Ketones as an oxolation source for the synthesis of titanium-oxo-organo clusters[†]

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Two titanium-oxo clusters, $[Ti_3O(OPr^i)_7(O_3C_9H_{15})]$ **1** and $[Ti_{11}O_{13}(OPr^i)_{18}]$ **2**, have been obtained through the reactions of $Ti(OPr^i)_4$ with ketones such as acetone, acetylacetone and diacetone alcohol. Complex **1** is composed of a trinuclear unit that is capped by a tridentate enolate ligand synthesized *in situ*. Complex **2** is a more condensed titanium cluster with a spherical oxo core. The titanium-oxo-organo cores of these clusters are preserved in solution as characterized by ^{17}O, ^{13}C, and ^{1}H NMR spectroscopy. The possible different reactions involved in the formation of these clusters are discussed.

Nanochemistry seems to be one of the most important scientific themes of the end of this century, providing material scientists with new perspectives in many different fields (optics, electronics, magnetism, catalysis, membranes, ...).[1–4] This field of chemistry is becoming more and more involved in the synthesis of advanced materials that can be made with large assemblies of molecules or metal ion based clusters. The synthesis of such materials through low temperature chemical routes allows a better control of their microstructure. Among the different processes belonging to the so-called "chimie douce", sol–gel processes are a way of making highly dispersed materials through the growth of metal-oxopolymers in a solvent.[5–8] They are based on hydrolysis-condensation reactions of molecular precursors such as metal alkoxides $M(OR)_4$ (M = Si, Ti, ...). Fundamental studies on transition metal alkoxide hydrolysis, are complicated for two main reasons: their extreme moisture sensitivity (hydrolysis and condensation rates are fast) and their tendency to form mixtures of structurally complex species upon hydrolysis. The resulting metal-oxopolymers are generally polydisperse in size and composition.[8,9]

An attractive solution is to use preformed metal-oxo clusters of well defined structure as precursors for making new metal oxides. Depending on the set of chosen experimental conditions these clusters can be considered as molecular building blocks or as a reservoir of matter with a lower reactivity than that of the starting metal alkoxide. Transition metal-oxo clusters capped with polymerizable complexing ligands can serve as nano building blocks to form hybrid organic–inorganic polymers.[10–13] This molecular nanobuilding block approach yields xerogels having microstructures, porosities and surface areas different from those obtained by sol–gel polymerization of the alkoxide precursors under the same conditions.[14–18]

Moreover, many transition metal-oxo-organo clusters are defined species whose structures have been resolved by X-ray diffraction. As a consequence, they can be used as a reference to provide structural information on the polydisperse and amorphous metal-oxopolymers that constitute the sols and gels from which materials can be processed.[12,19,20] General chemical formulae for some titanium- and zirconium-oxo-organo clusters whose structures were resolved by X-ray diffraction are reported in Table 1.

These transition metal-oxo-clusters are generally synthesized *via* substoichiometric hydrolysis ($H_2O/M < 1$) of metal alkoxides[21–23] or of metal alkoxides complexed by β-

Table 1 Some examples of titanium- and zirconium-oxo-organo clusters

Precursor[a]	Cluster formula	Reference
$Ti(OEt)_4$	$[Ti_7O_4(OEt)_{20}]$	27, 28
	$[Ti_{10}O_8(OEt)_{24}]$	22
	$[Ti_{16}O_{16}(OEt)_{32}]$	28
$Ti(OPr^i)_4$	$[Ti_3O(OPr^i)_9(OMe)]$	23
	$[Ti_3O(OPr^i)_9(O_3C_9H_{15})]$	29
	$[Ti_{12}O_{16}(OPr^i)_{16}]$	21, 30
	$[Ti_{11}O_{13}(OPr^i)_{13}(OEt)_5]$	21
$Ti(OCH_2C_6H_5)_4$	$[Ti_8O_4(OCH_2C_6H_5)_{20}]$	22
$Ti(OBu^t)_4$	$[Ti_{18}O_{27}(OBu^t)_{17}(OH)]$	31
$Hacac : Ti(OBu^t)_4 = 0.1$	$[Ti_{18}O_{22}(OBu^n)_{26}(acac)_2]$	32
$HOAc : Ti(OPr^i)_4 = 1$	$[Ti_6O_4(OPr^i)_{12}(OAc)]_4$	30, 33
$HOAc : Ti(OPr^i)_4 = 2$	$[Ti_6O_4(OR')_8(O_2CR)_8]^b$	10, 24, 25 26
$HOMc : Ti(OPr^n)_4 = 4$	$[Ti_9O_8(OPr^n)_4(OMc)_{16}]$	34
$Zr(OMe)_4$	$[Zr_{13}O_8(OMe)_{36}]$	35
$Hacac : Zr(OPr^n)_4 = 1$	$[Zr_4O(OPr^n)_{10}(acac)_4]$	36
$aaa : Zr(OPr^n)_4 = 0.6$	$[Zr_{10}O_6(OH)_4(OPr^n)_{18}(aaa)_6]$	12
$HOMc : Zr(OPr^n)_4 = 4$	$[Zr_6O_4(OH)_4(OMc)_{12}]$	13
$HOMc : Zr(OPr^n)_4 = 12$	$[Zr_4O_2(OMc)_{12}]$	13

[a] OMc: methacrylate; aaa: allylacetoacetate; acac: acetylacetonate.
[b] $R = CH_3$ and $R' = Et, Pr^i, Bu^n$ or $R = CH_3C{=}CH_2$ and $R' = Et$.

[†] *Supplementary material available:* ORTEP drawing of complex **2**, corresponding to the second molecule present in the asymmetric unit, and the NMR spectra of complexes **1** and **2**. For direct electronic access see http://www.rsc.org/suppdata/nj/1999/1079/, otherwise available from BLDSC (No. SUP 57658, 5 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/njc).

diketones or carboxylic acids.[10,13,24–26,32] Alternative strategies using *in situ* generation of water[30,37] or nonhydrolytic sol–gel processes[38,39] could also be developed to avoid stability problems arising from local over-concentrations of water or the presence of residual water in the synthetic medium.

This paper describes the structural and spectroscopic characterizations of two titanium-oxo-isopropoxo complexes, $[Ti_3O(OPr^i)_7(O_3C_9H_{15})]$ **1** and $[Ti_{11}O_{13}(OPr^i)_{18}]$ **2**, synthesized through the reactions of $Ti(OPr^i)_4$ with ketones, which is somewhat uncommon for the preparation of these complexes. The structure of complex **1** was first briefly reported by Barkley *et al.*,[29] but due to a large crystallographic disorder, it was difficult to unambiguously determine the nature of the enolate ligand. In this work, multinuclear NMR spectroscopy was used as a tool to complete the X-ray analysis. The structure of complex **2** has been resolved by single crystal X-ray diffraction. This cluster exhibits the same titanium-oxo core $[Ti_{11}O_{13}]$ as previously reported for the complex $[Ti_{11}O_{13}(OPr^i)_{13}(OEt)_5]$, but complex **2** does not contain any ethoxy groups. Multinuclear NMR spectroscopy was also used to identify unambiguously the alkoxo groups. There is ongoing interest in the identification and structural characterization of titanium(IV)-oxo-based clusters,[21–34] but numerous X-ray structures reported exhibit high crystallographic disorder. Multinuclear NMR techniques allow one to determine clearly the nature of the ligands. As a consequence, this paper presents an interesting cross-checking approach for the structural characterization of clusters by combining X-ray diffraction and multinuclear NMR techniques. Moreover, multinuclear NMR spectroscopy, especially ^{17}O NMR in natural abundance, was used to check the preservation of the metal-oxo cores in solution. Finally, possible mechanisms for the formation of the titanium-oxo clusters are also discussed.

Experimental

All manipulations were carried out under argon atmosphere using Schlenk techniques and a glove box in order to prevent hydrolysis with atmospheric water.

Synthesis of $[Ti_3O(OPr^i)_7(O_3C_9H_{15})]$ 1 and $[Ti_{11}O_{13}(OPr^i)_{18}]$ 2 complexes

Complex 1. $Ti(OPr^i)_4$ (3 mL, 10.18 mmol) and dry propan-2-one (acetone; 15 mL, 200 mmol) were stirred in a closed vessel until a clear yellow solution was obtained. Colorless crystals of complex **1** were obtained upon ageing this reaction mixture for about 24 h at room temperature. These crystals were suitable for X-ray structure determination. Yield 33.7%, anal. found: C, 47.7; H, 8.8; Ti, 21.9; O, 21.7%. $Ti_3O_{11}C_{30}H_{64}$ requires C, 48.4; H, 8.6; Ti, 19.3; O, 23.7%. δ_O (400 MHz, C_6D_6, H_2O): 556 (1O, *O*–Ti_3), 214, 293, 352, 380, (10 O, Ti–*O*R); δ_H (300 MHz, C_6D_6, TMS): 2.08 (1H, d, C*H*$_2$), 2.59 (1H, d, C*H*$_2$), 4.49 (1H, s, C*H*), 4.52, 4.58, 4.65, 4.75, 4.81, 4.815, 4.94 [7H, sept, O–C*H*$(CH_3)_2$], 1.2–1.6 [54H, d + s, O–CH(C*H*$_3$)$_2$ and O–C(C)(C*H*$_3$)$_2$]; δ_C (75.47 MHz, C_6D_6, TMS): 52 (*C*H$_2$), 115.7 [*C*H=C(O)], 76.7, 75.9, 76.0, 75.4, 76.9, 78.0, 78.4, 79.7, [O–*C*H$(CH_3)_2$], 79.9, 81.1 [O–*C*(C)$(CH_3)_2$], 149.7 [CH=*C*(O)], 26–33 [O–CH(*C*H$_3$)$_2$ and O–C(C)(*C*H$_3$)$_2$].

Complex 2. $Ti(OPr^i)_4$ (3 mL, 10.18 mmol) was added to dry 4-hydroxy-4-methyl-2-pentanone (diacetone alcohol; 1.27 mL, 10.18 mmol) at room temperature. During stirring the resulting solution turned a red-brown color. From the reaction bath two kinds of crystals corresponding to complex **2** and to a trinuclear cluster labelled $(Ti_3)^{\#}$ were grown after an ageing period of about 24 h. One suitable crystal of complex **2** was selected for an X-ray structure determination. But it was not possible to isolate enough crystals of complex **2** for NMR spectroscopy characterization. Yields: complex **2**: 70%; complex (Ti_3): 30% from the ^{17}O NMR spectrum. δ_O (400 MHz, C_6D_6, H_2O): complex **2**: 515, 529, 536 (10O, *O*–Ti_3), 711 (1O, *O*–Ti_2), 729 (1O, *O*–Ti_2), 770 (1O, *O*–Ti_2); complex $(Ti_3)^{\#}$: 553 (1O, *O*–Ti_3).

Crystal structure determination

For complexes **1** and **2**, transparent plate-like crystals were mounted on a STOE IPDS single φ axis diffractometer with a 2D area detector based on imaging plate technology. For complex **1**, 125 images were recorded at low temperature (150 K) by using the rotation method ($0 < \varphi < 250°$) with $\Delta\varphi = 2°$, an exposure time of 3 min, and a crystal-to-plate distance of 80 mm. For complex **2**, 210 images were recorded at low temperature (150 K) by using the rotation method ($0 < \varphi < 210°$) with $\Delta\varphi = 1°$, an exposure time of 3 min, and a crystal-to-plate distance of 80 mm. The images were recorded and processed with the set of programs from STOE (EXPOSE, DISPLAY, INDEX, CELL, PROFILE, INTEGRATE).[40] The structures were solved by direct methods with the SHELXS-86 program[41] and difference Fourier techniques and refined by full-matrix least-squares calculations (SHELXL-93).[42] The H atoms were not located for both complexes.

For the structure of complex **2**, two independent molecules are present in the unit cell, which correspond to the same titanium cluster $[Ti_{11}O_{13}(OPr^i)_{18}]$. Direct methods and successive Fourier maps were used to locate the positions of all atoms. The atomic positions, the isotropic thermal parameters and the atomic occupation factors as well were given by full-matrix least-squares refinement. For each molecule, the atomic occupation factors of two titanium atoms [Ti(5) and Ti(6) for the first molecule; Ti(11) and Ti(12) for the second one] were found to be less than one. This is in agreement with the presence of a metallic vacancy that is distributed over two positions. For the second titanium cluster present in the unit cell, some isopropoxy groups are highly disordered. Taking into account the atomic occupation factors given by the refinement, a model was proposed for these isopropoxy groups. Details concerning the crystallographic data collection and structure determination for complex **2** are reported in Table 2.

CCDC reference number 440/143. See http://www.rsc.org/suppdata/nj/1999/1079/for crystallographic files in .cif format.

NMR measurements

For solution NMR spectra, fresh crystals were easily dissolved in C_6D_6. For solution ^{17}O NMR spectra measured on the reaction bath (reaction mixture from which the crystals are grown), 1 mL of the reaction mixture was added to 2 mL of

Table 2 Crystallographic data collection and structure determination of complex **2**

Formula	$Ti_{11}O_{31}C_{54}H_{126}$
M	1798.5
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	25.560(2)
b/Å	14.1881(6)
c/Å	26.618(2)
β/°	108.478(7)
U/Å^3	9155.3(10)
Z	4
T/K	150
μ(MoKα)/mm^{-1}	0.970
Unique reflections	13974
Observed reflections $[I \geqslant 2\sigma(I)]$	8517
$R^a[I \geqslant 2\sigma(I)]$	0.1208
$R_w{}^b$ (all reflections)	0.3356

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

C_6D_6. The solution ^{17}O NMR spectra were recorded at 54.2 MHz on a Bruker MSL 400 spectrometer. A 90° pulse was used and the recycle delay was 0.2 s. A dead time of 36 μs, equal to 6 times the digitalization spacing, was set before signal acquisition.

The ^{17}O nucleus is particularly difficult to observe by NMR spectroscopy for two reasons. First, it has a spin $I = 5/2$ with an appreciable electric quadrupole moment ($Q = -2.6 \times 10^{-26}$ cm^2), which in general leads to rapid quadrupole relaxation. As a consequence, broad resonances are observed with poor spectral resolution and signal-to-noise ratios. Second, its low natural abundance (0.037%) limits observation of the NMR signals. Nevertheless, in sol–gel chemistry, this latter problem may be overcome by ^{17}O enrichment through the use of ^{17}O-labelled water. As a consequence, the oxo polymers and polyoxoalkoxides that result from the hydrolysis of metal alkoxides by ^{17}O-enriched water are selectively enriched at the oxo bridges.[19,43] In the present study, titanium alkoxide was not directly hydrolyzed, and selective enrichment was not possible. Consequently, the ^{17}O NMR spectra were recorded with extensive signal accumulation (2.5×10^5 transients for complex **1** and 4×10^5 transients for complex **2**) in order to get a good signal-to-noise ratio. Previously reported ^{17}O NMR results,[19,21,22,43] obtained for ^{17}O-enriched titanium-oxo-based clusters or titanium-oxo polymers, have been used as references for the characterization of the complexes reported in this study with natural abundance of ^{17}O.

The solution ^{13}C and ^1H NMR spectra for complexes **1** and **2** were recorded on a Bruker AC 300 spectrometer (300.13 MHz for ^1H and 75.47 MHz for ^{13}C). For the ^{13}C INEPT (insensitive nuclei enhanced to polarisation transfer) NMR spectrum for complex **1** the conditions of the measurement (mixing: 2 ms; refocalization: 3 ms) were chosen in order to allow spectral editing of the carbon groups. Signals of CH_2 groups appear negative and those of CH and CH_3 positive. For the quaternary carbons (CX_4, $X \neq H$) no signals are detected. The ^{13}C–^1H heteronuclear correlation spectrum (XHCORRD) spectrum for complex **1** was recorded on a Bruker AC 500 spectrometer. For the 2D ^{13}C–^1H heteronuclear shift correlation[44] (256 increments in the ^1H dimension) a delay of 4 ms corresponding to $J^1_{\text{C-H}} = 125$ Hz was chosen.

Results

X-Ray structure determination of complex 1

The X-ray structure of complex **1** was resolved‡ and was found to be identical to a titanium-oxo-isopropoxo cluster already reported in a short communication.[29] As a consequence, the main structural features of this complex will be simply summarized. The structure of complex $[Ti_3O(OPr^i)_7(O_3C_9H_{15})]$ is based on a trinuclear unit capped by a tridentate ligand that is statistically disordered over three positions. The CrystalMaker drawing presented in Fig. 1 shows the molecular structure of complex **1** with one peculiar position of the tridentate ligand.

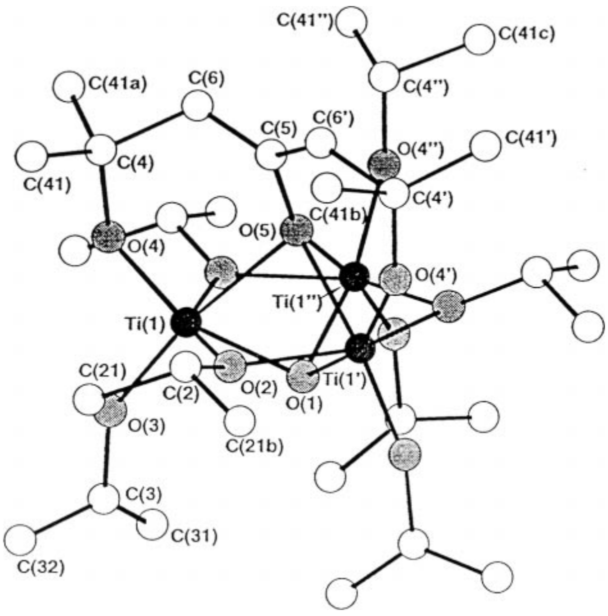

Fig. 1 Molecular structure of complex **1**. The symmetry transformations used to generate equivalent atoms are labelled as follow: ′ = *z*, *x*, *y*; ″ = *y*, *z*, *x*; a = *z*, *y*, *x*; b = *y*, *x*, *z*; c = *x*, *z*, *y*.

In the triangular unit of titanium atoms, each metal center is linked to the others *via* a bridging isopropoxy group. This unit is capped on one side by the oxygen atom, O(1), which is linked to the three titanium atoms (μ_3-O). The other side of the trinuclear unit is capped by the tridentate organic ligand *via* three oxygen atoms, namely: (*i*) the oxygen O(5) of an enol function [O(5)–C(5)=C(6)H] bound to the three titanium atoms and (*ii*) the oxygen atoms O(4) and O(4′) corresponding to tertiary alcohol functions $OC(CH_3)_2$. The coordination of the tridentate ligand to the titanium atoms constitutes two distinct metallacycles: Ti(1)–O(4)–C(4)–C(6)–C(5)–O(5) and Ti(1′)–O(4′)–C(4′)–C(6′)–C(5)–O(5) having a common edge O(5)–C(5). All the titanium atoms are sixfold coordinated. Their coordination is completed by terminal isopropoxy groups [two isopropoxo groups for Ti(1″) and one isopropoxo group for Ti(1) and Ti(1′)]. They are located in distorted oxygen octahedra TiO_6, whose particularity is to share faces. Such a compact arrangement of octahedra is particulary scarce because face-sharing between octahedra is known to promote strong repulsion between the metallic centers. However, this structural feature was previously observed in the titanium-oxo-based complex $[Ti_3O(OPr^i)_9(OMe)]$ whose structure is close to that of compound **1**.[23]

The presence of an enol function can be suggested because of the relatively short C(6)–C(5) = 1.402(13) Å bond. However, the important disorder could be responsible for these short bond lengths. The X-ray structure of $[Ti_3O(OPr^i)_7(O_3C_9H_{15})]$ reported in the literature[29] also exhibits the same crystallographic disorder. Nevertheless, no spectroscopic measurements have yet been performed in order to evidence unambiguously the presence of an enolate ligand. As a consequence, it was crucial to validate this structural model by NMR spectroscopy.

Solution NMR studies of complex 1

^{17}O NMR Spectroscopy. The ^{17}O NMR spectrum of complex **1** displays a sharp resonance (linewidth $\Delta\nu_{1/2} = 40$ Hz) located at 556 ppm, which can be assigned to the triply bridging oxygen. The remaining broad resonances located at 214, 293, 352 and 380 ppm are attributed to the oxygens of the organic ligands bound to titanium nuclei. It is difficult to assign these resonances since only a few ^{17}O NMR studies have been reported for the characterization of organic ligands bound to transition metals. The line width ($400 < \Delta\nu_{1/2} < 1000$ Hz) of these resonances is likely due to the high nuclear quadrupole relaxation of these oxygen atoms or to some exchange process. The integrated intensities for the oxo bridges and for the other oxygen atoms are in the expected 1 : 10 ratio.

^{17}O NMR experiments show that the titanium-oxo core of compound **1** is preserved when this cluster is dissolved in non-polar solvents. But this NMR investigation is not sufficient to

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‡ $Ti_3O_{11}C_{30}H_{64}$: M = 744.6 g mol^{-1}, rhombohedral, $R\bar{3}m$, $a = 12.580$ (2) Å, $\alpha = 91.64(2)°$, $U = 1988.2(4)$ Å^3, $Z = 2$, $D_c = 1.244$ g cm^{-3}, $\mu = 0.636$ mm^{-1}, $T = 150$ K.

characterize the tridentate ligand. The cluster was then studied by ^{13}C and ^{1}H NMR spectroscopy.

^{1}H NMR spectroscopy. The ^{1}H NMR data of complex **1** are reported in Table 3. The spectrum displays a complex signal between 1.2 and 1.6 ppm. This chemical shift region is typical of the methyl protons corresponding to the isopropoxo groups and to the tridentate ligand [methyl bond to C(4)]. The two doublets, located at 2.08 and 2.59 ppm, present an intensity distorsion characteristic of a second-order effect in coupled AB systems and can be assigned to the geminal hydrogens of a CH_2. The singlet located at 4.49 ppm can be assigned to the C*H* proton of the enol function since its chemical shift is very close to the one reported for the proton C*H*=CO of a titanium-enolate complex $[CH_3CH{=}C(C_6H_5)OTi(NEt_2)_3]$ used as reference.[45]

The spectrum also displays seven septuplets (4.52, 4.58, 4.65, 4.75, 4.81, 4.815, 4.94 ppm) that partially overlap. The chemical shifts, the multiplicity and the coupling constant $^{3}J_{H\text{-}H}$ = 6.1 Hz are characteristic of the resonance of the proton in $O\text{–}CH(CH_3)_2$. The integration of the spectrum, considering an intensity of seven for the septuplets, results in relative intensities of 0.9, 0.7 and 1 for the signals at 2.08, 2.59 and 4.49 ppm, respectively. Although quantification of the NMR spectra presents some inaccuracies, these results are in relatively good agreement with the presence of an enolate ligand coordinated to titanium atoms. In order to confirm this hypothesis, the cluster was studied by ^{13}C NMR spectroscopy.

^{13}C NMR and ^{13}C INEPT NMR spectroscopy. The ^{13}C NMR data of complex **1** are also reported in Table 3. In both spectra, a broad signal between 26 and 33 ppm is present and is composed of overlapping methyl carbon resonances corresponding to isopropoxy groups and to the tridentate ligand. Eight resonances are observed between 75.4 and 79.7 ppm and can be assigned to $O\text{–}CH(CH_3)_2$. This number of resonances is surprising as only seven nonequivalent isopropoxy groups were evidenced by ^{1}H NMR spectroscopy.

The signal at 52 ppm presents a negative intensity in the INEPT spectrum and can be attributed to a CH_2 carbon. As the signal at 115.7 ppm remains positive in the INEPT spectrum, this resonance likely corresponds to a *C*H carbon. The three resonances at 79.9, 81.1 and 149.7 ppm, which are not observed in the INEPT spectrum, can be assigned to quaternary carbons. In order to give a complete assignment of the NMR resonances, a 2D ^{13}C–^{1}H correlation spectrum was recorded.

2D ^{13}C–^{1}H correlation spectrum. The XHCORRD ^{13}C–^{1}H spectrum is presented in Fig. 2. If the resonances of methyl protons are not taken into account, ten correlations are observed in the spectrum: (*i*) Two correlations that confirm that the two protons at 2.08 and 2.59 ppm are both bound to the carbon at 52 ppm. This CH_2 group belongs to the tridentate ligand. (*ii*) One correlation that allows us to associate the proton at 4.49 ppm to the carbon at 115.7 ppm. At this step, it is actually obvious that the carbon group is a CH group. (*iii*) Seven correlations characteristic of $O\text{–}CH(CH_3)_2$ groups.

Table 3 ^{13}C and ^{1}H NMR data for complex **1**

δ_H	δ_C	Assignment
2.08 (d)	52	$CH{=}C(O)\text{–}CH_2$
2.59 (d)	52	$CH{=}C(O)\text{–}CH_2$
4.49 (s)	115.7	$CH{=}C(O)\text{–}CH_2$
4.52 (sept)	76.7	$O\text{–}CH(CH_3)_2$
4.58 (sept)	75.9 and 76.0	$O\text{–}CH(CH_3)_2$
4.65 (sept)	75.4	$O\text{–}CH(CH_3)_2$
4.75 (sept)	76.9	$O\text{–}CH(CH_3)_2$
4.81 and 4.815 (sept)	78.0 and 78.4	$O\text{–}CH(CH_3)_2$
4.94 (sept)	79.7	$O\text{–}CH(CH_3)_2$
—	79.9	$O\text{–}C(C)(CH_3)_2$
—	81.1	$O\text{–}C(C)(CH_3)_2$
—	149.7	$CH{=}C(O)\text{–}CH_2$

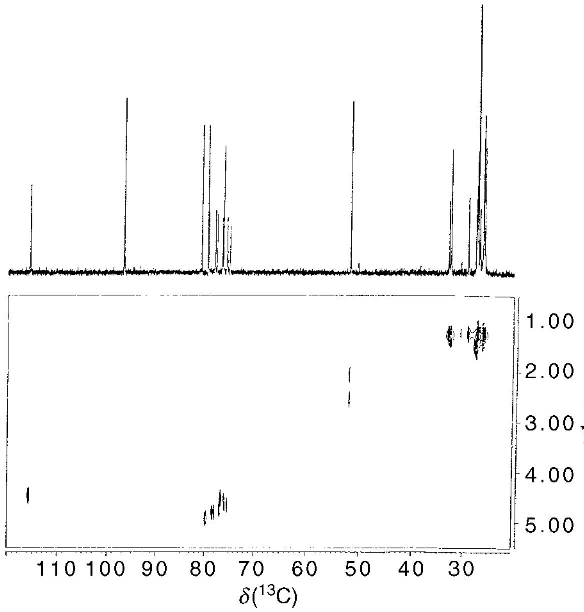

Fig. 2 XHCORRD ^{13}C–^{1}H spectrum of complex 1.

The complete assignment of the signals are given in Table 3.

The absence of correlations involving the carbon resonances at 79.9, 81.1 and 149.7 ppm confirms that these carbons are not protonated. These quaternary carbons and the *C*H carbon related to the signal at 115.7 ppm have been identified on the basis of their chemical shifts. The signals at 79.9 and 81.1 ppm correspond to the carbons $O\text{–}C(C)(CH_3)_2$ of the enolate ligand. Indeed, the characterization of the titanium alkoxide $Ti(OAm^{t})_4$ by ^{13}C NMR spectroscopy shows that the resonance of the quaternary carbon is close to 80 ppm.[46] Moreover, NMR data reported for the enolate complex $[CH_3CH{=}C(C_6H_5)OTi(NEt_2)_3]$ allow the final assignment of the resonances located at 149.7 (CH=*C*) and 115.7 (*C*H=C) ppm.[45]

These NMR experiments have allowed us to identify unambiguously the tridentate ligand as the enolate form of a trimeric condensation product of acetone $[(CH_3)_2C(OH)CH_2C(OH){=}CHC(OH)(CH_3)_2$: 2,6-dimethylhept-3-en-2,4,6-triol]. Moreover, they show that the titanium-oxo core of complex **1** is preserved in a nonpolar solvent. However, while the ^{1}H NMR and the 2D ^{1}H–^{13}C NMR spectra contain seven methine resonances, the ^{13}C NMR spectrum evidences eight methine resonances, which are difficult to justify compared to the presence of seven isopropoxy groups in each cluster. It could be due to the presence of two isomers in solution, which can be distinguished by a different orientation of one isopropoxy ligand.

X-Ray structure determination of complex 2

The molecular structure of compound **2** was determined by single crystal X-ray diffraction. An ORTEP drawing and a polyhedral representation are shown in Fig. 3(*a*) and 3(*b*), respectively. The unit cell contains two independent, but very similar, molecules that have a titanium-oxo core $[Ti_{11}O_{13}]$, which was previously proposed from NMR spectroscopy and by comparison with the X-ray structure of the complex $[Ti_{11}O_{13}(OPr^{i})_{13}(OEt)_5]$.[21] The complex $[Ti_{11}O_{13}(OPr^{i})_{18}]$ can result from a vacant arrangement of the complex $[Ti_{12}O_{16}(OPr^{i})_{16}]$, whose structure was resolved by single crystal X-ray diffraction.[21] Five titanium atoms are fivefold

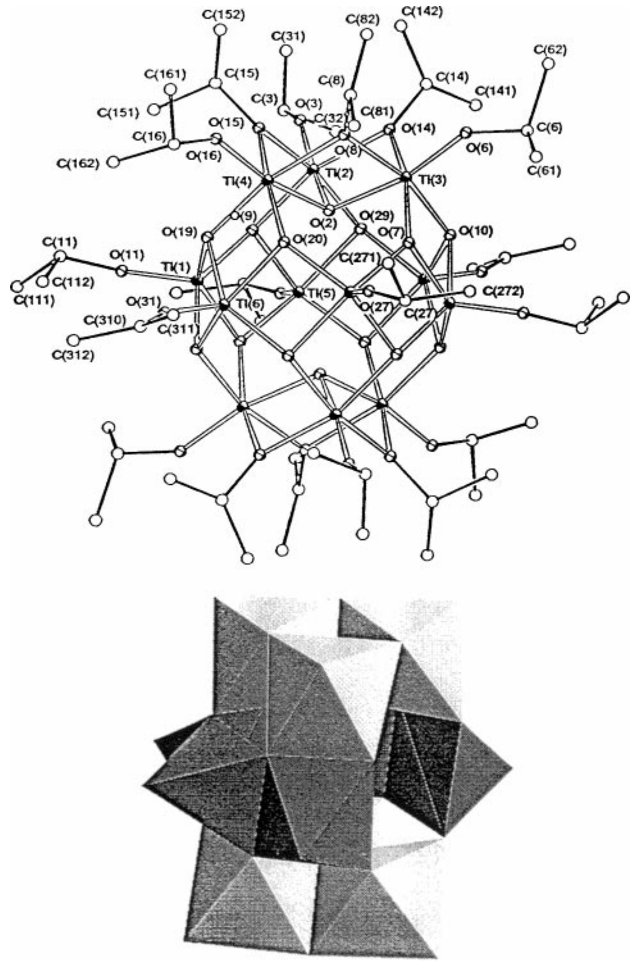

Fig. 3 (*a*) ORTEP drawing of complex **2** showing 20% displacement ellipsoids. (*b*) Polyhedral view of complex **2**.

coordinated and exhibit a square pyramidal environment, while six are sixfold coordinated and are located in oxygen-distorted octahedra. The titanium-oxo framework forms a nearly spherical cage. The cluster can be described as a incomplete cycle of pentacoordinated titanium atoms, which is capped on each side with a trimeric unit of six-coordinate titanium atoms. The metallic vacancy is located in the cycle but in the structure of compound **2**, the vacancy is disordered over two positions corresponding to five-coordinate titanium atoms, namely Ti(5) and Ti(6).§ The presence of the vacancy implies structural modifications in order to preserve the electroneutrality of the cluster compared to $[Ti_{12}O_{16}(OPr^i)_{16}]$. In the structure of compound **2**, the hexacoordinated titanium atoms are linked together by three isopropoxo bridges. Such a structural modification was also observed by NMR studies on the $[Ti_{11}O_{13}(OPr^i)_{18}]$ complex.[21]

Moreover, in $[Ti_{11}O_{13}(OPr^i)_{18}]$[21] the Ti–OPr^i vacancy is accompanied by the replacement of the four μ_3-oxo bridges directly linked to the Ti–OPr^i vacancy by three μ_2-oxo and one isopropoxy bridge. These structural modifications take place in the immediate vicinity of the vacancy and are difficult to observe for compound **2** since the vacancy is distributed over two distinct positions. As an example, in the first molecule the vacancy is located in the two crystallographic positions Ti(5) and Ti(6), whose atomic occupation factors are 0.9 and 0.6. If we consider only one OPr^i bridge position for each cluster, some electronic density is expected to be close to one of the four μ_3-oxo bridges linked to the Ti–OPr^i vacancy. Yet, the resolution of the structure has shown no electronic density that can correspond to carbon atoms. This is not so surprising as the carbon atoms corresponding to Ti(5)–OPr^i and Ti(6)–OPr^i vacancies should have atomic occupation factors of 0.1 and 0.4, respectively. These are so low that it is particularly difficult to locate the corresponding atoms. Moreover, it is possible that the OPr^i group is statistically distributed in the four positions corresponding to the four μ_3-oxo bridges linked to one Ti–OPr^i vacancy. In this case, its atomic occupation factor will be even smaller.

Significant molecular motion is evidenced for the isopropoxy groups. The high mobility of the carbons can also explain the difficulty in locating the OPr^i group position by Fourier maps. Moreover, molecular mobility is responsible for some of the poorly determined bond lengths in the isopropoxo groups.

The crystallographic structure of compound **2** has shown that this cluster contains only isopropoxy and oxo ligands. However, an uncertainty remains concerning the μ-OX ligand that results from the presence of the metallic vacancy. If this ligand is identical to μ-OPr^i, then compound **2** will be a cluster of formula $[Ti_{11}O_{13}(OPr^i)_{18}]$. The other possibility is the presence of one hydroxy bridging group and consequently the synthesized complex would be $[Ti_{11}O_{13}(OPr^i)_{17}(OH)]$. In order to resolve this ambiguity, complex **2** was also studied by NMR spectroscopy.

Solution NMR studies of complex 2

^{17}O NMR spectroscopy. Complex **2** was studied by ^{17}O NMR spectroscopy in solution. The assignment of all the ^{17}O NMR resonances was made according to previously reported data.[21]

The ^{17}O NMR spectrum of compound $[Ti_{11}O_{13}(OPr^i)_{18}]$ presents three resonances in the region of triply bridging oxygens (515, 529, 536 ppm) and three in the region of doubly bridging oxygens (711, 729, 770 ppm). These resonances are characteristic of the titanium-oxo core of the complex $[Ti_{11}O_{13}(OPr^i)_{18}]$.[21] As a consequence, this shows that complex **2** corresponds more likely to the cluster $[Ti_{11}O_{13}(OPr^i)_{18}]$ and that the structural hypothesis $[Ti_{11}O_{13}(OPr^i)_{17}(OH)]$ proposed from the crystallographic study is less probable. These ^{17}O NMR experiments show also that the titanium-oxo core of compound **2** is preserved in nonpolar solvents.

Moreover, the spectrum displays another resonance at 553 ppm, which can be assigned to a triply bridging oxygen. The chemical shift is close to those observed for the trinuclear complexes **1** ($\delta = 556$), $[Ti_3O(OPr^i)_9(OMe)]$ ($\delta = 554$)[23] and $[Ti_3O(OPr^i)_{10}]$ ($\delta = 558$).[23] The signal at 553 ppm indicates the presence of another titanium-oxo species [labeled $(Ti_3)^{\#}$ in this study], which presents probably the same titanium-oxo core $[Ti_3O_{11}]$. The spectrum presents also a broad resonance close to 290 ppm, which can be assigned to the Ti–*O*Pr^i oxygens, and a sharp one located at 38 ppm assigned to propan-2-ol.

^{13}C NMR and ^{13}C INEPT NMR spectroscopy. The characterization of the organic ligands was mainly investigated by ^{13}C NMR spectroscopy as the ^{1}H NMR spectrum did not provide significant information. The ^{13}C simple impulsion NMR spectrum exhibits 20 resolved resonances located between 72 and 80 ppm. From the INEPT spectrum 16 resonances can be attributed to *C*H carbons of isopropoxy groups and four resonances (79.8, 78.6, 75.4, 72.7 ppm) to quaternary carbons. The NMR characterization of compound **1** has shown that the ^{13}C resonances of O–*C*(C)(CH$_3$)$_2$ can be observed in this region. These non-protonated carbons can correspond to the diacetone alcohol ligand or to organic molecules that result from the condensation of diacetone alcohol.

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§ The Ti(5) and Ti(6) site occupancies are equal to 0.9 and 0.6. As the cluster is centrosymmetric, it contains 11 titanium atoms. For the second molecule, the vacancy is located on Ti(11) and Ti(12), whose atomic occupation factors are equal to 0.8 and 0.7.

It is possible that these ligands are coordinated to the titanium centers of the trinuclear complex $(Ti_3)^{\#}$, whose presence was suggested by ^{17}O NMR spectroscopy.

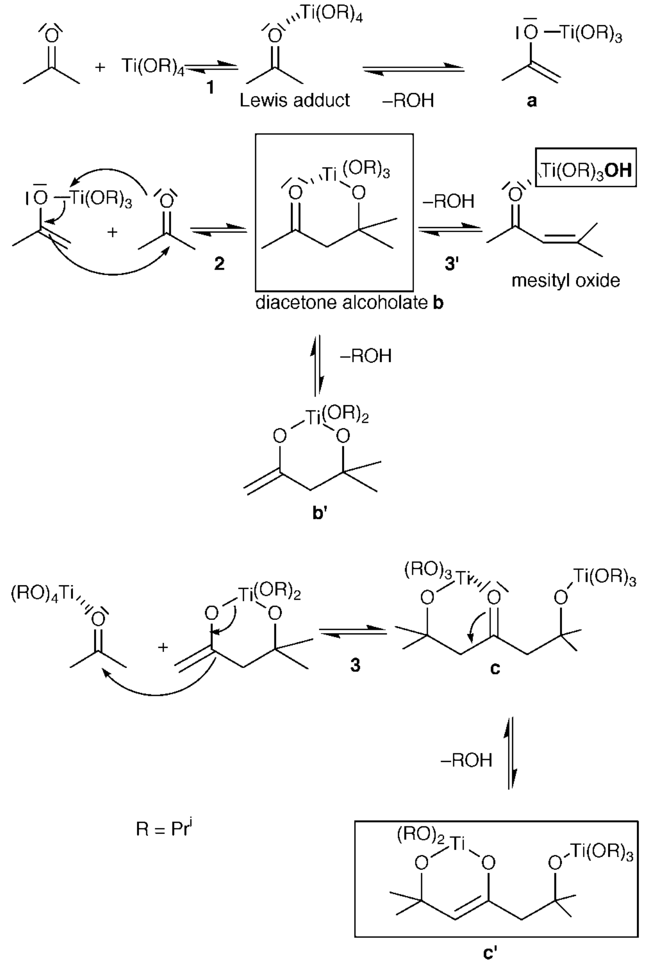
The ^{13}C NMR study shows also the presence of 4-methylpent-3-en-2-one (mesityl oxide) molecules. The resonances at 124, 154 and 197 ppm have been assigned respectively to the carbons $\mathit{C}H{=}C(CH_3)_2$, $CH{=}\mathit{C}(CH_3)_2$, and $\mathit{C}{=}O$ of mesityl oxide molecules from the comparison of the simple impulsion and the INEPT spectra. The assignment of the mesityl oxide resonances is fully confirmed by the spectrum of the pure compound.

Finally, one can observe four other resonances at 48.1, 49.1, 55.5 and 100.4 ppm that are difficult to identify and may correspond to the organic ligands of the trinuclear complex $(Ti_3)^{\#}$.

The ^{13}C NMR study has shown that the reaction of diacetone alcohol with $Ti(OPr^i)_4$ does not lead only to compound **2**. Other species are synthesized by this chemical route and in particular molecules of mesityl oxide were evidenced.

Discussion

At room temperature, the complex $[Ti_3O(OPr^i)_7(O_3C_9H_{15})]$ can be obtained in the presence of dry acetone while $[Ti_{11}O_{13}(OPr^i)_{18}]$ is obtained in the presence of dry diacetone alcohol. The formation of mesityl oxide and a new tridentate ligand ($O_3C_9H_{18}$ = 2,6-dimethylhept-3-en-2,4,6-triol) have been evidenced. The formation of $[Ti_3O(OPr^i)_7(O_3C_9H_{15})]$ from $Ti(OPr^i)_4$ and acetone can be described following Schemes 1 and 2. The proposed mechanism can be conveniently divided into three main formal steps: (*i*) synthesis of the tridentate ligand ($O_3C_9H_{18}$), (*ii*) hydroxylation of the titanium precursor, and (*iii*) condensation of hydroxylated precursors.



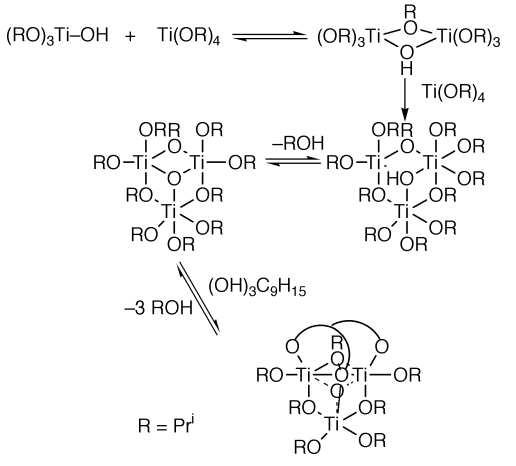
Scheme 1 Possible mechanism for the formation of $C_9O_3H_{18}$ through acetone condensation and for the hydroxylation of titanium alkoxide through crotonization of diacetone alcohol.

The first step involves the condensation reaction between two acetone molecules to form a ketoenolate complex (reaction 2 involving complex **b**). This reaction is probably catalyzed by the formation of a donor–acceptor Lewis adduct between a carbonyl function and a titanium nucleus. This adduct is converted to a titanium-enolate complex (complex **a**). This latter favors the stabilization of the enol form of the acetone, which is prone to condense with a second acetone molecule to form a titanium diacetone alcoholate (complex **b**). Ketoenol equilibria followed by a second condensation (reaction 3) between the complex **b′** and a third acetone molecule leads to the $O_3C_9H_{18}$ tridentate ligand (complexes **c** and **c′**).

The formation of the μ_3-oxo bridge requires a hydroxylation step. It is known that ketolization-enolization reactions are accompanied by crotonization reactions (dehydration reactions of condensed carbonyl compounds).[47] The main products of these reactions are unsaturated carbonyl compounds. Under our dilution conditions, it was not possible to detect the presence of mesityl oxide. However, mesityl oxide was clearly evidenced by ^{13}C NMR spectroscopy when a large quantity of diacetone alcohol was added to $Ti(OPr^i)_4$. As diacetone alcohol can result from the condensation of two acetone molecules, mesityl oxide is probably released during $[Ti_3O(OPr^i)_7(O_3C_9H_{15})]$ complex formation.

The crotonization reaction is presented in Scheme 1 (reaction 3′). This hydroxylation step is a nonhydrolytic process, catalyzed by the Lewis acid properties of titanium isopropoxide. Such a mechanism was also reported for the synthesis of the zinc hydroxide $Zn(OH)_2$, but the catalytic process was based on the basic character of the precursor $Zn(OCEt_3)_2$.[37] A metallic ketoenolate complex (**b**), which is involved in the ligand formation, is also a reaction intermediate in the hydroxylation step. In this entity, the titanium center is linked to an alkoxo function and solvated by the carbonyl function. Such a structural hypothesis was evidenced by NMR spectroscopy for an alkoxyaldehyde compound involved in a Grignard reaction.[48] This metallic ketoenolate complex (complex **b**) can lead to a nonhydrolytic hydroxylation of the metallic center and formation of mesityl oxide.

Finally, a possible mechanism for the formation of the trinuclear complex **1** is proposed in Scheme 2. Hydroxylated titanium isopropoxide precursors and titanium isopropoxide undergo olation and alcoholation reactions. These reactions are likely kinetically favored with respect to oxolation when the titanium centers present unsatisfied tetrahedral coordination.[8] The μ_3OH–Ti ligand being strongly acidic, the



Scheme 2 Possible mechanism for the formation of complex **1**.

proton can combine with an alkoxy group and be released as propan-2-ol. Finally, the cluster [$Ti_3O(OPr^i)_7(O_3C_9H_{15})$] can be obtained through the alcoholysis of three alkoxy groups by the tridentate ligand and the main driving force of this mechanism is the tendency of titanium to satisfy its preferred octahedral oxygen coordination.[8,9] One can notice that this mechanism can also be proposed for the formation of the homologous complexes [$Ti_3O(OPr^i)_9(OMe)$] and [$Ti_3O(OPr^i)_{10}$]. The only difference is the nature of the alcohol R′OH introduced in the last nucleophilic substitution step {[$Ti_3O(OPr^i)_9(OMe)$]: R′OH = MeOH; [$Ti_3O(OPr^i)_{10}$]: R′OH = $HOPr^i$; complex **1**: 3 R′OH = $(HO)_3C_9H_{15}$}. Another mechanism based on the condensation of titanium precursors complexed by the preformed tridentate ligand can also be proposed. The role of the tridentate ligand would be to assemble the titanium centers as its tridentate character contributes to the strength of the metal–ligand bonds and to the stabilization of the complex.

When diacetone alcohol and $Ti(OPr^i)_4$ react in a 1 : 1 ratio, the hydroxylation reaction is strongly favored and this pathway gives rise to more highly condensed species such as [$Ti_{11}O_{13}(OPr^i)_{18}$], instead of increasing the yield of trinuclear species. The formation of another trinuclear species, together with the [$Ti_{11}O_{13}(OPr^i)_{18}$] complex, was suggested by ^{17}O and ^{13}C NMR spectroscopy. This general tendency of forming trinuclear oxo clusters that transform into [$Ti_{11}O_{13}(OPr^i)_{18}$] when the hydrolysis ratio increases[23,49] has already been observed. ^{17}O NMR experiments have shown that upon direct hydrolysis of $Ti(OPr^i)_4$ the cluster [$Ti_3O(OPr^i)_{10}$] is obtained for a hydrolysis ratio $H_2O : Ti = 0.1$; when this hydrolysis ratio increases to 0.7 the [$Ti_3O(OPr^i)_{10}$] complex disappears and formation of the cluster [$Ti_{11}O_{13}(OPr^i)_{18}$] starts. For intermediate hydrolysis ratios (0.3–0.5) a mixture of both clusters is obtained.[49]

Mesityl oxide is formed immediately after mixing $Ti(OPr^i)_4$ and diacetone alcohol, as shown by the ^{17}O NMR spectrum recorded just after mixing and which exhibits the characteristic resonances of the complex [$Ti_{11}O_{13}(OPr^i)_{18}$] (515, 529, 536, 711, 729, 770 ppm). The ^{13}C NMR spectrum measured on the same solution shows the typical resonances of mesityl oxide (124, 154, 197 ppm). It proves that $Ti(OPr^i)_4$ is particularly reactive towards diacetone alcohol. In contrast, $Ti(OPr^i)_4$ is much less reactive towards acetone and mesityl oxide. Indeed, ^{17}O NMR experiments recorded on the mixtures acetone : $Ti(OPr^i)_4 = 1$ and mesityl oxide : $Ti(OPr^i)_4 = 1$ did not show new chemical species released just after mixing. This particular reactivity difference probably arises from the chemical nature of the carbonyl compound. The diacetone alcohol has necessarily better nucleophilic powers because of the presence of two nucleophilic functions. Indeed, alkoxide ligands can be easily transalcoholyzed and are consequently bound to a titanium center *via* a σ bond, although the interaction of titanium and a carbonyl function is based on a weaker π donor–acceptor bond. Moreover, the bidentate character of diacetone alcohol can favor the formation of the ketoenolate complex (complex **b**), which is the main reaction intermediate in the crotonization process.

It is interesting to point out that complexes **1** and **2** can also be obtained by refluxing (at 80 °C for two days) titanium isopropoxide with acetylacetone in the molar ratio acacH : $Ti(OPr^i)_4 = 0.1$, followed by a dilution in dry acetone. The ketone derivatives present in the reaction mixture act likely as oxolation sources for the synthesis of these titanium-oxo-organo clusters. However, the mechanism is not obvious as both isopropylacetate ester and condensation products of acetone have been detected in the reaction bath prior to acetone dilution through ^{17}O and ^{13}C NMR experiments. The ester compound is likely formed through a retro-Claisen reaction[50] from acetylacetone as already evidenced in the case of a yttrium alkoxide derived complex.[51]

Conclusions

It has been shown that ketones can be used through condensation-dehydration reactions as oxolation sources for the formation of metal-oxo-organo clusters from transition metal alkoxide precursors. This strategy is interesting because it provides oxolation *in situ* and therefore avoids the stability problems of the metal-oxo cores arising from local over-concentrations of water in the synthetic medium. Two titanium-oxo clusters, [$Ti_3O(OPr^i)_7(O_3C_9H_{15})$] and [$Ti_{11}O_{13}(OPr^i)_{18}$], were characterized by combining data provided by single crystal X-ray diffraction experiments and NMR spectroscopy. This study underlines that the simultaneous use of both techniques is of paramount importance to resolve accurately the structures of such clusters, which exhibit a high degree of structural disorder even at low temperatures.

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