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Titanium(III) Alkoxides. a New Synthetic Route and Solid State Properties (CP/MAS ^{13}C NMR, X-ray and IR)

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Abstract

$Ti(OR)_3$ compounds ($R = C_2H_5$, $C_4H_9{}^n$, C_6H_5) were prepared by reduction of titanium tetralkoxides with organosilicon compounds containing Si–H bonds. The reaction mechanism probably involves a four membered cyclic intermediate. The tervalent alkoxides have been characterized by elemental analyses, X-ray powder diffraction, infrared spectroscopy and solid-state magic angle sample spinning ^{13}C NMR.

The compounds are polymeric owing to the presence of alkoxide bridges. They are diamagnetic, insoluble materials which decompose on melting. Previously reported results are critically discussed and compared with the experimental findings from both infrared and NMR spectroscopy.

Introduction

The discovery of Ziegler–Natta catalysis in the early fifties prompted a great deal of interest in both the inorganic and organometallic chemistry of transition metal compounds of group IVB and VB. Among them Ti and V alkoxides have found industrial applications as components of soluble Ziegler Natta catalysts for olefin polymerization [1] More recently great interest has been shown in the development of new chemoselective reagents for the total synthesis or partial modification of multifunctional natural molecules [2, 3]. To this aim titanium alkoxides and dialkylamides have proved successful in achieving a fine 'tuning in' of the reactivity of conventional nucleophilic organometallic compounds of main-group metals (such as lithium and magnesium). Very high chemoselectivity has been reached obtaining exactly the reactivity desired for the planned application.

These two examples highlight the utility of transition metal alkoxides in solving practical problems connected with both catalysis and synthesis. The growing recognition of their importance mandates the development of more efficient synthetic routes.

Concerning Ti alkoxides $Ti(OR)_x$ (R = alkyl, aryl, $x = 3, 4$), their chemistry and properties have been comprehensively reviewed [4 6] Tetra-alkyl and tetra-aryl titanates are probably the most well known among transition metal alkoxides. Actually, presently available literature contains many scientific papers dealing either with their syntheses or properties. On the contrary, only a limited number of reports of Ti(III) and V(III) alkoxides can be found [7–10]. Moreover, there exist many contradictory results concerning their structure. $Ti(OR)_3$ compounds have been described both as tetrameric soluble compounds [10] and insoluble polymeric materials [7].

As part of our study of the chemistry and properties of low valent IVB and VB transition metal compounds, we recently reported the synthesis of alkoxy-chloro compounds $(RO)_2MCl$ (M = Ti, V; R = alkyl) [11]. Attention given to this class of compounds (as well as to $Ti(OR)_3$) is due to their possible application as low-valent intermediate in Ziegler–Natta catalysts [12].

In this paper we shall now report a new simple route to $Ti(OR)_3$ (R = alkyl, aryl) through the reaction of tetravalent derivatives and organosilicon compounds containing Si–H bonds. We will also briefly describe some of the solid state properties of the resulting materials.

Experimental

Experimental details concerning either analyses or synthetic procedures may be found elsewhere [11].

Materials

Solvents were purified by standard procedure and stored under nitrogen over pre-baked 3 Å Linde

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TABLE I. Analytical Data for $Ti(OR)_3$ Compounds[a]

Compound	Colour	Melting point[b] (°C)	Ti (%)	C (%)	H (%)	Si (%)
$Ti(OC_2H_5)_3$	pale green	236	25.9 (26.19)	39.0 (39.36)	8.1 (8.20)	0.31
$Ti(OC_4H_9{}^n)_3$	dark green	226	17.7 (17.94)	53.8 (53.95)	9.95 (10.11)	0.33
$Ti(OC_6H_5)_3$	yellow–green	265	14.3 (14.65)	66.2 (66.07)	4.58 (4.58)	0.41

[a] Calculated percentages are given in parentheses. [b] Extensive decomposition took place.

molecular sieves. $TiCl_3$ was used as received. Triethoxysilane was from Fluka and polymethylhydrosiloxane (PMHS) from Bayer (Baysilon MH 15).

Preparation of $Ti(OR)_3$ (R = alkyl). General Procedure (Method A)

Reactions were carried out in a nitrogen filled flask equipped with a dropping funnel, nitrogen inlet, magnetic stirrer and reflux condenser. A 50 ml heptane solution of 29 mmol $(RO)_3SiH$ (or an equivalent amount of PMHS) was slowly added to an equimolecular solution of $Ti(OR)_4$. The mixture was gently warmed at 50 °C for 10 h. After cooling, the resulting solid was separated by filtration, washed with n-hexane and dried under vacuum (10^{-3} mmHg). Yields were about 80%.

Preparation of $Ti(OC_6H_5)_3$ (Method B)

4 g of $Ti(OC_6H_5)_4$ were dissolved in 60 ml toluene. 1.4 g PMHS were added ([Si–H]/[Ti] = 3/1). The solution was allowed to react at 85 °C for 6 h. During this time its colour gradually turned from yellow–orange to mustard yellow. After cooling, the resulting solid was filtered off, washed with n-hexane and dried under vacuum. Yield was about 40% based on Ti.

Analytical data of the alkoxy Ti(III) compounds are reported in Table I. Only a limited amount of silicon was found indicating thus a low degree of contamination by the reducing agent. All are insoluble in both aprotic and protic, even strong solvating, solvents. They melt above 200 °C with decomposition.

^{13}C NMR Spectroscopy

Solid-state cross-polarization magic-angle sample spinning, dipolar decoupling (CP/MAS/DD) ^{13}C NMR spectra were recorded at 75 MHz using a Bruker AM-300 spectrometer equipped with a cross-polarization accessory. The radio-frequency amplifiers were adjusted to fulfil the Hartman–Hahn condition at approximately 48 kHz. The spectra were obtained using spin-lock cross-polarization and quadrature detection. Contact times for cross-polarization were 1.0 ms, with a 4 s delay between pulses. The magic angle spinning was around 4000 Hz for all samples.

Results

The reaction of hydrocarbon solutions of $Ti(OR)_4$ (R = alkyl) with organosilicon compounds containing Si–H bonds took place very smoothly. The solution gradually becomes turbid and a green colour develops. Hydrogen (0.5 mol per equivalent of Si–H bonds) was slowly released. The reaction between $Ti(OC_2H_5)_4$ and $(C_2H_5O)_3SiH$ was followed by gas chromatography. An equimolecular amount of $Si(OC_2H_5)_4$ was found at the end of the reaction. Accordingly, the overall stoichiometry can be deduced as follows:

$$Ti(OR)_4 + HSi(OR)_3 \longrightarrow Ti(OR)_3 + Si(OR)_4 + 0.5H_2\uparrow$$

The reaction between $Ti(OC_6H_5)_4$ and PMHS seems to be more complex. A higher [Si–H]/[Ti] was needed to achieve a complete reduction of the titanium compound. In this case no reaction was observed when $(C_6H_5)_3SiH$ was employed. On the contrary, $(C_2H_5O)_3SiH$ was still effective as a reducing agent. However alkoxy group exchange took place since the resulting solid contained variable amounts of ethoxy ligands. Hydrogen evolution was observed also in this case although the stoichiometry of the reaction was highly dependent on the experimental conditions. All these results clearly indicate that the reduction of Ti(IV) phenoxy compounds proceeds through a different reaction pathway.

X-ray Powder Diffraction

The X-ray powder diffraction patterns of the synthesized alkoxy compounds were recorded. '*d*' spacings and related line intensities from diffraction spectra of $Ti(OC_2H_5)_3$ and $Ti(OC_6H_5)_3$ are reported in Table II. In this Table we report also

TABLE II. X-ray Powder Diffraction Data for Ti(OR)$_3$ Compounds; '*d*' Spacing Values (Å)

$Ti(OC_2H_5)_3$	$Ti(OC_6H_5)_3$	$Ti(OCH_3)_3$[a]	$Ti(OC_2H_5)_2Cl$[b]
8.51(100)	10.78(100)	8.50(100)	11.1(100)
4.67(14)	6.11(10)	5.21(vw)	4.67(mb)
3.722(30)	4.04(15)	4.87(w)	3.63(w)
3.619(28)	2.95(7)	3.785(mw)	3.09(wb)
3.376(14)		3.625(w)	
3.142(16)		3.23(mw)	
2.315(10)		2.96(w)	
		2.565(vw)	

[a] Prepared according to ref. 7. [b] Ref. 11.

diffraction data from $Ti(OC_2H_5)_2Cl$ [11] and $Ti(OCH_3)_3$ prepared according to the method of Winter *et al.* [7]. It is worth noting that the diffraction pattern of trialkoxo Ti(III) compounds synthesized either by disproportionation between LiOR and $TiCl_3$ or through the route reported in this paper bear very close analogies. '*d*' spacing values of $Ti(OC_6H_5)_3$ were found to be completely different from those of both $Ti(OR)_3$ and alkoxy-chloro Ti(III) compounds [11].

Infrared Spectra

In Table III are listed the infrared absorption maxima and relative intensities of $Ti(OC_2H_5)_3$, $Ti(OC_4H_9{}^n)_3$, $Ti(OC_6H_5)_3$ and $Ti(O_6H_5)_4$. The infrared spectra for $Ti(OC_2H_5)_3$, $Ti(OC_4H_9{}^n)_3$ and $Ti(OC_6H_5)_3$ are given in Fig. 1.

TABLE III. Infrared Spectral Data for Ti(III) and Ti(IV) Alkoxides (cm^{-1})[a]

$Ti(OC_2H_5)_3$	$Ti(OC_4H_9{}^n)_3$	$Ti(OC_6H_5)_3$	$Ti(OC_6H_5)_4$[b]
1260(w)	1260(w)	1591(s)	1588(s)
1110(vs)	1235(vw)	1380(w)	1380(w)
1066(vs)	1119(msh)	1250(sh)	1250(vs)
910(s)	1070(vs)	1220(vsb)	1216(s)
590(sh)	1005(m)	1170(s)	1166(m)
542(sb)	970(mw)	1078(w)	1070(w)
438(mb)	900(mw)	1028(m)	1028(w)
	590(s)	961(w)	1001(w)
	547(m)	894(m)	912(s)
	470(sh)	861(s)	853(m)
	448(sb)	756(s)	840(m)
	400(m)	690(s)	758(s)
		625(m)	690(ms)
		540(m)	667(m)
		505(w)	577(m)
		365(w)	493(m)

[a] Nujol mull between CsI plates, unless otherwise stated. [b] KBr plates.

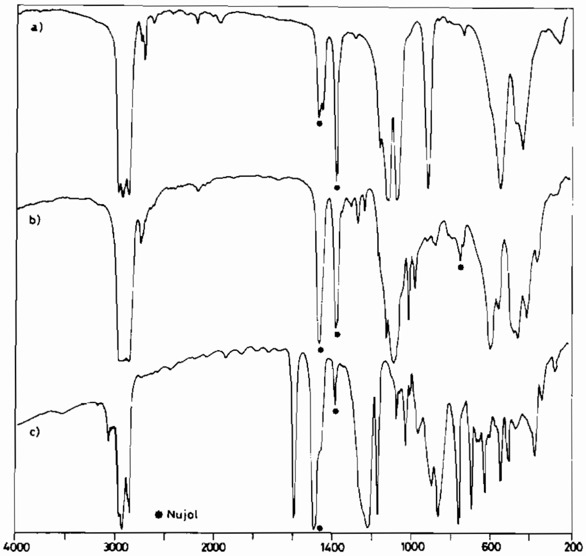


Fig. 1. Infrared spectra of: (a) $Ti(OC_2H_5)_3$; (b) $Ti(OC_4H_9{}^n)_3$; (c) $Ti(OC_6H_5)_3$.

The spectral behaviour of Ti(IV) tetralkoxides has been fully investigated by many authors [13–16]. Complete assignments have been made in the infrared for the methoxy derivative [16]. However, for the higher homologues it is difficult to make assignments with certainty as many such compounds are associated in varying degrees. This notwithstanding four distinctive regions can be clearly identified. Bands falling between 1470 and 1250–1150 cm^{-1} can be assigned to the usual deformation modes of CH_3– and $-CH_2-$ groups of the alkoxy ligands. The characteristic strong absorptions of alkoxy groups [ν_s(C–O) + ν_{as}(C–O)] appear around 1000 cm^{-1}. In this region the presence of a larger number of C–O stretching bands than expected on theoretical grounds is usually diagnostic for the polymeric nature of these compounds. ν(Ti–O) modes are expected to fall between 620 and 500 cm^{-1}. Finally, bending modes δ(Ti–O) give rise to a number of less intense bands between 450 and 400 cm^{-1}.

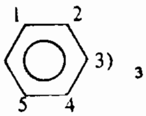
Up to now, however, to our knowledge no data have been published on the infrared spectra of IVB and VB tervalent transition metal alkoxides. Accordingly, Table IV lists some tentative IR assignments

TABLE IV. Tentative IR Assignment for Ti(OR)$_3$ Compounds (cm^{-1})[a]

Compound	ν(C–O)	ν(Ti–O)	δ(Ti–O)
$Ti(OC_2H_5)_3$	1110, 1066	542	438
$Ti(OC_4H_9{}^n)_3$	1070, 1005 (970)	590, (547)[b]	448

[a] Assignments in parentheses are doubtful. [b] Probably arising from interaction between ν_s(Ti–O) and δ(O–C–C) modes.

TABLE V. ^{13}C NMR CP/MAS for $Ti(OR)_{3,4}$ Alkoxides[a]

Compound	δ (ppm; TMS = 0)			
$Ti(O{-}\overset{1}{C}H_2{-}\overset{2}{C}H_3)_3$	$C_1 = \begin{cases}66.7(1.5)\\68.5(1.5)\end{cases}$	$C_2 = 21.4(1.5)$		
$Ti(O\overset{1}{C}H_2\overset{2}{C}H_3)_4$[b]	$C_1 = 70.3(2)$	$C_2 = 19.7(1.0)$		
$Ti(O\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_3)_3$	$C_1 = \begin{cases}72.9(1.5)\\71.7(1.5)\end{cases}$	$C_2 = 36.8(2.7)$	$C_3 = 20.2(0.9)$	$C_4 = 15.3(1.8)$
$Ti(O\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_2\overset{4}{C}H_3)_4$[b]	$C_1 = 75.7(1.8)$	$C_2 = 36.6(\sim 2)$	$C_3 = 20.3(1.5)$	$C_4 = 15.1(1.5)$
Ti(O )₃	$C_6 = \begin{cases}163.0(3)\\167.0(3)\end{cases}$	$C_1 \div C_5 = 123.(4), 127(4), 131(4)$		
$Ti(OC_6H_5)_4$	$C_6 = 167(4)$	$C_1 \div C_5 = 120(4), 130(4)$		

[a]Values in parentheses refer to linewidth in ppm. [b]Liquid alkoxides were supported on calcined SiO_2.

for $Ti(OC_2H_5)_3$ and $Ti(OC_4H_9{}^n)_3$ which have been deduced from the published data on the corresponding tetralkolates. No assignment has been made for both $Ti(OC_6H_5)_3$ and $Ti(OC_6H_5)_4$ although the intense, broad bands around 1250–1220 cm^{-1} and the peaks at 1585–1590 cm^{-1} can be clearly assigned to the ν(C–O) stretchings and to the out-of-plane deformations of phenyl rings, respectively.

CP/MAS/DD ^{13}C NMR Spectra

^{13}C NMR spectra have been run on $Ti(OC_2H_5)_3$, $Ti(OC_4H_9{}^n)_3$, $Ti(OC_6H_5)_3$ and the parent tetralkoxides by using the cross polarization-magic angle sample spinning technique. As shown in Fig. 2, well resolved spectra were obtained. Chemical shifts of resonances, line widths, and assignments are reported in Table V.

$Ti(OC_2H_5)_3$ and $Ti(OC_4H_9{}^n)_3$ show two resonances for the $^1CH_2$–O carbon having almost the same intensities. The splitting is probably due to the presence of alkoxy groups bonded as a bridge between two or more titanium atoms. Peaks having the same intensities may be diagnostic for polymeric structures with equivalent amounts of bridging and non-bridging groups. The parent Ti(IV) compounds don't show the analogous splitting although they too are considered polymeric. However they are liquid at room temperature and therefore, even if supported on silica, they dont lose the fluxional behaviour giving rise to spectra in which the chemical shifts arising from different bridging situations are averaged to a single value.

The phenoxy compound shows a quite different solid state structure. The Ti(III) compound shows splitting for the aromatic carbon C–O resonances into two peaks with relative intensities 2:1. It is likely that, in this case, the oligomerization degree and consequently the ratio between bridging and non-bridging alkoxy groups is different from the previous one. Also in this case, the parent Ti(IV) compound shows a single peak for the C–O carbon atoms.

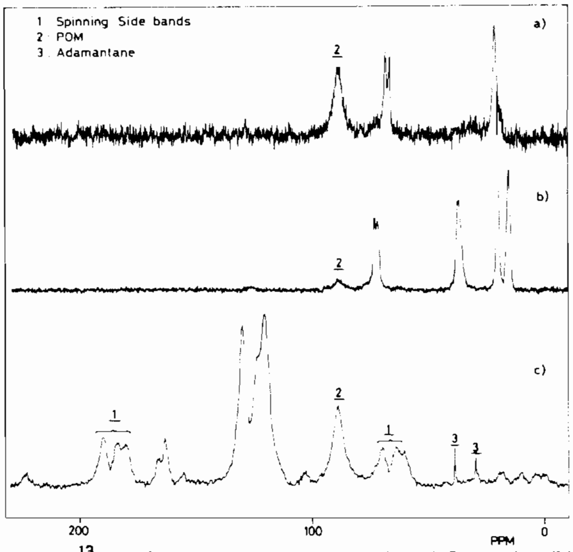


Fig. 2. ^{13}C CP/MAS NMR spectra of: (a) $Ti(OC_2H_5)_3$; (b) $Ti(OC_4H_9{}^n)_3$; (c) $Ti(OC_6H_5)_3$.

Attention has been addressed to the presence of paramagnetism in these compounds. As shown in Table V, Ti(III) alkoxides show practically the same chemical shifts and linewidth as Ti(IV) alkoxides. Literature is very limited concerning studies of high resolution solid state NMR of paramagnetic compounds. Accordingly, for a better understanding

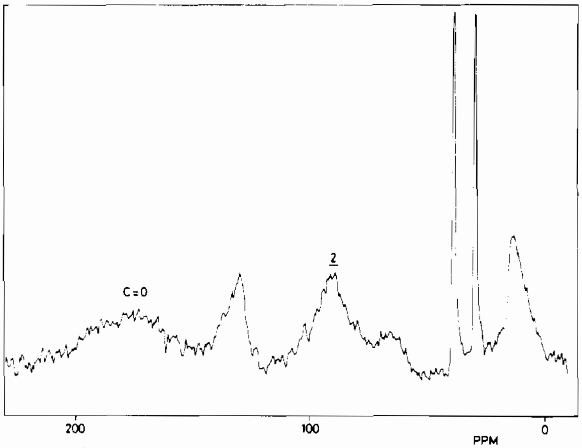
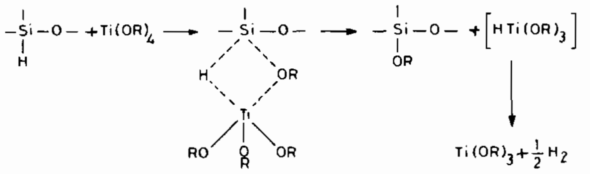


Fig. 3. ^{13}C CP/MAS NMR spectrum of $TiCl_3 \cdot C_6H_5COOC_2H_5$.

of the magnetic behaviour of Ti(III) alkoxides, we have synthesized the d^1 adduct $TiCl_3 \cdot C_6H_5COOC_2H_5$ and the corresponding d^0 compound $TiCl_4 \cdot C_6H_5COOC_2H_5$. As is well known [17, 18], complexes of $TiCl_3$ with Lewis bases exhibit a paramagnetic behaviour. Resonances due to the C=O groups are shown in Fig. 3. The ratio between the linewidth of the paramagnetic to the diamagnetic complex is about 20/1. It seems, therefore, reasonable to exclude for the Ti(III) alkoxides the presence of any contact shift or line broadening due to dipole–dipole interactions arising from the presence of unpaired electrons.

Discussion

Organosilicon compounds containing Si–H bonds are well known as mild reducing agents [19]. They have been employed in reactions with both organic and inorganic compounds. Thus, it has been shown that the trimer $(CH_3HSiO)_3$ is able to reduce very efficiently Fe(III) salts to Fe(II), Cu(II) to Cu(I), and Ag(I) compounds to metallic silver [20]. Shiihara and coworkers [21] employed PMHS in conjunction with $TiCl_4$ for the *in situ* preparation of $TiCl_3$-based Ziegler–Natta catalysts for olefin polymerization. During the reaction H_2 formation was observed. On these grounds, the hydrogen evolution during the reaction of $Ti(OR)_4$ with PMHS or $(C_2H_5O)_3SiH$ can be accounted for by a mechanism involving a four member cyclic intermediate leading to an alkoxy ligand exchange between titanium and silicon.



The intermediate titanium hydride complex is very unstable decomposing immediately to hydrogen and the desired trialkoxy compound.

Concerning the structure and properties of $Ti(OR)_3$ alkoxides there are a few contradictory reports in the literature. Adams *et al.* [7] first synthesized $Ti(OCH_3)_3$ and $Ti(OC_2H_5)_3$ by disproportionation between $TiCl_3$ and LiOR. The resulting alkoxides were described as polymeric insoluble materials. Since there is a close analogy between the X-ray powder diffraction pattern of $Ti(OCH_3)_3$ prepared according to these authors and $Ti(OC_2H_5)_3$ synthesized according to the new route described in this paper, the same solid state structure can be reasonably inferred. Lappert and Sanger [10] prepared $Ti(OR)_3$ ($R = CH_3$, C_2H_5) by addition of an excess of alcohol to a benzene solution of tris(dimethylamido)titanium(III). Diamagnetic green–blue crystals of tetrameric trialkoxytitanium(III) were obtained. An analogous result was reported by Nitzsche [22] who obtained a dark-blue benzene solution by reaction of titanium tetrabutylate with PMHS in an excess of alcohol. However no solid compound was isolated. Previously reported preparations of triethoxytitanium(III) by reduction of tetraethyltitanate with alkali metlas, yielded dark-blue [23] or pink–lilac crystals [24].

It seems likely to us that the structure of the resulting Ti(III) alkoxides are heavily dependent upon reaction conditions. Since Ti(III) compounds are highly electron deficient it seems quite reasonable that tervalent Ti(III) alkoxides synthesized in the presence of an excess of ligands which can act as electron donors, may have quite different solid state structures. Concerning this point, the formation of polynuclear molecular clusters dominates the chemistry of IVB and VB transition metal alkoxides [4]. The alkoxo ligand displays a great propensity to bridge two or more metal atoms giving rise to a large variety of highly complex structures. Useful informations concerning the bonding situation of the alkoxo ligands can be deduced from the infrared active ν(Ti–O) stretching modes. Kriegsman [16] described the infrared active modes of tetralkoxytitanates on the grounds of the distorted tetrahedral V_d point group. Total symmetric ν_s(Ti–O) stretchings were found to fall between 550 and 650 cm^{-1}. Owing to both varying degrees of association and the distortion from the T_d tetrahedral arrangement around the central metal atom, there are more bands than expected on theoretical grounds. However, when oxygen atoms are not shared in bridging situation, a double bonding is likely to occur between metal and oxygen. Then a contribution from a structure of the type $C{-}\overset{+}{O}{=}\overset{-}{M}$ would tend to drain electrons from the C–O σ bond imparting a certain degree of π double bonding to the M–O moiety with a resultant increasing of the ν_s(Ti–O) frequency.

TABLE VI. ν_s(Ti–O) Stretching Mode for Alkoxy Titanium Compounds

Ligand R	$Ti(OR)_4$ (cm^{-1})	$Ti(OR)_3$ (cm^{-1})	$Ti(OR)_2Cl$ (cm^{-1})	$\Delta\nu^a$ (cm^{-1})
CH_3	588^b	530^c	595^d	58
C_2H_5	621^b	542	545^d	59
$C_4H_9{}^n$	633^b	590		43

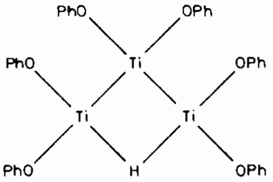
$^a\Delta\nu = \nu_s[Ti(OR)_4] - \nu_s[Ti(OR)_3]$. ^{b}Ref. 16. ^{c}Prepared according to ref. 7. ^{d}Ref. 11.

On the contrary, the higher the bridging degree, the lower the ν_s(Ti–O) frequency. The absorption frequencies of the ν_s(Ti–O) mode for $Ti(OR)_4$, $Ti(OR)_3$ and $Ti(OR)_2Cl$ are listed in Table VI. A frequency lowering of about $\Delta\nu \simeq 50$ cm^{-1} was observed for both classes of Ti(III) compounds in accordance with their polymeric nature due to a ligand bridging situation.

Much deeper insights into the solid state structure of the Ti(III) alkoxides can be gained by a close inspection of CP/MAS/DD ^{13}C NMR spectra. For both $Ti(OC_2H_5)_3$ and $Ti(OC_4H_9{}^n)_3$ the C–O resonances are split into two well resolved peaks having almost the same intensities. Also in this case both these features could be tentatively explained in terms of the bridging ability of the alkoxo groups. For nonbridging ligands contribution from a structure of the type $C{-}\overset{+}{O}{=}\overset{-}{M}$ would result in a carbon atom resonance downfield with respect to a bonding situation where such a contribution is not possible owing to double or triple bridging. In this respect, it is worth noting that X-ray diffraction studies of Ti alkoxides highlighted surprisingly complex structures [25–27]. Both double and triple bridging oxygens were present leading to a high degree of clustering. Although it is not possible to assign any well defined structure to the insoluble Ti(III) alkoxides, both infrared and solid state ^{13}C NMR spectra are in accordance with a polymeric network involving edge-sharing distorted octahedra and probably containing both double and triple bridging oxygens. The polymeric nature of these compounds is further confirmed by the absence of unpaired electrons as shown by the narrow linewidth of the CP/MAS/DD ^{13}C NMR resonances. A complete spin pairing can be accounted for only by strong electron exchange of neighbouring metal atoms in a clustering structure due to a highly bridging situation.

The phenoxy ligand exhibits a quite different behaviour either with respect to synthetic procedures or solid state properties. The only previous attempt to prepare $Ti(OC_6H_5)_3$ was by Lappert and Sanger [10]. They found that the reaction of phenol with tris(dimethylamido)titanium(III) occurs in two distinct stages. An initial solution of a Ti(III) complex formed. On standing decomposition took place and orange crystals of $Ti(OC_6H_5)_4 \cdot Me_2NH$ precipitated. This anomalous behaviour can be explained by considering the large variety of bonding situations that can be in principle forseen for Ti(III) phenoxide [28].

In this respect, we recall here the work of Wilkinson [29] who reported the reactions of $Ti(OC_6H_5)_2Cl_2$ with a number of reducing agents. The following structures have been suggested for the low valent titanium complexes:



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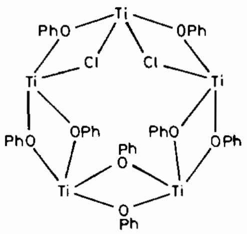

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Moreover the unstable $[Ti(OPh)_2Me_2]_n$ oligomer, on warming to 25 °C gave an orange insoluble complex whose analysis was consistent with its formation as $\{Ti_3(OPh)_4\}_2$. It is worth noting that the infrared absorption maxima reported for this compound match very closely those for $Ti(OC_6H_5)_3$ reported in Table III. However, also in this case, it is not possible to assign any definite structure to the $Ti(OC_6H_5)_3$ complex prepared by reaction of $Ti(OC_6H_5)_4$ and PMHS. The insolubility of the solid material is certainly due to a polymeric nature. The bonding situation for the phenoxide ligand should be, however, different from that in the alkyl alkoxo Ti(III) compounds as indicated by the CP/MAS/DD ^{13}C NMR spectrum. Moreover, the presence of η-bonded phenyl groups is likely to be ruled out since the chemical shifts of the aromatic carbon resonances do not change significantly.

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