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[((η^2-*tert*-Butylperoxo)titanatrane)$_2$· 3 Dichloromethane]: X-ray Crystal Structure and Oxidation Reactions

Gernot Boche,* Konrad Möbus, Klaus Harms, and
Michael Marsch

Fachbereich Chemie, Universität Marburg
D-35032 Marburg, Germany

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Titanium peroxides are of paramount importance in modern stereoselective oxidation reactions. Thus, in the catalytic enantioselective oxidation of allylic alcohols with alkyl hydroperoxides in the presence of titanium tetraisopropoxide and a chiral tartrate diester to give the corresponding epoxides (Sharpless oxidation), a titanium peroxide was formulated as the decisive intermediate.[1] A similar reagent was used by Kagan et al. and Uemura et al. for the enantioselective formation of sulfoxides from sulfides.[2] The stereoselective oxidation of tertiary amines to *N*-amine oxides was also reported by Sharpless et al.[3] More recently, a titanium tetraisopropoxide catalyzed intramolecular epoxidation of allylic hydroperoxides was established by Adam et al.[4] This reaction as well as the oxidation of titanium enolates with dioxygen[5] and *tert*-butyl hydroperoxide,[6] respectively, should similarly proceed via a titanium peroxide. There are several reports in the literature on the attempted isolation and characterization of the titanium peroxide complex involved in the Sharpless epoxidation; however, a species containing the peroxide moiety was never reported.[7] Because of the assumption that the peroxide should generally be bonded to the titanium atom in an η^2-fashion,[7] the vanadium(V) dipicolinato *tert*-butyl peroxide[8] deserves special interest: it is so far the only transition metal peroxide with such an η^2-bonding mode, as shown in an X-ray crystal structure determination. We found recently that in the crystalline (lithium *tert*-butyl peroxide)$_{12}$ the two oxygen atoms are similarly η^2-bridged by lithium.[9] In the following we report on the X-ray crystal structure determination of [((η^2-*tert*-butylperoxo)titanatrane)$_2$·3 dichloromethane] [(**4**)$_2$·3CH$_2$Cl$_2$] (Figure 1)[10] which was prepared from the reaction of (diethylamino)titanatrane **1**[12] with *tert*-butyl hydroperoxide **2** in dichloromethane at −78 °C (Scheme 1).

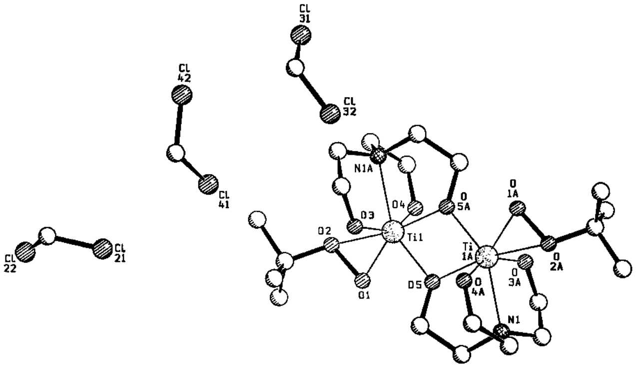

Figure 1. Crystal structure of [(**4**)$_2$·3 CH$_2$Cl$_2$]. Tables of crystallographic parameters along with a complete list of structural parameters are available in the supporting information. Hydrogen atoms have been omitted for clarity.

The dichloromethane molecules (mean value of the C−Cl bond lengths 174.1 pm (mean value in 1 044 crystal structure determinations 172.2 pm[13])) are independent of the (η^2-*tert*-butylperoxo)titanatrane dimers (**4**).[2] The bonding around Ti1 shows the η^2-coordination of the anionic O1 (Ti1−O1 191.3(3) pm) and the neutral O2 (Ti1−O2 226.9(2) pm) peroxide oxygen atoms. The bond to N1A amounts to 229.9(3) pm while the bonds to O3 (185.0(3) pm) and O4 (188.2(3) pm) are shorter than those to the bridging O5 (199.4(2) pm) and O5A (204.8(2) pm). The O1−O2 bond length (146.9(3) pm) corresponds closely to the mean value of the O−O bonds of 29 HOOR (146.5 pm) and 14 HOOH (145.3 pm) molecules in crystals.[13] The mean value of the O−O bond length in 18 compounds of the type η^1-MOOR amounts to 146.7 pm.[13]

There are many reports on model calculations of the Sharpless epoxidation reaction in the literature.[14] In agreement with the experimental result shown above η^2-coordination of the peroxide oxygens is found. In a density functional study[14a] of a model complex the calculated bond lengths of Ti to the anionic oxygen atom (190.6 pm) and to the neutral oxygen atom (229.4 pm) agree nicely with the corresponding bond lengths in [(**4**)$_2$·3CH$_2$Cl$_2$] (191.3(3) and 226.9(2) pm, respectively). The O−O bond length, however, is usually calculated to be longer than that in [(**4**)$_2$·3CH$_2$Cl$_2$]: (Ti(OCH$_2$)$_2$(η^2-OOCH$_3$)(OCH$_2$CH═CH$_2$)-

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[10] Crystals of [(**4**)$_2$·3CH$_2$Cl$_2$] were received after filtration of the crude product from the diethylamine containing dichloromethane solution and recrystallization from dichloromethane/pentane (2/1) at −65 °C: ^{1}H NMR (CD$_2$Cl$_2$, −30 °C, 400 MHz) δ 4.65 (dt, 4, J = 4.5, 11.1 Hz), 4.48 (t, 4, J = 5.7 Hz), 4.26 (dd, 4, J = 6.8, 11.2 Hz), 3.38 (dt, 4, J = 6.8, 11.1 Hz), 3.17 (dd, 4, J = 5, 11.3 Hz), 3.10 (t, 4, J = 5.7 Hz), 1.31 (s, 18); ^{13}C NMR (100 MHz) δ 83.93, 73.33, 68.76, 63.98, 56.81, 26.63; mass spectrum (EI) 252 (48) M$^+$ − O − CH$_3$, 237 (35) M$^+$ − O − 2CH$_3$, 194 (54) M$^+$ − OO*t*C$_4$H$_9$, 59 (100) C$_3$H$_7$O$^+$, 44 (51) CO$_2$, 32 (54) O$_2$. The ^{1}H NMR spectrum is in agreement with an η^2 coordination of the *tert*-butyl peroxide oxygen atoms as well as a dimeric structure of **4**.[11]

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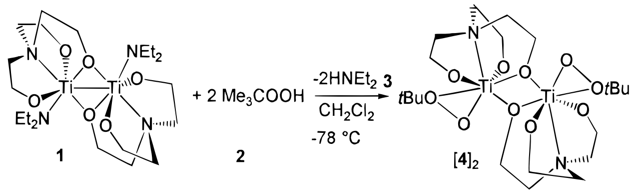
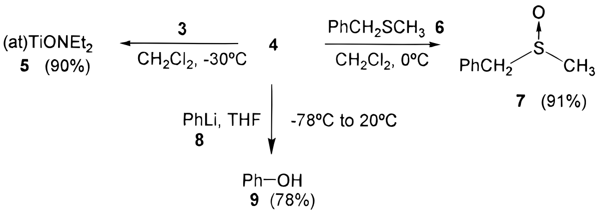
Scheme 1



Scheme 2



(OH_2) 156.6 pm;[14a] Ti(η^2-OOH)$(OH)_3$ 156.2 (149.3) pm;[14b] Ti(η^2-OOH)$(OH)_3$ 149.2;[14d] however, see also Ti(η^2-OOH)-$(SH_2)H_3$ 144.6 pm.[14c] We cannot explain the discrepancy between the shorter experimental bond length and longer calculated O−O bond lengths at the moment, especially since **4** shows strong oxenoid character in reactions with nucleophiles.[15] Thus, $[(\mathbf{4})_2{\cdot}3CH_2Cl_2]$ dissolved in dichloromethane oxidized diethylamine **3** at −30 °C to diethylhydroxylamine which finally led to the formation of the insoluble diethylhydroxylamine−titanatrane complex **5** (Scheme 2). Similarly, benzylmethylsulfide **6** was oxidized by $[(\mathbf{4})_2{\cdot}3CH_2Cl_2]$ in dichloromethane at 0 °C to benzylmethylsulfoxide **7** (Scheme 2). Addition of phenyllithium **8** in diethyl ether/cyclohexane at −78 °C to a THF suspension of microcrystalline **4** (prepared from $[(\mathbf{4})_2{\cdot}3CH_2Cl_2]$ by removal of CH_2Cl_2 at 20 °C and 10^{-2} Torr), followed by warming of the reaction mixture to 20 °C and protonation with 2 N HCl, yielded phenol **9** in 78% (Scheme 2). This is in agreement with our earlier findings that titanium alkyl peroxides transform organolithium and Grignard compounds at low temperature (−78 °C) into the corresponding alcohols (phenols) in good to excellent yields.[16]

In conclusion, we have determined for the first time the X-ray crystal structure of a titanium alkyl peroxide. The η^2-structure of $[(\mathbf{4})_2{\cdot}3CH_2Cl_2]$ is in agreement with earlier assumptions and calculations of the ground state structure of such alkyl peroxides, as well as with models of the transition states of oxidation reactions of various nucleophiles. The importance of η^2-bonded transition metal peroxides in oxidation reactions has been reemphasized recently.[17]

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Supporting Information Available: Tables giving a summary of crystal structure determination data, atomic coordinates, equivalent isotropic displacement parameters, bond lengths and angles, torsion angles, anisotropic displacement parameters, hydrogen coordinates, and observed and calculated structure factors for $[(\mathbf{4})_2{\cdot}3CH_2Cl_2]$ (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(15) In the case of carbenoids and nitrenoids the enhanced electrophilic character goes along with a marked elongation of the C(N)−X bond (X = Ha1, OR), see ref 14d and literature cited therein.

(16) Husemann, M. Ph.D. work in progress. The facile oxidation of nucleophiles with titanium peroxides may in part be caused by the titanium atom bridging the peroxide O−O atoms (η^2-bonding), thus leading to a titanium-assisted ionization of the O−O bond without changing the geometry of the complex in the transition state dramatically. It is interesting in this context that in the η^1-bonded Hf complex Cp_2*Hf(Et)(OO-*tert*-butyl) the oxidation of the ethyl to the ethoxy functionality takes place at 33 °C (van Asselt, A.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 8291−8293).

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