

Low-Nuclearity Titanium Alkoxides and Their Rhodium Derivatives

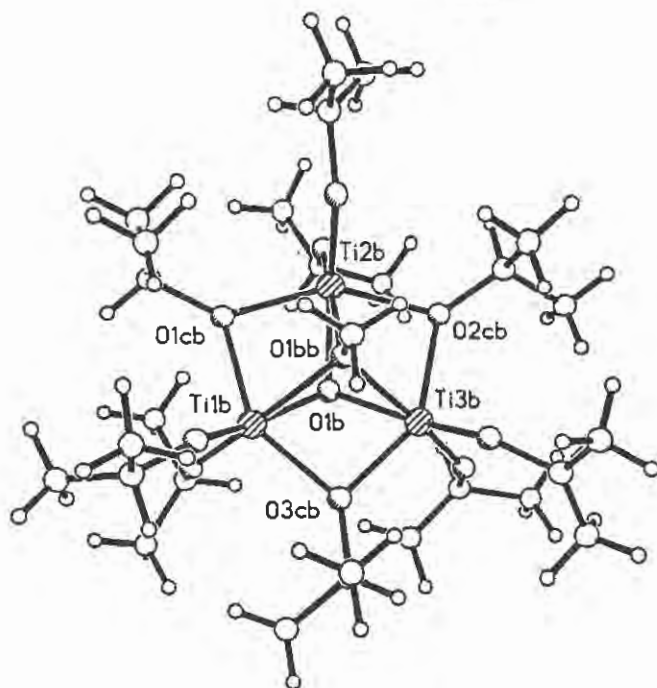
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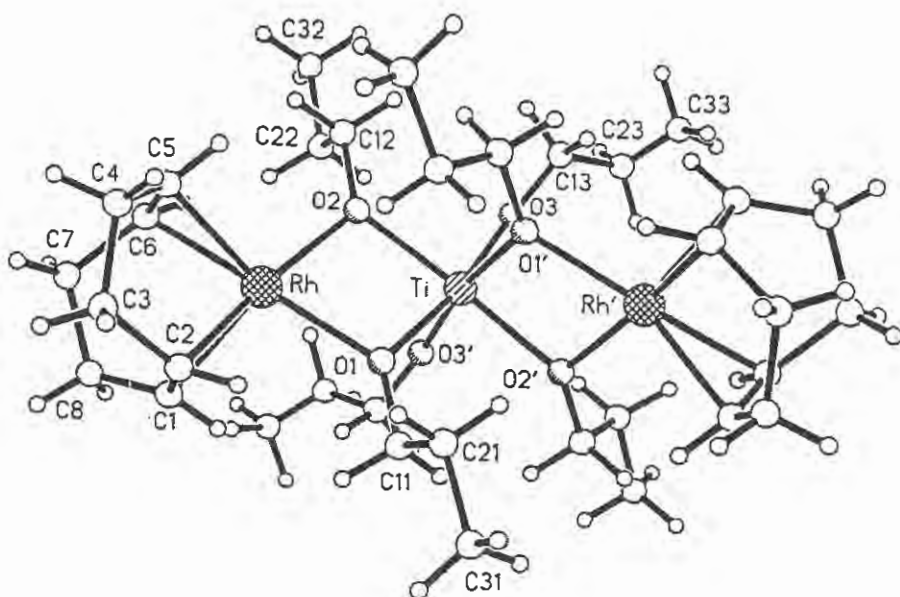
Titanium alkoxides and oxoalkoxides have received renewed interest in recent years as attention has focused on their role as titania sol-gel precursors and intermediates [1]. Porous metal oxides generated in this fashion have a number of interesting chemical applications as heterogeneous catalysts and catalyst supports [2,3]. This seminar treats three related aspects of titanium alkoxide chemistry: low nuclearity oxoalkoxides, organometallic alkoxides, and tetraalkylammonium alkoxides.

The reaction of $\text{Ti}(\text{OPr}^i)_4$ with 0.078 equivalents of water and 0.6 equivalents of methanol in *i*-PrOH solution gave $[\text{Ti}_3\text{O}](\text{OMe})(\text{OPr}^i)_9$ (**1**). A single crystal X-ray diffraction study of this material indicated that it contains two crystallographically-independent $[\text{Ti}_3(\mu_3\text{-O})](\mu_3\text{-OMe})(\mu_2\text{-OPr}^i)_3(\text{OPr}^i)_6$ molecules, one of which is shown below:



The analogous $[\text{Ti}_3\text{O}](\text{OPr}^i)_{10}$ molecule (**1a**) was generated in solution by hydrolysis of $\text{Ti}(\text{OPr}^i)_4$ with 0.02 equivalents of ^{17}O enriched water in Pr^iOH , and identified using ^{17}O , $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR techniques. Variable temperature ^1H , $^{13}\text{C}\{^1\text{H}\}$, and ^{17}O NMR spectroscopic studies show that **1** retains its solid state structure in hydrocarbon solvents at low temperature. It decomposes quickly at room temperature, however, to form $\text{Ti}(\text{OMe})_x(\text{OPr}^i)_{4-x}$, and more highly condensed oxoalkoxides. The stability of **1** and the other known titanium polyoxoalkoxides ($[\text{Ti}_x\text{O}_y](\text{OR})_{4x-2y}$) [4] in solution is known to be approximately a function of their degree of condensation, y/x . $[\text{Ti}_3\text{O}](\text{OMe})(\text{OPr}^i)_9$, with the smallest degree of condensation $y/x = 0.33$ known for titanium oxoalkoxides, therefore shows the lowest stability.

The reaction between $[\text{Rh}(\text{COD})(\text{OH})]_2$ and 3 equivalents of $\text{Ti}(\text{OPr}^n)_4$ results in the formation of $[\text{Rh}(\text{COD})]_2\text{Ti}(\text{OPr}^n)_6$ (**2**). An X-ray diffraction study showed that **2** adopts a butterfly structure with two $\text{Rh}(\text{COD})$ units acting as wings:



In solution, **2** exists in equilibrium with $[\text{Rh}(\text{COD})(\text{OPr}^n)]_2$ and $\text{Ti}(\text{OPr}^n)_4$. $[\text{Rh}(\text{COD})(\text{OPr}^n)]_2$ can also be prepared from the reaction of $[\text{Rh}(\text{COD})(\text{OH})]_2$ with 1 equivalent of $\text{Ti}(\text{OPr}^n)_4$.

The reaction of $\text{Ti}(\text{OMe})_4$ with 0.63 equivalents of $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_3]\text{OCH}_3$ in toluene/methanol leads to the formation of an analytically-pure, ionic titanium alkoxide $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_3][\text{Ti}_2(\text{OMe})_9]$ (**3**). A face-shared bioctahedral structure for $\text{Ti}_2(\text{OMe})_9^-$ is proposed based on its NMR spectroscopic properties at low temperature. Variable temperature ^1H NMR spectra of **3** also indicate that the $\text{Ti}_2(\text{OMe})_9^-$ anion is involved in a dynamic process, through which the bridging and terminal OCH_3 groups scramble. At -70°C , this process is sufficiently slow that two resonances for two types of OCH_3 protons with relative intensity 2:1 are observed.

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