Synthesis and Characterization of New Alkyl−Carbon Dioxide Compounds and the First Neutral Acyl−Carbonyl Niobocene Complexes

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The olefin−hydride complexes $Cp'_2Nb(H)(\eta^2$-RHC=CH_2) ($Cp' = \eta^5$-C_5H_4SiMe_3; R = H (**3**), C_6H_5 (**4**, endo isomer)) were prepared by the alkylation reactions of $[Cp'_2NbCl]_2$ (**1**) with the appropriate Grignard reagents RMgX (R = CH_2CH_3, CH_2CH_2C_6H_5) followed by a stereoselective β-elimination from the intermediate alkyl complexes $Cp'_2Nb(CH_2CH_2R)$. Complexes $Cp'_2Nb(H)(\eta^2$-RHC=CH_2) (R = C_6H_4CH_3 (**5**), C_6H_4OCH_3 (**6**)) were prepared as a mixture of endo and exo isomers by reaction of Cp'_2NbH_3 (**2**) with the corresponding olefin. Furthermore, reactions of CO with **3** and **4**, and the reactions of CO_2 with **3**−**6**, afforded the alkylniobocene complexes $Cp'_2Nb(CO)R$ (R = CH_2CH_3 (**7**), CH_2CH_2C_6H_5 (**8**)) $Cp'_2Nb(\eta^2$-CO_2)(R) (R = CH_2CH_3 (**9**)), CH_2CH_2C_6H_5 (**10**), CH_2CH_2C_6H_4CH_3 (**11**), CH_2CH_2C_6H_4OCH_3 (**12**)). The reactivity of **9** and **10** toward the strong Lewis acid $B(C_6F_5)_3$ was also studied; in a first step the adducts $Cp'_2Nb(\eta^2$-CO_2−B(C_6F_5)_3)(CH_2CH_2R) (R = H (**13**), C_6H_5 (**14**)) were formed and subsequently evolved to give the oxo−alkyl complexes $Cp'_2Nb(O−B(C_6F_5)_3)(CH_2CH_2R)$ (R = H (**15**), C_6H_5 (**16**)) with the loss of CO. Finally, reactions of **3** and **4** with CO under appropriate conditions gave the neutral acylniobocene complexes $Cp'_2Nb(CO)(\eta^1$-C(O)CH_2CH_2R) (R = H (**17**), C_6H_5 (**18**)), which were alternatively prepared from the reactions of **7** and **8** with CO. The different complexes were characterized by spectroscopic methods.

Introduction

Olefin−hydride metal systems, including those corresponding to group 5 metals, are of great interest in a host of catalytic processes. Particularly, insertion of olefins into metal−hydride bonds and its microscopic reverse, β-elimination, are very common steps in industrial catalytic reactions, such as olefin polymerization, hydrogenation, and hydroformylation.[1]

After the preparation of the first olefin−hydride bis(cyclopentadienyl) complex of group 5 metals, $Cp_2Nb(H)(\eta^2$-C_2H_4) (Cp = η^5-C_5H_5), by Tebbe and Parshall,[2] several olefin−hydride complexes of Nb and Ta were synthesized by employing two alternative processes, namely the reaction of Cp_2MCl_2 and Cp_2MH_3 (M = Nb, Ta) with various alkylmagnesium halides and olefins, respectively.[3] The first process takes place via a stereospecific β-H elimination from the monoalkyl complexes Cp_2MR and the second by thermal elimination

of H_2 followed by olefinic coordination of the Cp_2MH species. In addition, elegant and extensive work of Bercaw, Green, and co-workers have described NMR studies of the dynamic processes in the olefin−hydride niobocene and tantalocene complexes.[3d,e,g] Furthermore, the metal-promoted transformation of carbon dioxide into organic products of practical interest is an attractive goal in the field of organometallic chemistry.[4] In this context, there have been recent reports[5] on the

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(1) (a) Parshall, G. A. *Homogeneous Catalysis*; Wiley: New York, 1980. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987.
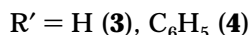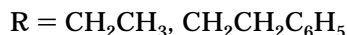(2) Tebbe, F. N.; Parshall, G. W. *J. Am. Chem. Soc.* **1971**, *93*, 3794.

(3) (a) Klazinga, A. H.; Teuben, J. H. *J. Organomet. Chem.* **1978**, *157*, 413. (b) Eichiner, M. E.; Att, H. G.; Rausch, M. D. *J. Organomet. Chem.* **1984**, *264*, 309. (c) Klazinga, A. H.; Teuben, J. H. *J. Organomet. Chem.* **1980**, *194*, 309. (d) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670. (e) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134. (f) Bercaw, J. E.; Burger, B. J.; Green, M. L. H.; Santarsiero, B. D.; Sella, A.; Trimmer, M. S.; Wong, L.-L. *J. Chem. Soc., Chem. Commun.* **1989**, 734. (g) Green, M. L. H.; Sella, A.; Wong, L.-K. *Organometallics* **1992**, *11*, 2650. (h) Antiñolo, A.; Carrillo, F.; Garcia-Yuste, S.; Otero, A. *Organometallics* **1994**, *13*, 2761. (i) Antiñolo, A.; Chaudret, B.; Commenges, G.; Fajardo, M.; Jalón, F.; Morris, R. H.; Otero, A.; Schweitzer, C. T. *J. Chem. Soc., Chem. Commun.* **1988**, 1210.
(4) See for example the following reviews: (a) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. (b) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (c) Walther, D. *Coord. Chem. Rev.* **1987**, *79*, 135.
(5) (a) Fu, P.-F.; Masood, A. K.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 6579. (b) Fu, P.; Khan, M. A.; Nicholas, K. M. *J. Organomet. Chem.* **1996**, *506*, 49.

isolation and reactivity of several alkyl−carbon dioxide niobocene complexes obtained by oxidation of the corresponding alkyl−carbonyl species with molecular oxygen and on the chemical and electrochemical reduction of the niobocene dichlorides in the presence of carbon dioxide.[6] Following on from studies on olefin−hydride[3h] and heterocumulene complexes,[7] we report here the outcome of recent studies on the preparation of new olefin−hydride niobocene complexes by alkylation of the $[Cp'_2NbCl]_2$ species and the subsequent β-elimination process and by reaction of Cp'_2NbH_3 with the corresponding olefin, the coordination of carbon dioxide on alkylniobocene species to give the corresponding carbon dioxide alkylniobocenes, and the first well-established insertion process of carbon monoxide into a niobium−carbon bond of a niobocene complex to give the corresponding acyl derivatives.
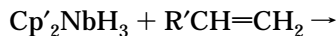
Results and Discussion

Synthesis and Characterization of Olefin- and Alkyl-Containing Niobocene Complexes. Aspects of the reactivity of the chloroniobocene complex $[Cp'_2NbCl]_2$ (**1**)[8] suggest it to be ideal for studying its behavior with alkylating agents, such as Grignard compounds, and thus extending the knowledge of the alkylation processes in haloniobocene species.

In fact, the starting niobium complex $[Cp'_2NbCl]_2$ (**1**;[8a] $Cp' = \eta^5\text{-}C_5H_4SiMe_3$) reacts with 1 equiv of RMgX (R = Et, $CH_2CH_2C_6H_5$) to generate at room temperature in high yields the corresponding olefin−hydride complexes $Cp'_2Nb(H)(\eta^2\text{-}RHC=CH_2)$ (R = H (**3**) C_6H_5 (**4**, endo isomer)) by a highly stereoselective β-elimination from the initially formed monoalkyl species $Cp'_2Nb(CH_2CH_2R)$, which have not been detected (eq 1).

$$[Cp'_2NbCl]_2 + RMgX \rightarrow [Cp'_2NbR] \rightarrow$$
$$Cp'_2Nb(H)(CH_2=CHR') \quad (1)$$
$$\mathbf{3,4}$$

$$R = CH_2CH_3, CH_2CH_2C_6H_5$$

$$R' = H \ (\mathbf{3}), C_6H_5 \ (\mathbf{4})$$
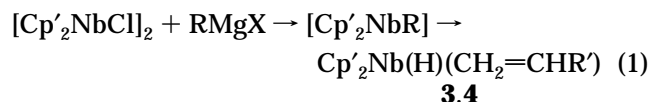
This synthetic method, which was initially described several years ago by Teuben,[3a,c] has subsequently been employed by others.[3d,e,g,h] In addition, styrene hydride complexes, $Cp'_2Nb(H)(\eta^2\text{-}RHC=CH_2)$ (R = C_6H_5 (**4**),[3h] $C_6H_4CH_3$ (**5**), $C_6H_4OCH_3$ (**6**)) were also obtained, as a mixture of endo and exo isomers, by reaction of the niobocene trihydride complex Cp'_2NbH_3[3i] (**2**) and the corresponding olefin (eq 2).

Furthermore, the reactions of complexes **3** and **4** with CO and of **3**−**6** with CO_2 favored the insertion process to give the alkyl tautomer with isolation of the corre-

(6) El Krami, S.; Mourad, Y.; Mugnier, Y.; Antiñolo, A.; Del Hierro, I.; García-Yuste, S.; Otero, A.; Fajardo, M.; Brunner, H.; Gehart, G.; Wachter, J.; Amaudrut, J. *J. Organomet. Chem.* **1995**, *498*, 165.
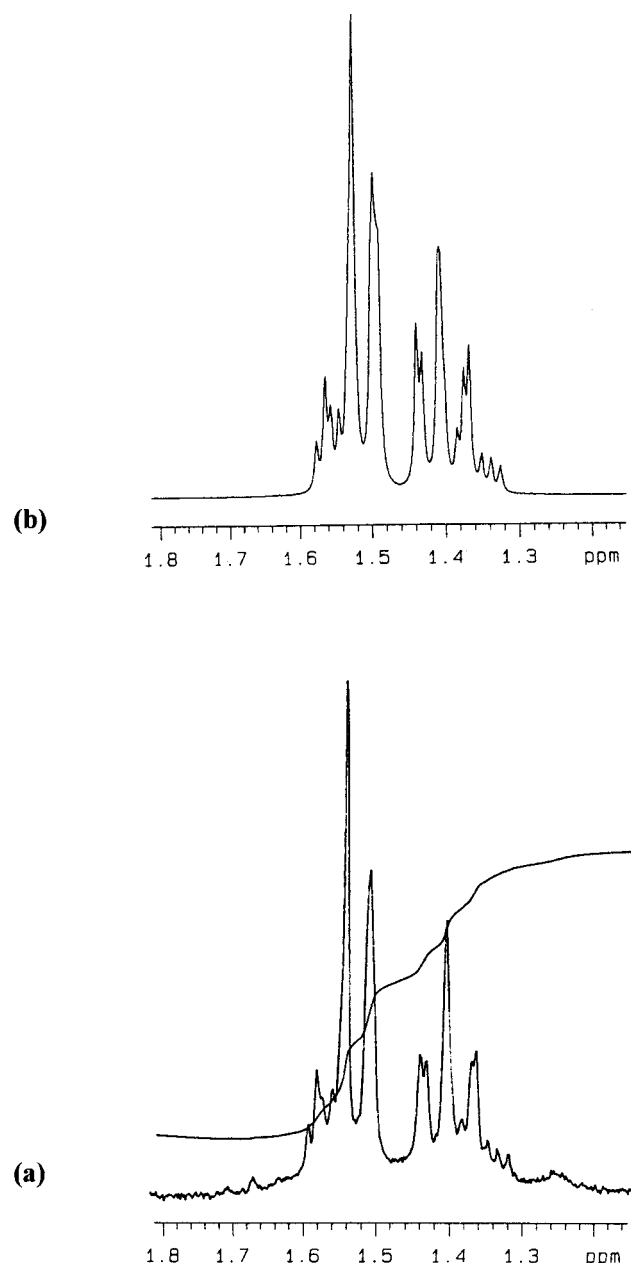
(7) (a) Antiñolo, A.; Fajardo, M.; López-Mardomingo, C.; Otero, A.; Mourad, Y.; Mugnier, Y.; Sanz-Aparicio, J.; Fonseca, I.; Florencio, F. *Organometallics* **1990**, *9*, 164. (b) Antiñolo, A.; Fajardo, M.; García-Yuste, S.; Del Hierro, I.; Otero, A.; El Krami, S.; Mourad, Y.; Mugnier, Y. *J. Chem. Soc., Dalton Trans.* **1995**, 3409.

(8) See, for example: (a) Antiñolo, A.; García-Lledó, S.; Martínez de Ilarduya, J. M.; Otero, A. *J. Organomet. Chem.* **1987**, *335*, 85. (b) Antiñolo, A.; Espinosa, P.; Fajardo, M.; Gómez-Sal, P.; López-Mardomingo, C.; Martín-Alonso, A.; Otero, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1007.

$$Cp'_2NbH_3 + R'CH=CH_2 \rightarrow$$
$$Cp'_2Nb(H)(CH_2=CHR') \ (endo + exo) \quad (2)$$

$$R' = C_6H_5 \ (\mathbf{4}), C_6H_4CH_3 \ (\mathbf{5}), C_6H_4OCH_3 \ (\mathbf{6})$$

sponding alkylniobocene complexes $Cp'_2Nb(CO)(R)$ (R = CH_2CH_3 (**7**), $CH_2CH_2C_6H_5$ (**8**)) and $Cp'_2Nb(\eta^2\text{-}CO_2)(R)$ (R = CH_2CH_3 (**9**), $CH_2CH_2C_6H_5$ (**10**), $CH_2CH_2C_6H_4CH_3$ (**11**), $CH_2CH_2C_6H_4OCH_3$ (**12**) (eq 3).

$$Cp'_2Nb(H)(CH_2=CHR') + L \rightarrow Cp'_2Nb(L)(R) \quad (3)$$
$$\mathbf{3-6} \qquad\qquad\qquad\qquad \mathbf{7-12}$$

L = CO, R' = H (**3**), C_6H_5 (**4**); R = CH_2CH_3 (**7**),
$$CH_2CH_2C_6H_5 \ (\mathbf{8})$$

L = CO_2, R' = H (**3**), C_6H_5 (**4**), $C_6H_4CH_3$ (**5**),
$C_6H_4OCH_3$ (**6**); R = CH_2CH_3 (**9**), $CH_2CH_2C_6H_5$ (**10**),
$$CH_2CH_2C_6H_4CH_3 \ (\mathbf{11}), CH_2CH_2C_6H_4OCH_3 \ (\mathbf{12})$$
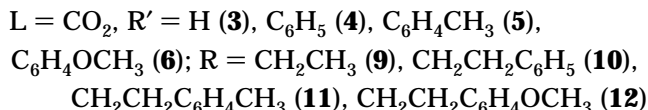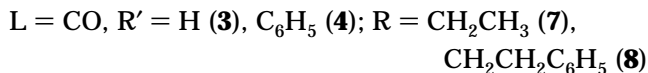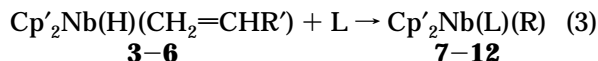
The reaction with a mixture of endo and exo styrene−hydride isomers gave complexes **8** and **10**−**12** only. Transformation of the exo to the endo isomers to give the corresponding alkyl complexes probably occurs, as the primary alkyl-containing complexes **8** and **10**−**12** would be the expected kinetic products on the basis of steric arguments. We have previously observed similar results in the reaction of olefin−hydride niobocene complexes with carbon disulfide.[9] Alkyl−carbonyl niobocene complexes were previously prepared by alkylation of halo−carbonyl complexes,[10] while Nicholas *et al.*,[5a] in an elegant study, reported (as noted above) for the first time the isolation of several alkyl−carbon dioxide niobocene complexes. However, this is one of the first reports on group 5 metallocene-promoted coordination of CO_2 and it is noteworthy that the process proceeds in acceptable yield (ca. 60%) and under mild conditions (3 and 4 atm of CO_2 are required to isolate **9** and **10**−**12**, respectively; see Experimental Section). Lappert and co-workers reported[11] for the first time the preparation of $Cp'_2Nb(\eta^2\text{-}CO_2)(CH_2SiMe_3)$ ($Cp' = \eta^5\text{-}C_5H_4Me$) by the reaction of $Cp'_2Nb(Cl)(CH_2SiMe_3)$ with sodium amalgam under an atmosphere of carbon dioxide, and several related complexes were recently prepared by Nicholas and co-workers[5b] in a similar way in modest yield (ca. 20%).

Spectral characterizations of complexes **3**−**12** are as follows. The IR spectra for **3** and **6** show a weak broad band at ca. 1740 cm^{-1}, assigned to $\nu(Nb-H)$, and for complexes **7**, **8** and **9**−**12**, intense bands at ca. 1896 and 1697 cm^{-1} are seen, which correspond respectively to $\nu(CO)$ of coordinated CO and CO_2. The ^1H NMR spectra of **3**−**6** show the hydride resonance at δ ca. −3 ppm. The ^{13}C NMR spectra of **7**−**12** show diagnostic resonances of coordinated CO and CO_2 at δ 270 and ca. 200 ppm, respectively (see Experimental Section).

Especially noteworthy is the ^1H NMR spectral pattern of the ethyl group in **9**, as illustrated in Figure 1, because it displays an ABM_3 pattern, indicating the

(9) Antiñolo, A.; del Hierro, I.; Fajardo, M.; Garcia-Yuste, S.; Otero, A.; Blaque, O.; Kubicki, M. M.; Amaudrut, J. *Organometallics* **1996**, *15*, 1966.

(10) Antiñolo, A.; Gomez-Sal, P.; Martinez de Ilarduya, J. M.; Otero, A.; Royo, P. *J. Chem. Soc., Dalton Trans.* **1988**, 2865.

(11) Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145.

Scheme 1

R= CH₂CH₃ **9**
R= CH₂CH₂C₆H₅ **10**

R= CH₂CH₃ **13**
R= CH₂CH₂C₆H₅ **14**

R= CH₂CH₃ **15**
R= CH₂CH₂C₆H₅ **16**

(b)

(a)

Figure 1. ^{1}H NMR spectra of [Cp′₂Nb(η^2-CO₂)(CH₂CH₃)] in the ethyl region: (a) experimental; (b) simulated.

presence of an unusually weak agostic interaction between an α-hydrogen atom of the ethyl group and the metal center (J_{MB} = 7.0 Hz, J_{MA} = 7.5 Hz, J_{AB} = 18 Hz).[12] This proposal, however, should be considered cautiously, because in the ^{13}C NMR spectrum we have not been able to distinguish the two $^1J(^{13}C-^1H)$ constants corresponding to the CH₂ group.

Reactivity of η^2-CO₂ Complexes with Lewis Acids. Insertion Processes. Complexes **9** and **10** react instantaneously with B(C₆F₅)₃ to initially give the
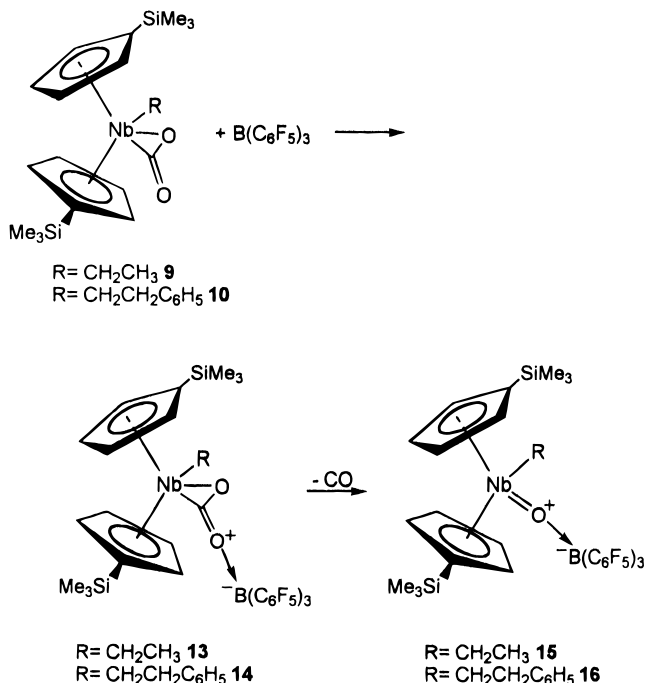
adducts Cp′₂Nb(η^2-CO₂−B(C₆F₅)₃)(CH₂CH₂R) (R = H (**13**), C₆H₅ (**14**)), which subsequently evolved to the oxo−alkyl complexes Cp′₂Nb(O−B(C₆F₅)₃)(CH₂CH₂R) (R = H (**15**), C₆H₅ (**16**); see Scheme 1), with the loss of CO.

Nicholas and co-workers[16] have studied the behavior of an analogous complex, Cp′₂Nb(η^2-CO₂)(CH₂SiMe₃) (Cp′ = η^5-C₅H₄Me), toward different Lewis acids, namely LiPF₆, BF₃·OEt₂, and ZnCl₂, and they have found that initial coordination of the Lewis acid to the niobocene moiety, through the CO₂ ligand, was followed by a decarbonylation instead of a migratory insertion promotion into the Nb−C bond. Complexes **13** and **14** are very unstable toward the loss of CO and were isolated from the reaction mixture by evaporation of the solvent after a brief reaction time (see Experimental Section). The formation of these adducts can be considered the result of the interaction of the Lewis acid B(C₆F₅)₃ with the noncoordinated oxygen atom of the CO₂ ligand. Their IR spectra exhibited an absorption band at ca. 1570 cm⁻¹ which corresponds to ν(CO₂), which is significantly lower than the value for ν(CO₂) found in the starting complexes, indicating an appreciable reduction of electron density in the C=O bond as a result of the coordination of the Lewis acid. Complexes **13** and **14** were found to be unstable in solution, gradually decomposing to the new complexes **15** and **16** with loss of CO, where the B(C₆F₅)₃ molecule is coordinated to the oxo ligand, through a Nb−O−B linkage. These compounds can alternatively be prepared by the direct reaction of the oxo complexes Cp′₂Nb(O)(R) (R = CH₂CH₃, CH₂-CH₂C₆H₅) with B(C₆F₅)₃. The IR spectra of the decarbonylated products **15** and **16** exhibit ν(Nb=O) at ca. 839 cm⁻¹, which is slightly shifted with regard to the oxo complexes (ν(Nb=O) at ca. 875 cm⁻¹), indicating that the electron density around the Nb=O bond is reduced through the coordination of the Lewis acid B(C₆F₅)₃. The formation of adducts such as **13** and **14**,

(12) A similar weak α-interaction was described for the 18-electron Cp₂Nb(CH₃C≡CCH₃)(CH₂CH₃) complex: Yasuda, H.; Yamamoto, H.; Arai, T.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1991**, *10*, 4058. Other examples of group 5 alkyl complexes with α-agostic interactions are (C₅^{t}Bu₅)TaCl₂(CH₂^{t}Bu)(CH₂CMe₂CH₂)₂[13] (C₅H₅)Nb(N-2,6-C₆H₃^{i}Pr₂)(CH₂^{t}Bu)₂,[14] and Tp′NbCl(CH₂CH₃)(RC≡CR′).[15]

(13) van der Heidjen, H.; Gal, A. W.; Pasman, P.; Orpen, A. G. *Organometallics* **1985**, *4*, 1847.

(14) Poole, A. D.; Williams, D. N.; Kenwright, A. M.; Gibson, V. C.; Clegg, W.; Hockless, D. C. R.; O'Neil, P. A. *Organometallics* **1993**, *12*, 2549.

(15) Etienne, M. *Organometallics* **1994**, *13*, 410.

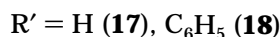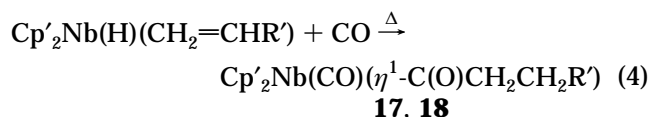(16) Fu, P.-F.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1992**, *11*, 2607.

where the C=O band of the coordinated CO_2 is polarized and the electron density around the metal center is reduced, opens up new prospects for reactivity studies on these molecules with, for example, unsaturated compounds. ^{1}H and ^{13}C NMR spectra of **13** and **14** show little differences from the corresponding spectra of **9** and **10**, although all attempts to detect the resonances of the coordinated CO_2 were unsuccessful. ^{19}F NMR spectra for complexes **13**−**16** (see Experimental Section) have confirmed the presence of the $B(C_6F_5)_3$ group bonded to the niobocene moieties.

Finally, in an effort to perform a more in-depth study on the reactivity of the olefin−hydride complexes **3** and **4** toward carbon monoxide, toluene solutions of these complexes were refluxed under pressure of CO and led to the isolation of acylniobocene species $Cp'_2Nb(CO)(\eta^1\text{-}C(O)CH_2CH_3)$ (**17**) and $Cp'_2Nb(CO)(\eta^1\text{-}C(O)CH_2\text{-}CH_2C_6H_5)$ (**18**) after appropriate workup (eq 4).

$$Cp'_2Nb(H)(CH_2{=}CHR') + CO \xrightarrow{\Delta}$$
$$Cp'_2Nb(CO)(\eta^1\text{-}C(O)CH_2CH_2R') \quad (4)$$
$$\mathbf{17}, \mathbf{18}$$

$$R' = H\ (\mathbf{17}),\ C_6H_5\ (\mathbf{18})$$

The same complexes were obtained from the reaction of **7** and **8** with CO under similar experimental conditions. Furthermore, reactions of **17** and **18** with CF_3-COOH in acetone as solvent gave the corresponding aldehydes and the niobocene trifluoroacetato complex $Cp'_2Nb(CO)(\eta^1\text{-}(OC(O)CF_3))$,[17] in agreement with eq 5.

$$R' = H\ \mathbf{17},\ C_6H_5\ \mathbf{18}$$
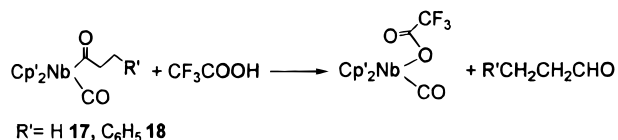
Although cyclopentadienylacylniobium and -tantalum species arising from migratory insertion of alkyl−carbonyl complexes have been claimed to participate as intermediates in different processes,[18] no neutral acyl-metallocenes have been isolated or characterized. It is noteworthy that Bercaw and co-workers have previously reported[19] the formation of similar neutral acyl−carbonyl niobocene complexes but no spectroscopic details were presented. Furthermore, several cationic acyl complexes, $Cp'_2Nb^+Cl(R_1R_2HCC{=}O)$, formed by the protonation of niobocene ketene complexes, have been described.[20] Spectroscopic data are consistent with the proposed formulas for complexes **17** and **18**. The IR spectra contain an acyl C=O stretch at 1599 cm^{-1}, and although this value is lower that reported for the foregoing cationic acylniobocenes which contain an η^2-acyl (ca. 1620 cm^{-1}), an η^1-acyl coordination must be proposed in our complexes in order to attain an 18-

electron configuration for a Nb(III) ion.[21] This represents an unusual situation, because η^2-acyl coordination is very commonly encountered among the early transition metals.[22] In addition, the IR carbonyl C≡O stretches for complexes **17** and **18** appear at 1895 and 1897 cm^{-1}, respectively, similar to the values found for **7** and **8**. The ^{13}C NMR spectra provide additional information. The acyl carbon resonates downfield at 278 and 277 ppm for **17** and **18**, thus appearing at higher field than in the cationic acylniobocenes (ca. 285 ppm). Finally, the carbon atoms of the carbonyl ligands resonate at 263 and 262 ppm, respectively (see Experimental Section).

In conclusion, we have described in this paper the activation of carbon dioxide by alkylniobocenes to give stable carbon dioxide complexes and established examples of migratory insertion of alkyl−carbonyl niobocene complexes to give the first characterized neutral acylniobocene complexes

Experimental Section

All reactions were performed using standard Schlenk-tube techniques under an atmosphere of dry nitrogen. Different styrenes, $C_6H_5CH_2CH_2MgBr$ and CH_3CH_2MgCl, were purchased from Aldrich and used as received. Solvents were distilled from appropriate drying agents and degassed before use. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyzer. Infrared spectra were obtained in the region 200−4000 cm^{-1} using a Perkin-Elmer 883 spectrophotometer. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on Varian-Unity FT-300 and Gemini FT-200 spectrometers, and the chemical shifts were determined by reference to the residual deuterated solvent peaks.

Preparation of $[(C_5H_4SiMe_3)_2Nb(H)(CH_2{=}CH_2)]$ (3). To an Et$_2$O (40 mL) solution of $[(C_5H_4SiMe_3)_2NbCl]_2$ (490 mg, 1.36 mmol) was added an equimolar quantity of CH_3CH_2MgCl (2 M, Et$_2$O) at 0 °C. The solution was stirred and warmed to room temperature for 3 h. The solvent was removed in vacuo, and the resulting solid was extracted with cold pentane (20 mL). Complex **3** was obtained as a microcrystalline yellow solid (387 mg, 0.98 mmol, 72%) after concentration and cooling of the solution.

3: ^{1}H NMR (C_6D_6) δ (ppm) −3.20 (s, 1H, Nb**H**), 0.24 (s, 18H, Si**Me**$_3$), 0.7 and 1.05, (4H, **CH**$_2${=}**CH**$_2$), 3.44 (2H), 3.71 (2H), 4.99 (4H) (m, C_5**H**$_4$SiMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ (ppm) 0.64 (Si**Me**$_3$), 10.34 and 14.73 (**CH**$_2${=}**CH**$_2$), 92.15, 93.67, 93.77, 99.82 (**C**$_5$H$_4$SiMe$_3$). Anal. Calcd for $C_{18}H_{31}Si_2Nb$: C, 54.50; H, 7.80. Found: C, 54.40; H, 7.90. For complex **4** see ref 3h.

Preparation of $[(C_5H_4SiMe_3)_2Nb(H)(CH_2{=}CHR)]$ (R = $C_6H_4CH_3$ (5), $C_6H_4OCH_3$ (6) (Endo + Exo Mixtures)). To a solution of $(C_5H_4SiMe_3)_2Nb(H)_3$ (300 mg, 0.81 mmol) in 20 mL of toluene was added by syringe a 1.62 mmol portion of the corresponding styrene. The mixture was warmed to 65 °C and stirred for 3 h. Alternatively, the reaction can be carried out at room temperature over 48 h. The resulting solution was filtered and evaporated to dryness for several hours. The yellow-brown oily residue was extracted with diethyl ether (20 mL). Complexes **5** and **6** were isolated on cooling as yellow crystalline needles (356 mg, 0.73 mmol, 90% yield for **5**; 365 mg, 0.73 mmol, 90% yield for **6**).

5-exo: ^{1}H NMR (C_6D_6) δ (ppm) −3.20 (s, 1H, Nb**H**), 0.09 (s, 9H, Si**Me**$_3$), 0.15 (s, 9H, Si**Me**$_3$), 0.90 (dd, $J_{AB} = 2$ Hz, $J_{AM} = 5$ Hz, 1H, C**H**H=CHR), 1.40 ($J_{BA} = 2$ Hz, $J_{BM} = 5$ Hz, 1H, CH**H**=CHR), 2.20 (s, 3H, C**H**$_3$), 3.30 ($J_{MA} = 5$ Hz, $J_{MB} = 5$ Hz, 1H, CH$_2$=C**H**R), 3.51 (1H), 3.61 (1H), 3.72 (2H), 4.61 (1H), 4.81 (1H), 5.02 (2H) (m, C_5**H**$_4$SiMe$_3$), 7.00−7.40 (m, 4H, C_6**H**$_4$).

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5-endo: ^{1}H NMR (C$_6$D$_6$) δ (ppm) −2.60 (s, 1H, Nb**H**), 0.10 (s, 9H, SiMe$_3$), 0.12 (s, 9H, SiMe$_3$), 1.30 (J_{AB} = 2 Hz, J_{AM} = 5 Hz, 1H, C**H**H=CHR), 1.60 (J_{BA} = 2 Hz, J_{BM} = 5 Hz, 1H, CH**H**=CHR), 2.30 (s, 3H, C**H**$_3$), 2.60 (J_{MA} = 5 Hz, J_{MB} = 5 Hz, 1H, CH$_2$=C**H**R), 3.31 (1H), 3.51 (1H), 3.80 (2H), 4.21 (1H), 4.81 (1H), 5.11 (1H), 5.52 (1H) (m, C$_5$**H**$_4$SiMe$_3$), 7.00−7.40 (m, 4H, C$_6$**H**$_4$). Anal. Calcd for C$_{25}$H$_{37}$Si$_2$Nb: C, 61.70; H, 7.66. Found: C, 61.50; H, 7.63.

6-exo: ^{1}H NMR (C$_6$D$_6$) δ (ppm) −3.20 (s, 1H, Nb**H**), 0.10 (s, 9H, SiMe$_3$), 0.20 (s, 9H, SiMe$_3$), 0.90 (J_{AB} = 2 Hz, J_{AM} = 5 Hz, 1H, C**H**H=CHR), 1.30 (J_{BA} = 2 Hz, J_{BM} = 5 Hz, 1H, CH**H**=CHR), 3.20 (s, 3H, C**H**$_3$), 3.30 (J_{MA} = 5 Hz, J_{MB} = 5 Hz, 1H, CH$_2$=C**H**R), 3.51 (1H), 3.70 (1H), 3.82 (1H), 3.90 (1H), 4.61 (1H), 4.81 (1H), 5.09 (2H) (m, C$_5$**H**$_4$SiMe$_3$), 7.00−7.40 (m, 4H, C$_6$**H**$_4$).

6-endo: ^{1}H NMR (C$_6$D$_6$) δ (ppm) −2.60 (s, 1H, Nb**H**), 0.14 (s, 9H, SiMe$_3$), 0.15 (s, 9H, SiMe$_3$), 1.40 (J_{AB} = 2 Hz, J_{AM} = 5 Hz, 1H, C**H**H=CHR), 1.50 (J_{BA} = 2 Hz, J_{BM} = 5 Hz, 1H, CH**H**=CHR), 3.40 (s, 3H, C**H**$_3$), 2.60 (J_{MA} = 5 Hz, J_{MB} = 5 Hz, 1H, CH$_2$=C**H**R), 3.31 (1H), 3.41 (1H), 3.50 (1H), 4.31 (2H), 5.01 (1H), 5.52 (2H) (m, C$_5$**H**$_4$SiMe$_3$), 7.00−7.40 (m, 4H, C$_6$**H**$_4$). Anal. Calcd for C$_{25}$H$_{37}$Si$_2$ONb: C, 59.74; H, 7.42. Found: C, 59.65; H, 7.35.

Preparation of [(C$_5$H$_4$SiMe$_3$)$_2$Nb(CO)(CH$_2$CH$_3$)] (7). A yellow hexane solution (30 mL) of [(C$_5$H$_4$SiMe$_3$)$_2$Nb(H)(CH$_2$=CH$_2$)] (298 mg, 0.78 mmol) under a CO atmosphere was stirred for 16 h at room temperature. The solution became increasingly green, and finally a green oily residue was obtained after removing the solvent. All attempts to crystallize this oily material in several solvents, namely pentane, diethyl ether, acetonitrile, dichloromethane, etc., were unsuccessful. Nevertheless, the green oily product showed spectroscopic purity by NMR (90% yield).

The reaction can be speeded up at higher temperature (50 °C), taking 6 h instead of 16 h.

7: IR (KBr) 1895 cm^{-1} (ν_{CO}); ^{1}H NMR(C$_6$D$_6$) δ (ppm) 0.09 (s, 18H, SiMe$_3$), 0.5 (q, 2H, CH$_2$), 1.36 (t, 3H, CH$_3$, J = 7.0 Hz), 4.39 (2H), 4.40 (2H), 4.67 (2H), 4.95 (2H) (m, C$_5$**H**$_4$SiMe$_3$); ^{13}C-{^{1}H} NMR (C$_6$D$_6$) δ 0.39 (SiMe$_3$), 10.20 (CH$_2$CH$_3$), 23.53 (CH$_2$CH$_3$), 91.80 (C$_{ipso}$), 90.20, 93.73, 98.29, 101.23 (C$_5$H$_4$SiMe$_3$), 266 (CO).

Preparation of [(C$_5$H$_4$SiMe$_3$)$_2$Nb(CO)(CH$_2$CH$_2$C$_6$H$_5$)] (8). A hexane solution (30 mL) of [(C$_5$H$_4$SiMe$_3$)$_2$Nb(H)(C$_6$H$_5$-CH=CH$_2$)] (endo and exo isomers) (162 mg, 0.30 mmol) under a CO atmosphere was stirred for 48 h at room temperature. The solution became increasingly green, and finally a green oily residue was obtained after removing solvent. All attempts to crystallize this oily material in several solvents, namely pentane, diethyl ether, acetonitrile, dichloromethane, etc., were unsuccessful. Nevertheless, the green oily product showed spectroscopic purity by NMR (90% yield).

The reaction can be speeded up at higher temperature (50 °C), taking 12 h instead of 48 h.

8: IR (KBr) 1897 cm^{-1} (ν_{CO}); ^{1}H NMR (C$_6$D$_6$) δ (ppm) 0.08 (s, 18H, SiMe$_3$), 0.4 (m, 2H, CH$_2$CH$_2$Ph), 2.52 (m, 2H, CH$_2$CH$_2$-Ph), 4.37 (2H), 4.49 (2H), 4.68 (2H), 4.97 (2H) (m, C$_5$**H**$_4$SiMe$_3$), 7−7.25 (C$_6$**H**$_5$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 0.24 (SiMe$_3$), 7.17 (CH$_2$CH$_2$Ph), 46.64 (CH$_2$CH$_2$Ph), 95.98 (C$_{ipso}$), 90.20, 96.95, 98.68, 101.08 (C$_5$H$_4$SiMe$_3$), 150.11 (C$_{ipso}$), 124.96, 127.82, 128.47 (C$_6$H$_5$), 266 (CO).

Preparation of [(C$_5$H$_4$SiMe$_3$)$_2$Nb(η^2-CO$_2$)(CH$_2$CH$_3$)] (9). A yellow hexane solution (30 mL) of [(C$_5$H$_4$SiMe$_3$)$_2$Nb(H)-(CH$_2$=CH$_2$)] (464 mg, 1.17 mmol) under a CO$_2$ atmosphere (3 atm in a Fisher−Porter bottle) was stirred for 48 h at room temperature, and a white precipitate was formed. The solid was isolated by filtration, washed with cold hexane, and then recrystallized from toluene to give white needles of **9** (384 mg, 0.90 mmol, 77% yield).

9: IR (KBr) 1697 cm^{-1} (ν_{CO}); ^{1}H NMR (CDCl$_3$) δ (ppm) 0.20 (s, 18H, SiMe$_3$), 1.41 (q, 2H, C**H**$_2$), 1.54 (t, 3H, C**H**$_3$, J = 7.0 Hz), 5.26 (2H), 5.64 (2H), 5.83 (2H), 6.02 (2H) (m, C$_5$**H**$_4$SiMe$_3$);

^{13}C{^{1}H} NMR (C$_6$D$_6$) δ (ppm) −0.88 (SiMe$_3$), 23.48 (**C**H$_2$CH$_3$), 19.53 (CH$_2$**C**H$_3$), 117.37 (C$_{ipso}$), 99.81, 101.33, 107.09, 119.47 (C$_5$H$_4$SiMe$_3$), 198.24 (CO$_2$). Anal. Calcd for C$_{19}$H$_{31}$Si$_2$NbO$_2$: C, 51.80; H, 7.09. Found: C, 51.50; H, 6.90.

Preparations of [(C$_5$H$_4$SiMe$_3$)$_2$Nb(η^2-CO$_2$)(CH$_2$CH$_2$-C$_6$H$_4$R)] (R = H (10), CH$_3$ (11), OCH$_3$ (12)). A yellow hexane solution (30 mL) of [(C$_5$H$_4$SiMe$_3$)$_2$Nb(H)(C$_6$H$_5$CH=CH$_2$)] (a mixture of isomers, exo:endo ratio 2:1; 800 mg, 1.67 mmol) under a CO$_2$ atmosphere (4 atm in a Fisher−Porter bottle) was stirred for 48 h at room temperature, and a white precipitate was formed. The solid was isolated by filtration, washed with cold hexane, and then recrystallized from toluene to obtain white needles of **10** (515 mg, 1 mmol, 60% yield).

Complexes **11** (529 mg, 1 mmol, 60% yield) and **12** (515 mg, 1 mmol, 60% yield) were prepared in a similar way.

10: IR (KBr) 1697 cm^{-1} (ν_{CO}); ^{1}H NMR (CDCl$_3$) δ (ppm) 0.18 (s, 18H, SiMe$_3$), 1.63 (m, 2H, C**H**$_2$CH$_2$Ph), 2.95 (m, 2H, CH$_2$C**H**$_2$Ph), 5.32 (2H), 5.72 (2H), 5.86 (2H), 6.07 (2H) (m, C$_5$**H**$_4$SiMe$_3$), 7.2−7.4 (C$_6$**H**$_5$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ (ppm) −1.01 (SiMe$_3$), 32.43 (**C**H$_2$CH$_2$Ph), 40.38 (CH$_2$**C**H$_2$Ph), 116.57 (C$_{ipso}$), 101.58, 101.67, 108.55, 117.64 (C$_5$H$_4$SiMe$_3$), 147.12 (C$_{ipso}$), 125.06, 127.56, 128.21 (C$_6$H$_5$), 200.94 (CO$_2$). Anal. Calcd for C$_{25}$H$_{35}$Si$_2$O$_2$Nb: C, 58.12; H, 6.80. Found: C, 58.30; H, 6.70.

11: IR (KBr) 1710 cm^{-1} (ν_{CO}); ^{1}H NMR (CDCl$_3$) δ (ppm) 0.17 (s, 18H, SiMe$_3$), 1.64 (m, 2H, C**H**$_2$CH$_2$C$_6$H$_4$CH$_3$), 2.95 (m, 2H, CH$_2$C**H**$_2$C$_6$H$_4$CH$_3$), 2.30 (s, 3H, C**H**$_3$), 5.29 (2H), 5.69 (2H), 5.84 (2H), 6.04 (2H) (m, C$_5$**H**$_4$SiMe$_3$), 7.00−7.22 (C$_6$**H**$_4$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ (ppm) −1.12 (SiMe$_3$), 20.74 (CH$_2$CH$_2$C$_6$H$_4$**C**H$_3$), 32.55 (CH$_2$**C**H$_2$C$_6$H$_4$CH$_3$), 39.84 (CH$_3$), 116.44 (C$_{ipso}$), 101.50, 101.66, 108.43, 117.52 (C$_5$H$_4$SiMe$_3$), 144.00 (C$_{ipso}$), 127.34, 128.79 (C$_6$H$_4$), 198.00 (CO$_2$). Anal. Calcd for C$_{26}$H$_{37}$Si$_2$O$_2$Nb: C, 58.85; H, 7.03. Found: C, 58.30; H, 6.80.

12: IR (KBr) 1720 cm^{-1} (ν_{CO}); ^{1}H NMR (CDCl$_3$) δ (ppm) 0.20 (s, 18H, SiMe$_3$), 1.60 (m, 2H, C**H**$_2$CH$_2$C$_6$H$_4$OCH$_3$), 2.92 (m, 2H, CH$_2$C**H**$_2$C$_6$H$_4$OCH$_3$), 3.81 (s, 3H, C**H**$_3$), 5.33 (2H), 5.73 (2H), 5.87 (2H), 6.08 (2H) (m, C$_5$**H**$_4$SiMe$_3$), 6.88−7.20 (C$_6$**H**$_4$); ^{13}C-{^{1}H} NMR (C$_6$D$_6$) δ (ppm) −1.03 (SiMe$_3$), 32.68 (**C**H$_2$CH$_2$C$_6$H$_4$-OCH$_3$), 39.42 (CH$_2$**C**H$_2$C$_6$H$_4$OCH$_3$), 55.09 (CH$_3$), 116.56 (C$_{ipso}$), 101.55, 101.62, 108.55, 113.63 (C$_5$H$_4$SiMe$_3$), 157.19 (C$_{ipso}$), 128.40, 139.35 (C$_6$H$_4$), 200.96 (CO$_2$). Anal. Calcd for C$_{26}$H$_{37}$-Si$_2$O$_3$Nb: C, 57.13; H, 6.82. Found: C, 57.10; H, 6.70.

Preparations of [(C$_5$H$_4$SiMe$_3$)$_2$Nb(η^2-CO$_2$-B(C$_6$F$_5$)$_3$)-(CH$_2$CH$_2$R)] (R = H (13), C$_6$H$_5$ (14)). To a solution of [(C$_5$H$_4$-SiMe$_3$)$_2$Nb(η^2-CO$_2$)(CH$_2$CH$_3$)] (85 mg, 0.20 mmol) in 10 mL of dichloromethane at −70 °C was added an equimolar amount of B(C$_6$F$_5$)$_3$ (99 mg, 0.20 mmol), dissolved in 10 mL of the same cold solvent. The colorless solution became yellow immediately. The solution was warmed and the solvent removed under vacuum as fast as possible to give a pale yellow solid of complex **13** (181 mg, 0.19 mmol, 95% yield). Attempts to crystallize this solid from toluene or dichloromethane solutions were unsuccessful, because the liberation of CO was observed and the complex **15** was isolated.

Complex **14** (195 mg, 0.19 mmol, 95% yield) was prepared in a similar way.

Solutions of compounds **13** and **14** were monitored by ^{1}H NMR to observe their evolution to complexes **15** and **16**, respectively.

13: IR (KBr) 1570 cm^{-1} (ν_{CO}), 1600, 1514, 978 cm^{-1} (ν_{CF}); ^{1}H NMR (C$_6$D$_6$) δ (ppm) −0.11 (s, 18H, SiMe$_3$), 1.04 (t, 3H, CH$_3$), 1.28 (q, 2H, CH$_2$, J = 7.0 Hz), 4.71 (2H), 5.21 (4H), 5.35 (2H) (m, C$_5$**H**$_4$SiMe$_3$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ (ppm) −0.64 (SiMe$_3$), 17.60 (**C**H$_2$CH$_3$), 29.10 (CH$_2$**C**H$_3$), 108.71, 111.94, 111.91, 115.49 (C$_5$H$_4$SiMe$_3$), 135.97, 139.37, 146.67, 149.98 (B(**C**$_6$F$_5$)$_3$); ^{19}F NMR (C$_6$D$_6$) −134.22 (**F**$_o$, dd), −160.72 (**F**$_p$, t), −165.11 (**F**$_m$, td). Anal. Calcd for C$_{37}$H$_{31}$F$_{15}$BSi$_2$NbO$_2$: C, 46.66; H, 3.28. Found: C, 46.30; H, 3.21.

14: IR (KBr) 1575 cm^{-1} (ν_{CO}), 1610, 1513, 968 cm^{-1} (ν_{CF}); ^{1}H NMR (C$_6$D$_6$) δ (ppm) −0.09 (s, 18H, SiMe$_3$), 1.62 (m, 2H, C**H**$_2$-CH$_2$Ph), 2.34 (m, 2H, CH$_2$C**H**$_2$Ph), 4.84 (2H), 5.28 (2H), 5.30 (2H), 5.42 (2H, m, C$_5$**H**$_4$SiMe$_3$), 7.00−7.20 (C$_6$**H**$_5$); [13]C{[1]H}

NMR (C_6D_6) δ (ppm) -0.66 (Si**Me**$_3$), 37.66 (**C**H$_2$CH$_2$Ph), 39.07 (CH$_2$**C**H$_2$Ph), 111.62 (**C**$_{ipso}$), 108.57, 111.33, 112.27, 115.62 (**C**$_5$H$_4$SiMe$_3$), 146.41 (**C**$_{ipso}$), 135.98, 139.29, 147.05, 150.10 (B(**C**$_6$F$_5$)$_3$); ^{19}F NMR (C_6D_6) δ (ppm) -134.72 (**F**$_o$, dd), -159.09 (**F**$_p$, t), -163.12 (**F**$_m$, td). Anal. Calcd for $C_{43}H_{35}F_{15}BSi_2$-NbO$_2$: C, 50.21; H, 3.43. Found: C, 50.40; H, 3.40.

Preparations of [($C_5H_4SiMe_3$)$_2$Nb(O$-$B(C_6F_5)$_3$)(CH$_2$-CH$_2$R)] (R = H (15), C_6H_5 (16)). To a solution of [(C_5H_4-SiMe$_3$)$_2$Nb(η^2-CO$_2$)(CH$_2$CH$_3$)] (200 mg, 0.45 mmol) in 20 mL of dichloromethane was added an equimolar amount of B(C_6F_5)$_3$ (230 mg, 0.45 mmol) in 10 mL of dichloromethane, at room temperature. The colorless solution became yellow immediately. The mixture was stirred for 12 h and the solvent removed under vacuum to give a yellow solid, which was recrystallized from CH$_2$Cl$_2$ to give rise to yellow crystals of **15** (380 mg, 0.40 mmol, 90% yield).

Complex **15** can be also prepared by reaction of a dichloromethane solution (20 mL) of ($C_5H_4SiMe_3$)$_2$Nb(O)(CH$_2$CH$_3$) (200 mg, 0.50 mmol) with an equimolar amount of B(C_6F_5)$_3$ (256 mg, 0.50 mmol) at room temperature. The solution was stirred over 30 min, and after workup similar to that described above, yellow crystals of **15** were obtained.

Complex **16** (410 mg, 0.40 mmol, 90% yield) was prepared in a similar way.

15: IR (KBr) 897 cm^{-1} ($\nu_{Nb=O}$), 1640, 1514, 974 cm^{-1} (ν_{CF}); ^{1}H NMR (C_6D_6) δ (ppm) -0.08 (s, 18H, Si**Me**$_3$), 1.25 (t, 3H, CH$_3$), 2.01 (q, 2H, CH$_2$, $J = 7.0$ Hz), 5.44 (2H), 5.62 (2H), 5.84 (2H), 5.98 (2H) (m, C_5**H**$_4$SiMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ (ppm) -0.54 (Si**Me**$_3$), 21.26 (**C**H$_2$CH$_3$), 42.03 (CH$_2$**C**H$_3$), 119.96 (**C**$_{ipso}$), 110.51, 118.94, 120.73, 122,52 (**C**$_5$H$_4$SiMe$_3$), 135.75, 139.06, 146.95, 150.13 (B(**C**$_6$F$_5$)$_3$); ^{19}F NMR(C_6D_6) δ (ppm) -132.04 (**F**$_o$, dd), -58.73 (**F**$_p$, t), -164.71 (**F**$_m$, td). Anal. Calcd for $C_{36}H_{31}$-F$_{15}BSi_2NbO$: C, 46.77; H, 3.38. Found: C, 46.20; H, 3.80.

16: IR (KBr) 894 cm^{-1} ($\nu_{Nb=O}$), 1600, 1514, 980 cm^{-1} (ν_{CF}); ^{1}H NMR (C_6D_6) δ (ppm) -0.07 (s, 18H, Si**Me**$_3$), 2.29 (m, 2H, CH$_2$CH$_2$Ph), 2.75 (m, 2H, CH$_2$**C**H$_2$Ph), 5.58 (2H), 5.61 (2H), 5.92 (2H), 6.10 (2H) (m, C_5**H**$_4$SiMe$_3$), 7.00$-$7.20 (C_6**H**$_5$); ^{13}C-{^{1}H} NMR (C_6D_6) δ (ppm) -0.50 (Si**Me**$_3$), 42.20 (**C**H$_2$CH$_2$Ph), 49.34 (CH$_2$**C**H$_2$Ph), 119.80 (**C**$_{ipso}$), 110.01, 119.15, 120.99, 123.48 (**C**$_5$H$_4$SiMe$_3$), 135.97, 139.31, 147.08, 150.28 (B(**C**$_6$F$_5$)$_3$); ^{19}F NMR (C_6D_6) δ (ppm) -132.41 (**F**$_o$, dd), -158.80 (**F**$_p$, t), -164.91 (**F**$_m$, td). Anal. Calcd for $C_{42}H_{35}F_{15}BSi_2NbO$: C, 50.40; H, 3.53. Found: C, 50.01; H, 3.43.

Preparation of [($C_5H_4SiMe_3$)$_2$Nb(CO)(η^1-C(O)CH$_2$CH$_3$)] (17). A yellow toluene solution (20 mL) of [($C_5H_4SiMe_3$)$_2$Nb-(H)(CH$_2$=CH$_2$)] (210 mg, 0.52 mmol) under a CO atmosphere (3 atm in a Fisher$-$Porter bottle) at 80 °C was stirred for 48

h. The yellow solution became red-brown. The solvent was removed in vacuo, giving rise to a brown oily material (yield almost quantitative by NMR). All attempts to crystallize this product from several solvents, namely pentane, diethyl ether, acetonitrile, dichloromethane, etc., were unsuccessful; therefore, complex **17** was isolated as a pure oily material.

17: IR (KBr) 1599, 1895 cm^{-1} (ν_{CO}); ^{1}H NMR (C_6D_6) δ (ppm) -0.07 (s, 18H, Si**Me**$_3$), 0.99 (t, 3H, CH$_3$), 2.68 (q, 2H, CH$_2$, $J = 7.20$ Hz), 4.51 (2H), 4.62 (2H), 4.86 (2H), 5.03 (2H) (m, C_5**H**$_4$-SiMe$_3$); ^{13}C{^{1}H} NMR (C_6D_6) δ (ppm) 0.04 (Si**Me**$_3$), 9.54 (CH$_2$**C**H$_3$), 59.91 (**C**H$_2$CH$_3$), 91.81, 96.42, 98.03. 100.87 (**C**$_5$H$_4$-SiMe$_3$), 263 (**C**O), 277.97 (**C**(O)R).

Preparation of [($C_5H_4SiMe_3$)$_2$Nb(CO)(η^1-C(O)CH$_2$CH$_2$-C_6H_5)] (18). A yellow toluene solution (20 mL) of [(C_5H_4-SiMe$_3$)$_2$Nb(H)(C_6H_5CH=CH$_2$)] (300 mg, 0.63 mmol) under a CO atmosphere (3 atm in a Fisher$-$Porter bottle) at 80 °C was stirred for 48 h. The yellow solution became red-brown. The solvent was removed in vacuo, giving a brown oily material (yield almost quantitative by NMR). All attempts to crystallize this product from several solvents, namely pentane, diethyl ether, acetonitrile, dichloromethane, etc., were unsuccessful. Complex **18** was isolated as a pure oily material.

18: IR (KBr) 1599, 1897 cm^{-1} (ν_{CO}); ^{1}H NMR (C_6D_6) δ (ppm) 0.05 (s, 18H, Si**Me**$_3$), 2.80 (m, 2H, CH$_2$CH$_2$Ph), 2.99 (m, 2H, CH$_2$**C**H$_2$Ph), 4.45 (2H), 4.49 (2H), 4.81 (2H), 4.95 (2H) (m, C_5**H**$_4$SiMe$_3$), 7.00$-$7.20 (m, 5H, C_6**H**$_5$); ^{13}C{^{1}H} NMR (C_6D_6) δ (ppm) 0.00 (Si**Me**$_3$), 31.21 (**C**H$_2$CH$_2$Ph), 68.49 (CH$_2$**C**H$_2$Ph), 96.58 (**C**$_{ipso}$), 91.75, 96.52, 98.32, 101.37 (**C**$_5$H$_4$SiMe$_3$), 143.79 (**C**$_{ipso}$), 125.58, 128.52, 129.19 (**C**$_5$H$_5$), 262.52 (**C**O), 277.14 (**C**(O)R).

Protonation of 17 and 18 with CF$_3$COOH. CF$_3$COOH was added to an acetone-d_6 solution of **17** or **18** in a 5 mm NMR tube, at room temperature, to give the corresponding aldehydes and the niobocene trifluoroacetato complex [(C_5H_4-SiMe$_3$)$_2$Nb(CO)(OC(O)CF$_3$)].[17]

CH$_3$CH$_2$CHO: ^{1}H NMR (acetone-d_6) δ (ppm) 1.02 (**C**H$_3$), 2.43 (**C**H$_2$), 9.73 (**C**HO).

PhCH$_2$CH$_2$CHO: ^{1}H NMR (acetone-d_6) δ (ppm) 2.60 (Ph**C**H$_2$), 2.80 (**C**H$_2$CHO), 7.00$-$7.42 (C_5**H**$_5$), 9.78 (**C**HO).

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