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Mass-Spectrometric and Kinetic Studies on the Mechanism and Degradation Pathways of Titanium Salalen Catalysts for Asymmetric Epoxidation with Aqueous Hydrogen Peroxide

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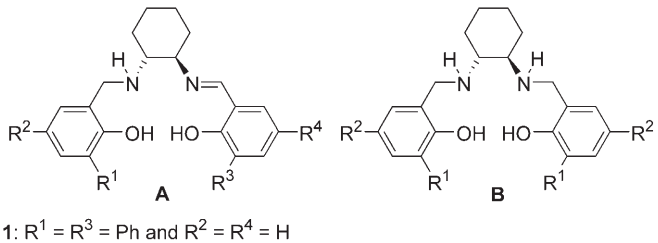
Abstract: The composition and degradation of a highly active and enantioselective titanium salalen *in situ* catalyst for the asymmetric epoxidation of olefins with aqueous hydrogen peroxide was investigated. Kinetic data and ESI-MS studies point to a mononuclear titanium salalen as the catalytically active species. By means of ESI-MS and selective monodeuteration of the salalen ligand, the oxidative degradation was studied. Upon exposure to aqueous hydrogen peroxide, the amine functionality of the salalen ligand is converted to the hydroxylamine, followed by loss of water and generation of the inactive titanium-salen complex. This transformation limits the activity of the catalyst in the epoxidation of less electron-rich olefins, such as 1-octene.

Keywords: alkenes; asymmetric catalysis; catalyst design; epoxidation; hydrogen peroxide; titanium

Introduction

Asymmetric epoxidation (AE) of olefins is the most direct approach for the preparation of enantiomerically enriched epoxides.[1] In terms of convenience and atom efficiency, aqueous hydrogen peroxide is the oxidant of choice, as it is cheap, safe, easy to handle, and produces water as the sole by-product.[2] Significant effort has been devoted to the development of AE methods using hydrogen peroxide as the oxidant.[3] Recent work by Katsuki et al. is based on the use of titanium in combination either with a semi-reduced salen-type ligand (a so-called salalen, **A**, Scheme 1), or a fully reduced salen (salan, **B**, Scheme 1). High yields and enantioselectivities were achieved for a number of conjugated olefins.[4]



Scheme 1. Reduction stages of salens: half-reduced (salalen **A**), fully reduced (salan **B**).

Recently, our group has developed a practical and versatile method for the preparation of salalen ligands **A** (and complexes) which allows easy access to a variety of both "symmetrical ($R^1=R^3$ and $R^2=R^4$)" and "non-symmetrical" salalen ligands **A**, with easily tunable steric and electronic properties.[5] In our study, we exploited the versatility of our method for the optimization of simple salalen ligands **A** in the Ti-catalyzed AE with H_2O_2. Furthermore, improved practicability results from the fact that the Ti catalyst can be generated *in situ* by just combining stock solutions of titanium tetraisopropoxide [Ti(O-*i*-Pr)$_4$] and of the chiral ligand. We obtained good to excellent yields and enantioselectivities with phenyl-substituted salalen **1** ($R^1=R^3=$Ph; $R^2=R^4=$H) as ligand for non-functionalized olefins [such as 1,2-dihydronaphthalene (91% yield and 96% *ee*) and indene (88% yield and 97% *ee*)].

Besides the investigations on the catalysis performance, we also determined the structure of the titanium complex [after exposure to air (moisture)] as a dimer ([Ti(salalen **1**)O]$_2$) by X-ray crystallography (Figure 1, *left*). High resolution mass spectrometry from the catalytically active solution indicated mononuclearity. On the basis of these results we formulated a proposal for a mononuclear active peroxotitanium species, which is activated for the oxygen transfer by intramolecular hydrogen bonding (dashed green lines,

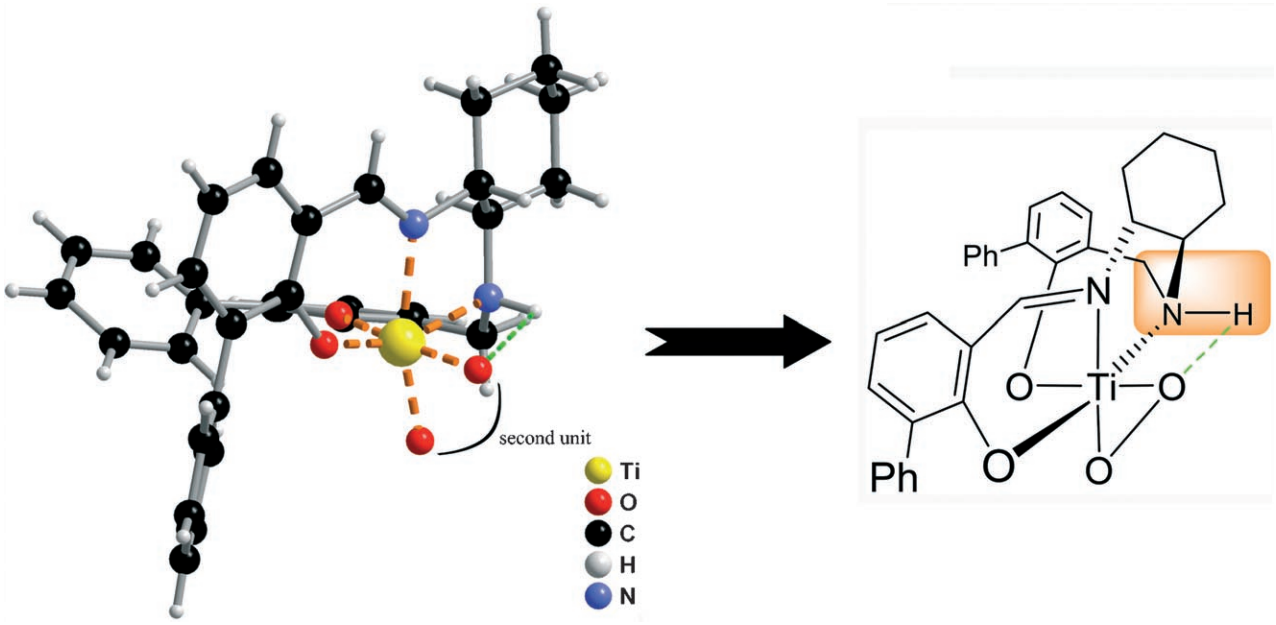


Figure 1. X-ray structure of the [Ti(salalen **1**)O]$_2$-complex (*left*) and the resultant putatitive mononuclear peroxotitanium complex (*right*); dashed green lines indicate intramolecular hydrogen bonding.

Figure 1, *right*). Activation by "external protonation" appears unlikely, as buffering of the reaction mixture around neutral pH was found to be beneficial.[4d]

Results and Discussion

Our current kinetic study further supports our proposal of a mononuclear catalytically active species. We determined yield/time profiles for the epoxidation of 1,2-dihydronaphthalene as a function of the Ti(O-*i*-Pr)$_4$/salalen **1** concentrations (5 mol% and 10 mol%). All other experimental parameters were kept constant. Under these conditions the velocity ν of the reaction is dependent only on the concentration of titanium: $\nu = k \times [Ti]^c$.

From the yield/time profile, the velocities ν were determined for the two titanium loadings (Figure 2) Double logarithmic analysis gives the reaction order c in titanium. The value of $c = 1.09$ indicates that the reaction exhibits first-order kinetics in titanium which is consistent with a mononuclear catalytically active titanium complex.

In the course of our investigation, we encountered a limitation of the method, namely that it is particularly well suited for electron-rich olefins. We also tested non-conjugated olefins such as vinylcyclohexane (VCH) and 1-octene. Whereas the enantioselectivity was encouraging for VCH (84% *ee*), the epoxide yield (<10%) was unsatisfactory. Prolonging of the reaction time from 18 h to a couple of days or addition of hydrogen peroxide in portions and up to 10 equivalents, did not increase the epoxide yield significantly. These observations led us to the assumption that the life-time of the active titanium salalen species is limited in the presence of hydrogen peroxide, and that its deactivation proceeds more rapidly than oxygen transfer to electron-poor olefins.

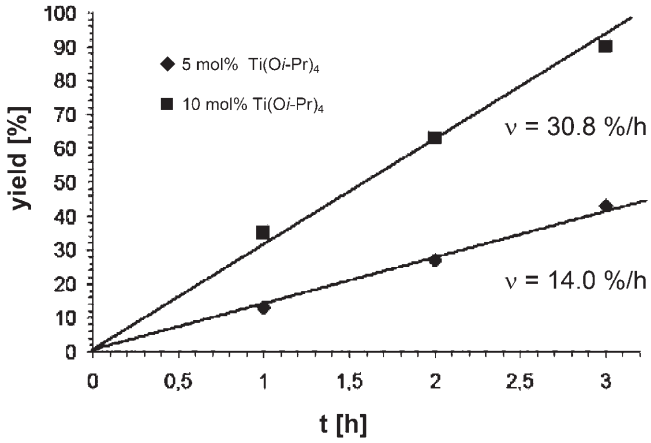


Figure 2. Velocities of the reaction at different concentrations of Ti(O-*i*-Pr)$_4$.

In this paper, we report our investigation on the deactivation of the titanium complex catalyst Ti(salalen **1**) in the presence of aqueous hydrogen peroxide. For this purpose, we first monitored the Ti catalyst prepared *in situ* from the salalen ligand **1** and Ti(O-*i*-Pr)$_4$ in dichloromethane by ESI-MS, *without* addition of hydrogen peroxide (Figure 3).

The main peak of the spectrum was characterized as a *mononuclear* species by HR-ESI-MS ($m/z =$

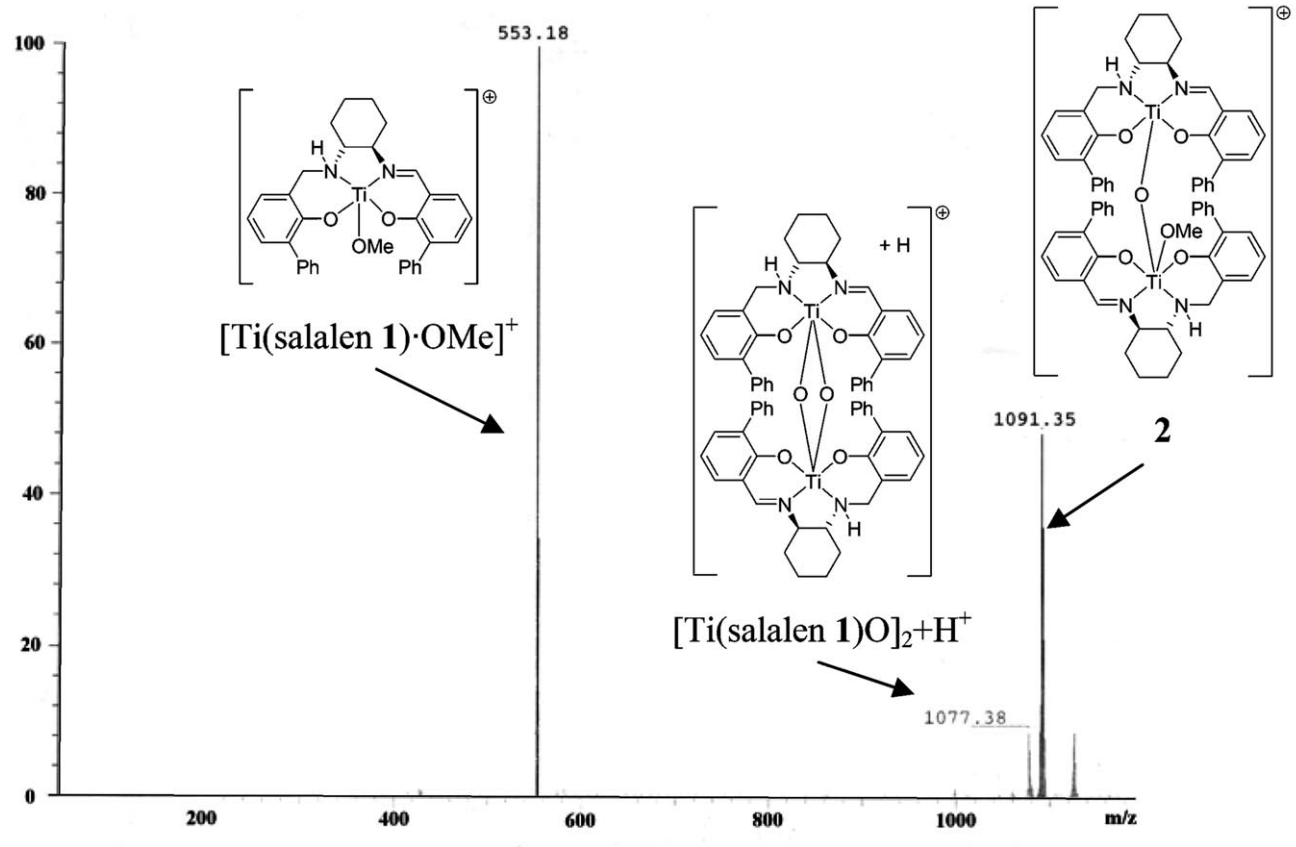


Figure 3. ESI mass spectrum of the Ti(salalen **1**) complex in CH_2Cl_2/MeOH (spray solvents).

553.197: [Ti(salalen **1**)·OMe]$^+$, $^-$OMe from spray solvent). Besides this peak, two more signals are visible and indicate dimeric species [Ti(salalen **1**)O]$_2$+H$^+$], and **2** {[Ti(salalen **1**)$^1/_2$O]$_2$·OMe}$^+$ (Figure 3). Upon addition of aqueous hydrogen peroxide (30%), the mass spectrometric appearance of the titanium complex solution changes dramatically (Figure 4).

As shown in Figure 4, the most intensive signal (m/z = 553.13) still belongs to the *mononuclear* species [Ti(salalen **1**)·OMe]$^+$. Also, the signal of the dimer **2** [Ti(salalen **1**)$^1/_2$O]$_2$·OMe]$^+$ (m/z = 1091.25) is still present. Additionally, the newly occurring mass of m/z = 477.20 clearly indicates incipient demetallation of the titanium salalen catalyst to the free ligand **1**. The appearance of two new monomeric species is the most striking effect of H_2O_2 addition. The peak at m/z = 569.12 has exactly the mass of the main peak *plus one oxygen atom* [Ti(salalen **1**)·OMe + O]$^+$ which is consistent with a mono-oxygenated monomeric titanium complex. The second new signal with m/z = 537.06 corresponds to a titanium sal*en* complex [Ti(sal*en*)·OH]$^+$ in which the hydroxide counterion results from the use of aqueous H_2O_2. In the mass range of the dimers, similar species can be identified. The signal with m/z = 1109.21 points at a doubly oxygenated titanium dimer {[Ti(salalen **1**)O]$_2$+2O+H$^+$}, and the mass of m/z = 1075.18 to a salen/salalen mixed titanium complex **3**.

The positions of the ligand which can be mono-oxygenated most easily are the benzylic CH and the amine NH bonds (Scheme 2, *top*).[6] To distinguish between these two possibilities, we substituted a benzylic proton for a deuterium atom. Based on the most reasonable assumption that, after hydroxylation, exchange of hydroxylic protons with aqueous hydrogen peroxide will take place, the level of deuterium content should not change after oxidation if the amine functionality is oxidized. By the same token, the level of deuterium content should decrease if the oxidation takes place at the benzylic position (Scheme 2, *middle*). Additionally, information concerning the regioselectivity of subsequent water elimination can be obtained from the D content. If a salen is formed, the D content should decrease. On the other hand, elimination to an "iso-salen" should not be accompanied by loss of deuterium (Scheme 2, *bottom*).

Deuterium was incorporated into the benzylic position of the salalen ligand **9** as shown in Scheme 3. First, *trans*-1,2-diaminocyclohexane **4** (DACH), in the form of its anhydrous monohydrochloride **5**,[8] was condensed with one equivalent of 3-phenylsalicylic aldehyde **6**, and the resulting imine **7** was reduced to

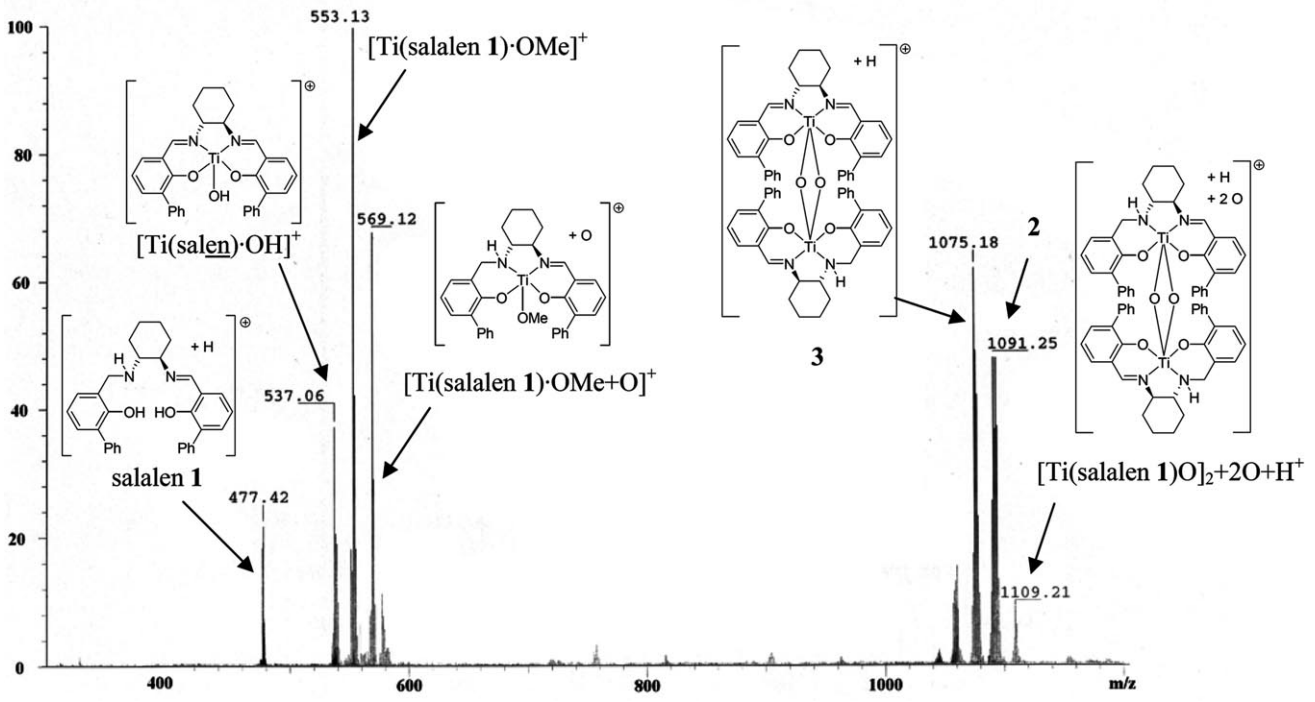
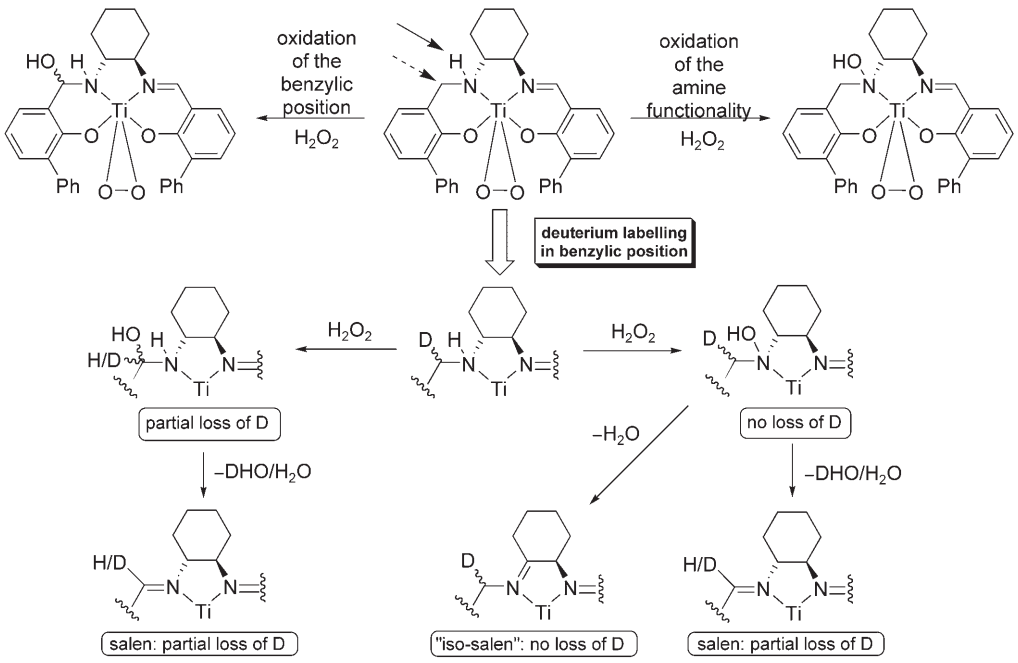
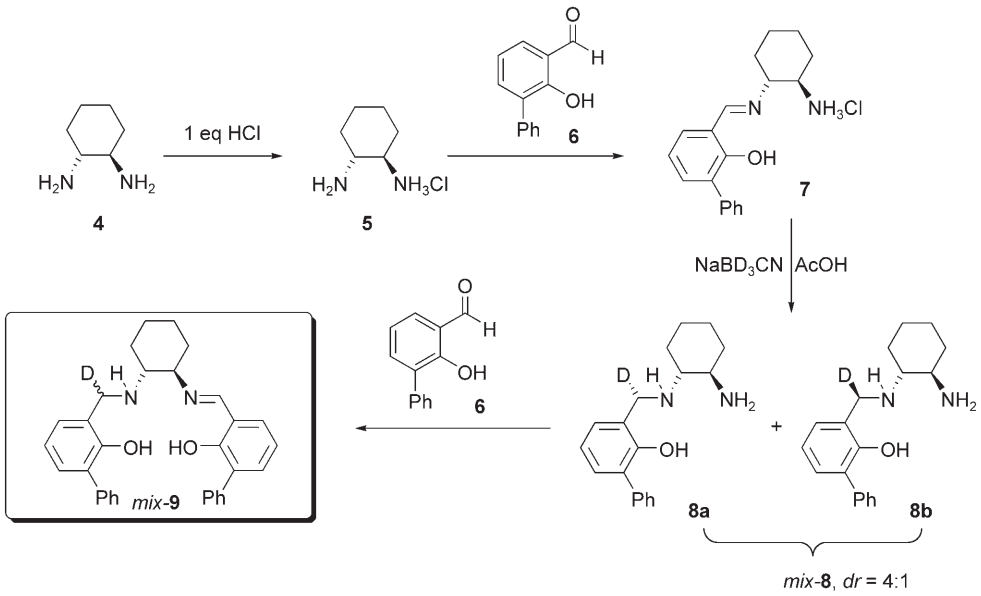


Figure 4. ESI mass spectrum of the Ti(salalen **1**) complex in the presence of 50 equivalents of aqueous hydrogen peroxide in CH_2Cl_2/MeOH (spray solvents).



Scheme 2. Hydroxylation reactions of the catalytically active mononuclear Ti(salalen **1**)-species (*top*), and strategy of the deuterium labelling experiment for distinguishing between possible pathways (*bottom*).

the monoalkylated diamine *mix*-**8**. The diastereomeric ratio **8a**:**8b** was determined as 4:1 by NMR spectroscopy (see Supporting Information for details). For the reduction step, sodium cyanoborodeuteride in pure acetic acid proved best. With the monodeuterated amine component *mix*-**8** in hand, condensation with one equivalent of 3-phenylsalicylic aldehyde **6** afforded the mixture of diastereomeric deuterio-salalen ligands *mix*-**9**.



Scheme 3. Synthesis of the monodeuterated DACH-salalen ligand *mix*-**9**.

Analogous to the nondeuterated ligand **1**, the titanium deuterio-salalen complex was prepared *in situ* from the deuterio-salalen ligand *mix*-**9** and Ti(O-*i*-Pr)$_4$ in dichloromethane. The mass spectra of the resultant complex before and after addition of aqueous hydrogen peroxide are shown in Figure 5. Before addition of hydrogen peroxide, two well-defined signals can be identified analogous to the spectrum of the non-deuterated Ti complex (Figure 3). The signal at $m/z = 554.20$ once again points to the *mononuclear* species: [Ti(salalen *mix*-**9**)·OMe]$^+$ ($^-$OMe from spray solvent) and the second with $m/z = 1093.30$ to the dimeric structure **10** (Figure 5, *left*). After addition of hydrogen peroxide, the spectrum shows identical changes as in the case of the non-deuterated Ti complex (Figure 4). Besides the signal at $m/z = 554.19$ for [Ti(salalen *mix*-**9**)·OMe]$^+$, the masses for a mono-oxygenated titanium complex [Ti(salalen *mix*-**9**)·OMe + O]$^+$ ($m/z = 570.18$) and a titanium sal*en* complex [Ti(sal*en*)·OH]$^+$ ($m/z = 538.15$) could be detected (Figure 5, *right*). Analogous to the spectrum of the non-deuterated Ti complex (Figure 4) the peaks at $m/z = 1077.24$ and $m/z = 1095.18$ can be assigned to dimeric species.

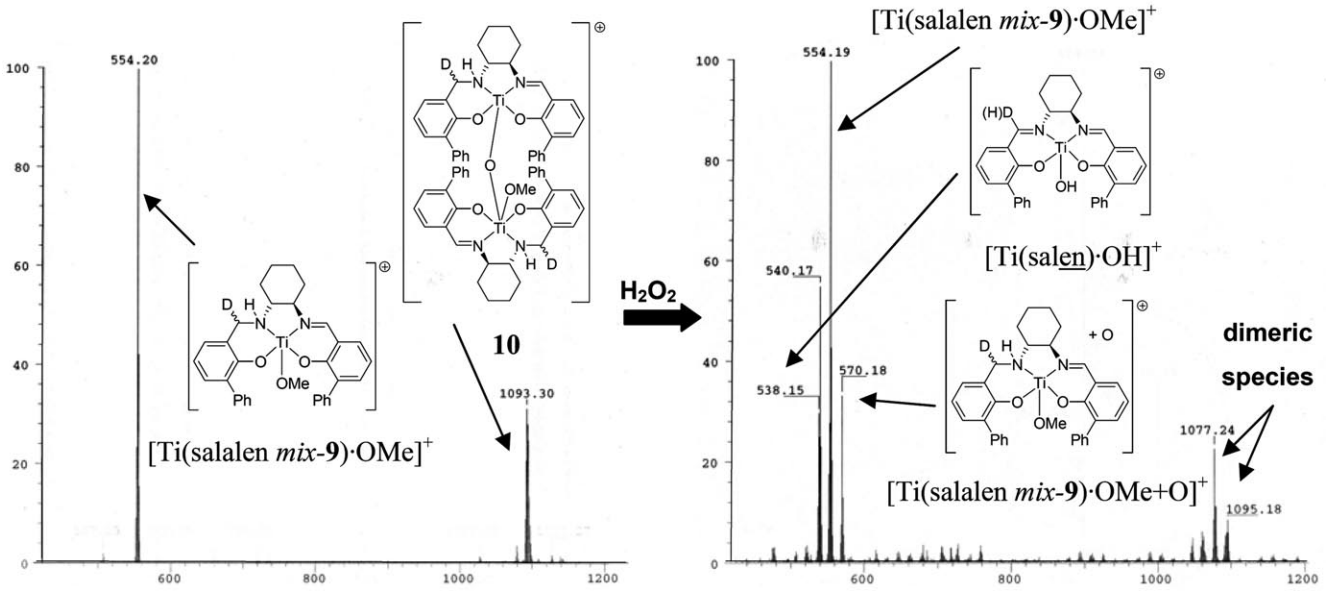


Figure 5. ESI mass spectra of the Ti(deuterio-salalen *mix*-**9**) complex before (*left*) and after (*right*) addition of H_2O_2 (50 equiv.) in CH_2Cl_2/MeOH (structures of the dimeric species are omitted for clarity).

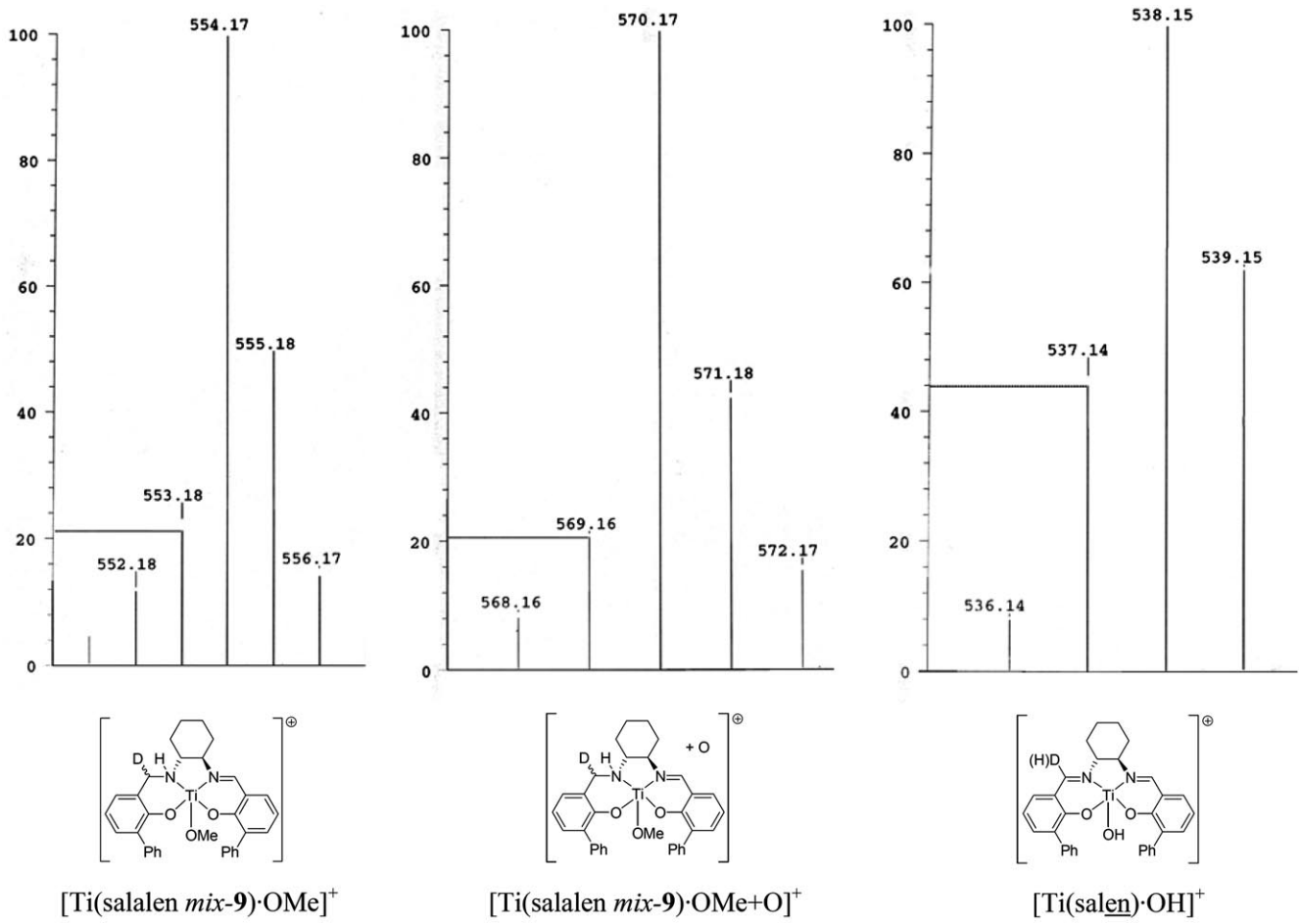


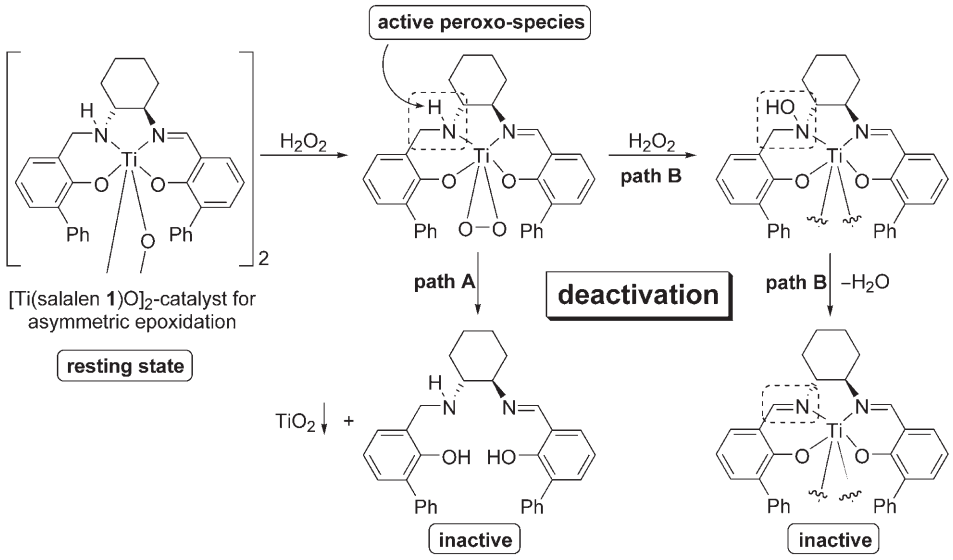
Figure 6. Isotopic patterns of the peaks belonging to [Ti(salalen *mix*-**9**)·OMe]$^+$ (*left*) before addition of H_2O_2 and [Ti(salalen *mix*-**9**)·OMe + O]$^+$ after addition of H_2O_2 (*middle*) as well as the [Ti(sal*en*)·OH]$^+$ (*right*). The peak heights relative to the 100% signals reflect the H content.

A comparison of the isotopic patterns of the peaks belonging to the deuterated mononuclear titanium complex [Ti(salalen·*mix*-**9**)·OMe]$^+$ (Figure 6, *left*) and its oxygenated form [Ti(salalen *mix*-**9**)·OMe + O]$^+$ (Figure 6, *middle*) indicate that the deuterium level did not change upon incorporation of an oxygen atom [compare the horizontal lines for $m/z = 553.18$ and $m/z = 569.16$, the peak heights relative to the 100% signals (554.14, 570.14) reflect the H content].

In the case of deuterium loss, the intensity of the signal at $m/z = 569.16$ would have increased. Consequently, oxygenation of the ligand in [Ti(salalen *mix*-**9**)·OMe]$^+$ is *not* accompanied by loss of deuterium. This, in turn, indicates that the benzylic position is not hydroxylated but the amine functionality, affording a hydroxylamine. The signal at $m/z = 537.14$ (Figure 6, *right*) which corresponds either to the mononuclear Ti-salen or Ti-"iso-salen" complex shows a diminished level of deuterium. Consequently, dehydration resulted in a sal*en*-complex, and not in an "iso-salen" Ti complex (Scheme 2, *bottom*). In fact, dehydration of the hydroxylamine to form the salen is the expected mode of reaction, as imine formation from alkylhydroxylamines is known in the literature, and salen formation should additionally be favoured by the generation/extension of the conjugated system.[6,7] It is especially worthy of note that imine formation from *N*,*N*-dialkylated amines was reported to proceed already at very low temperatures in the presence of titanium halides.[7]

Conclusions

The results of our study can be summarized as follows (Scheme 4). One of the deactivation pathways of the Ti catalyst derived from salalen ligand **1**, in the presence of aqueous hydrogen peroxide, consists in hydrolytic demetallation (path A), affording the free ligand **1** and catalytically inactive titanium dioxide. More importantly, the amine functionality of the Ti(salalen **1**) catalyst is oxidized to the hydroxylamine (path B). Subsequent loss of water leads to the inactive titanium salen complex.



Scheme 4. Degradation pathways of the Ti(salalen **1**)-catalyst in the presence of hydrogen peroxide (these pathways do not necessarily occur on the stage of the peroxo-species).

The life time of the Ti(salalen **1**) catalyst and its active peroxotitanium species in the presence of hydrogen peroxide is long enough for the epoxidation of electron-rich, conjugated olefins, such as 1,2-dihydronaphthalene. However, it seems to be too short for effectively transferring an oxygen atom to less reactive (i.e., electron-poor), non-conjugated olefins, such as vinylcyclohexane.

Experimental Section

Deuterio-(1*R*,2*R*)-Ph,H;Ph,H-DACH-salalen (*mix*-9)

Anhydrous HCl (1.31 mL, 2.61 mmol, 2 M in diethyl ether) was added to a solution of (1*R*,2*R*)-*trans*-1,2-diaminocyclohexane **4** (298 mg, 2.61 mmol) in dry diethyl ether (10 mL) over a period of 15 min. The mixture was stirred at room temperature for 18 h. The precipitate was collected by vacuum filtration, washed with diethyl ether and dried under vacuum. The colourless solid was then dissolved in a methanol/ethanol mixture (50/50 v/v, 20 mL), and 3-phenyl-2-hydroxybenzaldehyde **6** (466 mg, 2.35 mmol) was added in small portions. The reaction mixture was stirred overnight. After removal of the solvent, the remaining yellow solid was washed twice with diethyl ether and suspended in glacial acetic acid (15 mL). Sodium cyanoborodeuteride (132 mg, 2.00 mmol) was added in one single portion. After one hour, additional $NaBD_3CN$ (68 mg, 1.04 mmol) was added, and the solution was stirred for three hours to ensure complete reduction. 6 M KOH (aqueous) was added until pH 8 was reached. The resulting suspension was extracted with CH_2Cl_2, and the combined organic phases were washed with saturated aqueous $NaHCO_3$. After drying over $MgSO_4$, filtration and evaporation, the remaining oil was dissolved in a methanol/ethanol mixture (50/50 v/v, 50 mL). 3-Phenyl-2-hydroxybenzaldehyde **6** (252 mg, 1.27 mmol) was added in small portions. The mixture was stirred overnight. The solvent was removed, and the remaining yellow solid was dried under vacuum over phosphorus pentoxide at 40 °C. The product *mix*-**9** was obtained as a pale yellow powder; yield: 607 mg (1.27 mmol, 49%); mp 71 °C; ^{1}H NMR ($CDCl_3$): δ = 1.23–1.35 (m, 1H), 1.26–1.41 (m, 1H), 1.29–1.41 (m, 1H), 1.55–1.67 (m, 1H), 1.61–1.82 (m, 1H), 1.73–1.82 (m, 1H), 1.76–1.84 (m, 1H), 2.14–2.28 (m, 1H), 2.72–2.84 (m, 1H), 3.01–3.13 (m, 1H), 3.83–3.89 (m, 1H), 6.76–6.88 (m, 1H), 6.88–6.99 (m, 1H), 6.91–6.99 (m, 1H), 7.17–7.26 (m, 1H), 7.20–7.29 (m, 1H), 7.25–7.32 (m, 1H), 7.29–7.35 (m, 1H), 7.34–7.40 (m, 2H), 7.37–7.43 (m, 1H), 7.40–7.46 (m, 1H), 7.52–7.55 (m, 1H), 7.61–7.67 (m, 2H), 8.46 (s, 1H), 13.78 (br. s, 2H); ^{13}C NMR ($CDCl_3$): δ = 24.4 (t), 24.5 (t), 30.0 (t), 34.0 (t), 49.9 (d, $J_{C\text{-}D}$ = 19.5 Hz), 61.4 (s), 73.4 (d), 118.8 (s), 118.9 (d), 119.1 (d), 123.6 (s), 126.8 (d), 127.2 (d), 127.5 (d), 128.1 (d), 128.2 (d), 129.2 (s), 129.3 (d), 129.4 (d), 129.8 (d), 129.9 (s), 131.1 (d), 133.6 (d), 137.7 (s), 138.5 (s), 155.1 (s), 158.3 (s), 166.1 (d); IR (ATR): $\tilde{\nu}$ = 3054, 2930, 2856, 1623, 1623, 1496, 1456, 1428, 1289, 1098, 1070, 1029, 831, 757, 697 cm^{-1}; HR-MS (ESI): *m*/*z* [u] = 478.260, exact mass calcd. for $[C_{32}H_{32}DN_2O_2]^+$ ($[M+H]^+$): 478.261.

[Ti(salalen *mix*-9)O]$_2$

Titanium isopropoxide (5.9 μL, 20 μmol) was added to a solution of the deuterio-(1*R*,2*R*)-Ph,H;Ph,H-DACH-salalen *mix*-**9** (9.6 mg, 20 μmol) in 1 mL of dry CH_2Cl_2. The resulting yellow solution was stirred for two hours and exposed to air for 24 h. Drying under vacuum afforded the Ti complex as a yellow solid; yield: 10.8 mg (10 μmol, quant.). HR-MS (ESI; CH_2Cl_2, MeOH): *m*/*z* [u] = 554.204, exact mass calcd. for $[C_{33}H_{32}DN_2O_3Ti]^+$ ($[M+OMe]^+$): 554.203.

General Procedure for the Mass Spectrometric Monitoring of Titanium Salalen Complexes in the Presence of Aqueous Hydrogen Peroxide

[Ti(salalen **1**)O]$_2$ (2.0 mg, 1.9 μmol, 2 equiv.) and [Ti(salalen *mix*-**9**)O]$_2$ (2.0 mg, 1.9 μmol, 2 equiv.), respectively, were dissolved in a solvent mixture consisting of 200 μL of dry CH_2Cl_2 and 200 μL of dry MeOH. Fifty equivalents (18.9 μL, 186 μmol) of aqueous hydrogen peroxide (30%) were added. An aliquot of the solution was analyzed by ESI mass spectrometry on a Finnigan MAT 900S instrument (for further details concerning ESI-MS experiments: see Supporting Information).

Acknowledgements

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