



# Formation, solution structure and reactivity of alkylperoxo complexes of titanium

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## Abstract

A detailed in situ <sup>13</sup>C and <sup>1</sup>H NMR spectroscopic characterization of the following families of alkylperoxo complexes of titanium is presented: Ti(η<sup>2</sup>-OO*t*Bu)(O*i*Pr)<sub>4-n</sub>, where *n* = 1–4; binuclear complexes [(*i*PrO)<sub>3</sub>Ti(μ-O*i*Pr)<sub>2</sub>Ti(O*i*Pr)<sub>2</sub>(η<sup>2</sup>-OO*t*Bu)] and [(η<sup>2</sup>-OO*t*Bu)(*i*PrO)<sub>2</sub>Ti(μ-O*i*Pr)<sub>2</sub>Ti(O*i*Pr)<sub>2</sub>(η<sup>2</sup>-OO*t*Bu)]; complexes with β-diketonato ligands: Ti(LL)<sub>2</sub>(OEt)(η<sup>2</sup>-OO*t*Bu), Ti(LL)<sub>2</sub>(O*i*Pr)(η<sup>2</sup>-OO*t*Bu), Ti(LL)<sub>2</sub>(η<sup>2</sup>-OO*t*Bu)<sub>2</sub>, Ti(LL)<sub>2</sub>(O*t*Bu)(η<sup>1</sup>-OO*t*Bu), where HLL = acetylacetonate, dipivaloylmethane. These alkylperoxo complexes could not be isolated due to their instability and were studied in situ at low temperatures. Whereas the side-on (η<sup>2</sup>) coordination mode of *tert*-butylperoxo ligand is generally preferable, the end-on (η<sup>1</sup>) coordination caused by spatial hindrance from surrounding bulky ligands is found in two cases. The quantitative data on the reactivity of alkylperoxo complexes found towards sulfides and alkenes were obtained. The system TiO(acac)<sub>2</sub>/*t*BuOOH in C<sub>6</sub>H<sub>6</sub> was reinvestigated using <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy. The structure of the complex TiO(acac)<sub>2</sub>{CH<sub>3</sub>C(O)(OO*t*Bu)COO} actually formed in this system was elucidated. Four types of titanium(IV) alkylperoxo complexes were detected in the Sharpless–Katsuki catalytic system using <sup>13</sup>C NMR spectroscopy.

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**Keywords:** Alkylperoxo complexes of titanium(IV); Intermediates of selective epoxidation; <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy

## 1. Introduction

It is postulated that titanium(IV) alkylperoxo species are the reactive intermediates of the catalytic systems based on Ti(IV) and alkylhydroperoxides (see [1–7], and references therein). However, the experimental data on the isolation or spectroscopic characterization of titanium(IV) alkylperoxo complexes are very restricted. The solid state structure of the achiral (η<sup>2</sup>-*tert*-butylperoxo)titanatrane dimer is the only

reported X-ray structure of Ti(IV) alkylperoxo complex so far [7]. Recently, the alkylperoxo complexes formed upon interaction of *tert*-butylhydroperoxide with enantioselective Ti(IV) sulfoxidation catalysts bearing C<sub>3</sub>-symmetric trialkanolamine ligands were characterized by <sup>1</sup>H NMR and ESI–MS analysis [8].

In this work, we report a detailed in situ <sup>13</sup>C and <sup>1</sup>H NMR spectroscopic characterization of various families of *tert*-butylperoxo complexes of titanium with β-diketones (acetylacetonate and dipivaloylmethane) and alkoxo ligands (–O*t*Bu, –O*i*Pr, –OEt). The quantitative data on the reactivity of alkylperoxo complexes found towards sulfides and alkenes are also presented. Based on the elucidated <sup>13</sup>C NMR spectroscopic features of alkylperoxo complexes of titanium,

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the attempt was undertaken to detect these intermediates in the Sharpless–Katsuki catalytic system.

## 2. Experimental

CH<sub>2</sub>Cl<sub>2</sub>, CDCl<sub>3</sub>, Ti(OiPr)<sub>4</sub>, dipivaloylmethane, acetylacetone, diisopropyl L-tartrate, *tert*-butyl alcohol, isopropyl alcohol and benzyl phenyl sulfide were purchased from Aldrich and used without further purification. Cyclohexene was distilled prior to use. *tert*-Butyl hydroperoxide (99%) was prepared using standard procedures [9]. Reactions were carried out directly in standard 5 mm or 10 mm NMR tubes at –100 to +20 °C. The rate of *t*BuOOH decomposition (monitored by the appearance of the signals of *t*BuOH in <sup>1</sup>H and <sup>13</sup>C NMR spectra) was negligible below –30 °C for the systems studied.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400.13 and 100.61 MHz, respectively, using a Bruker MSL-400 spectrometer. The following operating conditions were used: sweep width 6 kHz (<sup>1</sup>H) or 25 kHz (<sup>13</sup>C), 10–20° pulse of 1–2 μs (<sup>1</sup>H), 45° pulse of 10 μs (<sup>13</sup>C), relaxation delay 5–60 s and 20–1000 scans. Quantitative <sup>13</sup>C NMR relative intensity measurements were made with inverse gated proton decoupling (to avoid the nuclear Overhauser effect) and long relaxation delays. Mutual correlations of NMR peaks were verified by <sup>13</sup>C–<sup>1</sup>H and <sup>1</sup>H–<sup>1</sup>H double resonance techniques.

## 3. Results and discussion

### 3.1. Mononuclear complexes

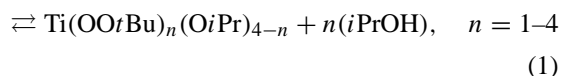
Ti(η<sup>2</sup>-OO*t*Bu)<sub>n</sub>(OiPr)<sub>4–n</sub> with *n* = 1–4

#### 3.1.1. Solution structure of alkylperoxo complexes

Ti(OO*t*Bu)<sub>n</sub>(OiPr)<sub>4–n</sub> with *n* = 1–4 [10]

<sup>13</sup>C and <sup>1</sup>H NMR monitoring of the interaction of Ti(OiPr)<sub>4</sub> with *t*BuOOH in CH<sub>2</sub>Cl<sub>2</sub> (CDCl<sub>3</sub>) at –70 to –30 °C has shown unambiguously that alkoxo ligands of Ti(OiPr)<sub>4</sub> are successively displaced by alkylperoxo ones with the increase of *t*BuOOH concentration from 1:1 to 10:1 with respect to Ti(OiPr)<sub>4</sub> to form an equilibrium mixture of alkylperoxo complexes Ti(OO*t*Bu)<sub>n</sub>(OiPr)<sub>4–n</sub>, where *n* = 1–4 (Table 1). The equilibrium (1) between all these complexes and Ti(OiPr)<sub>4</sub> is rapidly established even at –70 °C.

Ti(OiPr)<sub>4</sub> + *n*(*t*BuOOH)



Recently, analogous ligand displacement was observed for alkylperoxo complexes of vanadium. Using <sup>51</sup>V, <sup>17</sup>O, <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy, vanadium (V) alkylperoxo complexes VO(OO*t*Bu)<sub>k</sub>(O*n*Bu)<sub>3–k</sub>, where *k* = 1–3, were characterized in the reaction of VO(O*n*Bu)<sub>3</sub> with *t*BuOOH in CH<sub>2</sub>Cl<sub>2</sub> [11].

The molecular composition of the alkylperoxo complexes formed was determined using relative

Table 1

<sup>13</sup>C and <sup>1</sup>H NMR chemical shifts<sup>a</sup> of titanium(IV) alkylperoxo complexes Ti(OO*t*Bu)<sub>n</sub>(OiPr)<sub>4–n</sub>, *n* = 1–4

| <i>n</i>                    | C*(CH <sub>3</sub> ) <sub>3</sub> | C*H(CH <sub>3</sub> ) <sub>2</sub> | C(CH <sub>3</sub> ) <sub>3</sub> | CH(CH <sub>3</sub> ) <sub>2</sub> | CH(CH <sub>3</sub> ) <sub>2</sub> | C(C*H <sub>3</sub> ) <sub>3</sub> | CH(C*H <sub>3</sub> ) <sub>2</sub> |
|-----------------------------|-----------------------------------|------------------------------------|----------------------------------|-----------------------------------|-----------------------------------|-----------------------------------|------------------------------------|
| 0                           | –                                 | 76.59                              | –                                | 4.491                             | 1.270                             | –                                 | 26.73                              |
| 1                           | 86.93                             | 77.51                              | 1.444                            | 4.564                             | 1.276                             | 26.26                             | 26.52                              |
| 2                           | 87.42                             | 78.18                              | 1.450                            | 4.656                             | 1.269                             | 26.41                             | 26.01                              |
| 3                           | 87.21                             | 78.95                              | 1.421                            | 4.724                             | 1.286                             | 26.63                             | 25.89                              |
| 4                           | 87.54 <sup>b</sup>                | –                                  | 1.426                            | –                                 | –                                 | 26.80                             | –                                  |
| <i>i</i> PrOH <sup>c</sup>  | –                                 | 64.2                               | –                                | 4.02                              | 1.18                              | –                                 | 25.3                               |
| <i>t</i> BuOOH <sup>c</sup> | 80.1 <sup>d</sup>                 | –                                  | 1.26                             | –                                 | –                                 | 26.0 <sup>e</sup>                 | –                                  |

<sup>a</sup> <sup>13</sup>C NMR spectra were recorded at –30 °C in CH<sub>2</sub>Cl<sub>2</sub>; <sup>1</sup>H NMR spectra were recorded at –40 °C in CDCl<sub>3</sub>.

<sup>b</sup> The value 87.04 reported earlier [10] was erroneous.

<sup>c</sup> Chemical shifts depend on concentration.

<sup>d</sup> Due to the presence of *i*PrOH; chemical shift for dilute CH<sub>2</sub>Cl<sub>2</sub> solution of *t*BuOOH itself is 81.1 ppm and further increases with increase of its concentration (to 81.4 ppm for 2.6 M solution) and decrease of the temperature.

<sup>e</sup> Due to the presence of *i*PrOH; chemical shift for CH<sub>2</sub>Cl<sub>2</sub> solutions of *t*BuOOH itself is 25.80 ± 0.01 ppm and is almost independent on concentration and temperature.

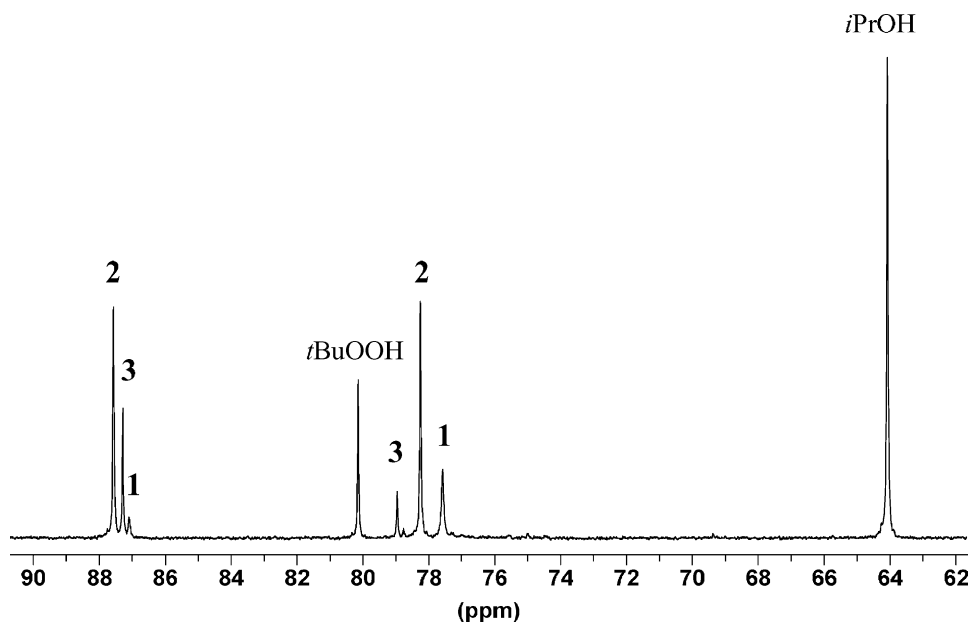


Fig. 1.  $^{13}\text{C}$  NMR spectrum of the system  $\text{Ti}(\text{O}i\text{Pr})_4/t\text{BuOOH}$  in  $\text{CH}_2\text{Cl}_2$  at  $-30^\circ\text{C}$  (initial concentrations:  $[\text{Ti}(\text{O}i\text{Pr})_4] = 0.3\text{ M}$ ,  $[t\text{BuOOH}] = 0.6\text{ M}$ ). The signals belonging to complexes **1–3** are marked correspondingly.  $i\text{PrOH}$  is a product of ligand substitution.

intensities of the  $^{13}\text{C}$  NMR signals of the quaternary carbon atoms of  $^- \text{OO}t\text{Bu}$  ligands and the ternary carbon atoms of  $^- \text{O}i\text{Pr}$  ligands, which were 1:3, 2:2 and 3:1 for  $\text{Ti}(\text{OO}t\text{Bu})(\text{O}i\text{Pr})_3$  (**1**),  $\text{Ti}(\text{OO}t\text{Bu})_2(\text{O}i\text{Pr})_2$  (**2**) and  $\text{Ti}(\text{OO}t\text{Bu})_3(\text{O}i\text{Pr})$  (**3**), respectively. Only the signals of the  $^- \text{OO}t\text{Bu}$  ligands correspond to complex  $\text{Ti}(\text{OO}t\text{Bu})_4$  (**4**) in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. The coupling constants and multiplicities of the  $^1\text{H}$  and  $^{13}\text{C}$  resonances of complexes **1–4** are the same as those for corresponding signals of  $i\text{PrOH}$  and  $t\text{BuOOH}$ . As an example, Fig. 1 shows  $^{13}\text{C}$  NMR spectrum of the system  $\text{Ti}(\text{O}i\text{Pr})_4 + 2(t\text{BuOOH})$  in  $\text{CH}_2\text{Cl}_2$  at  $-30^\circ\text{C}$ . The signals of the quaternary carbon atoms of  $^- \text{OO}t\text{Bu}$  ligands and the ternary carbon atoms of  $^- \text{O}i\text{Pr}$  ligands of complexes **1–3** are clearly seen.

Intensities of the signals belonging to  $\text{OO}t\text{Bu}$  and  $\text{O}i\text{Pr}$  groups of a particular complex  $\text{Ti}(\text{OO}t\text{Bu})_n(\text{O}i\text{Pr})_{4-n}$  successively reached their maximums and then decreased in the order of  $n = 1–3$  with the gradual increase of  $t\text{BuOOH}$  concentration. In the case of  $n = 4$ , the maximal intensity of the corresponding signals of  $\text{OO}t\text{Bu}$  groups was observed at the highest  $t\text{BuOOH}$  concentration.

The difference in the chemical shifts for the quaternary carbon atom of the  $t\text{Bu}$  group in  $\text{Ti}(\text{OO}t\text{Bu})_n(\text{O}i\text{Pr})_n$  ( $n = 1–4$ ) and in  $t\text{BuOOH}$  is 6.9–7.5 ppm. The corresponding difference for the primary carbon atoms of the  $t\text{Bu}$  group is 0.25–0.75 ppm (Table 1). The difference in the chemical shifts for the ternary carbon atom of the  $i\text{Pr}$  group in  $\text{Ti}(\text{OO}t\text{Bu})_n(\text{O}i\text{Pr})_{4-n}$  and in  $i\text{PrOH}$  is 14–15 ppm (Table 1). To define the mode of  $^- \text{OO}t\text{Bu}$  ligand coordination to the titanium atom in complexes **1–4**, we have compared the above differences with those for specially prepared alkoxo complexes  $\text{Ti}(\text{O}t\text{Bu})_n(\text{O}i\text{Pr})_{4-n}$ , where  $n = 1–4$  (Table 2). The corresponding differences for the  $\alpha$ -carbon atom of  $\text{O}i\text{Pr}$  and  $\text{O}t\text{Bu}$  groups are 11.2–12.2 ppm, whereas those for the  $\beta$ -carbon atom of  $\text{O}t\text{Bu}$  groups are 1.04–1.09 ppm. Thus, in the case of  $\eta^1$ -coordination of  $^- \text{OO}t\text{Bu}$  ligand, one would expect a difference in the chemical shifts for the quaternary carbon atom of the  $t\text{Bu}$  group in **1–4** and in  $t\text{BuOOH}$  of about 1 ppm, whereas in the case of  $\eta^2$ -coordination a difference up to 11–12 ppm is expected. Based on these data, it is natural to conclude that  $\eta^2$ -coordination of  $\text{OO}t\text{Bu}$  moieties is preferable for alkylperoxo complexes **1–4**, where this difference

Table 2

 $^{13}\text{C}$  and  $^1\text{H}$  NMR chemical shifts<sup>a</sup> of titanium(IV) alkoxy complexes  $\text{Ti}(\text{O}t\text{Bu})_n(\text{O}i\text{Pr})_{4-n}$ ,  $n = 1-4$ 

| $n$ | $\text{C}^*(\text{CH}_3)_3$ | $\text{C}^*\text{H}(\text{CH}_3)_2$ | $\text{C}(\text{CH}_2)_3$ | $\text{CH}(\text{CH}_3)_2$ | $\text{CH}(\text{CH}_2)_2$ | $\text{C}(\text{C}^*\text{H}_3)_3$ | $\text{CH}(\text{C}^*\text{H}_3)_2$ |
|-----|-----------------------------|-------------------------------------|---------------------------|----------------------------|----------------------------|------------------------------------|-------------------------------------|
| 0   | –                           | 76.59                               | –                         | 4.491                      | 1.253                      | –                                  | 26.73                               |
| 1   | 81.28                       | 76.36                               | 1.316                     | 4.488 <sup>b</sup>         | 1.248 <sup>c</sup>         | 32.35 <sup>c</sup>                 | 26.71 <sup>c</sup>                  |
| 2   | 80.98                       | 76.14                               | 1.313                     | 4.484 <sup>b</sup>         | 1.248 <sup>c</sup>         | 32.35 <sup>c</sup>                 | 26.71 <sup>c</sup>                  |
| 3   | 80.68                       | 75.85                               | 1.308                     | 4.476                      | 1.243                      | 32.35 <sup>c</sup>                 | 26.71 <sup>c</sup>                  |
| 4   | 80.33                       | –                                   | 1.298                     | –                          | –                          | 32.35 <sup>c</sup>                 | –                                   |

<sup>a</sup>  $^{13}\text{C}$  NMR spectra were recorded at  $0^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$ ;  $^1\text{H}$  NMR spectra were recorded at  $20^\circ\text{C}$  in  $\text{CDCl}_3$ .<sup>b</sup> Partially resolved.<sup>c</sup> Unresolved.

is 6.9–7.5 ppm. According to the  $\eta^2$ -coordination mode of  $^-\text{OO}t\text{Bu}$  ligands, the coordination number of the titanium atom increases from 5 to 8 for complexes **1–4**, respectively (Fig. 2). The above results are the first example of a direct NMR detection of alkylperoxo complexes of titanium with **1–4** alkylperoxo ligands.

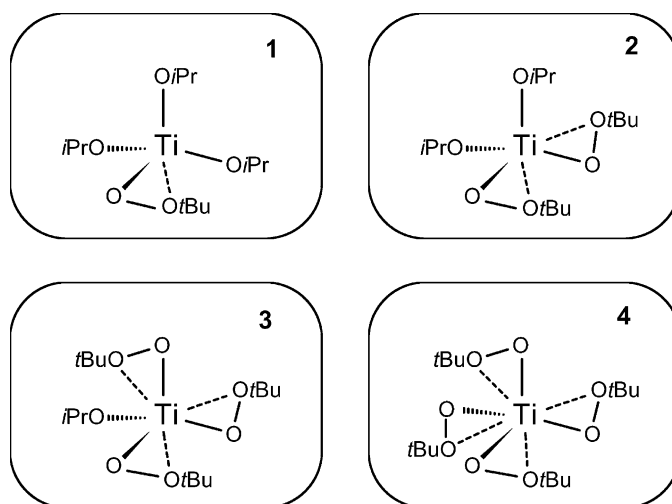
It is noteworthy that only one set of  $^{13}\text{C}$  and  $^1\text{H}$  NMR signals was observed for ligands of any particular complex  $\text{Ti}(\text{OO}t\text{Bu})_n(\text{O}i\text{Pr})_{4-n}$  with  $n = 1-4$ . This fact evidences in favor of fast (even at  $-70^\circ\text{C}$ ) intra-molecular rearrangements in the coordination sphere, which lead to observed magnetic symmetry of the ligands and to fast inter-conversion of all possible structural isomers of a particular alkylperoxo complex.

### 3.1.2. Reactivity of alkylperoxo complexes

$\text{Ti}(\text{OO}t\text{Bu})_n(\text{O}i\text{Pr})_{4-n}$ , where  $n = 1-4$  towards benzyl phenyl sulfide

The reaction of  $\text{Ti}(\text{OO}t\text{Bu})_n(\text{O}i\text{Pr})_{4-n}$ ,  $n = 1-4$  with benzyl phenyl sulfide was studied by  $^1\text{H}$  NMR spectroscopy in deuterio-chloroform at  $-30^\circ\text{C}$ . At this temperature, these alkylperoxo complexes are stable and their concentrations do not noticeably change during several hours.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR data show that at the reactants ratio  $[\text{tBuOOH}]/[\text{Ti}(\text{O}i\text{Pr})_4] \leq 0.5$  complex **1** is a major form of the alkylperoxo complexes. The reactivity of complex **1** towards sulfide can be readily determined by the  $^1\text{H}$  NMR monitoring of **1**, sulfide and sulfoxide concentration changes with time. The reaction was performed directly in an NMR tube. Thus

Fig. 2. The structures proposed for complexes **1–4**.

obtained rate constant  $k_1$  for the reaction of complex **1** with benzyl phenyl sulfide at  $-30^\circ\text{C}$  is  $(8 \pm 2) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ .

At the initial concentration ratio  $[t\text{BuOOH}]/[\text{Ti}(\text{OiPr})_4] \approx 2$ , complex **2** is the predominant species in the system  $\text{Ti}(\text{OiPr})_4 + t\text{BuOOH}$  in  $\text{CH}_2\text{Cl}_2$ . Reactivity of complex **2** towards benzyl phenyl sulfide is noticeably higher than that of **1**,  $k_2 = (3.2 \pm 0.6) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  at  $-30^\circ\text{C}$ .

At the reactants ratio  $[t\text{BuOOH}]/[\text{Ti}(\text{OiPr})_4] > 10$ , complexes **3** and **4** predominate in solution. They are much more reactive towards benzyl phenyl sulfide. We could only evaluate corresponding rate constants at  $-30^\circ\text{C}$ :  $k_3, k_4 \geq 1.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ . Thus, the reactivity of alkylperoxo complexes of titanium  $\text{Ti}(\text{OO}i\text{Bu})_n(\text{OiPr})_{4-n}$ ,  $n = 1-4$  towards this sulfide grows with the increase of the number of alkylperoxo ligands. Moreover, the reactivity per each alkylperoxo group also increases in this row.

In the course of the oxidation of benzyl phenyl sulfide in the above system, the formation of  $\text{Ti}(\text{O}i\text{Bu})_n(\text{OiPr})_{4-n}$  complexes is observed, where  $n = 1-4$ , which participate in equilibrium reactions with  $t\text{BuOH}$ ,  $i\text{PrOH}$  and  $t\text{BuOOH}$ . Their concentrations simply reflect that of the oxidation by-product  $t\text{BuOH}$ . At the initial stage of the oxidation, when  $t\text{BuOH}$  concentration is much less than that of  $i\text{PrOH}$ , the formation of  $\text{Ti}(\text{O}i\text{Bu})_n(\text{OiPr})_{4-n}$  complexes can be neglected.

### 3.1.3. Reactivity of alkylperoxo complex $\text{Ti}(\text{OO}i\text{Bu})(\text{OiPr})_3$ towards alkenes

Complex **1** is far less reactive towards olefins than towards sulfides. Thus, its reactions with olefins were studied at  $20^\circ\text{C}$ . At this temperature self-decomposition of **1** takes place with the rate constant  $k_d = 4 \times 10^{-4} \text{ s}^{-1}$ . In the course of this decomposition, one molecule of acetone is formed via oxidation of one of the  $^- \text{OiPr}$  ligands by the  $\text{OO}i\text{Bu}$  moiety. Reaction of **1** with an olefin must be competitive with this self-decay for the formation of epoxide to be detected. For the sample with  $[\text{cyclo-C}_6\text{H}_{10}] = 1.4 \text{ M}$ ,  $[\text{Ti}(\text{OiPr})_4] = 0.24 \text{ M}$ ,  $[t\text{BuOOH}] = 0.14 \text{ M}$ , the molar ratio of the oxidation products  $[\text{acetone}]/[\text{epoxide}]$  was about 3. The rate constant for the reaction of **1** with cyclohexene at  $20^\circ\text{C}$  is  $10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ . Styrene and stilbene were unreactive towards **1**. Allylic alcohols react very rapidly

with **1** at  $20^\circ\text{C}$  to form corresponding epoxides. In this case, self-decomposition of **1** with a formation of acetone can be entirely suppressed.

### 3.2. Binuclear complexes

$[(i\text{PrO})_3\text{Ti}(\mu\text{-OiPr})_2\text{Ti}(\text{OiPr})_2(\text{OO}t\text{Bu})]$  (**5**) and  $[(t\text{BuOO})(i\text{PrO})_2\text{Ti}(\mu\text{-OiPr})_2\text{Ti}(\text{OiPr})_2(\text{OO}t\text{Bu})]$  (**6**)

It is known that  $\text{Ti}(\text{OiPr})_4$  exists in solution in monomeric and dimeric forms [14], the latter predominates at low temperatures.  $^{13}\text{C}$  NMR spectrum of  $[\text{Ti}(\text{OiPr})_4]_2$  in  $\text{CH}_2\text{Cl}_2$  at  $-100^\circ\text{C}$  displays peak at 74.45 ppm from ternary carbon atoms of two bridging  $^- \text{OiPr}$  ligands and that at 77.68 ppm from corresponding carbon atoms of six terminal  $^- \text{OiPr}$  ligands. With the temperature increase, the exchange of terminal and bridging  $\text{OiPr}$  groups of  $[\text{Ti}(\text{OiPr})_4]_2$  is accelerated, and the only resonance at 76.67 ppm is observed for the ternary carbon atoms at  $-40^\circ\text{C}$ .

The  $^{13}\text{C}$  NMR monitoring of the titanium(IV) species in the system  $\text{Ti}(\text{OiPr})_4/t\text{BuOOH}$  ( $[t\text{BuOOH}]/[\text{Ti}(\text{OiPr})_4] < 1$ ,  $\text{CH}_2\text{Cl}_2$ ,  $-95^\circ\text{C}$ ) shows that besides signals of mononuclear complexes considered above, those of binuclear alkylperoxo intermediates **5** and **6** can be observed (Fig. 3). The equilibrium between all detected titanium species is rapidly es-

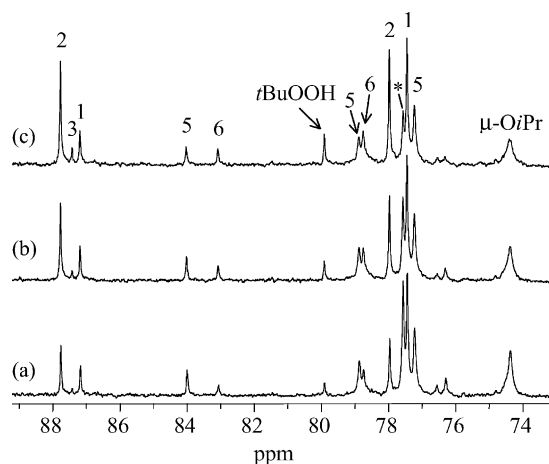


Fig. 3.  $^{13}\text{C}$  NMR spectra of the system  $\text{Ti}(\text{OiPr})_4/t\text{BuOOH}$  in  $\text{CH}_2\text{Cl}_2$  at  $-95^\circ\text{C}$ . Initial concentration of  $\text{Ti}(\text{OiPr})_4$  was 0.3 M, that of  $t\text{BuOOH}$  was 0.16 M (a), 0.2 M (b) and 0.24 M (c). The signals belonging to complexes **1–3**, **5** and **6** are marked correspondingly. Ternary carbon atom signal of terminal  $^- \text{OiPr}$  ligands of  $[\text{Ti}(\text{OiPr})_4]_2$  is marked with an asterisk.

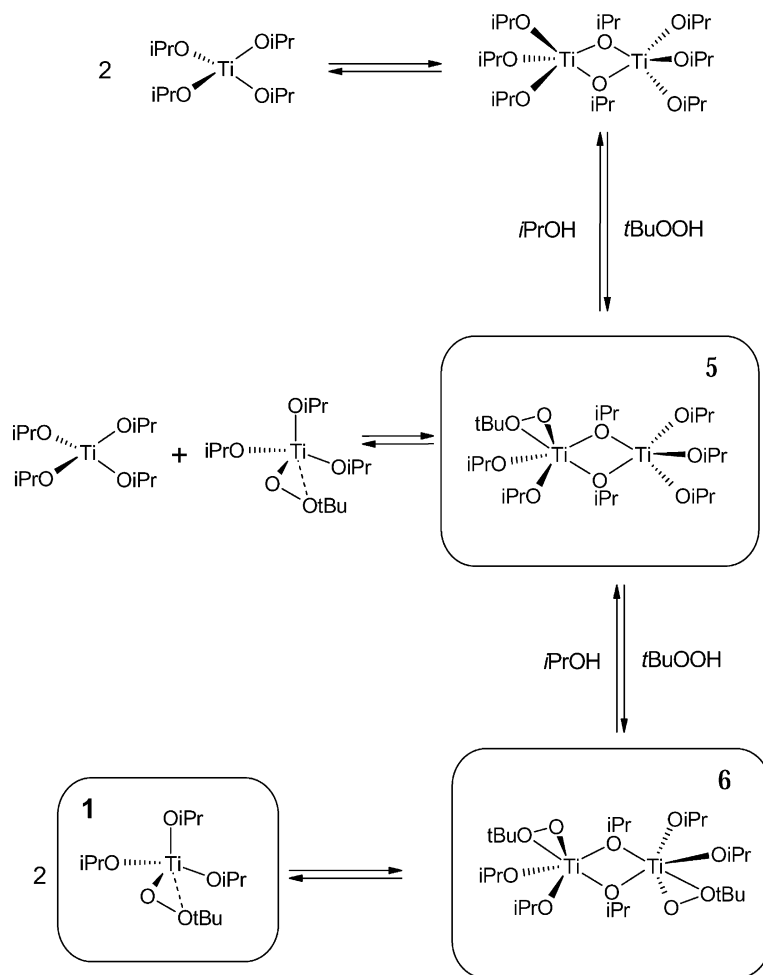


Fig. 4. The structures proposed for binuclear titanium(IV) alkylperoxy complexes **5** and **6**, and a possible scheme of their formation.

established even at  $-100^{\circ}\text{C}$ . The signals of **5** and **6** successively reach their maximums and then diminish with the gradual increase of *t*BuOOH concentration. Complexes **5** and **6** are converted to complexes **2–4** at a large excess of *t*BuOOH.

Complex **5** exhibits three  $^{13}\text{C}$  NMR signals of ternary carbon atoms of  $^{-}\text{O}i\text{Pr}$  ligands at 78.97 (2C), 77.41 (3C) and 74.59 ppm (2C), and one signal of quaternary carbon atom of  $^{-}\text{OO}t\text{Bu}$  ligand at 84.00 ppm (1C). The relative intensities of the signals are shown in parenthesis. Peaks at 78.97 ppm (2C) and 77.41 ppm (3C) are in the range of chemical shifts of terminal  $^{-}\text{O}i\text{Pr}$  ligands, whereas that at 74.59 ppm (2C) is in

the range for bridging  $^{-}\text{O}i\text{Pr}$  ligands. Thus, complex **5** incorporates two bridging and five terminal  $^{-}\text{O}i\text{Pr}$  ligands, and one  $^{-}\text{OO}t\text{Bu}$  ligand. The binuclear structure  $[(i\text{PrO})_3\text{Ti}(\mu\text{-O}i\text{Pr})_2\text{Ti}(\text{O}i\text{Pr})_2(\text{OO}t\text{Bu})]$  (Fig. 4) fits well to the  $^{13}\text{C}$  NMR spectrum of complex **5**.

Complex **6** displays two  $^{13}\text{C}$  NMR signals of ternary carbon atoms of terminal and bridging  $^{-}\text{O}i\text{Pr}$  ligands at 78.86 ppm (4C) and 74.75 ppm (2C), respectively, and one resonance at 83.04 ppm (2C) from quaternary carbon atoms of  $^{-}\text{OO}t\text{Bu}$  ligands. In principle, the observed pattern 1:2:1 could be assigned to mononuclear complex with one  $^{-}\text{OO}t\text{Bu}$  and three  $^{-}\text{O}i\text{Pr}$  ligands. However, previously considered mononuclear

complex **1** of this molecular composition exhibits strictly different  $^{13}\text{C}$  NMR spectrum (Table 1). Thus, complex **6** is a symmetrical binuclear complex  $[(t\text{BuOO})(i\text{PrO})_2\text{Ti}(\mu\text{-O}i\text{Pr})_2\text{Ti}(\text{O}i\text{Pr})_2(\text{OO}t\text{Bu})]$  (Fig. 4). Fig. 4 also shows a possible scheme of the complexes **5** and **6** formation.

The chemical shifts for quaternary carbon atoms of  $\text{OO}t\text{Bu}$  groups of complexes **5** (84.00 ppm) and **6** (83.04 ppm) are close to that for X-ray characterized  $\eta^2$ -(*tert*-butylperoxy)titanatrane dimer (83.93 ppm, in  $\text{CD}_2\text{Cl}_2$ ) [7]. Thus, most likely,  $\eta^2$ -coordination of  $\text{OO}t\text{Bu}$  ligands is preferable for complexes **5** and **6**.

### 3.3. Alkylperoxo complexes of titanium(IV) with $\beta$ -diketonato ligands

Tetra(alkoxo) complexes of titanium(IV) ( $\text{Ti}(\text{OR})_4$ ) interact with  $\beta$ -diketones with a formation of complexes *cis*- $\text{Ti}(\text{diketonato})_2(\text{OR})_2$ . They are coordinatively saturated and thus the exchange of  $\text{OR}$  ligands is very slow in contrast to fast exchange observed for coordinatively unsaturated complexes  $\text{Ti}(\text{OR})_4$ . Consequently, our attempts to prepare titanium alkylperoxo complexes via displacement of alkoxo ligands in  $\text{Ti}(\text{LL})_2(\text{OR})_2$  with  $\text{OO}t\text{Bu}$  ligand (by *t*BuOOH

addition) were unsuccessful, since the displacement was slower than  $\text{OO}t\text{Bu}$  ligands decomposition ( $\text{LL} = \text{acetylacetonato (acac)}$  or  $\text{dipivaloylmethanato (DPM)}$ ,  $\text{R} = \text{Et, } i\text{Pr, } t\text{Bu}$ ).

This problem can be avoided via addition of two equivalents of  $\beta$ -diketone to the pre-formed equilibrium mixture of complexes  $\text{Ti}(\text{OO}t\text{Bu})_n(\text{OR})_{4-n}$ ,  $n = 1\text{--}4$  in  $\text{CH}_2\text{Cl}_2$  at  $-40^\circ\text{C}$ . In this case, complexes  $\text{Ti}(\text{LL})_2(\text{OR})_2$ ,  $\text{Ti}(\text{LL})_2(\text{OR})(\text{OO}t\text{Bu})$  and  $\text{Ti}(\text{LL})_2(\text{OO}t\text{Bu})_2$  are immediately formed with the relative ratios depending on the composition of the initial mixture. The  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopic study of the systems thus obtained allowed to unequivocally characterize the following alkylperoxo complexes:  $\text{Ti}(\text{acac})_2(\text{OEt})(\text{OO}t\text{Bu})$  (**7**),  $\text{Ti}(\text{acac})_2(\text{O}i\text{Pr})(\text{OO}t\text{Bu})$  (**8**),  $\text{Ti}(\text{acac})_2(\text{O}t\text{Bu})(\text{OO}t\text{Bu})$  (**9**),  $\text{Ti}(\text{acac})_2(\text{OO}t\text{Bu})_2$  (**10**),  $\text{Ti}(\text{DPM})_2(\text{OEt})(\text{OO}t\text{Bu})$  (**11**),  $\text{Ti}(\text{DPM})_2(\text{O}i\text{Pr})(\text{OO}t\text{Bu})$  (**12**),  $\text{Ti}(\text{DPM})_2(\text{O}t\text{Bu})(\text{OO}t\text{Bu})$  (**13**) and  $\text{Ti}(\text{DPM})_2(\text{OO}t\text{Bu})_2$  (**14**). The structure of these complexes is shown in Fig. 5 and some parameters of their  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are collected in Table 3.

Two  $\beta$ -diketonato ligands in alkylperoxo complexes  $\text{Ti}(\text{LL})_2(\text{OR})(\text{OO}t\text{Bu})$  (**7–9, 11–13**) exhibit two peaks of equal intensity (1:1) from their CH groups, and four

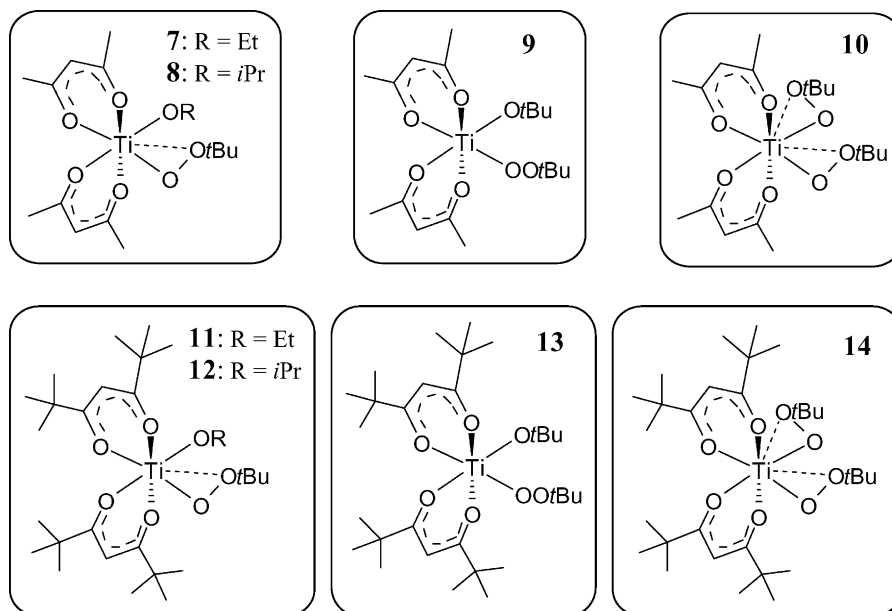


Fig. 5. The structures proposed for titanium(IV) alkylperoxo complexes **7–14**.



Table 3

<sup>13</sup>C and <sup>1</sup>H NMR chemical shifts of titanium(IV) alkylperoxo complexes Ti(β-diketonato)<sub>2</sub>(OO*t*Bu)<sub>*n*</sub>(OR)<sub>2-*n*</sub> in CH<sub>2</sub>Cl<sub>2</sub> at -30 °C.

| Complex   | OOC*(CH <sub>3</sub> ) <sub>3</sub> | OOC(C*H <sub>3</sub> ) <sub>3</sub> | OOC(CH <sub>3</sub> ) <sub>3</sub> | OR(α- <sup>13</sup> C) | OR(β- <sup>13</sup> C)                  |
|---|-------------------------------------|-------------------------------------|------------------------------------|------------------------|---|
| Ti(acac) <sub>2</sub> (OEt)(OO <i>t</i> Bu) ( <b>7</b> ) <sup>a</sup> | 86.22                               | 26.84                               | 1.35                               | 72.81                  | 18.01                                   |
| Ti(acac) <sub>2</sub> (O <i>i</i> Pr)(OO <i>t</i> Bu) ( <b>8</b> )    | 85.47                               | 26.77                               | 1.33                               | 80.14                  | 24.65 <sup>b</sup> , 24.88 <sup>b</sup> |
| Ti(acac) <sub>2</sub> (O <i>t</i> Bu)(OO <i>t</i> Bu) ( <b>9</b> )    | 82.56                               | 26.50                               | 1.17                               | 87.44                  | 30.74 <sup>c</sup>                      |
| Ti(acac) <sub>2</sub> (OO <i>t</i> Bu) <sub>2</sub> ( <b>10</b> )     | 85.83                               | 26.57                               | 1.32                               | –                      | –                                       |
| Ti(DPM) <sub>2</sub> (OEt)(OO <i>t</i> Bu) ( <b>11</b> )              | 85.43                               | 27.02                               | 1.33                               | 72.74                  | 18.13                                   |
| Ti(DPM) <sub>2</sub> (O <i>i</i> Pr)(OO <i>t</i> Bu) ( <b>12</b> )    | 84.57                               | 26.99                               | 1.31                               | 77.77                  | 24.83 <sup>b</sup> , 25.29 <sup>b</sup> |
| Ti(DPM) <sub>2</sub> (O <i>t</i> Bu)(OO <i>t</i> Bu) ( <b>13</b> )    | 82.24                               | 26.89                               | 1.20                               | 85.81                  | 31.15 <sup>d</sup>                      |
| Ti(DPM) <sub>2</sub> (OO <i>t</i> Bu) <sub>2</sub> ( <b>14</b> )      | 84.28                               | 26.97                               | 1.31                               | –                      | –                                       |

<sup>a</sup> <sup>13</sup>C NMR chemical shifts of acac<sup>-</sup> ligands of complex **7** are the following: 190.68, 190.19, 188.88 and 188.65 ppm (C=O); 103.04 and 103.37 ppm (CH); 26.77, 26.73, 26.44 and 25.50 ppm (CH<sub>3</sub>). The enol form of free Hacac exhibits <sup>13</sup>C NMR peaks at 191.68 ppm (C=O), 100.62 ppm (CH) and 24.95 ppm (CH<sub>3</sub>).

<sup>b</sup> The splitting of peaks is caused by diastereotopic surrounding of CH<sub>3</sub>-groups of *i*PrO<sup>-</sup>-ligands.

<sup>c</sup> <sup>1</sup>H NMR chemical shift of the corresponding CH<sub>3</sub>-group is 1.29 ppm.

<sup>d</sup> <sup>1</sup>H NMR chemical shift of the corresponding CH<sub>3</sub>-group is 1.27 ppm.

peaks (1:1:1:1) from both CH<sub>3</sub> and CO-groups in <sup>1</sup>H and <sup>13</sup>C NMR spectra. Complexes **11–13** additionally display four <sup>13</sup>C NMR peaks (1:1:1:1) from C(CH<sub>3</sub>)<sub>3</sub> quaternary carbon atoms of dipivaloylmethanato ligands. Thus, two β-diketonato ligands in complexes **7–9** and **11–13** are non-equivalent and asymmetric. Such low symmetry is characteristic of *cis*-isomers of octahedral complexes M(LL)<sub>2</sub>XY with different monodentate ligands X and Y. The structures proposed for complexes **7–9** and **11–13**, shown in Fig. 5, are in agreement with these spectroscopic features.

The number of <sup>13</sup>C and <sup>1</sup>H NMR signals of β-diketonato ligands in complexes Ti(LL)<sub>2</sub>(OO*t*Bu)<sub>2</sub> (**10** and **14**) is twice less than that in complexes Ti(LL)<sub>2</sub>(OR)(OO*t*Bu) (**7–9**, **11–13**). Therefore, β-diketonato ligands in Ti(LL)<sub>2</sub>(OO*t*Bu)<sub>2</sub> (**10** and **14**) are equivalent but asymmetric in agreement with the structures shown in Fig. 5.

Complexes Ti(LL)<sub>2</sub>(OR)(OO*t*Bu) (**7–9**, **11–13**) differ only by the nature of R (R = Et, *i*Pr and *t*Bu, respectively). When passing from **7** to **9** and **11** to **13**, α-hydrogen atoms of R are successively replaced by Me-groups. The comparison of <sup>1</sup>H and <sup>13</sup>C NMR data for complexes **7–9** and **11–13** shows that chemical shifts of OO*t*Bu moiety change insignificantly when going from R = Et to R = *i*Pr, and sharply decrease when going from R = *i*Pr to R = *t*Bu (Table 3). This effect cannot be explained by the change of donor properties of <sup>-</sup>O*t*Bu ligand with respect to <sup>-</sup>O*i*Pr one, because, in this case, the similar great difference of

chemical shifts should be observed also for complexes with R = Et and *i*Pr. Most likely, the observed “jump” of the chemical shifts is caused by a different mode of coordination of the alkylperoxo moiety in complexes Ti(LL)<sub>2</sub>(O*t*Bu)(OO*t*Bu) (**9**, **13**). The bulky neighboring <sup>-</sup>O*t*Bu ligand prevents coordination of the second (ether-like) oxygen atom of <sup>-</sup>OO*t*Bu ligand and, therefore, η<sup>2</sup>-mode of its coordination. Accordingly, η<sup>1</sup>-coordination mode takes place. The values of <sup>1</sup>H NMR chemical shifts of coordinated <sup>-</sup>OO*t*Bu ligands for complexes **9** and **13** (1.17 and 1.20 ppm) are smaller, whereas those for complexes **7**, **8**, **10**, **11**, **12** and **14** (1.31–1.35 ppm) are larger than that for uncoordinated *t*BuOOH (1.24 ppm) (Table 3). This fact supports the different mode of coordination of OO*t*Bu moiety in complexes **9** and **13** from that in complexes **7**, **8**, **10**, **11**, **12** and **14**.

It is noteworthy that methyl groups of dipivaloylmethanato ligands alone do not prevent η<sup>2</sup>-coordination of <sup>-</sup>OO*t*Bu ligand (complexes **11**, **12** and **14**), since these groups are placed further away from coordination center, than methyl groups of <sup>-</sup>O*t*Bu ligand.

All presented data show that η<sup>2</sup>-coordination of <sup>-</sup>OO*t*Bu ligand is generally preferable for alkylperoxo complexes of titanium. Alternative η<sup>1</sup>-mode takes place only when the bulky neighboring ligand (<sup>-</sup>O*t*Bu) prevents coordination of the second (ether-like) oxygen atom of the alkylperoxo ligand.

Alkylperoxo complexes with β-diketonato ligands (**7–14**) are far less reactive than alkylperoxo



complexes **1–4** under comparable conditions. Probably, strongly coordinating chelating ligands diminish the reactivity of  $^-OO-$  moiety as in the case of peroxo complexes of molybdenum [12].

#### 3.4. Reinvestigation of the reaction system $TiO(acac)_2/tBuOOH$

Formation of the alkylperoxo complex  $Ti(acac)_2(OOtBu)OH$  in the initial stage of interaction of  $TiO(acac)_2$  with  $tBuOOH$  in benzene was reported earlier, based on  $^1H$  NMR studies [13]. However,  $^{13}C$  and  $^1H$  NMR reinvestigation of the above system showed that this assignment was in error. The structure of complex **15** actually formed in this system is shown in Fig. 6 (only one of two possible diastereomeric forms is shown). Complex **15** incorporates two acetylacetonato ligands and, additionally, one bidentate ligand  $CH_3C(O^-)(OOtBu)COO^-$  formed upon interaction of pyruvic acid ( $CH_3COCO(OH)$ ) with  $tBuOOH$  (pyruvic acid might be formed as an intermediate in the course of acetylacetone oxidation in this system).

The structure proposed for complex **15** is based on  $^{13}C$  NMR data ( $10^\circ C$ ,  $C_6H_6$ )  $\delta$  21.47 ( $CH_3$ , 1C,  $^1J_{CH} = 130$  Hz,  $CH_3-OC(OTi)$ ), 25.56 ( $CH_3$ , 4C,  $^1J_{CH} = 129$  Hz, acac), 26.87 ( $CH_3$ , 3C,  $^1J_{CH} = 126$  Hz,  $tBu$ ), 80.60 (C, 1C,  $tBu$ ), 106.70 (CH, 2C,  $^1J_{CH} = 165$  Hz, acac), 117.78 (C, 1C,  $MeC(OTi)$ ), 180.27 (C, 1C,  $COOTi$ ), 192.72 (C, 4C, acac); and

$^1H$  NMR data ( $10^\circ C$ ,  $C_6H_6$ ):  $\delta$  1.29 (9H,  $tBu$ ), 1.76 (3H,  $CH_3-C(OTi)$ ). Signal assignments were also confirmed by  $^{13}C$ - $^1H$  double resonance experiments.

The observed magnetic symmetry of acetylacetonato ligands in complex **15** is caused, most likely, by fast intra-molecular ligand rearrangements, which might start with de-coordination of the weakest ( $-COO^-$ ) side of the bidentate ligand  $CH_3C(O^-)(OOtBu)COO^-$ . To support this explanation,  $^{13}C$  NMR spectra of complex **15** were recorded at lower temperatures (down to  $-80^\circ C$ ) using toluene as a solvent. With the temperature decrease, the signals of  $CH_3C(O^-)(OOtBu)COO^-$  ligand remain narrow, but widths of those of acetylacetonato ligands increases (especially that of CO-signal at 192.59). This broadening is about 7 Hz to the half-height-width of CO-signal at  $-30^\circ C$  and evidences in favor of chemical exchange phenomenon proposed above. However, even at  $-80^\circ C$ , the rate of this exchange process is high enough to prevent detection of separate signals for non-equivalent CO-groups of acetylacetonato ligands. Note that two possible diastereomeric forms of complex **15** can easily inter-convert through such ligand rearrangement, which is, therefore, most probable reason of the detection of only one set of NMR signals for complex **15**.

To confirm the structure proposed above, complex **15** was prepared independently. For this purpose, the ligand  $CH_3C(OH)(OOtBu)COOH$  was obtained in benzene via reversible addition reaction of  $tBuOOH$

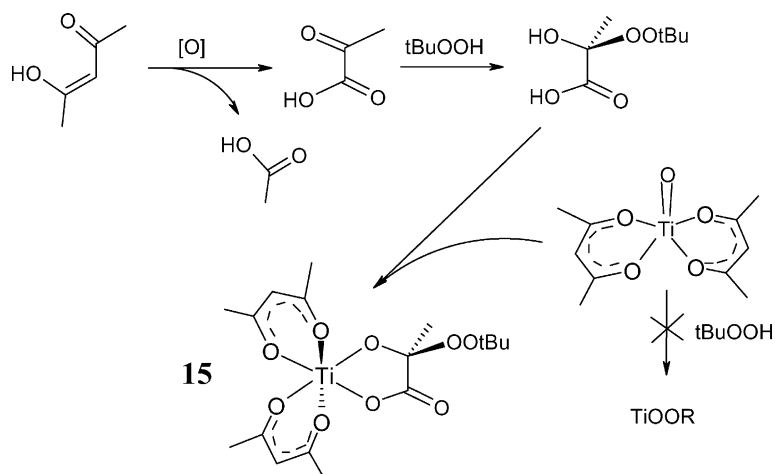


Fig. 6. The structure proposed for complex **15**, and a scheme of its formation.

to pyruvic acid, and characterized by  $^{13}\text{C}$  NMR ( $10^\circ\text{C}$ ,  $\text{C}_6\text{H}_6$ )  $\delta$  21.25 ( $\text{CH}_3$ , 1C,  $^1J_{\text{CH}} = 130\text{ Hz}$ ,  $\text{CH}_3\text{-C(OH)}$ ), 26.59 ( $\text{CH}_3$ , 3C,  $^1J_{\text{CH}} = 126\text{ Hz}$ ,  $t\text{Bu}$ ), 81.14 (C, 1C,  $t\text{Bu}$ ), 99.07 (C, 1C,  $\text{MeC(OH)}$ ), 174.93 (C, 1C,  $\text{COOH}$ ). Subsequent addition of one equivalent of  $\text{TiO}(\text{acac})_2$  to this ligand in solution immediately gave complex **15**, as detected by its  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals.

The attempts to study the reactivity of this complex towards cyclohexene undertaken in reference [13] were inadequate, since its decomposition in the presence of cyclohexene reflects the  $t\text{BuOOH}$  consumption (e.g. in the substrate oxidation catalyzed by some other species), but not the reaction of complex **15** with cyclohexene. Moreover, since **15** is not an alkylperoxy complex (it contains no metal-coordinated alkylperoxy ligands), it is most likely unreactive.

### 3.5. $^{13}\text{C}$ NMR spectroscopic detection of alkylperoxy complexes of titanium in the Sharpless–Katsuki catalytic system

As far as oxygen-transfer catalysis is concerned, the Sharpless–Katsuki epoxidation system launched the rich field of titanium-mediated asymmetric oxidations [1–3,14]. Although chiral, metal-centered  $\eta^2$ -alkylperoxy species have been postulated as reactive intermediates [3], these species were never detected spectroscopically in the above system. Based on the spectroscopic data for various alkylperoxy complexes of titanium obtained in this work, we have undertaken  $^{13}\text{C}$  NMR search of such species in the Sharpless–Katsuki system  $\text{Ti}(\text{O}i\text{Pr})_4/\text{L}$ -diisopropyltartrate/ $t\text{BuOOH}$  in  $\text{CH}_2\text{Cl}_2$  at  $-100^\circ\text{C}$ . Such low temperature was used to decrease the rate of ligand exchange in the coordination sphere of titanium, which otherwise would lead to dramatic broadening of NMR signals. To favor the formation of alkylperoxy species,  $i\text{PrOH}$  formed upon reaction of  $\text{Ti}(\text{O}i\text{Pr})_4$  with diisopropyl  $\text{L}$ -tartrate was removed in vacuo and a large excess of  $t\text{BuOOH}$  was then used.

In the range 75–95 ppm, the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of this catalytic system displays a number of signals, which might belong to quaternary carbon atoms of  $^-\text{OO}t\text{Bu}$  ligands or ternary carbon atoms of  $^-\text{O}i\text{Pr}$  and diisopropyl  $\text{L}$ -tartrate ligands (Fig. 7b). In order

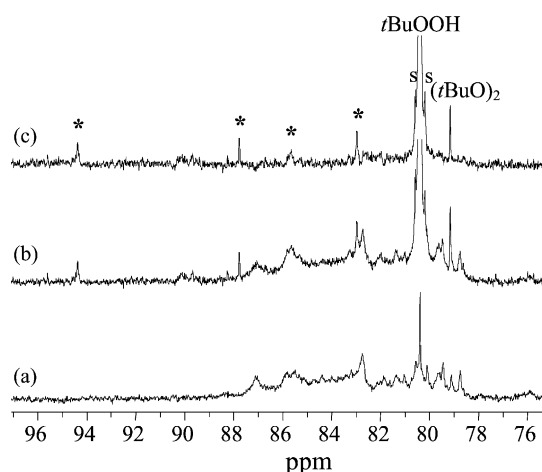


Fig. 7.  $^{13}\text{C}$  NMR spectra of the system  $\text{Ti}(\text{O}i\text{Pr})_4/\text{diisopropyl L-tartrate}/t\text{BuOOH}$  in  $\text{CH}_2\text{Cl}_2$  at  $-100^\circ\text{C}$  (initial concentrations:  $[\text{Ti}(\text{O}i\text{Pr})_4] = 0.3\text{ M}$ ,  $[\text{diisopropyl L-tartrate}] = 0.36\text{ M}$ ,  $[t\text{BuOOH}] = 1.6\text{ M}$ ): spectrum DEPT (a), spectrum  $^{13}\text{C}\{^1\text{H}\}$  (b), difference between spectra (b) and (a) (c). Quaternary carbon atom signals of coordinated  $^-\text{OO}t\text{Bu}$  ligands are marked with asterisks.  $(t\text{BuO})_2$  is an impurity (about 1% (w/w)) in  $t\text{BuOOH}$  reagent. Signals marked by “s” are  $^{13}\text{C}$  satellites due to  $^{13}\text{C}(\text{CH}_3)_2(^{13}\text{CH}_3)\text{OOH}$  isotopomer.

to distinguish those of quaternary carbon atoms, the following procedure was used. Spectrum DEPT adjusted to select only ternary carbon atoms (Fig. 7a) was subtracted from the spectrum of Fig. 7b. Thus obtained sub-spectrum (Fig. 7c) displays only the signals of quaternary carbon atoms. The most intensive peak at 80.3 ppm belongs to  $t\text{BuOOH}$  and rather small signals at 94.5, 87.8, 85.6 and 82.9 ppm marked with asterisks arise from four types of  $t\text{BuOO}$  moieties coordinated to titanium. The latter signals cannot be assigned to  $t\text{BuO}^-$  ligands, since the decomposition of  $t\text{BuOOH}$  does not occur at  $-100^\circ\text{C}$ . Thus, four types of alkylperoxy complexes of titanium(IV) can be detected in the Sharpless–Katsuki catalytic system. The detection of several alkylperoxy complexes in comparable concentrations in the Sharpless–Katsuki catalytic system raises some interesting questions: which species are most active intermediates, and which are most selective? Is it possible to tune enantioselectivity by changing relative concentrations of the alkylperoxy complexes detected? Further studies are needed to elucidate their molecular composition and actual role in epoxidation.

#### 4. Conclusions

Using  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy, the following titanium (IV) alkylperoxo complexes were characterized in  $\text{CH}_2\text{Cl}_2$  and  $\text{CDCl}_3$  solutions at low temperatures:  $\text{Ti}(\text{OO}t\text{Bu})_n(\text{O}i\text{Pr})_{4-n}$  ( $n = 1-4$ ); binuclear complexes  $[(i\text{PrO})_3\text{Ti}(\mu\text{-O}i\text{Pr})_2\text{Ti}(\text{O}i\text{Pr})_2(\text{OO}t\text{Bu})]$  and  $[(t\text{BuOO})(i\text{PrO})_2\text{Ti}(\mu\text{-O}i\text{Pr})_2\text{Ti}(\text{O}i\text{Pr})_2(\text{OO}t\text{Bu})]$ ; complexes with  $\beta$ -diketonato ligands  $\text{Ti}(\text{acac})_2(\text{OR})(\text{OO}t\text{Bu})$ ,  $\text{Ti}(\text{acac})_2(\text{OO}t\text{Bu})_2$ ,  $\text{Ti}(\text{DPM})_2(\text{OR})(\text{OO}t\text{Bu})$ ,  $\text{Ti}(\text{DPM})_2(\text{OO}t\text{Bu})_2$ , where Hacac = acetylacetonate, HDPM = dipivaloylmethane, R = Et, *i*Pr and *t*Bu. The side-on ( $\eta^2$ ) coordination of the *tert*-butylperoxo ligand is generally preferable for titanium(IV) alkylperoxo complexes. The end-on ( $\eta^1$ ) coordination observed for octahedral  $\beta$ -diketonato complexes bearing *cis-t*BuO<sup>-</sup> ligand is caused by spatial hindrance created by this ligand. The coordination numbers of titanium atoms in the complexes studied are in the range of 5–8. The quantitative data on the reactivity of alkylperoxo complexes found towards sulfides and alkenes were obtained. It was shown that the reactivity of alkylperoxo complexes of titanium grows with the increase of the number of alkylperoxo ligands in the coordination sphere of titanium. Coordination of strong chelating ligands (e.g. acetylacetonate) suppresses the reactivity. The system  $\text{TiO}(\text{acac})_2/t\text{BuOOH}$  in  $\text{C}_6\text{H}_6$  was reinvestigated using  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectroscopy. The structure of the complex  $\text{Ti}(\text{acac})_2\{\text{CH}_3\text{C}(\text{O})(\text{OO}t\text{Bu})\text{COO}\}$  actually formed in this system was elucidated. Four types of titanium(IV) alkylperoxo complexes were detected in the Sharpless–Katsuki catalytic system.

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