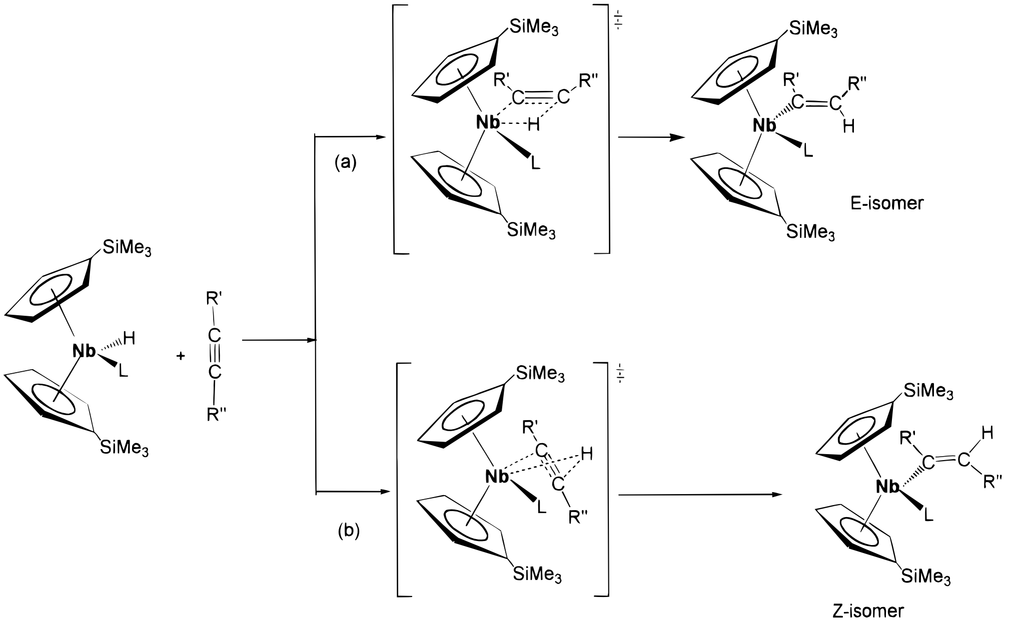
Scheme 1. Proposed Mechanism for the Insertion of Activated Alkynes into Nb−H Bonds



recently explored.[4,5] Continuing in this field, we report here our results on the reactivity of Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CNR), Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CO), and Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)$_3$ with activated alkynes which has permitted the preparation of new niobocene isocyanide or carbon monoxide alkenyl complexes, Nb(η^5-$C_5H_4SiMe_3$)$_2$(L)(C(R′)=CH(R″)), L = CNR, CO, as well as hydride olefin complexes, Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)[η^2-$RO_2C(H){=}C(H)CO_2R'$].

Results and Discussion

We have previously prepared the hydride isocyanide complexes, Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CNR)[6] and viewed it as an ideal complex for studying its behavior with activated alkynes bearing electron-withdrawing substituents with the principal aim of extending the knowledge of the insertion processes of these reagents into the Nb−H bond. This is the first time that such a study has been carried out with niobocenes containing isocyanides as ancillary ligands.

Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CNR) complexes react with the corresponding activated alkynes to give, in a straightforward manner, the corresponding alkenyl isocyanide complexes (eq 1).

$$\mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2(H)(CNR) + R'C{\equiv}CR'' \rightarrow \mathrm{Nb}(\eta^5\text{-}C_5H_4SiMe_3)_2(CNR)(C(R'){=}CH(R''))$$

1, $R = \text{xylyl}, R' = R'' = CO_2Me$

2, $R = \text{xylyl}, R' = R'' = CO_2{}^tBu$

3, $R = \text{xylyl}, R' = CO_2Me, R'' = H$

4, $R = \text{xylyl}, R' = CO_2Me, R'' = Me$

5, $R = Cy, R' = R'' = CO_2Me$

6, $R = Cy, R' = R'' = CO_2{}^tBu$

7, $R = Cy, R' = CO_2Me, R'' = Me$

8, $R = {}^tBu, R' = R'' = CO_2Me$

9, $R = {}^tBu, R' = R'' = CO_2{}^tBu$ (1)

With an excess of alkyne and varying the experimental conditions of the reaction the only isolable product remained the alkenyl derivative, Nb(η^5-$C_5H_4SiMe_3$)$_2$(L)(C(R′)=CH(R″)), and therefore an alternative insertion in the Nb−isocyanide bond or coupling in the primary insertion reactions of alkenyl and isocyanide ligands were not observed. However reactions of Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CN^{t}Bu) with esters $HC{\equiv}CCO_2Me$ and $MeC{\equiv}CCO_2Me$ and Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CNCy) with $HC{\equiv}CCO_2Me$ gave a mixture of unidentifiable products.

The alkenyl niobocene complexes **1**−**9** behave as air-sensitive products, and they were all isolated exclusively as the (*E*)-alkenyl isomer, probably as result of a stereoselective *cis*-insertion of the alkyne into the Nb−H bond via a four-centered transition state (see route a, Scheme 1).[2c]

It is noteworthy that most of the processes of hydride metallocenes with disubstituted activated alkynes occur via stereospecific *trans*-insertion reactions that give rise to kinetic products of (*Z*)-configuration.[7] However in some cases of sterically more crowded metallocenes, for example Nb(η^5-C_5H_5)$_2$(H)($Me_3SiC{\equiv}CSiMe_3$),[21] the (*E*)-isomer is exclusively formed under kinetic control probably via the aforementioned four-centered transition state. With these precedents, we must consider that in the reactions reported here, the presence of bulky isocyanide ligands favors the proposed stereospecific *cis*-insertion to give exclusively (*E*)-isomers.

However, in the reaction of Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CO) with the activated alkynes, under kinetic control, a mixture of the (*Z*)- and (*E*)-alkenyl niobocene complexes were obtained (eq 2).

As in the reactions of the isocyanide-containing complexes, derivatives **10**−**12** were the only species to be isolated. No reaction was observed with the ester $MeC{\equiv}CCO_2Me$. We propose, in accordance with data

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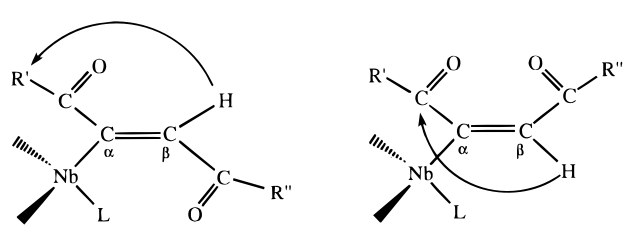
$$\begin{array}{l}\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\mathrm{H})(\mathrm{CO}) + \mathrm{R'C{\equiv}CR''} \rightarrow \\ \quad \mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\mathrm{CO})(\mathrm{C(R')}{=}\mathrm{CH(R'')}) \\ \qquad \mathbf{10},\ \mathrm{R'} = \mathrm{R''} = \mathrm{CO_2Me} \\ \qquad \mathbf{11},\ \mathrm{R'} = \mathrm{R''} = \mathrm{CO_2{}^tBu} \\ \qquad \mathbf{12},\ \mathrm{R'} = \mathrm{CO_2Me},\ \mathrm{R''} = \mathrm{H} \end{array} \quad (2)$$

previously described,[3] that a primary *trans* stereospecific insertion occurs via a four-centered transition state[2c] (see route b, Scheme 1) to give the kinetic (*Z*)-isomer (**10a** and **11a**), and a subsequent isomerization gives (*E*)-isomer (**10b** and **11b**) resulting in the mixture of (*E*)- and (*Z*)-isomers. In fact, the (*Z*)-isomer is the major product from the reaction mixture (*Z*/*E* ratio of *ca.* 4/1), but in solution at room temperature isomerization takes place slowly and after 2 days the *Z*/*E* ratio was *ca.* 3/2. It has previously been reported that Nb(η^5-C_5H_5)$_2$(H)(CO) reacts with dimethylacetylene dicarboxylate or cyanoethyne to give, under kinetic control, a mixture of (*Z*)- and (*E*)-isomers, although exclusive formation of the (*Z*)-isomer was observed with hexafluorobut-2-yne.[2h,3] In the case of **10** the (*Z*)-isomer was isolated, by means of differing solubilities, and slowly evolved (2 days) to give a mixture of (*E*)- and (*Z*)-isomers (*Z*/*E* ratio of *ca.* 3/2). As a consequence of these results and other reported in the literature, we can establish that in the presence of bulky ancillary ligands, such as some alkynes and isocyanides, a primary *cis* stereospecific insertion under kinetic control affords the (*E*)-isomer probably via the four-centered transition state shown in route a, Scheme 1, which is favored by steric arguments.

The structural characterization of the different alkenyl niobocene complexes was carried out by IR and NMR spectroscopy. The IR spectra show the characteristic bands of the alkenyl and the different isocyanide or carbonyl ancillary ligands (see Experimental Section).

In NMR spectroscopy the value of the vicinal coupling constant of the alkenyl protons with the carbonyl carbon atom of the α-carbon has been used as a useful tool to establish (*E*)- or (*Z*)-stereochemistry for the alkenyl group (Figure 1).[21,7a,b]

In the alkenyl isocyanide niobocene complexes (except **3**), the coupling constant $^3J(^1H-^{13}C)$ of *ca.* 15 Hz agrees with a *trans*-disposition of the α-ester and the alkenyl proton in the (*E*)-isomer. In the case of **4** and **7** a quartet and a doublet were observed ($^2J(^1H-^1H)$ *ca.* 6.5 Hz) showing the existence of a C═CHMe moiety. Furthermore, NMR spectra of the carbonyl alkenyl derivatives **10** and **11** indicate, in accordance with the coupling constants $^3J(^1H-^{13}C)$ of *ca.* 9 Hz and *ca.* 15 Hz (see Experimental Section), that a mixture of (*E*)- and (*Z*)-isomers were present. Finally in ^{1}H NMR spectra of **3** and **12**, a doublet with a small coupling constant of ($^2J(^1H-^1H)$) *ca.* 3.5 Hz indicates that a C═CH$_2$ moiety is present[8] as a result of a regiospecific α-insertion.



(Z)-isomer (E)-isomer

Figure 1.

Following the study on the insertion processes of activated alkynes into the niobium−hydride bond in niobocenes, we have examined the behavior of the trihydride complex Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)$_3$ with some of these activated reagents. Reactions of niobocene trihydride with alkynes are well known and generally give rise to alkyne hydride complexes.[9] However Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)$_3$ reacts with the activated alkynes affording the new hydride olefin complexes Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)[η^2-RO$_2$C(H)═C(H)CO$_2$R′] and Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)[η^2-MeO$_2$C(H)═CH$_2$] (eq 3).

$$\begin{array}{l}\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\mathrm{H})_3 + \mathrm{RC{\equiv}CR'} \rightarrow \\ \quad \mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2(\mathrm{H})[\eta^2\text{-}\mathrm{RC(H){=}C(H)R'}] \\ \qquad \mathbf{13},\ \mathrm{R} = \mathrm{R'} = \mathrm{CO_2Me} \\ \qquad \mathbf{14},\ \mathrm{R} = \mathrm{R'} = \mathrm{CO_2{}^tBu} \\ \qquad \mathbf{15},\ \mathrm{R} = \mathrm{CO_2Me},\ \mathrm{R'} = \mathrm{H} \end{array} \quad (3)$$

The reaction takes place virtually instantaneously in THF with the disubstituted alkynes, giving rise to **13** and **14**, but requires 6 h at room temperature for the monosubstituted alkyne **15**; nevertheless, with nonactivated alkynes the corresponding alkyne hydride niobocene complexes are the only products to be isolated.[10] This is the first example of hydride olefin niobocene complexes that have been prepared by the reaction of a niobocene trihydride with alkynes, since this type of complexes was synthesized by employing two alternative processes, namely the reaction of Nb(η^5-C_5R_5)$_2$Cl$_2$ and Nb(η^5-C_5R_5)$_2$(H)$_3$ with various alkylmagnesium halides and olefins, respectively.[11] A similar behavior was reported in the reaction of a tantalocene trihydride with activated alkynes containing electron-withdrawing substituents where Ta(η^5-C_5H_5)$_2$(H)$_3$ reacts with the esters RO$_2$CC≡CCO$_2$R (R = Me, SiMe$_3$) to give the corresponding fumaric ester complexes Ta(η^5-C_5H_5)$_2$(H)(*trans*-RO$_2$CCH═CHCO$_2$R),[12] but with simple alkynes, as our trihydride complex, the corresponding alkyne hydride tantalocenes were isolated. Complexes **13**−**15** were isolated as air-sensitive materials, and their special inertness towards several unsaturated reagents is noteworthy, namely CO, CNR, CS$_2$, and activated alkynes, thus preventing insertion processes even under drastic conditions. This is in contrast with the behavior that has been previously observed for other hydride olefin niobocene complexes.[13]

Although we have not been able to detect any intermediate species on following the reactions by variable

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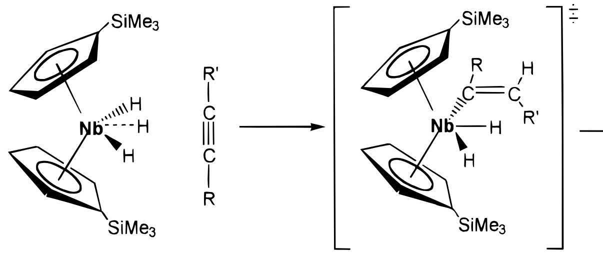
Scheme 2. Proposed Mechanism for the Formation of the Hydride Olefin Complexes 13−15



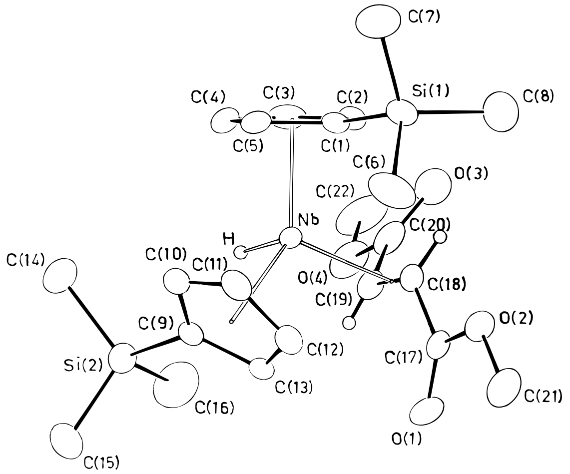


Figure 2. View of complex **13** with atom-numbering scheme (30% probability ellipsoids).

temperature ^{1}H NMR studies, the formation of **13**−**15** may be explained by a similar rationale to that previously described for the tantalocene trihydride (see Scheme 2).[12]

A stereospecific *trans*-insertion to give a dihydride alkenyl intermediate is suggested in the first step, followed by an intramolecular rearrangement which leads to the final hydride olefin complexes, although alternative plausible pathways cannot be excluded.

The structural characterization of **13**−**15** was carried out by spectroscopic and X-ray diffraction studies. ^{1}H and ^{13}C NMR spectra exhibit eight and ten resonances for the proton and carbon atoms, respectively, for the two cyclopentadienyl ligands, indicating that they are nonequivalent, and this behavior is in agreement with the structural disposition (*vide infra*) observed for these complexes where the olefinic carbon atoms are coplanar with the niobium and hydride atoms in such a way that their substituents (in a *trans*-disposition) are situated in a plane orthogonal to that containing the aforementioned atoms. This structural confirmation leads to the presence of two resonances for the inequivalent $SiMe_3$ groups. Finally, the presence in the ^{1}H NMR spectra of AB spin systems for the olefinic protons must also be emphasized (see Experimental Section).

In addition the X-ray crystal structures were determined for **13** and **14**. Views, of the two similar complexes, which adopt the typical bent-metallocene structure are shown in Figures 2 and 3 together with the atom-numbering schemes.

The chirality of the two complexes is due to the configuration of the coordinated C(18) and C(19) atoms. In complex **13** only the (*S*,*S*) enantiomer is present while in **14** the enantiomers (*S*,*S*) and (*R*,*R*) are found. Selected bond distances and angles are given in Table 1.

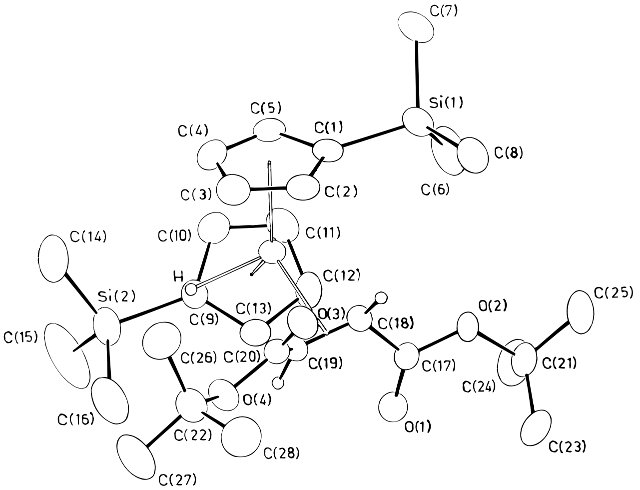


Figure 3. View of complex **14** with atom-numbering scheme (30% probability ellipsoids).

The Cp′ ligands (Cp′ = $C_5H_4SiMe_3$), nearly staggered with the two $SiMe_3$ groups *trans* to each other, are coordinated to the Nb atom in the conventional η^5-fashion (range of the Nb−C distances: 2.391(6)−2.422(5), 2.384(6)−2.433(5) Å for **13**, and 2.370(4)−2.427(5) and 2.386(4)−2.411(4) Å for **14**), the distances between the Nb atom and the centroids CE(1) and CE(2) of the rings being 2.091(5) and 2.086(5) Å for **13** and 2.084(4) and 2.081(4) Å for **14**. The angles between the weighted least-squares planes of the Cp′ ring carbon atoms are not significantly different in the two complexes (47.3(2)° for **13** and 46.8(2)° for **14**). The niobium atom is also bound to the C(18) and C(19) carbon atoms of the dihapto coordinated alkene. The metal coordination description obviously requires positioning of the light hydride atom which was clearly in evidence, for both compounds, in the final Δ*F* map. (The Nb−H bond lengths are 1.54(6) Å for **13** and 1.84(6) Å for **14**, the distance for **13** being somewhat shorter than expected). The resultant coordination around the metal atom may be described as an irregular flattened tetrahedron with the centroids CE(1), CE(2), M(1) (the midpoint of the olefinic C(18)═C(19) bond), and the hydride at the vertices of the polyhedron. The NbM(1)H plane is essentially perpendicular to the NbCE(1)CE(2) plane (96.5(20)° for **13** and 93.1(9)° **14**). The four atoms Nb, C(18), C(19), and the hydride are practically coplanar (the hydride ligand is out of the NbC(18)C(19) plane by 0.17(6) Å in **13** and 0.06(4) Å in **14**), and the Nb−H bond is parallel to the C(18)═C(19) bond. In fact the angles subtended by the two weighted least-squares lines NbH

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Table 1. Selected Bond Distances (Å) and Angles (deg) for 13 and 14 with ESDs in Parentheses[a]

	13	14
Nb−CE(1)	2.091(5)	2.084(4)
Nb−CE(2)	2.086(5)	2.081(4)
Nb−M(1)	2.194(5)	2.184(4)
Nb−H	1.54(6)	1.84(6)
Nb−C(18)	2.316(5)	2.308(4)
Nb−C(19)	2.299(5)	2.294(4)
C(18)−C(19)	1.429(7)	1.448(6)
C(18)−C(17)	1.468(7)	1.462(6)
C(19)−C(20)	1.451(8)	1.470(6)
C(17)−O(1)	1.224(7)	1.207(5)
C(17)−O(2)	1.352(7)	1.355(6)
O(2)−C(21)	1.431(8)	1.478(6)
C(20)−O(3)	1.205(8)	1.204(5)
C(20)−O(4)	1.373(8)	1.366(6)
O(4)−C(22)	1.432(8)	1.462(7)
CE(1)−Nb−CE(2)	134.4(2)	134.5(2)
CE(1)−Nb−M(1)	111.5(2)	112.1(2)
CE(2)−Nb−M(1)	111.7(2)	112.1(2)
CE(1)−Nb−H	102.0(22)	97.9(14)
CE(2)−Nb−H	89.4(22)	92.0(14)
M(1)−Nb−H	93.2(21)	90.3(14)
C(17)−C(18)−C(19)	121.1(4)	119.6(3)
C(18)−C(19)−C(20)	121.0(5)	120.4(4)
C(18)−C(17)−O(1)	126.3(5)	126.3(4)
C(18)−C(17)−O(2)	111.9(4)	110.2(3)
O(1)−C(17)−O(2)	121.8(5)	123.4(4)
C(17)−O(2)−C(21)	116.3(4)	121.7(3)
C(19)−C(20)−O(3)	127.4(6)	127.4(4)
C(19)−C(20)−O(4)	111.3(5)	108.9(4)
O(3)−C(20)−O(4)	121.3(6)	123.7(4)
C(20)−O(4)−C(22)	115.4(5)	120.9(4)

[a] CE(1) and CE(2) are the centroids of the C(1)···C(5) and C(9)···C(13) Cp′ rings, respectively, M(1) the midpoint of the C(18)═C(19) bond.

and C(18)C(19) are 6.7(21)° for **13** and 1.8(14)° for **14**. The NbC(18)C(19) plane bisects the two Cp′ rings (the angles between the weighted least-squares plane NbC(18)C(19) and the C(1)···C(5) Cp′ ring and the C(9)···C(13) Cp′ ring are 23.6(2)° and 23.6(2)° for **13** and 25.8(2) and 21.9(2)° for **14**, respectively).

With the exception of **13** and **14**, only one structurally characterized hydride alkene complex with the positioning of the hydride ligand, Nb(η^5-C_5Me_5)$_2$(H)[η^2-C(H)H═C(H)C_6H_5], has been reported.[14] In the case of [Nb(η-C_4H_6)$_2$(H)(dmpe)$_2$] the hydride was not located.[15] In the styrene complex Nb(η^5-C_5Me_5)$_2$(H)[(η^2-C(H)H═C(H)-C_6H_5] the Nb−C_{Cp*}, Nb−CE distances and the CE(1)−Nb−CE(2) angle (Nb−C range: 2.415(4)−2.506(4), 2.439(4)−2.484(4) Å; Nb−CE: 2.140, 2.143 Å; CE(1)−Nb−CE(2) = 141.4°) are obviously larger than in the present complexes although the olefinic carbon−carbon bond length (1.431(6) Å) is very similar to those found in **13** (1.429(7) Å) and in **14** (1.448(6) Å). These values are larger than that of a free olefin and may be indicative of substantial back donation from the metal to the olefin, introducing some metallacyclopropane−Nb(V) character into the formally Nb(III) olefin adduct. The C═C bond distances do not seem to be significantly different to that found in the ethylene complex Nb(η^5-C_5H_5)$_2$((C_2H_5))[(η^2-C(H)H═C(H)H] (1.406(13) Å).[16] The Nb−C olefin bond lengths in the styrene complex (2.289(4), 2.309(4) Å) and in the ethylene complex (2.277(9), 2.320(9) Å) are similar to those found in **13** (2.316(5), 2.299(5) Å) and in **14** (2.308(4), 2.294(4) Å).

The most remarkable differences between the π-bonded alkene ligands in the two parent complexes are the bond angles C(17)−O(2)−C(21) [116.3(4)° for **13** and 121.7(3)° for **14**] and C(20)−O(4)−C(22) [115.4(5)° for **13** and 120.9(4)° for **14**] due to the steric hindrance of the bulky ^{t}Bu groups in **14**. Some π delocalization occurs which involves the O(1)C(17)C(18)C(19) and the O(3)C(20)C(19)C(18) fragments although the torsion angles τ[C(17)−C(18)−C(19)−C(20)] = −134.3(5)° **13**, ±127.9(4)° **14** reveal a deformation from planarity of the C(17)C(18)C(19)C(20) moiety due to the "$\sigma-\pi$"-interaction with the metal.

Experimental Section

General Procedures. All reactions were performed using standard Schlenk-tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use.

The complexes Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CN(2,6-Me_2-C_6H_3), Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CNC_6H_{11}), Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CN^{t}Bu), Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CO), and Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)$_3$ were prepared as described earlier.[6,10,17] IR spectra were recorded on a Perkin-Elmer PE 883 IR spectrophotometer. ^{1}H and ^{13}C spectra were recorded on Varian FT-300 and Varian Gemini FT-200 spectrometers and referenced to the residual deuteriated solvent. Microanalyses were carried out with a Perkin-Elmer 2400 microanalyzer.

Nb(η^5-$C_5H_4SiMe_3$)$_2$(CNR)(C(R′)═CH(R″) [R = xylyl, R′ = R″ = CO_2Me **1**; R = xylyl, R′ = R″ = $CO_2{}^tBu$ **2**; R = xylyl, R′ = CO_2Me, R″ = H **3**; R = xylyl, R′ = CO_2Me, R″ = Me **4**; R = Cy, R′ = R″ = CO_2Me **5**; R = Cy, R′ = R″ = $CO_2{}^tBu$ **6**; R = Cy, R′ = CO_2Me, R″ = Me **7**; R = ^{t}Bu, R′ = R″ = CO_2Me **8**; R = ^{t}Bu, R′ = R″ = $CO_2{}^tBu$ **9**]. The activated alkyne, $MeO_2CC{\equiv}CCO_2Me$ (0.062 mL, 0.50 mmol), was added to a solution of Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)(CN(2,6-Me_2-C_6H_3)) (0.25 g, 0.50 mmol) in THF (*ca.* 30 mL). The resulting mixture was stirred for 15 min at room temperature, and the solvent was removed, *in vacuo*, to give a red oily solid which was washed with cold hexane (20 mL at −30 °C) to yield the red solid **1** (0.26 g, 81%). **2**, **5**, **6**, **8**, and **9** were prepared in a similar manner to **1**; for **3**, **4**, and **7**, the reaction mixture was stirred for 5 h at 50 °C. Yields of 60−80% were recorded for **2**−**9**.

1: IR (Nujol) ν_{CN} 2037 cm^{-1}, $\nu_{C=C}$ 1624 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.01 (s, 18H, SiMe$_3$), 4.79 (2H), 5.10 (2H), 5.15 (2H), 5.55 (2H) (m, C_5*H_4*), 2.21 (s, 6H, *Me*CNR), 6.67 (m, 3H, C_6*H_3*CNR), 3.36 (3H), 3.46 (3H) (s, CO_2*Me*), 6.24 (s, 1H, C═C*H*). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): δ 0.18 (SiMe$_3$), 90.80, 94.61 (C^1), 98.43, 100.95, 105.15 (*C*$_5H_4$), 18.96 (*Me*CNR), 230.00 (*C*NR), 187.00 (*C*═CH), 129.74 (C═*C*H), 162.02, 179.93 (*C*O$_2$-Me), 50.18, 50.37 (CO$_2$*Me*). ^{13}C NMR (300 MHz, C_6D_6): $^3J(^{13}C_1-{}^1H_\beta)$ 15.96 Hz. Anal. Calcd for $C_{31}H_{42}NNbO_4Si_2$: C, 58.02; H, 6.60; N, 2.18. Found: C, 57.83; H, 6.54; N, 2.16.

2: IR (Nujol) ν_{CN} 2038 cm^{-1}, $\nu_{C=C}$ 1575 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.04 (s, 18H, SiMe$_3$), 4.87 (2H), 5.14 (2H), 5.20 (2H), 5.57 (2H) (m, C_5*H_4*), 2.29 (s, 6H, *Me*CNR), 6.71 (m, 3H, C_6*H_3*CNR), 1.40 (9H), 1.55 (9H) (s, CO$_2$*^{t}Bu*), 6.62 (s, 1H, C═C*H*). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): δ 0.17 (SiMe$_3$), 90.69, 94.21 (C^1) 98.24, 101.36, 104.88 (*C*$_5H_4$), 19.00 (*Me*CNR), 228.63 (*C*NR), 183.50 (*C*═CH), 131.56 (C═*C*H), 161.19, 179.21 (*C*O$_2{}^t$Bu), 28.46, 29.01, 77.76, 78.03 (CO$_2$*^{t}Bu*). ^{13}C NMR (300 MHz, C_6D_6): $^3J(^{13}C_1-{}^1H_\beta)$ 15.10 Hz. Anal. Calcd for $C_{37}H_{54}NNbO_4Si_2$: C, 61.22; H, 7.50; N, 1.93. Found: C, 61.15; H, 7.51; N, 1.88.

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3: IR (Nujol) ν_{CN} 2045 cm^{-1}, $\nu_{C=C}$ 1591 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.07 (s, 18H, SiMe$_3$), 4.85 (2H), 5.19 (2H), 5.23 (2H), 6.71 (2H) (m, C$_5$*H*$_4$), 2.22 (s, 6H, *Me*CNR), 6.71 (m, 3H, C$_6$*H*$_3$CNR), 3.33 (s, 3H, CO$_2$*Me*), 5.53 (1H), (d, C=C*H*), $^{2}J(^{1}H-^{1}H)$ 4.34 Hz. $^{13}C\{^{1}H\}$ NMR (300 MHz, C_6D_6): δ 0.27 (SiMe$_3$), 90.83, 94.30 (C^1), 97.63, 101.31, 104.68 (*C*$_5$H$_4$), 19.02 (*Me*CNR), 225.72 (*C*NR), 166.17 (*C*=CH), 135.20 (C=*C*H), 181.31 (*C*O$_2$Me), 49.95 (CO$_2$*Me*). Anal. Calcd for $C_{29}H_{40}NNbO_2Si_2$: C, 59.67; H, 6.91; N, 2.40. Found: C, 59.40; H, 6.80; N, 2.35.

4: IR (Nujol) ν_{CN} 2032 cm^{-1}, $\nu_{C=C}$ 1604 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.09 (s, 18H, SiMe$_3$), 4.88 (2H), 5.13 (2H), 5.26 (2H), 5.65 (2H) (m, C$_5$*H*$_4$), 2.31 (s, 6H, *Me*CNR), 6.75 (m, 3H, C$_6$*H*$_3$CNR), 3.27 (s, 3H, CO$_2$*Me*), 1.67 (d, 3H, C=C*Me*), 6.58 (q, 1H, C=C*H*), $^{2}J^{1}H-^{1}H)$ 6.30 Hz. $^{13}C\{^{1}H\}$ NMR (300 MHz, C_6D_6): δ 0.43 (SiMe$_3$), 90.74, 93.20 (C^1), 97.29, 101.63, 105.42 (*C*$_5$H$_4$), 19.11 (*Me*CNR), 220.45 (*C*NR), 170.87 (*C*=CH), 135.40 (C=*C*H), 21.67 (C=C*Me*), 180.87 (*C*O$_2$Me), 49.76 (CO$_2$*Me*). ^{13}C NMR (300 MHz, C_6D_6): $^{3}J(^{13}C_1-^{1}H_\beta)$ 15.35 Hz. Anal. Calcd for $C_{30}H_{42}NNbO_2Si_2$: C, 60.28; H, 7.08; N, 2.34. Found: C, 59.98; H, 6.97; N, 2.25.

5: IR (Nujol) ν_{CN} 2100 cm^{-1}, $\nu_{C=C}$ 1616 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.09 (s, 18H, SiMe$_3$), 4.68 (2H), 5.00 (2H), 5.08 (2H), 6.40 (2H) (m, C$_5$*H*$_4$), 0.94−1.60, 3.53 (m, 11H, CNC$_6$*H*$_{11}$), 3.42 (3H), 3.76 (3H) (s, CO$_2$*Me*), 6.40 (s, 1H, C=C*H*). $^{13}C\{^{1}H\}$ NMR (300 MHz, C_6D_6): δ 0.36 (SiMe$_3$), 89.75, 93.93 (C^1), 99.50, 99.97, 102.87 (*C*$_5$H$_4$), 23.85, 25.22, 25.83, 33.67, 56.69 (C^1), 67.79 (CN*C*$_6$H$_{11}$), 208.68 (*C*NC$_6$H$_{11}$), 188.65 (*C*=CH), 131.41 (C=*C*H), 161.85, 181.26 (*C*O$_2$Me), 50.50, 56.69 (CO$_2$*Me*). ^{13}C NMR (300 MHz, C_6D_6): $^{3}J(^{13}C_1-^{1}H_\beta)$ 13.70 Hz. Anal. Calcd for $C_{29}H_{44}NNbO_4Si_2$: C, 56.20; H, 7.16; N, 2.26. Found: C, 56.22; H, 7.16; N, 2.29.

6: IR (Nujol) ν_{CN} 2091 cm^{-1}, $\nu_{C=C}$ 1605 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.14 (s, 18H, SiMe$_3$), 4.82 (2H), 5.02 (2H), 5.59 (2H), 6.09 (2H) (m, C$_5$*H*$_4$), 0.91−1.62, 3.53 (m, 11H, CNC$_6$*H*$_{11}$), 1.42 (9H), 1.69 (9H) (s, CO$_2$^{t}*Bu*), 6.45 (s, 1H, C=C*H*). $^{13}C\{^{1}H\}$ NMR (300 MHz, C_6D_6): δ 0.45 (SiMe$_3$), 88.82 (C^1), 89.89, 100.66, 104.83, 112.06 (*C*$_5$*H*$_4$), 24.05, 25.53, 26.18, 33.84, 57.07 (C^1), 67.79 (CN*C*$_6$H$_{11}$), 215.73 (*C*NC$_6$H$_{11}$), 180.53 (*C*=CH), 132.86 (C=*C*H), 165.78, 179.91 (*C*O$_2$^{t}Bu), 29.21, 29.63, 77.53, 78.13 (CO$_2$^{t}*Bu*). ^{13}C NMR (300 MHz, C_6D_6): $^{3}J(^{13}C_1-^{1}H_\beta)$ 15.72 Hz. Anal. Calcd for $C_{35}H_{56}NNbO_4Si_2$: C, 59.72; H, 8.02; N, 1.99. Found: C, 59.54; H, 7.91; N, 1.95.

7: IR (Nujol) ν_{CN} 2032 cm^{-1}, $\nu_{C=C}$ 1609 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.07 (s, 18H, SiMe$_3$), 4.67 (2H), 4.92 (2H), 5.05 (2H), 5.51 (2H) (m, C$_5$*H*$_4$), 0.75−1.41, 3.47 (m, 11H, CNC$_6$*H*$_{11}$), 3.47 (s, 3H, CO$_2$*Me*), 1.68 (d, 3H, C=C*Me*), 5.65 (q, 1H, C=C*H*), $^{2}J(^{1}H-^{1}H)$ 6.4 Hz. $^{13}C\{^{1}H\}$ NMR (300 MHz, C_6D_6): δ 0.42 (SiMe$_3$), 89.95, 92.71 (C^1), 98.92, 101.13, 102.75 (*C*$_5$H$_4$), 23.98, 25.37, 25.80, 33.89, 57.40 (C^1), 67.73 (CN*C*$_6$H$_{11}$), 224.53 (*C*NC$_6$H$_{11}$), 149.63 (*C*=CH), 136.81 (C=*C*H), 20.08 (C=C*Me*), 181.65 (*C*O$_2$Me), 49.49 (CO$_2$*Me*). ^{13}C NMR (300 MHz, C_6D_6): $^{3}J(^{13}C_1-^{1}H_\beta)$ 15.80 Hz. Anal. Calcd for $C_{28}H_{44}NNbO_2Si_2$: C, 58.41; H, 7.70; N, 2.43. Found: C, 58.13; H, 7.68; N, 2.45.

8: IR (Nujol) ν_{CN} 2085, 1825 cm^{-1}, $\nu_{C=C}$ 1630 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.06 (s, 18H, SiMe$_3$), 4.64 (2H), 5.00 (2H), 5.11 (2H), 5.52 (2H) (m, C$_5$*H*$_4$), 1.08 (s, 9H, CN^t*Bu*), 3.41 (3H), 3.78 (3H) (s, CO$_2$*Me*), 6.40 (s, 1H, C=C*H*). $^{13}C\{^{1}H\}$ NMR (300 MHz, C_6D_6): δ 0.35 (SiMe$_3$), 89.52, 93.96 (C^1), 99.16, 99.76, 103.43 (*C*$_5$H$_4$), 30.74, 58.32 (CN^t*Bu*), 278.39 (*C*N^{t}Bu), 189.20 (*C*=CH), 161.78, 181.17 (*C*O$_2$Me), 52.58, 67.77 (CO$_2$*Me*). ^{13}C NMR (300 MHz, C_6D_6): $^{3}J(^{13}C_1-^{1}H_\beta)$ 15.70 Hz. Anal. Calcd for $C_{27}H_{42}NNbO_4Si_2$: C, 54.62; H, 7.13; N, 2.36. Found: C, 54.80; H, 7.22; N, 2.42.

9: IR (Nujol) ν_{CN} 2093, 1836 cm^{-1}, $\nu_{C=C}$ 1598 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.13 (s, 18H, SiMe$_3$), 4.72 (2H), 5.00 (2H), 5.02 (2H), 5.55 (2H) (m, C$_5$*H*$_4$), 1.13 (s, 9H, CN^t*Bu*), 1.40 (9H), 1.67 (9H) (s, CO$_2$^{t}*Bu*), 6.44 (s, 1H, C=C*H*). $^{13}C\{^{1}H\}$ NMR (300 MHz, C_6D_6): δ 0.49 (SiMe$_3$), 84.57, 89.62, 90.56 (C^1), 101.4, 102.5 (*C*$_5$H$_4$), 28.50, 58.36 (CN^t*Bu*), 265.4 (*C*N^{t}Bu), 187.15 (*C*]-dbdCH), 132.61 (C=*C*H), 179.95, 160.94 (*C*O$_2$^{t}Bu), 28.70, 28.86, 77.33, 78.17 (CO$_2$^{t}*Bu*). ^{13}C NMR (300 MHz, C_6D_6): $^{3}J(^{13}C_1-^{1}H_\beta)$ 14.61 Hz. Anal. Calcd for $C_{33}H_{54}NNbO_4Si_2$: C, 58.47; H, 8.03; N, 2.07. Found: C, 58.15; H, 7.87; N, 2.11.

Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(CO)(C(R′)=CH(R″) [R′ = R″ = CO$_2$Me **10**; R′ = R″ = CO$_2$^{t}Bu **11**; R′ = CO$_2$Me, R″ = H **12**]. **10**, **11**, and **12** were prepared in a similar manner to **1** in yields of 60−80%.

10: IR (Nujol) ν_{CO} 1904 cm^{-1}, $\nu_{C=C}$ 1566 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): **10a** δ 0.05 (s, 18H, SiMe$_3$), 4.80 (2H), 4.92 (2H), 5.20 (2H), 5.55 (2H) (m, C$_5$*H*$_4$), 3.35 (3H), 3.70 (3H) (s, CO$_2$*Me*), 6.80 (s, 1H, C=C*H*); **10b** δ 0.15 (s, 18H, SiMe$_3$), 4.85 (2H), 4.89 (2H), 5.20 (2H), 5.39 (2H) (m, C$_5$*H*$_4$), 3.39 (3H), 3.60 (3H) (s, CO$_2$*Me*), 6.28 (s, 1H, C=C*H*). $^{13}C\{^{1}H\}$ NMR (300 MHz, C_6D_6): **10a** δ 0.32 (SiMe$_3$), 95.72 (C^1), 99.53, 100.51, 101.94, 105.01 (*C*$_5$H$_4$), 260.06 (*C*O), 181.64 (*C*=CH), 131.55 (C=*C*H), 169.07, 180.19 (*C*O$_2$Me), 50.16, 50.46 (CO$_2$*Me*); **10b** δ 0.23 (SiMe$_3$), 90.55, 92.53 (C^1), 94.06, 96.07, 98.57 (*C*$_5$H$_4$), 258.32 (*C*O), 184.32 (*C*=CH), 128.53 (C=*C*H), 162.11, 181.64 (*C*O$_2$Me), 51.53, 52.52 (CO$_2$*Me*). ^{13}C NMR (300 MHz, C_6D_6): **10a** $^{3}J(^{13}C_1-^{1}H_\beta)$ 8.62 Hz; **10b** $^{3}J(^{13}C_1-^{1}H_\beta)$ 13.50 Hz. Anal. Calcd for $C_{23}H_{33}NbO_5Si_2$: C, 51.29; H, 6.18. Found: C, 51.62; H, 6.24.

11: IR (Nujol) ν_{CO} 1920 cm^{-1}, $\nu_{C=C}$ 1558 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): **11a** δ 0.13 (s, 18H, SiMe$_3$), 4.84 (2H), 5.06 (2H), 5.16 (2H), 5.51 (2H) (m, C$_5$*H*$_4$), 1.37 (9H), 1.48 (9H) (s, CO$_2$^{t}*Bu*), 6.72 (s, 1H, C=C*H*); **11b** δ 0.22 (s, 18H, SiMe$_3$), 4.82 (2H), 5.10 (2H), 5.20 (2H), 5.31 (2H) (m, C$_5$*H*$_4$), 1.40 (9H), 1.62 (9H) (s, CO$_2$^{t}*Bu*), 6.21 (s, 1H, C=C*H*). $^{13}C\{^{1}H\}$ NMR (300 MHz, C_6D_6): **11a** δ 0.08 (SiMe$_3$), 90.79, 95.39, 95.89 (C^1), 100.21, 105.54 (*C*$_5$H$_4$), 259.81 (*C*O), 161.50 (*C*=CH), 133.46 (C=*C*H), 168.79, 180.10 (*C*O$_2$^{t}Bu), 28.39, 28.80, 78.22, 78.93 (CO$_2$^{t}*Bu*); **11b** δ 0.16 (SiMe$_3$), 90.83, 92.34 (C^1), 94.26, 98.41, 102.32 (*C*$_5$H$_4$), 256.52 (*C*O), 141.84 (*C*=CH), 132.15 (C=*C*H), 161.76, 178.81 (*C*O$_2$^{t}Bu), 28.40, 29.00, 78.31, 79.11 (CO$_2$^{t}*Bu*). ^{13}C NMR (300 MHz, C_6D_6): **11a** $^{3}J(^{13}C_1-^{1}H_\beta)$ 9.50 Hz; **11b** $^{3}J(^{13}C_1-^{1}H_\beta)$ 14.83 Hz. Anal. Calcd for $C_{29}H_{45}NbO_5Si_2$: C, 55.93; H, 7.28. Found: C, 56.25; H, 7.36.

12: IR (Nujol) ν_{CO} 1912 cm^{-1}, $\nu_{C=C}$ 1570 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 0.04 (s, 18H, SiMe$_3$), 4.68 (2H), 4.86 (2H), 4.89 (2H), 5.44 (2H) (m, C$_5$*H*$_4$), 3.29 (3H), (s, CO$_2$*Me*), 6.29 (1H), 6.31 (1H) (d, C=C*H*$_2$) $^{2}J(^{1}H-^{1}H)$ 3.84 Hz. $^{13}C\{^{1}H\}$ NMR (300 MHz, C_6D_6): δ 0.00 (SiMe$_3$), 74.89 (C^1), 90.80, 98.57, 99.17, 101.92 (*C*$_5$H$_4$), 260.76 (*C*O), 152.95 (*C*=CH), 133.84 (C=*C*H), 180.79, (*C*O$_2$Me), 50.24 (CO$_2$*Me*). Anal. Calcd for $C_{21}H_{31}NbO_3Si_2$: C, 52.49; H, 6.50. Found: C, 52.63; H, 6.56.

Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(H)[η^2-RO$_2$C(H)=C(H)CO$_2$R′] [R = R′ = Me **13**: R = R′ = ^{t}Bu **14**] **and Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(H)[η^2-MeO$_2$C(H)=CH$_2$] 15.** Nb(C$_5$H$_4$SiMe$_3$)$_2$(H)$_3$ (0.30 g, 0.80 mmol) was dissolved in 40 mL of THF to give a light brown solution. To this solution was added 0.80 mmol of the corresponding activated alkyne. The mixture was stirred at room temperature for 15 min for **13** and **14**, and for 24 h for **15**. The resulting yellow-brown solution was filtered, and solvent was removed, from the filtrate, *in vacuo*. After washing the solid with 30 mL of hexane and recrystallization from diethyl ether, **13** and **14** were isolated as yellow (**13**, yield: 80%) or light blue crystals (**14**, yield: 75%). **15** was isolated as a yellow-brown oily material (yield: 90%).

13: IR (Nujol) ν_{CO} 1700 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ −1.65 (s, 1H, Nb*H*), 0.23 (9H), 0.28 (9H) (s, Si*Me*$_3$), 2.68, 2.72 (dd, AB system, 2H, CO$_2$Me(*H*)C=C(*H*)CO$_2$Me) $^{1}J_{AB}$ = 13.23 Hz, 3.46 (s, 3H, CO$_2$*Me*), 3.51 (s, 3H, CO$_2$*Me*), 3.95, 4.01, 4.29, 4.36, 4.52, 5.12, 5.15, 5.30 (s, 8H, C$_5$*H*$_4$). $^{13}C\{^{1}H\}$ NMR (300 MHz, C_6D_6): δ 0.10, 0.14, (Si*Me*$_3$), 29.92, 30.23 (MeO$_2$C(H)*C*=*C*(H)CO$_2$Me), 50.24, 50.50, (CO$_2$*Me*), 91.98, 95.79, 98.21, 100.07, 102.26, 102.86, 103.12(C^1), 106.50, 107.79, 107.99(C^1) (*C*$_5$H$_4$), 180.29, 178.0 (*C*O$_2$Me). Anal. Calcd for $C_{22}H_{35}NbO_4Si_2$: C, 51.50; H, 6.83. Found: C, 51.55; H, 6.83.

14: IR (Nujol) ν_{CO} 1665 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ −1.80 (s, 1H, Nb*H*), 0.25 (9H), 0.26 (9H) (s, Si*Me*$_3$), 1.41 (s, 9H, CO$_2$^{t}*Bu*), 1.44 (s, 9H, CO$_2$^{t}*Bu*), 2.54, 2.72 (dd, AB system, 2H, CO$_2$^{t}Bu(*H*)C=C(*H*)CO$_2$^{t}Bu) $^{1}J_{AB}$ = 11.21 Hz, 3.83, 4.30, 4.40, 4.65, 4.85, 5.10, 5.35, 5.45 (s, 8H, C$_5$*H*$_4$). $^{13}C\{^{1}H\}$ NMR

Table 2. Summary of Crystallographic Data for Complexes 13 and 14

	13	14
mol formula	$C_{22}H_{35}O_4Si_2Nb$	$C_{28}H_{47}O_4Si_2Nb$
mol wt	512.594	596.755
crystal system	orthorhombic	monoclinic
space group	$P2_12_12_1$	$P2_1/n$
radiation (Mo Kα)	λ = 0.71073 Å graphite monochromated	
a, Å	12.227(2)	14.171(4)
b, Å	14.183(2)	19.725(3)
c, Å	14.903(4)	12.390(3)
β, deg		110.43(2)
V, Å^3	2584.4(9)	3245.4(14)
Z	4	4
D_{calcd}, g cm^{-3}	1.317	1.221
F(000)	1072	1264
cryst dimens, mm	0.25 × 0.30 × 0.35	0.27 × 0.32 × 0.40
μ(Mo Kα), cm^{-1}	5.81	4.72
diffractometer	Philips PW 1100	Siemens AED
2θ range, deg	6−60	
reflns measd	h,k,l	$h,k,\pm l$
unique total data	4196	9456
unique obsd data [$I \geq 2\sigma(I)$]	2580	3966
goodness of fit	1.02	1.20
$R^a R_w^b$	0.0335, 0.0372	0.0430, 0.0450
$\Delta\rho_{max}$, e Å^{-3}	0.47	0.78

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

(300 MHz, C_6D_6): δ −0.86, −0.55 (Si*Me*$_3$), 27.68, 27.83 ($CO_2{}^tBu$), 29.50, 34.56 ($^tBuO_2C(H)\mathit{C}{=}\mathit{C}(H)CO_2{}^tBu$), 89.42, 90.29, 96.35, 99.20 (C^1), 100.10, 101.52, 104.39, 105.44 (C^1), 107.63, 113.81 (C_5H_4), 178.00, 180.29 ($\mathit{C}O_2{}^tBu$). Anal. Calcd for $C_{28}H_{47}NbO_4Si_2$: C, 56.31; H, 6.87. Found: C, 56.45; H, 6.90.

15: IR (Nujol) ν_{CO} 1650 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ −2.15 (s, 1H, Nb*H*), 0.32 (s, 9H, Si*Me*$_3$), 0.36 (s, 9H, Si*Me*$_3$), 0.80−1.20 (m, ABC system, 2H, $CO_2Me(H)C{=}C\mathit{H}_2$), 1.91 (dd, ABC system, 1H, $CO_2Me(\mathit{H})C{=}CH_2$) $^2J_{AC}$ = 13.53 Hz, $^2J_{BC}$ = 12.13 Hz, 3.88 (s, 3H, $CO_2\mathit{Me}$), 3.51 (s, 3H, $CO_2\mathit{Me}$), 4.10, 4.36, 4.49, 4.53, 5.42, 5.53, 5.63, 5.70 (s, 8H, $C_5\mathit{H}_4$). $^{13}C\{^1H\}$ NMR (300 MHz, C_6D_6): δ 0.19, 0.21 (Si*Me*$_3$), 18.40 ($MeO_2C(H)C{=}\mathit{C}H_2$), 23.84 ($MeO_2C(H)\mathit{C}{=}CH_2$), 52.86 ($CO_2\mathit{Me}$), 95.34, 96.89, 97.22, 97.26, 97.32, 101.77 (C^1), 102.77, 103.87, 104.85(C^1), 105.35 (C_5H_4), 177.00 ($\mathit{C}O_2Me$).

X-ray Data Collection, Structure Determination, and Refinement for Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)[η^2-$MeO_2C(H){=}C(H)CO_2Me$] 13 and Nb(η^5-$C_5H_4SiMe_3$)$_2$(H)[η^2-$^tBuO_2C(H){=}C(H)CO_2{}^tBu$] 14. A crystal of each compound was sealed in Lindemann capillary under dry nitrogen and used for data collection. The crystallographic data are summarized in Table 2. Accurate unit-cell parameters were determined by least-squares treatment of the setting angles of 30 carefully centered reflections in the θ range 9.2−17.3° for **13** and 10.2−18.0° for **14**. Data (3 < θ < 30°) were collected at 22 °C on a Philips PW 1100 for **13** and on a Siemens AED for **14** single-crystal diffractometer, using the graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and the $\theta/2\theta$ scan method. The reflections were collected with a variable scan speed of 3−9° min^{-1} and a scan width of 1.20 + 0.34 tan θ. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collections. The individual profiles have been analyzed following the method of Lehmann and Larsen.[18] Intensities were corrected for Lorentz and polarization effects. Only the observed reflections were used in the structure refinements.

The structures were solved by direct and Fourier methods and refined by full-matrix least-squares, first with isotropic thermal parameters and then with anisotropic thermal parameters for all the non-hydrogen atoms. The hydride anions, the hydrogen atoms of the Cp′ rings and of the C(18), C(19) atoms of the η^2 coordinated ligands were clearly located in the ΔF map and refined isotropically, all the others were placed at their geometrically calculated positions (C−H = 0.96 Å) and refined "riding" on the corresponding carbon atoms (with isotropic thermal parameters). The final cycles of refinement were carried out on the basis of 310 for **13** and 364 for **14** variables; after the last cycles no parameters shifted by more than 0.48 for **13** and 0.51 for **14** esd. The highest remaining peak in the final difference map was equivalent to about 0.47 for **13** and 0.78 for **14** e/Å^3. In the final cycles of refinement a weighting scheme, $w = k[\sigma(F_o) + gF_o{}^2]^{-1}$, was used; at convergence the k and g values were 0.3961 and 0.00138 for **13**, 1.3373 and 0.00029 for **14**, respectively. Since the space group $P2_12_12_1$ for **13** leads to a chiral configuration in the structure, a refinement of the non-hydrogen atoms with anisotropic thermal parameters was carried out using the coordinates $-x$, $-y$, $-z$; an increase of the R and Rw values was obtained [$R(x,y,z)$] = 0.0445, $Rw(x,y,z)$ = 0.0598; $R(-x,-y,-z)$ = 0.0457, $Rw(-x,-y,-z)$ = 0.0617]. The former model was selected. Also the final refinement with the hydrogen atoms was performed and confirmed the selected model [$R(-x,-y,-z)$ = 0.0352, $Rw(-x,-y,-z)$ = 0.0393]. Although the Nb−hydride distance results somewhat short in **13** after the refinement, the direction of the Nb−H bond seems to be correct; in fact the positional parameters were tested by means of a "potential energy" technique using the HYDEX program.[19] The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions, were taken from ref 20. All calculations were carried out on the GOULD POWERNODE 6040 and ENCORE 91 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma. The system of computer programs SIR92,[21] SHELXS-86 and SHELX-76,[22] Parst,[23] and ORTEP[24] were used. The final atomic coordinates for the non-hydrogen atoms are given in Table 3 for **13** and Table 4 for **14** in the supporting information. The atomic coordinates of the hydrogen atoms and thermal parameters are also given in the supporting information.

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Supporting Information Available: Tables of hydrogen atom coordinates (Tables SI, SII), anisotropic thermal parameters (Tables SIII, SIV), complete bond distances and angles (Tables SV, SVI), complete crystallographic data (Tables SVII, SVIII), and non-hydrogen atom coordinates (12 pages). Ordering information is given on any current masthead page. A list of structure factors is available upon request from the authors.

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