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Formation of titanium *tert*-butylperoxo intermediate from cubic silicon–titanium complex with *tert*-butyl hydroperoxide and its reactivity for olefin epoxidation

Masahiro Fujiwara,[a,*,†] Helge Wessel,[b] Park Hyung-Suh[b] and Herbert W. Roesky[b]

[a]*Kansai Center, National Institute of Advanced Industrial Science and Technology, 1 Midorigaoka, Ikeda, Osaka 563-8577, Japan*
[b]*Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-37077 Göttingen, Germany*

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Abstract—Epoxidation of olefins by *tert*-butyl hydroperoxide (TBHP) was effectively catalyzed by a cubic silicon–titanium μ-oxo-complex, which is obtained from a bulky silanetriol and titanium alkoxides. The stoichiometric reaction of the complex with TBHP in the absence of olefin formed a novel complex as white solid. The comparison of this product with analogous complexes in ^{1}H and ^{13}C NMR spectra indicated that the titanium *tert*-butylperoxo complex; this kind of intermediate is considered to be active for epoxidation in titanium-based catalysts, was first isolated. This titanium peroxo complex reacted with cyclohexene to produce cyclohexene oxide without additional oxidant accompanying the formation of titanium *tert*-butoxide. All pathways of the catalytic cycle of the epoxidation using titanium catalysts were verified experimentally.

1. Introduction

The catalytic oxidation of hydrocarbons, especially epoxidation of olefins, in liquid phase by titanium catalysts with peroxides is one of the most actively studied and rapidly improved reactions.[1] The real active species for this epoxidation is assumed to be titanium peroxo moieties, derived from four-coordinated titanium and peroxide.[1–3] In spite of some significant researches by synchrotron[2] or computer chemistry,[3] the isolation of the active intermediates and the experimental elucidation of their reaction behaviors have not been reported probably because of their low stability. Even in the case of model silicon–titanium complexes obtained from silsesquioxane silanetriols,[4–6] the isolation of the active titanium peroxo intermediate was not achieved because the active species readily decomposes.[6c]

We reported another type of cubic silicon–titanium μ-oxo-complex **1**,[4,7] which is obtained from a bulky silanetriol and titanium alkoxides (Fig. 1). In the solid state, this complex was monomeric as confirmed by single crystal X-ray diffraction,[7a] whereas the complexes from silsesquioxane[5,6] or triethanolamine[8] are dimeric or the mixture of monomer and dimer. The complex **1** is considered as a suitable model system of titanosilicates and related catalysts, where titanium species active for epoxidation might be four-coordinated, isolated and monomeric fixed in silica matrix.[1–3] The catalytic activity of our complex **1** for epoxidation was lower than the reported complexes from silsesquioxane (see Section 2).[6] However, less reactive intermediates are generally advantageous to isolation. In this paper, we wish to report the first isolation and the reaction behavior of the active titanium *tert*-butylperoxo intermediate for the epoxidation of olefins. In addition, the discussion on the catalytic

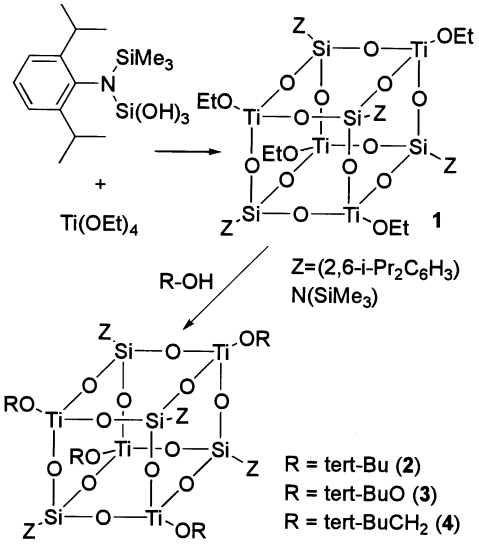

Figure 1.

Keywords: catalysts; epoxidation; silicon and compounds; titanium and compounds.

* Corresponding author. Tel.: +81-727-51-9253; fax: +81-727-51-9628; e-mail: m-fujiwara@aist.go.jp

† Stayed in Göttingen University as a visiting researcher.

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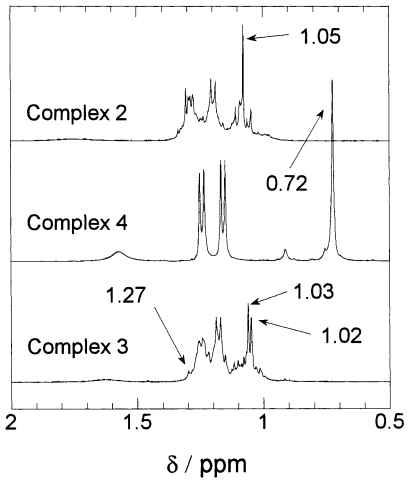

Figure 2. ^{1}H NMR spectra of complexes **2**–**4** at high magnetic field.

cycle of the epoxidation of olefins by titanium-based catalysts is described.

2. Results and discussion

Our first examination was the catalytic epoxidation using the complex **1**. The use of aqueous solution of hydrogen peroxide as an oxidant resulted in no epoxidation because of the decomposition of the complex **1** (titania anatase was formed). When the solution of cyclohexene or cyclooctene was stirred with the dichloromethane solution of *tert*-butyl hydroperoxide (TBHP) in the presence of catalytic amount of the complex **1** (1 mol% to TBHP) at room temperature for 21 h, cyclohexene oxide or cyclooctene oxide were obtained in 61 and 78% yields, respectively (based on TBHP used). The selectivities of olefins to the corresponding epoxides and the efficiency of TBHP to the epoxidation were very high (>95%). A considerable amount of TBHP still remained in the solution even after 21 h. On the other hand, the epoxidation reaction by a titanium complex from silsesquioxane is complete in a few hours and the perfect conversion of TBHP is observed in almost cases.[6] It is also reported by Crocker et al. that this complex reacts with TBHP in the absence of olefin to afford the titanium *tert*-butoxy group immediately.[6c] It is likely that the active intermediate from the complex **1** and TBHP is more stable than the reported complex from silsesquioxane[6] and is advantageous to isolation. The titanium *tert*-butylperoxo complex has already been isolated from titanium-triethanolaminate as a five-coordinated titanium complex.[8c] Although this complex oxidizes amines and sulfides to the corresponding oxides,[8] we confirmed that it had no activity for epoxidation. In our experiment, no epoxidation of cyclohexene with TBHP using titanium (triethanolaminato) isopropoxide analogous to the reported complexes[8] occurred at room temperature or at 70°C even after over 24 h with considerable conversion of TBHP (19% at 70°C after 24 h). As claimed, the epoxidation of olefins requires a four-coordinated titanium species as a catalyst.[1–3]

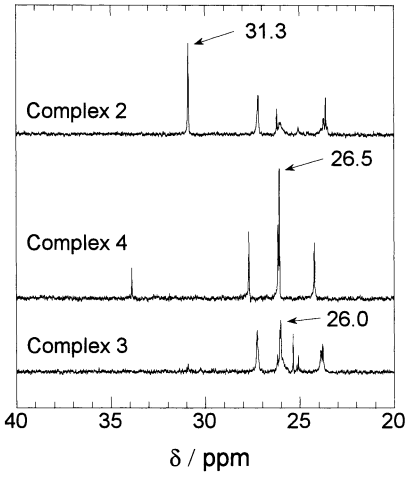

Figure 3. ^{13}C NMR spectra of complexes **2**–**4** at high magnetic field.

The simple reaction of the complex **1** with TBHP (equivalent to titanium in the complex **1**) in the absence of olefin at room temperature was not successful. After the reaction, only the peaks derived from the complex **1** and TBHP were observed in ^{1}H NMR spectra. The reaction of the complex **1** with excess TBHP (20 equiv.) at room temperature afforded a red color solution. ^{1}H and ^{13}C NMR spectra showed that various complicated compounds were formed and their identifications were not performed. The refluxing of the mixture in carbon tetrachloride produced another complex **2**. The same complex can be also obtained from the complex **1** and *tert*-butyl alcohol (Fig. 1). All the analytical results such as NMR spectra and mass spectrometry indicated that the complex **2** had *tert*-butoxy substituent on titanium. Next, the reaction of the complex **1** and TBHP at lower temperature was examined. The stoichiometric mixture (TBHP/complex **1**=4) in dry hexane was placed in a refrigerator (at about −20°C). After about 3 days, a white solid was formed in the solution. After the decantation of the solution and the removal of the residual volatiles in vacuo without heating, this solid (complex **3**) was analyzed by ^{1}H and ^{13}C NMR spectra quickly without further purification. Unfortunately, the recrystallization from hexane was not successful. However, the crude solid was pure enough for NMR analyses.

Table 1. Comparison of representative peaks of the complexes **1**–**4** and related compounds in ^{1}H and ^{13}C NMR spectra

Complex	^{1}H NMR (ppm)	^{13}C NMR (ppm)	
	$-C(CH_3)_3$	$-C(CH_3)_3$	$-C(CH_3)_3$
1	0.96[a], 3.95[b]	18.9[c]	73.8[d]
2	1.05	31.3	86.2
3	1.02, 1.03	26.5	88.8
4	0.72 (3.65)[e]	26.0	33.8, (88.5)[f]
TBHP	1.26	25.7	80.8
tert-BuOH	1.27	31.2	69.1
Reported complex[g]	1.31	26.6	83.9

[a] $O-CH_2CH_3$.
[b] $O-CH_2CH_3$.
[c] $O-CH_2CH_3$.
[d] $O-CH_2CH_3$.
[e] $O-CH_2C(CH_3)_3$.
[f] $O-CH_2C(CH_3)_3$.
[g] Reported titanium *tert*-butylperoxo complex from five-coordinated titanium alkoxide in Ref. 8c.

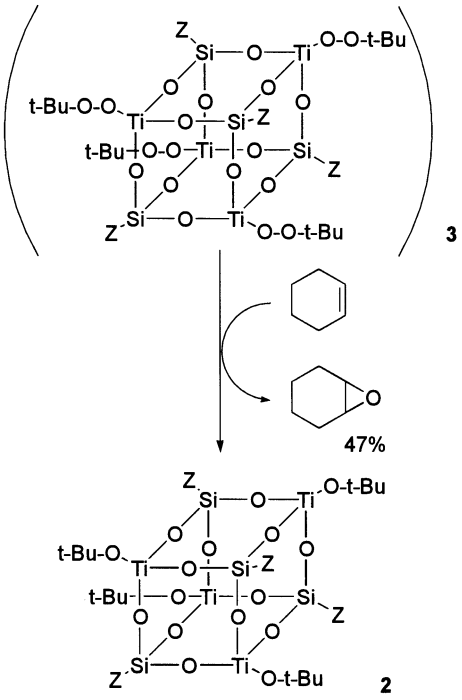

Figure 4. Epoxidation of cyclohexene by complex **3**.

Figs. 2 and 3 show ^{1}H and ^{13}C NMR spectra of the complexes **2**–**4** at high magnetic field, respectively. Table 1 summarizes some representative peaks of ^{1}H and ^{13}C NMR spectra of the complexes **1**–**4** and related compounds. The complex **4** with *tert*-butylmethoxy groups on the titanium atoms also participated for the comparison of the peaks of substituents on titanium. As shown in Fig. 2, two sharp singlet peaks (δ=1.02 and 1.03) were observed in ^{1}H NMR spectrum of the complex **3**. These two singlet peaks were different from the complex **1** (δ=0.95, 1.19), the complex **2** (δ=1.05), complex **4** (δ=0.72), TBHP (δ=1.26) and *tert*-butyl alcohol (δ=1.27). These peaks were also distinct from those of the substituents on silicon (*N*-trimethylsilyl-2,6-diisopropylanilino group), because in the complex **4**, no peak was observed in the field (δ=1.00–1.10). Therefore, these singlet peaks were derived from the substituents on titanium and were not *tert*-butoxy titanium moiety. On the other hand, ^{13}C NMR spectra (Fig. 3) showed that the peak at δ=31.3 in complex **2**, assigned to the methyl carbon in *tert*-butyl group (a quartet peak in off-resonance ^{13}C NMR spectrum), was absent in the complex **3**. From the comparison of tertiary carbon (singlet peaks in off-resonance ^{13}C NMR spectrum) in *tert*-butyl groups among the complexes **2**–**4** and other related compounds (Table 1), the complex **3** was considered to have a *tert*-butyl group different from other listed compounds. The peaks of methyl carbon in the complex **3** (δ=26.5) was observed in the same field of the carbon in the isolated titanium *tert*-butylperoxo complex with triethanolamine (δ=26.6).[8c] The complex **3** was unstable under various conditions. In ^{1}H NMR spectrum of the complex **3**, a slight amount of *tert*-butyl alcohol (δ=1.27) was detected, although volatiles must be removed by high vacuum evaporation. The intensity of this peak gradually increased with the decrease of the peaks at δ=1.02 and 1.03, when the solution used for NMR measurement was left at room temperature. Thus, the complex **3** eliminated *tert*-butyl alcohol. The complex **3** was thermally unstable not only in solution, but also as solid. When the solid of the complex **3** was stored at room temperature under argon atmosphere for 1 day, it converted into the complex **2** quantitatively. This labile character of the complex **3** suggested that it has an unstable group bearing *tert*-butyl moiety like as a *tert*-butylperoxo group.

The complex **3** had the activity for the stoichiometric epoxidation. When the mixed solution of complex **3** and excess cyclohexene without additional oxidant was stirred at room temperature for 7 h under dry argon, cyclohexene oxide was obtained in 47% yield base on titanium in the complex **3** (Fig. 4). The resulting residue of this reaction contained the complex **2**, and no complex **3** was detected in ^{1}H and ^{13}C NMR spectra. The comparatively low yield of the epoxide is thought to result from the partial decomposition of the complex **3**. It is assumed that one oxygen atom in the complex **3** was transferred to olefin, giving epoxide and the complex **2**. From all results obtained here, we concluded that the complex **3** has titanium *tert*-butylperoxo species, which is active for epoxidation. However, the complex **3** had no activity for alkane oxidation. When the cyclohexane solution (excess) of the complex **3** was refluxed for 21 h, only trace amounts of cyclohexanol and cyclohexanone were detected in the resulting solution with the perfect conversion of the complex **3**. As far as we know, this is the first isolated example of a titanium *tert*-butylperoxo intermediate, which is formed from a four-coordinated titanium complex and is effective in epoxidation. This result also supported that the four-coordinated titanium species is reactive and the five-coordinated one is inert for epoxidation.

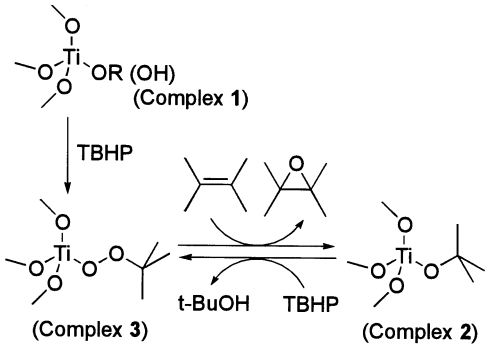

Figure 5. Catalytic cycle of epoxidation of olefins by titanium catalysts.

From all results revealed in this study, the catalytic cycle of the epoxidation of olefins catalyzed by four-coordinated titanium alkoxide species is represented in Fig. 5. Although this kind of scheme is often presented in previous papers,[1–3] the active titanium peroxo intermediate for epoxidation was not observed or isolated in these reports. On the other hand, we ascertained here all pathways of the catalytic cycle by the isolations of key compounds; the complex **1** (regarded as a titanium alkoxide or a titanium hydroxide) as the starting species of the catalyst, the complex **3** (regarded as a titanium *tert*-butylperoxide) as the active intermediate for epoxidation and the complex **2** (regarded as a titanium *tert*-butoxide) as the regenerated catalytic part. At first, a four-coordinated titanium alkoxide

(or hydroxide) and TBHP forms the titanium *tert*-butylperoxo group. From this peroxo intermediate, one oxygen atom is transferred into a double bond of olefin to produce the corresponding epoxide and titanium *tert*-butoxy group. The oxygen atom in the *tert*-butylperoxo group binding to titanium is thought to participate in this reaction, because titanium *tert*-butoxy group is produced. The catalytic cycle is completed by the regeneration of the active species from the titanium *tert*-butoxy group and TBHP. This step was also realized by that the complex **2** catalyzed the epoxidation of cyclohexene effectively (cyclohexene oxide was obtained from cyclohexene using the complex **2** as a catalyst in 40% yield with 90% efficiency of TBHP at room temperature for 21 h). Although we tried to prepare a good crystal for single crystal X-ray diffraction for determining its precise structure, all our attempts were still unsuccessful because of its low stability. However, we observed the active intermediate for epoxidation as the complex **3** with titanium *tert*-butylperoxo groups, by NMR technique as an isolated form. It is thought that our study revealed the catalytic cycle of the epoxidation of olefins using TBHP by titanium catalysts including titanosilicate.

3. Conclusions

The cubic silicon–titanium complex readily obtained from a bulky silanetriol and titanium alkoxide, catalyzed the epoxidation of olefins with TBHP. The titanium *tert*-butylperoxo intermediate could be first isolated by the stoichiometric reaction of the cubic complex and TBHP. The *tert*-butylperoxo intermediate thus formed had the activity for epoxidation of olefin without additional oxidant. These results support the elucidation of the catalytic cycle of the epoxidation using titanium catalysts including titanosilicates.

4. Experimental

^{1}H, ^{13}C and ^{29}Si NMR spectra were obtained by JEOL AL-400 spectrometer using $CDCl_3$ as solvent. Tetramethylsilane was used as internal standard. Infrared spectra were measured by Jasco FT/IR-230 spectrometer (only strong absorption bands are given). Mass spectra were obtained on a Finnigan MAT System 8230 and a Varian MAT CH5 mass spectrometer. CHN analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at Göttingen University. Small variations in analytical data are likely to be due to metal carbide formation in these systems.[9] Olefins employed for epoxidation were distilled over calcium hydride before use. The dichloromethane solution of TBHP was prepared by the described method.[10] The cubic silicon–titanium complex (complex **1**) was prepared as reported previously.[7a] Titanium (triethanolaminato) isopropoxide purchased from Aldrich was used after removing mixed isopropanol in vacuo.

4.1. Procedure of epoxidation

The dichloromethane solution (4.5 M) of TBHP (10 mmol) was added to the solution of an olefin (10 mL) with silicon–titanium complex (0.1 mmol, Ti 0.4 mmol) at room temperature under dry argon. The resulting mixture was stirred at room temperature for 21 h. The conversion of TBHP and the yield of the products were determined by the common iodometric titration or by a capillary GC (Shimadzu GC-17A with Silicon OV-101, capillary column; 50 m), respectively. The efficiency of TBHP was estimated by [(amount of epoxide formed)/(amount of TBHP converted)]×100.

4.1.1. Preparation of [(2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)SiO_3Ti(O-*t*-Bu)]$_4$ (2). Complex **2** was obtained by the reaction of complex **1** (0.5 mmol) with *tert*-butyl alcohol (2 mmol) in toluene (5 mL) at 80°C for 21 h. After removing the solvent, purification was performed by recrystallization from pentane; mp: 330°C (decomposition). FT-IR (Nujol): 1465, 1438, 1250, 1183, 1043, 995, 957, 902, 840, 801, 669, 538, 456 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 0.06 (s, 36H, $SiMe_3$), 1.05 (s, 36H, Me), 1.16 (d, 24H; Me), 1.26 (d, 24H, Me), 3.53 (m, 8H, CH), 6.98 (m, 12H, aromatic). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 1.11 ($SiMe_3$), 24.06 (Me), 26.64 (Me), 27.63 (CH), 31.30 (Me), 86.15 (C), 123.06 (aromatic), 124.20 (aromatic), 140.36 (aromatic), 146.90 (aromatic). ^{29}Si NMR (79.3 MHz, $CDCl_3$, TMS): −96.2 (SiO_3), 6.5 ($SiMe_3$). Mass spectrum (EI, 70 eV): *m/e* 1781 (M^+). Anal. Calcd for $C_{76}H_{140}N_4O_{16}Si_8Ti_4$: C, 54.7; H, 8.4; N, 3.7. Found: C, 49.0; H, 7.5; N, 3.0.

4.1.2. Preparation of [(2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)SiO_3-Ti(OO-*t*-Bu)]$_4$ (3). The hexane solution (1 mL) of complex **1** (0.501 g; 0.3 mmol) was mixed with TBHP (4.5 M of dichloromethane solution; 1.2 mmol) at 5°C for 10 min. The resulting solution was placed in a refrigerator (about −20°C). After about 3 days, a white solid was formed in the colorless solution. The solid was separated from the solution by decantation (0.273 g; 0.15 mmol, yield: 50%). The remaining volatiles were removed in vacuo without heating. Further purification of this solid was unsuccessful because of its low stability; FT-IR (Nujol): 1438, 1261, 1248, 1181, 1053, 994, 967, 957, 903, 838, 802, 744, 658, 449 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 0.06 (s, 36H, $SiMe_3$), 1.02, 1.03 (s, 36H, Me), 1.16 (d, 24H, Me), 1.26 (d, 24H, Me), 3.53 (m, 8H, CH), 6.98 (m, 12H, aromatic). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 1.89 ($SiMe_3$), 24.25 (Me), 26.45 (Me), 26.51 (CH), 27.69 (Me), 88.76 (C), 123.19 (aromatic), 124.21 (aromatic), 140.08 (aromatic), 147.05 (aromatic). ^{29}Si NMR (79.3 MHz, $CDCl_3$, TMS): −96.2 (SiO_3), 6.5 ($SiMe_3$).

4.1.3. Preparation of [(2,6-*i*-$Pr_2C_6H_3$)N($SiMe_3$)SiO_3-Ti(OCH_2-*t*-Bu)]$_4$ (4). Complex **4** was obtained by the same procedure as complex **2** using 2,2-dimethyl-1-propanol instead of *tert*-butyl alcohol; mp: 340°C (decomposition). FT-IR (Nujol): 1465, 1438, 1250, 1183, 998, 969, 959, 904, 841, 802, 713, 538 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): 0.04 (s, 36H, $SiMe_3$), 0.72 (s, 36H, Me), 1.16 (d, 24H, Me), 1.24 (d, 24H, Me), 3.51 (m, 8H, CH), 3.65 (s, 8H, CH_2), 6.99 (m, 12H, aromatic). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): 1.38 ($SiMe_3$), 24.15 (Me), 26.01 (Me), 26.08 (Me), 27.62 (CH), 33.8 (C), 88.76 (CH_2), 123.17 (aromatic), 124.39 (aromatic), 139.82 (aro matic), 146.92 (aromatic). ^{29}Si NMR (79.3 MHz, $CDCl_3$, TMS): −96.1 (SiO_3), 6.9 ($SiMe_3$). Mass spectrum (EI, 70 eV): *m/e* 1837 (M^+). Anal. Calcd for

$C_{80}H_{148}N_4O_{16}Si_8Ti_4$: C, 55.7; H, 8.6; N, 3.3. Found: C, 52.5; H, 8.2; N, 3.1.

4.2. Stoichiometric epoxidation of cyclohexene by the complex 3

Complex **3** (0.257 g; 0.14 mmol) was dissolved in cyclohexene (3 mL) and the resulting solution was stirred for 7 h at room temperature under dry argon. The yield of cyclohexene oxide was determined by GLC, and after the evaporation of volatiles and evacuation, the residue was analyzed by ^1H and ^{13}C NMR spectra.

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