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# Crystal Structure of a Binuclear N,N'-Disalicylidene-(*R*,*R*)-1,2-cyclohexanediamine-Titanium(IV) Complex and Asymmetric Oxidation of Methyl Phenyl Sulfide with Trityl Hydroperoxide Catalyzed by the Complex

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A binuclear titanium(IV) complex with N,N'-disalicylidene-(*R*,*R*)-1,2-cyclohexanediamine was prepared and the structure was determined by X-ray analysis. The complex catalyzes asymmetric oxidation of methyl phenyl sulfide with trityl hydroperoxide in methanol at 0 °C to give (*R*)-methyl phenyl sulfoxide with an optical yield of 53%.

In recent years, much attention is being attracted to the usefulness of optically active sulfoxides in the asymmetric synthesis of organic compounds.1) An efficient asymmetric oxidation of prochiral organic sulfides into optically active sulfoxides has been reported, using a stoichiometric amount of modified Sharpless reagent ($Ti(OPr^i)_4$/diethyl (*R*,*R*)-tartrate/$Bu^tOOH$) for asymmetric epoxidation.2,3) Very recently, we succeeded in a similar asymmetric oxidation of sulfides with organic hydroperoxides in the presence of a catalytic amount of optically active Schiff base-oxovanadium(IV) complexes.4) These results led us to study the catalytic properties of titanium(IV) analogs, although the stereochemistry of a titanium(IV)-Schiff base complex has not been well studied. This letter reports the preparation and X-ray crystal structure determination of

[TiCl(sal-(RR)-chxn)]$_2$O (H$_2$(sal-(RR)-chxn)=N,N'-disalicylidene-(*R*,*R*)-1,2-cyclohexanediamine), and the asymmetric oxidation of methyl phenyl sulfide with trityl hydroperoxide catalyzed by this complex.

The complex was prepared by treating $TiCl_4$ with an equimolar amount of H$_2$(sal-(RR)-chxn)$^{5)}$ in pyridine, and the product was recrystallized from dichloromethane-acetone to give orange crystals. Yield: 70%. Found: C, 58.79; H, 5.49; N, 6.05%. Calcd for [TiCl(sal-(RR)-chxn)]$_2$O·2(CH$_3$)$_2$CO: C, 58.80; H, 5.58; N, 5.96%. Although several titanium(IV) complexes with quadridentate Schiff bases of this type have been prepared in the same way as that described above, they have been formulated differently.$^{6,7)}$ Thus, the complex was subjected to X-ray analysis.

Crystal data of the complex are as follows: $Ti_2C_{40}N_4H_{40}Cl_2O_5 \cdot 2C_3H_6O$, MW 939.7, monoclinic, C2, a=22.189(6), b=9.616(2), c=23.452(6) Å, β=115.21(2)°, V=4527(2) Å$^3$, Z=4, $D_m$=1.44(3), $D_x$=1.38 g cm$^{-3}$, μ(Mo Kα)=5.11 cm$^{-1}$. Intensity measurements were carried out for $2\theta \leqq 45°$ on a RIGAKU AFC-5 diffractometer. Among 3340 ±h, -k, +l reflections measured, those of 2494 had $|F_o| \geqq 3\sigma(|F_o|)$. The structure was solved by direct methods and refined by a block-diagonal least squares procedure to

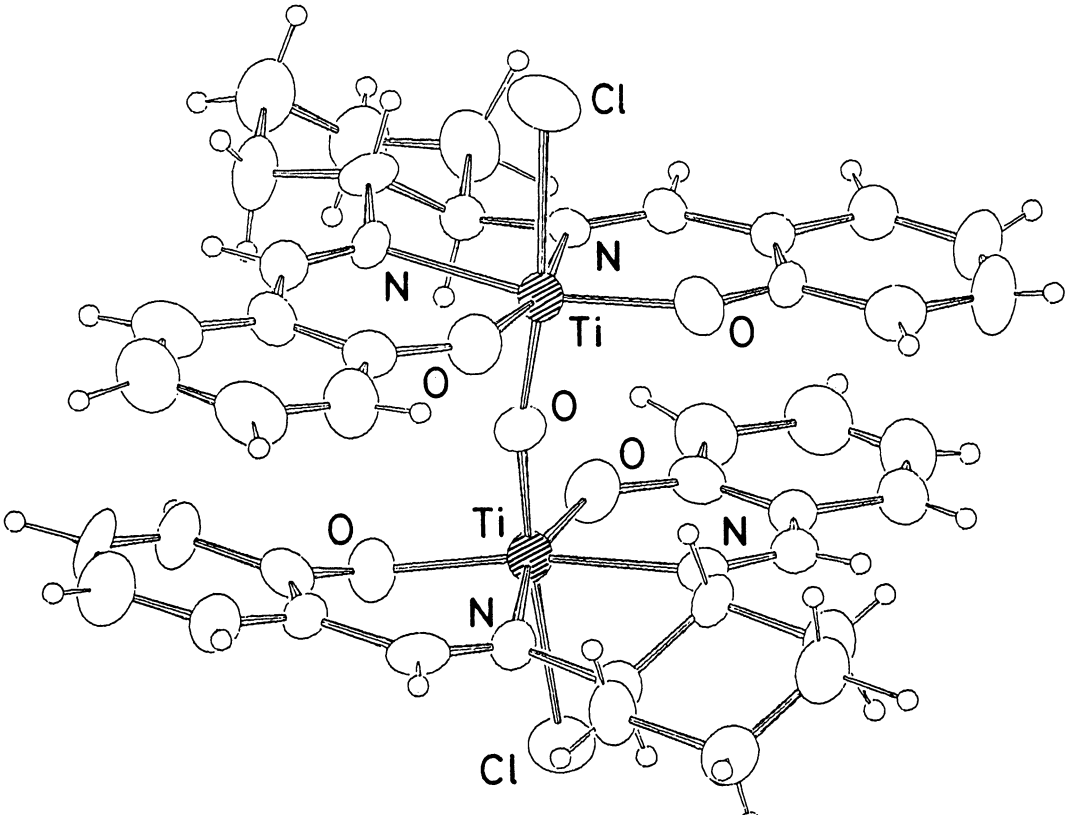

Fig. 1. An ORTEP drawing of [TiCl(sal-(RR)-chxn)]$_2$O.

Table 1. Asymmetric Oxidation of Methyl Phenyl Sulfide to the Sulfoxide[a)]

| Solvent | Peroxide[b)] | Temp/°C | Time/h | Yield/%[c)] | e.e./%[d)] | Sulfoxide configuration |
|---|---|---|---|---|---|---|
| MeOH | THP | 0 | 110 | 87 | 53 | (*R*) |
| EtOH | THP | 0 | 140 | 66 | 15 | (*R*) |
| $CH_3CN$ | THP | 5 | 140 | 73 | 5 | (*R*) |
| $CH_2Cl_2$ | THP | 0 | 170 | 48 | 23 | (*R*) |
| $CH_2Cl_2$ | THP | -20 | 960 | 44 | 28 | (*R*) |
| $CH_2Cl_2$ | THP | 20 | 64 | 60 | 12 | (*R*) |
| $CH_2Cl_2$ | THP | 40 | 20 | 58 | 5 | (*R*) |
| $CH_2Cl_2$ | CHP | 0 | 170 | 32 | 19 | (*R*) |
| $CH_2Cl_2$ | TBHP | 0 | 144 | 61 | 8 | (*R*) |

a) All reactions were performed as described in detail in the text. Molar ratio of $[TiCl(sal\text{-}(RR)\text{-}chxn)]_2O$ : organic hydroperoxide : methyl phenyl sulfide = 0.45 : 10 : 10. b) Peroxides: THP, trityl hydroperoxide; CHP, cumene hydroperoxide; TBHP, t-butyl hydroperoxide. c) Isolated yields, based on the sulfide. d) Based on the optical rotation of the pure enantiomer reported in Ref 9.

R=0.037 and wR=0.042 for 2421 unique reflections.[8)] The absolute structure was assigned on reference to the known absolute configuration of (*R*,*R*)-1,2-cyclohexanediamine moieties. The molecular structure is shown in Fig. 1. The complex is binuclear. The bridging oxygen atom seems to come from water in pyridine or from moisture in the air. The complex has a pseudo center of symmetry at the bridging O atom except for the (*R*,*R*)-1,2-cyclohexanediamine moieties. The Ti-O(bridge)-Ti angle is 168.3(3)° and the Cl-Ti-O(bridge) angles are 167.6(2) and 168.9(2)°. The Ti atoms are coordinated octahedrally and the planes composed of Ti and a Schiff base are nearly parallel to each other. The Ti-Cl distances are 2.437(3) and 2.453(3) Å, and the Ti-O(bridge) distances are 1.798(6) and 1.814(6) Å.

A typical run of the asymmetric oxidation of methyl phenyl sulfide was performed as follows. To a methanol solution (20 $cm^3$) of $[TiCl(sal\text{-}(RR)\text{-}chxn)]_2O\cdot 2(CH_3)_2CO$ (68 mg, $7.24 \times 10^{-5}$ mol) cooled to 0 °C were added trityl hydroperoxide (463 mg, $1.68 \times 10^{-3}$ mol) and methyl phenyl sulfide (209 mg, $1.68 \times 10^{-3}$ mol). The mixture was allowed to stand at 0 °C for 110 h, and the solvent was then removed under reduced pressure. The residue was extracted with diethyl ether,

which was evaporated under reduced pressure. From the resulting oil, methyl phenyl sulfoxide was isolated and purified by column chromatography on silica gel (eluent: cyclohexane-ethyl acetate (1:1 v/v)). Yield: 204 mg (87%).
The enantiomeric excess (e.e.) was determined on the basis of the reported optical rotation of the pure enantiomer;9) $[\alpha]_{589}^{24}$ (c 1.94, acetone) +79.1° ; e.e. 53% (*R* configuration).

Several solvents and peroxides were used for the asymmetric oxidation of methyl phenyl sulfide and the results are given in Table 1. The $[TiCl(sal-(RR)-chxn)]_2O$ complex catalyst gives always (*R*)-methyl phenyl sulfoxide, although the optical yield (e.e) decreases with an increase in temperature between -20 and +40 °C. It is to be noted that the oxovanadium(IV) complex catalyst, VO(sal-(RR)-chxn) gives the antipode, (*S*)-sulfoxide, in a similar oxidation.4) The optical yield shows a remarkable solvent dependence, and the result may be attributed to the difference in structure of the complex in solution. For example, the $^{13}C\{^1H\}$ NMR spectrum of the complex in $CD_2Cl_2$ shows 20 signals as expected from the crystal structure. However, the spectrum in $CD_3OD$ is quite complicated, suggesting the existence of several species. A mechanistic study is now under way.

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