

Synthesis and Characterization of Nb(OR)₄[OC(O)OR] (R = Me, Et, Allyl) and Their Reaction with the Parent Alcohol To Afford Organic Carbonates

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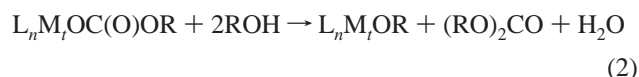
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Nb(OR)₄[OC(O)OR] (R = Me, Et, allyl) compounds have been synthesized by the reaction of dimeric alkoxo complexes [Nb(OR)₅]₂ with CO₂. The kinetics of the reaction has shown that the monomer in equilibrium with the dimer is the species that reacts with CO₂. The resulting compounds are monomeric with a η²-O,O-bonded hemicarbonate group. The CO₂ uptake is reversible. The hemicarbonates react with the parent alcohol to afford the relevant organic carbonate (RO)₂CO with a turnover number (TON) of >2.

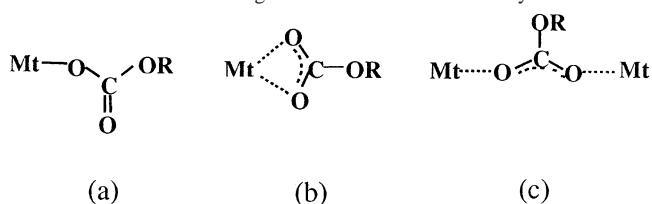
Introduction

The insertion of CO₂ into M–OR bonds of transition-metal alkoxo complexes¹ (eq 1) is well-known for both early^{2,3} and late transition metals.⁴ The reaction usually occurs under mild conditions and, for several metal centers, it is found to be reversible.^{2,4,5} The CO₂ insertion may have a practical interest, because the resulting metal hemicarbonate may generate the organic carbonate (eq 2).



The hemicarbonate moiety resulting from the insertion of CO₂ into the M–OR bond can act as a η¹-monodentate ligand

Chart 1. Mode of Bonding of the Hemicarbonate Moiety



(panel a in Chart 1) or η²-bidentate ligand⁶ (panel b in Chart 1) to a single metal center, or as a η²-μ² ligand, bridging two metal centers (panel c in Chart 1). In the latter case, dimers or polymers can be formed, whereas in cases a and b, monomers are obtained.

The existing literature data show that when two –OR groups are linked to a metal center, only the product of the mono insertion of CO₂ is easily isolated, although the insertion of CO₂ into the second M–OR bond has been reported to have favorable thermodynamics.^{7a} In this case, the available –OR group may react intermolecularly with the hemicarbonate moiety, under the appropriate conditions, with the formation of an organic carbonate.^{5,7b} This event generally converts the catalyst to an inactive form. Niobium

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penta-alkoxo complexes (R = Me, Et) have been known for a long time⁸ and have been reported to be dimeric [Nb(OR)₅]₂ in the solid state and in solution. Their reaction with CO₂ has been investigated only scarcely,³ and the resulting hemicarbonates have not been isolated or characterized in solution. In our previous work, we found that niobium complexes are catalysts in the carboxylation of epoxides⁹ and in the oxidative carboxylation of olefins¹⁰ to afford cyclic organic carbonates. We have now investigated the reaction of CO₂ with [Nb(OR)₅]₂ (R = Me, Et, allyl) and report on the characterization of Nb(OEt)₄[OC(O)OEt], a monomer with a chelating hemicarbonate moiety, and on its reactivity with the parent alcohol. We also describe the synthesis and reactivity of relevant systems with methyl and allyl substituents.

Experimental Section

All alcohols and solvents were RP Aldrich reagents. They were further purified, distilled,¹¹ and stored under dinitrogen over anhydrous calcium sulfate. [Nb(OEt)₅]₂ was synthesized as described below, using a modification of the method reported in the literature.⁸ Their molecular mass determination was performed using the apparatus for cryoscopy described in refs 12 and 13. NMR experiments were conducted using a 500 MHz or 300 MHz Bruker apparatus, as specified in the text. Deuterated CIL solvents were used. High-pressure reactions were conducted in a 100 mL autoclave thermostated with an electric heating jacket (maximum temperature of 675 K). The autoclaves were equipped with an inner glass reactor, to avoid metal contamination of the reagents, and with a valve for the continuous withdrawal of liquid samples. Reactions in supercritical CO₂ were performed in SITEC equipment with automatic temperature and pressure control. In the text, the symbol α represents the molar ratio of converted alcohol to initial alcohol.

Synthesis of [Nb(OEt)₅]₂ (1). To a reddish solution of NbCl₅ (3.72 g, 13.77 mmol) in toluene (100 mL), 20 mL (347.8 mmol) of ethanol was dropwise added. To the colorless resulting solution, NEt₃ (10 mL, 72.1 mmol) was added. After the solution was stirred for 3 h at 300 K, the mixture was filtered and the white solid that formed was removed. The resulting solution was pumped in vacuo at room temperature until toluene and ethanol were eliminated, and the residual liquid was distilled in vacuo (0.1 mmHg, 413 K) twice to obtain 3.591 g (11.28 mmol) of pure Nb(OEt)₅ (82% yield), which was shown to be a dimer.

The following analysis results were obtained. Anal. Calcd for C₂₀H₅₀Nb₂O₁₀ (%): C, 37.74; H, 7.91; Nb, 29.19. Found (%): C,

37.5; H, 7.7; Nb, 28.9. IR (KBr disks, neat; given in units of cm⁻¹): 2972 (s), 2930 (s), 2891 (s), 2863 (s), 2739 (w), 2697 (w), 1470 (m), 1441 (s), 1374 (s), 1352 (m), 1274 (w), 1114 (vs), 1069 (vs), 1030 (s), 915 (s), 880 (s), 837 (m), 799 (w), 569 (vs), 489 (s), 414 (m). ¹H NMR (recorded soon after the dissolution of [Nb(OEt)₅]₂ in toluene-*d*⁸, 500 MHz, 298 K): methyl protons at 1.30 (12 H, CH₃, ³J_{H,H} = 7.04 Hz, terminal OEt) and 1.38 ppm (3 H, CH₃, ³J_{H,H} = 6.68 Hz, bridging OEt), methylene protons at 4.50 (8 H, CH₂, ³J_{H,H} = 7.01 Hz, terminal OEt) and 4.29 ppm (2 H, CH₂, ³J_{H,H} = 6.31 Hz, bridging OEt). ¹³C NMR (toluene-*d*⁸, 500 MHz, 298 K): 19.17, 20.30, 69.47, and 70.37 ppm. With a HETCOR acquisition at 300 MHz, it was possible to assign the signals at 19.17 and 20.30 ppm to the methyl carbons of the bridging and terminal OEt groups, respectively; the signals at 69.47 and 70.37 ppm were assigned to the relevant respective methylene carbons.

If the ¹H NMR spectrum was recorded at intervals of time after the preparation of the sample, new signals were detected, in the regions of 4.80–4.60 and 1.40–1.30 ppm, that were attributed to the monomer. Their intensity grew with time and reached a maximum value in ~1–2 h, depending on the temperature. The integration of the signals allowed the equilibrium amount of monomer to be calculated, and that value was equal to 1.43 mol %. The equilibrium constant *K*_{eq} for the dissociation was evaluated to be 2.07 × 10⁻⁴.

Synthesis of [Nb(OMe)₅]₂ (2). This compound was prepared following the previously described procedure, starting from 3.21 g (11.89 mmol) of NbCl₅ and 15 mL (370.8 mmol) of methanol in toluene (100 mL). Nb(OMe)₅ was isolated as a white solid, and it was shown to be a dimer (2.35 g, 4.74 mmol; 79.7% yield).

Analysis results for this compound are as follows. Anal. Calcd for C₁₀H₃₀Nb₂O₁₀ (%): C, 24.21; H, 6.09; Nb, 37.45. Found (%): C, 24.0; H, 5.9; Nb, 37.4. IR (in hexachlorobutadiene mull; given in units of cm⁻¹): bands at 2910 (s), 2810 (w), 1455 (m), 1430 (s), 1375 (w), 1100 (vs), 1030 (s), 860 (m), 800 (m), 540 (s). ¹H NMR (toluene-*d*⁸, 500 MHz, 298 K): 4.53 (singlet, terminal OCH₃), 4.31 ppm (singlet, bridging OCH₃).

Synthesis of [Nb(O-allyl)₅]₂ (3). To 1.54 g (2.24 mmol) of [Nb(OEt)₅]₂, 2.0 mL (29.41 mmol) of allyl alcohol was added, and the solution was stirred for 50 min at 323 K. The formed ethanol was distilled in vacuo at 300 K, and the residual solution was stirred at 323 K for 50 min. This cycle was repeated twice, until no more ethanol was formed. The residue was distilled in vacuo at 440 K to afford the residual allyl alcohol and a yellow liquid that was identified to be Nb(O-allyl)₅. It was shown to be a dimer (1.44 g, 1.90 mmol, 84.8% yield).

Analysis results for this compound are as follows. Anal. Calcd for C₃₀H₅₀Nb₂O₁₀ (%): C, 47.63; H, 6.66; Nb, 24.56. Found (%): C, 47.3; H, 6.5; Nb, 24.3. IR (KBr disks, neat; given in units of cm⁻¹): bands at 3080 (m), 3002 (m), 2980 (m), 2900 (m), 2840 (s), 2750 (w), 2690 (w), 1640 (m), 1440 (m), 1410 (s), 1400 (m), 1350 (m), 1340 (m), 1240 (w), 1230 (w), 1090 (vs), 1010 (vs), 920 (s), 830 (s), 670 (s). ¹H NMR (toluene-*d*⁸, 500 MHz, 298 K) spectroscopy showed that the multiplicity of the signals is not well defined at room temperature; however, the analysis does show that the system is fluxional. Nevertheless, it was still possible to distinguish signals of allyloxo-terminal groups at 5.02, 5.04, 5.40, and 6.01 ppm from allyloxo bridging groups at 4.87, 5.07, 5.45, and 6.08 ppm. The signals at 5.02 and 4.87 ppm coalesce into a signal at 5.00 ppm at 355 K. Similarly, signals at 5.04 and 5.07 ppm, 5.40 and 5.45 ppm, 6.01 and 6.08 ppm afford three signals, at 5.06, 5.35, and 6.02 ppm, respectively, at the same temperature. ¹³C NMR (toluene-*d*⁸, 500 MHz, 298 K): 74.01, 75.15, 114.02, 114.12, 137.05, 138.62 ppm.

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Synthesis of Nb(OEt)₄[OC(O)OEt] (4), Nb(OMe)₄[OC(O)OMe] (5), and Nb(O-allyl)₄[OC(O)O-allyl] (6). For compound **4**, 1.32 g (2.07 mmol) of [Nb(OEt)₅]₂ was dissolved in ethanol (5 mL, 85.85 mmol) under CO₂ (0.1 MPa) and the solution was stirred for 70 h. The solvent was then evaporated at 290 K by bubbling CO₂. A yellow viscous liquid remained, which was characterized as the hemicarbonate (0.67 g, 1.863 mmol; 90% yield). The molecular mass determination by cryoscopy^{12,13} gave an experimental molecular mass of 391 uma, versus a theoretical value of 362 uma for the monomer Nb(OEt)₄[OC(O)OEt].

The analysis results for structure **4** are as follows. Anal. Calcd for C₁₁H₂₅NbO₇ (%): C, 36.48; H, 6.96; Nb, 25.65. Found (%): C, 36.0; H, 6.75; Nb, 25.4. IR (KBr disks, neat; given in units of cm⁻¹): bands at 2974 (s), 2928 (s), 2866 (s), 2700 (w), 1600 (s), 1472 (m), 1442 (s), 1414 (m), 1377 (s), 1353 (m), 1330 (m), 1275 (w), 1105 (vs), 1065 (vs), 917 (s), 880 (s), 807 (w), 664 (s). ¹H NMR (toluene-*d*⁸, 500 MHz, 298 K): methylene protons at 4.30 (broad signal, CH₂ of terminal OEt) and 4.09 ppm (quartet, ³J_{H,H} = 7.03 Hz, CH₂ of OC(O)OEt group); methyl protons at 1.2 (broad signal, CH₃ of terminal OEt) and 1.10 ppm (triplet, ³J_{H,H} = 6.98 Hz, CH₃ of OC(O)OEt group). ¹H NMR (toluene-*d*⁸, 500 MHz, 220 K): 3.97 (quartet, ³J_{H,H} = 7.04 Hz, CH₂ of OC(O)OEt group), 4.43 (quartet, ³J_{H,H} = 7.01 Hz, CH₂ of equatorial OEt group), and 4.51 ppm (quartet, ³J_{H,H} = 7.01 Hz, CH₂ of axial OEt group). ¹³C NMR (toluene-*d*⁸, 500 MHz, 298 K): 161.66 ppm [OC(O)O-].

Nb(OMe)₄[OC(O)OMe] (**5**) was synthesized in a manner similar to that for **4** from Nb(OMe)₅ in methanol under CO₂. A yellow solid was obtained, in a yield of 77.8%.

Analysis results for **5** are as follows. Anal. Calcd for C₆H₁₅NbO₇ (%): C, 24.67; H, 5.18; Nb, 31.81. Found (%): C, 24.3; H, 4.9; Nb, 31.4. IR (KBr disks, Nujol mull; given in units of cm⁻¹): 1600 [$\nu_{\text{asym}}(\text{OC}(\text{O}))$] and 1350 [$\nu_{\text{sym}}(\text{OC}(\text{O}))$]. ¹H NMR (toluene-*d*⁸, 500 MHz, 298 K): 3.73 ppm (singlet, -OC(O)OCH₃), 4.00 ppm (broad singlet, OCH₃ axial and equatorial). ¹³C NMR (toluene-*d*⁸, 500 MHz, 298 K): 160.22 ppm [OC(O)O-].

Nb(O-allyl)₄[OC(O)O-allyl] (**6**) was obtained from Nb(O-allyl)₅ and CO₂. The reaction was monitored by a parallel ¹H NMR and ¹³C NMR study. [Nb(O-allyl)₅]₂ (30 mg, 0.0397 mmol) dissolved in toluene-*d*⁸ (3 mL) was stirred under a CO₂ atmosphere for 70 h. The ¹H and ¹³C NMR spectra of the resulting solution were repeatedly recorded until no more changes were observed. When the new signals reached the maximum intensity, the bulk reaction was stopped and the hemicarbonate was isolated using the previously described procedure. The ¹H NMR (toluene-*d*⁸, 500 MHz, 298 K) spectrum showed, in addition to the weak signals of the residual Nb(O-allyl)₅, new strong signals: namely, a doublet of triplet centered at 4.54 ppm, a doublet of quartet centered at 5.26 ppm, and a multiplet at 5.83 ppm that was due to the hemicarbonate. The ¹³C NMR (toluene-*d*⁸, 500 MHz, 298 K) spectrum showed four new signals, at 68.04, 117.29, 133.40, and 161.12 ppm. The latter was assigned to the carbonate carbon.

Kinetics of Absorption of CO₂ by [Nb(OEt)₅]₂. [Nb(OEt)₅]₂ (0.5189 g, 1.63 mmol) was dissolved in benzene or ethanol that had been saturated with CO₂ in a thermostated (298 K) absorption cell connected to a gas buret. The gas adsorption was monitored for 70 h when the CO₂ uptake reached 0.9 mol/(mol niobium) (see Figure 1). The reaction was stopped at this time, and the product was isolated and confirmed to be Nb(OEt)₄[OC(O)OEt].

Reactivity of Nb(OR)₄[OC(O)OR]. Various methods were used to study the reactivity of Nb(OR)₄[OC(O)OR]. In one procedure, a quantity of the ethyl derivative (0.100 g, 0.28 mmol) was pumped in vacuo at 310 K for 30 min. The resulting liquid was analyzed

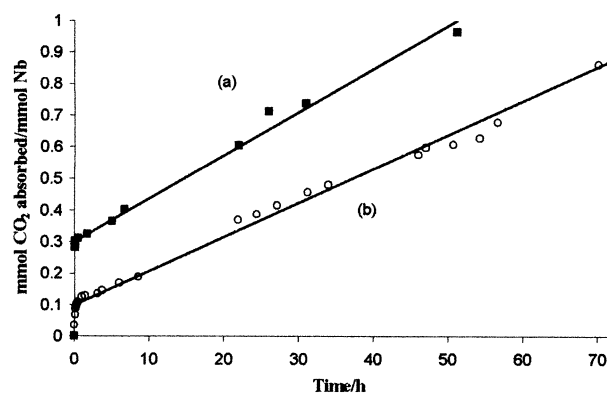


Figure 1. Kinetics of absorption of CO₂ by [Nb(OEt)₅]₂ in (a) ethanol and (b) benzene.

by IR spectroscopy, which showed the disappearance of the bands due to asymmetric and symmetric OC(O) stretching and the reappearance of the band at 1030 cm⁻¹ due to the bridging OEt groups. The resulting compound was identical with an authentic sample of [Nb(OEt)₅]₂. A similar behavior was shown by the methyl and allyl derivatives.

In another method, a quantity of the ethyl hemicarbonate (0.100 g, 0.28 mmol) was heated at 400 K in toluene for 15 h under 0.1 or 6 MPa of CO₂. The resulting solution was analyzed by GC-MS and did not show the formation of (EtO)₂CO. The starting complex was isolated after the solvent was evaporated by bubbling CO₂ at 300 K. A similar behavior was observed with the methyl and allyl derivatives.

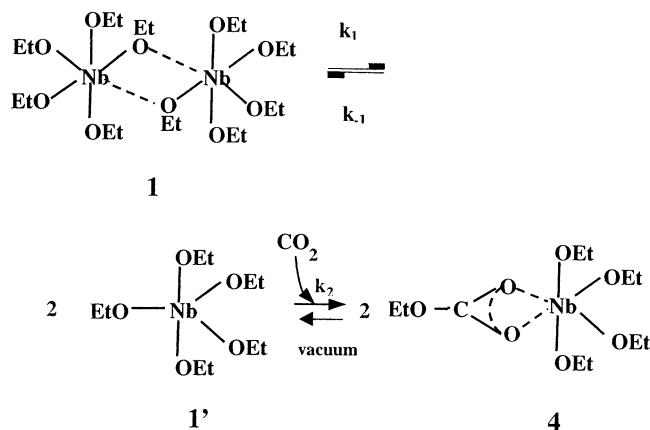
Another procedure heated 1.20 g (3.31 mmol) of the ethyl derivative dissolved in 4 mL (68.78 mmol) of ethanol at 410 K under 5.5 MPa of CO₂ in the previously described stainless steel autoclave. The solution was continuously monitored by GC-MS until the formation of the diethyl carbonate (DEC) reached a constant value. At this time (30 h), the autoclave was discharged, the solvent was evaporated in vacuo, the carbonate was isolated, and the catalyst was recovered and reused in a new cycle. The alcohol conversion ($\alpha \approx 0.02$ mol, on the basis of the carbonate formed) was determined per each cycle. This procedure was repeated for 10 cycles without loss of the catalytic properties of the niobium complex.

Another procedure reacted [Nb(OEt)₅]₂ with ethanol. The reaction was repeated under various partial pressures of CO₂ (P_{CO_2}). The following values of α were determined: for $P_{\text{CO}_2} = 0.1$ MPa, $\alpha = 0.001$; for $P_{\text{CO}_2} = 5.5$ MPa, $\alpha = 0.021$. The same reaction was conducted with Nb(OMe)₄[OC(O)OMe] under 6 MPa of CO₂ in methanol to afford (MeO)₂CO, with $\alpha = 0.022$. Performance of this reaction using Nb(O-allyl)₄[OC(O)O-allyl] in allyl alcohol under 6 MPa of CO₂ afforded (allylO)₂CO, with $\alpha = 0.035$.

Reaction in supercritical CO₂ also was used. [Nb(OEt)₅]₂ (1.21 g, 3.80 mmol) was dissolved in 5 mL of ethanol (85.85 mmol), and the resulting solution was transferred into a SITEC reactor for supercritical fluids and kept at 380 K and 25.0 MPa for 10 h. After the solution was cooled, the reactor was depressurized and the solution was analyzed using GC-MS. The carbonate yield was 4%, with respect to the starting ethanol.

Results and Discussion

Niobium(V) alkoxides, [Nb(OR)₅]₂ (with R = Me, Et), are well-known to be dimeric species with OR bridges, as demonstrated by XRD¹⁴ or pioneering NMR studies.¹⁵ Although a great amount of interest has been shown toward

Scheme 1. Reaction of Niobium Pentaethoxide with CO_2


the elucidation of the structure of the alkoxo complexes, their reaction with CO_2 has never been investigated in detail and the product of the reaction of the niobium alkoxo species with CO_2 has neither been isolated nor characterized in solution. We have performed a detailed study on the reaction of $[\text{Nb}(\text{OEt})_5]_2$ (**1**), $[\text{Nb}(\text{OMe})_5]_2$ (**2**), and $[\text{Nb}(\text{O-allyl})_5]_2$ (**3**) with CO_2 and have isolated the relevant reaction products. The hemicarbonate derivative of **1** has been characterized as $\text{Nb}(\text{OEt})_4[\text{OC}(\text{O})\text{OEt}]$ (**4**) by NMR spectroscopy and IR spectroscopy, and the molar mass determination was made using cryoscopy. A careful ^1H NMR investigation performed at 500 MHz has shown that $[\text{Nb}(\text{OEt})_5]_2$ in solution undergoes a dissociation equilibrium. In fact, if the ^1H NMR spectrum is monitored soon after the solution is prepared and repeated at intervals of time, besides the intense signals due to the dimer (see Experimental Section), low-intensity signals, not observed at lower fields, become evident in the ranges 4.80–4.60 and 1.40–1.30 ppm. Such signals are attributed to the monomeric species. Their intensity reaches a maximum within ~ 1 –2 h (depending on the temperature), and the integral of the signals allows estimation of the equilibrium concentration of the monomer: that is, 1.43 mol % of the starting dimer at 300 K. The calculated constant for the dissociation equilibrium (Scheme 1) is $K_{\text{eq}} = 2.07 \times 10^{-4}$. The previously given ^1H NMR signals cannot be due to hydrolyzed forms of $[\text{Nb}(\text{OEt})_5]_2$, because signals due to ethanol, which is the product generated in the hydrolysis of niobium ethoxo complexes, are completely absent.

Also, the fact that such signals are not due to impurities is demonstrated by their growth with the time of permanence of **1** in solution (see Experimental Section). A change of the spectral features of **1** was observed when $[\text{Nb}(\text{OEt})_5]_2$ was reacted with CO_2 in dry toluene in a NMR tube sealed under CO_2 . The signals attributed to the monomer quickly disappear, while new proton resonances appear (located at

1.10 (2.7 H, $^3J_{\text{H,H}} = 7.27$ Hz, CH_3) and 4.09 ppm (1.8 H, $^3J_{\text{H,H}} = 7.21$ Hz, CH_2)); the intensity of these signals increases with time. Also, the starting ^1H NMR signals due to the bridging OEt groups progressively disappear with time. The reaction was 90% complete in 70 h, when it was stopped. The signals at 1.10 and 4.09 ppm are attributed to the methyl and methylene protons, respectively, of the $\text{OC}(\text{O})\text{OCH}_2\text{-CH}_3$ group of the hemicarbonate complex $\text{Nb}(\text{OEt})_4[\text{OC}(\text{O})\text{OEt}]$ (**4**) that was also isolated and fully characterized (see below). The resonances of the terminal OEt groups of **4** appear as broad signals located at 4.3 and 1.2 ppm. The ^{13}C NMR of **4** shows five new signals, at 15.95, 18.23, 64.63, 71.85, and 161.66 ppm. The HETCOR acquisition allows correlation of the ^{13}C signal at 15.95 ppm to the ^1H triplet at 1.10 ppm (methyl group of the hemicarbonate moiety), the signal at 18.23 ppm to the ^1H signal at 1.20 ppm, the signal at 64.63 ppm to the quartet at 4.09 ppm (methylene group of the hemicarbonate group), and the signal at 71.85 ppm to the signal at 4.30 ppm. The signal at 161.66 ppm is attributed to the hemicarbonate carbon. A low-temperature study (220 K) has made it possible to separate signals of residual unreacted **1** from those of **4** and to establish, for the carboxylation, a yield of 90%. The low-temperature ^1H NMR spectrum has also made it possible to separate the equatorial and axial terminal ethyl groups for **1** and **4**. The terminal CH_2 groups of unreacted **1** (ca. 10%) are found as quartets at 4.21 ($^3J_{\text{H,H}} = 6.98$ Hz, equatorial) and 4.30 ppm ($^3J_{\text{H,H}} = 6.89$ Hz, axial), and the relevant bridging CH_2 groups are found at 3.82 ppm ($^3J_{\text{H,H}} = 7.08$ Hz). The intense signals of **4** are located at 3.97 (CH_2 of the $\text{OC}(\text{O})\text{OEt}$ moiety, $^3J_{\text{H,H}} = 7.04$ Hz), 4.43 ($^3J_{\text{H,H}} = 7.02$ Hz, equatorial), and 4.51 ppm ($^3J_{\text{H,H}} = 7.10$ Hz, axial), because of the CH_2 species of terminal ethoxo groups. The triplets of the methyl groups are less separated, and an unambiguous attribution is not possible. From these data, it was possible to infer that **4** is not a dimer as the parent compound. Note that, although the IR spectrum of **1** in Nujol mull shows a typical band at 1030 cm^{-1} , which is due to the bridging OEt group,¹⁶ such a band is not present in the IR spectrum of the isolated hemicarbonate species. New bands at 1600 (attributed to the asymmetric stretching of the carbonyl group of the hemicarbonate moiety), 1414, 1330 ($\nu_{\text{sym}}(\text{OCOO})$), and 807 cm^{-1} appear. The IR data also suggest, for the ethyl carbonate group, an η^2 -coordination to the metal center through two O atoms. In fact, the experimental value of $\Delta\nu = \nu_{\text{as}} - \nu_{\text{sym}}$ for the OCOO moiety has been found to be 270 cm^{-1} , which is the correct value reported for bridging or chelating OCOO moieties.⁶ Noteworthy is the fact that a bridging hemicarbonate moiety would generate dimers or polymers, whereas a chelating moiety would give a monomer. To eliminate the uncertainty about the possible coordination mode of the hemicarbonate moiety, a cryoscopic determination of the molecular mass^{12,13} of **4** was performed in benzene. The CO_2 -insertion product has been shown to be a monomer of formula $[\text{Nb}(\text{OEt})_4(\text{OC}(\text{O})\text{OEt})]$ (362 uma calculated, 391 uma found). The carboxylation pathway, represented in

(14) XRD data confirmed the existence of dimeric $\text{Nb}(\text{OMe})_5$. See: Pinkerton, A. A.; Schwarzenbach, D.; Hubert-Pfalzgraf, L. G.; Riess, J. G. *Inorg. Chem.* **1976**, *15*, 1196–1199.

(15) ^1H NMR spectra of $\text{Nb}(\text{OEt})_5$ recorded at 306 and 202 K with a Varian model A60 apparatus showed the resonance of bridging and terminal OEt groups, separated into axial and equatorial components. See: (a) Hubert-Pfalzgraf, L. G.; Riess, J. G. *Bull. Soc. Chim. Fr.* **1968**, 4348–4353. (b) Bradley, D. C.; Holloway, C. E. *J. Chem. Soc. A* **1968**, 219–223.

(16) Barraclough, C. G.; Bradley, D. C.; Lewis, J.; Thomas, I. M. *J. Chem. Soc.* **1961**, 2601–2605.

Scheme 1, most likely proceeds through the dissociation of the dimer and the carboxylation of the monomer, as supported by the ^1H NMR data, which show that the monomer in equilibrium with the dimer is immediately carboxylated upon reaction with CO_2 .

We have studied the kinetics of absorption of CO_2 by **1** in anhydrous ethanol or benzene. The overall process is slow, and the absorption of 0.9 mol CO_2 /(mol of niobium complex) requires 70 h under 0.1 MPa of CO_2 (Figure 1b) in benzene. Conversely, under 5 MPa of CO_2 , the uptake of 1 mol of CO_2 is completed in a few hours.

However, in any case, a slower rate is observed in C_6H_6 (Figure 1b) than in ethanol (Figure 1a). It is known that alcohol favors the conversion of the dimer to the monomer.^{15b} This can explain the fastest kinetics observed in ethanol, with respect to benzene (Scheme 1). The absorption curves reported in Figure 1 show, both in benzene and in ethanol, a fast absorption of CO_2 during the first few minutes, followed by a slow, continuous absorption over several hours. Such features well match the hypothesis that the carboxylation of the monomer is a process that is faster than the dissociation of the dimer to afford the monomer. Thus, the fast CO_2 uptake corresponds to the carboxylation of **1'**, which is present at the equilibrium in the solution of **1**, as demonstrated also by ^1H NMR (see above). The absorption of CO_2 at various pressures and temperatures and with different niobium concentrations in different solvents is still under study.¹⁷ The single-temperature (293 K) study under 0.1 MPa of CO_2 performed so far has allowed the preliminary evaluation of the kinetic constant for the carboxylation or dissociation process. Assuming a second-order kinetics (eq 3) for the carboxylation of **1'** (Scheme 1), the first part of the absorption curve allows calculation of a value of $k_2 = 1.19 \times 10^{-1} \text{ L mol}^{-1} \text{ s}^{-1}$ for the carboxylation step—that is, the same value as that observed in benzene and in ethanol.

$$v_{\text{carb}} = k_2[\text{Nb}(\text{OEt})_5][\text{CO}_2] \quad (3)$$

The second part of the curve allows the kinetic constant of the dissociation process to be calculated. Under the previously reported conditions, it is possible to calculate a k_1 value of $1.15 \times 10^{-5} \text{ s}^{-1}$ in ethanol and $0.97 \times 10^{-5} \text{ s}^{-1}$ in benzene. Similarly, $\text{Nb}(\text{OMe})_5$ reacts with CO_2 to afford a yellow solid that is sparingly soluble in toluene; analyses have identified this solid as $\text{Nb}(\text{OMe})_4[\text{OC}(\text{O})\text{OMe}]$ (**5**). Also, in this case, the IR band at 1030 cm^{-1} disappears after reaction with CO_2 , supporting the loss of bridging OMe groups. Analogously, $\text{Nb}(\text{O-allyl})_5$ reacts with CO_2 to afford the relevant hemicarbonate $\text{Nb}(\text{O-allyl})_4[\text{OC}(\text{O})\text{O-allyl}]$ (**6**), as demonstrated by IR and molecular mass determination.

The insertion of CO_2 into the Nb–OEt bond has been found to be fully reversible. Under vacuum, CO_2 was released by the hemicarbonate, as demonstrated by the fact that the IR signal due to the carbonate group disappeared and the starting $[\text{Nb}(\text{OEt})_5]_2$ complex was quantitatively regenerated. If **4** was heated in toluene (400 K) under CO_2 (at 0.01–6 MPa), no further reaction was observed. Such

behavior is different from that reported for $\text{Bu}_2\text{Sn}[\text{OC}(\text{O})\text{OR}](\text{OR})$, which undergoes $(\text{RO})_2\text{C}(\text{O})$ elimination when heated in toluene^{7b} at 423 K under 8 MPa of CO_2 . Conversely, if the niobium hemicarbonate species **4** was heated at 413 K in strictly anhydrous ethanol under CO_2 (5 MPa), DEC was formed. A kinetic study has shown that the formation of the carbonate has an induction time of ca. 1 h and continues for several hours until equilibrium is reached. The induction time can be explained, considering that the organic carbonate is formed only after the hemicarbonate is present in solution at an appropriate concentration. The reaction is 100% selective, and the equilibrium concentration of the carbonate depends on the temperature: $\alpha = 0.021$ at 410 K and rises to a value of 0.035 at 470 K under 6 MPa of CO_2 in a batch reactor. The CO_2 pressure also has a great influence. With $P_{\text{CO}_2} = 0.1 \text{ MPa}$ at 410 K, the value of α decreases from 0.021 to 0.001. Interestingly, if the catalyst was recovered from the batch reactor and reused under CO_2 with fresh anhydrous alcohol, DEC was again formed, with a similar value of α . The catalyst has been recycled up to 10 times with only a minor decrease in the value of α , which has the same order of magnitude of, but is higher than, that reported for a zirconium system.¹⁸ In our case, the overall observed turnover number (TON) after 10 cycles is 2.3 and the catalyst remains active. Recycling is of fundamental importance, to overcome the thermodynamic intrinsic limitation of the reaction. The reaction was also conducted in SC– CO_2 , using the same alcohol/niobium-hemicarbonate ratio. The conversion TON was 0.88 mol of EtOH converted/(mol of catalyst) or 0.44 mol of carbonate/(mol of catalyst) over a single step, with a slight improvement with respect to the reaction conducted in the batch reactor. Under the operative conditions ($\chi_{\text{CO}_2} = 0.9$, $\theta = 380 \text{ K}$, $P = 25 \text{ MPa}$), the CO_2 –ethanol system should most probably behave as a two-phase system.¹⁹ In all these systems, there may be an influence of water that is formed in the reaction; water may either react with the catalyst or reverse reaction 2. Either the capture of water or a better use of SC– CO_2 may help to improve the yield of the reaction with a more significant production of carbonates.

When pure $\text{Nb}(\text{OMe})_5$ or $\text{Nb}(\text{Oallyl})_5$ was reacted with CO_2 , the relevant hemicarbonates were obtained, which were characterized as reported for the ethyl derivative. (See the Experimental Section.) The hemicarbonates were reacted with the parent alcohol to afford dimethyl carbonate (DMC, TON = 2.1, 10 cycles) or diallyl carbonate (DAC, TON = 2.3, 10 cycles). Note that this is the first report on the synthesis of DAC from allyl alcohol and CO_2 .

We have also investigated the reaction of $\text{Nb}(\text{OEt})_5$ with CO_2 using other alcohols as a solvent under 6 MPa of CO_2 , or in supercritical CO_2 using the alcohol (5 mL) as a cosolvent and reagent. When methanol was reacted with $\text{Nb}(\text{OEt})_5$ under CO_2 , DMC was obtained, together with ethyl

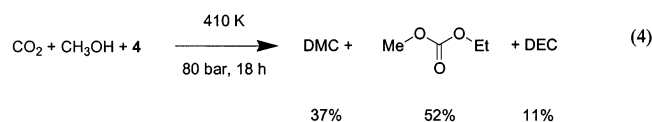
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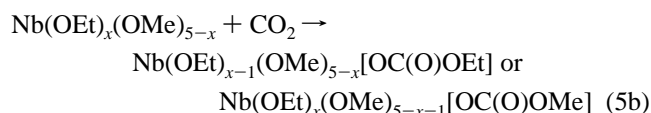
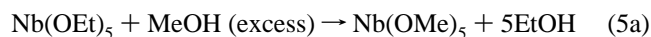
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Synthesis and Characterization of $Nb(OR)_4[OC(O)OR]$

methyl carbonate (EMC) and DEC, with an abundance of 37%, 52%, and 11%, respectively (eq 4). The overall TON was ~ 0.25 for a single cycle.



To gain an insight into the formation of the three carbonates, we have investigated the reaction of methanol with $Nb(OEt)_5$ in the absence of CO_2 and shown that methanol promptly reacts with niobium pentaethylate at room temperature with a progressive substitution of all five ethoxo groups (eq 5a). The intermediate mixed complexes $Nb(OEt)_x(OMe)_{5-x}$ ($x = 1-4$) may eventually react with CO_2 to afford hemicarbonates, either ethoxo or methoxo species (eq 5b), that may generate the DMC, MEC, and DEC.



Considering that the OEt/OMe exchange is faster than the CO_2 insertion, the preliminary conversion of $Nb(OEt)_5$ to $Nb(OMe)_5$ that would generate DMC cannot be ruled out. The subsequent trans-esterification reaction of DMC would generate EMC and DEC. As a matter of fact, $[Nb(OR)_5]_2$ can catalyze trans-esterification reactions.²⁰ Allyl alcohol reacts in a similar way with CO_2 and $Nb(OEt)_5$ to afford allyl ethyl carbonate, DEC, and DAC. When phenol was used, the relevant diphenyl carbonate (DPC) was not formed, confirming that there is thermodynamic control of the reaction.

(20) Aresta, M.; Dibenedetto, A.; Pastore, C., unpublished work.

Table 1. Heat of Formation (ΔH) of Alkyl and Aryl Carbonates

R	$\Delta H/\text{kcal mol}^{-1}$
CH_3	-4.00
CH_3CH_2	-3.80
CH_2CHCH_2	-3.91
C_6H_5	+12.06

In fact, although the formation of alkyl carbonates from the parent alcohol and CO_2 shows a favorable enthalpy,²¹ DPC formation has a positive heat of reaction (ΔH) (see Table 1).

These data allow us to conclude that, under the same operational conditions, the formation of DPC from phenol and CO_2 is less favorable than the formation of alkyl carbonates.

In conclusion, $[Nb(OR)_5]_2$ compounds ($R = Me, Et, \text{allyl}$) react with CO_2 to afford monomer $Nb(OR)_4[OC(O)OR]$ complexes. The alkoxo complexes are catalysts for the synthesis of dimethyl carbonate, diethyl carbonate, or diallyl carbonate, respectively, from the relevant alcohol and CO_2 . The mechanism of formation of the carbonate is intermolecular. The niobium catalysts have a long enough life to be recycled for several cycles (up to 10, so far) to reach a total turnover number (TON) of >2 . Although this value represents the best reported achievement in the synthesis of an organic carbonate from the parent alcohol and CO_2 , it is too low for any practical application. To overcome the thermodynamic constraints, the elimination of water may help to shift the equilibrium to the right and to increase the TON of the process. Also, a shift from the batch reactor to a continuous-flow system may produce better results. Further work is in progress along these lines.

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(21) The heats of formation of carbonates have been calculated according to the additivity method proposed by Benson and Cohen. (See: Benson, S. W.; Cohen, N. *Chem. Rev.* **1993**, *93*, 2419–2438.)