nicely with Pt-Pt distance (Table I), as predicted by a model[5] based on a SCF-X$\alpha$ calculation[13] for *cis*-diammineplatinum $\alpha$-pyridone blue.

In summary, a platinum pyrimidine blue has been structurally and magnetically characterized for the first time. The ability to prepare this species in pure cyrstalline form will facilitate further evaluation of this class of compounds as antitumor drugs. The geometric, magnetic, and spectroscopic properties of *cis*-diammineplatinum 1-methyluracil blue substantially extend the amplify our understanding of platinum blues as based on earlier studies of the $\alpha$-pyridone analogue.

**Acknowledgment.** This work was supported by grants from the Bristol-Myers Co. and the National Cancer Institute under Research Grant CA-34992. We also thank Engelhard Industries for a loan of $K_2PtCl_4$, from which all platinum compounds were made, and W. H. Armstrong and T. V. O'Halloran for experimental assistance and helpful discussions.

**Supplementary Material Available:** Atomic positional and thermal parameters for compound **3** (2 pages). Ordering information is given on any current masthead page.

(13) Ginsberg, A. P.; O'Halloran, T. V.; Fanwick, P. E.; Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 5430.

## Crystal Structures of Two Titanium Tartrate Asymmetric Epoxidation Catalysts

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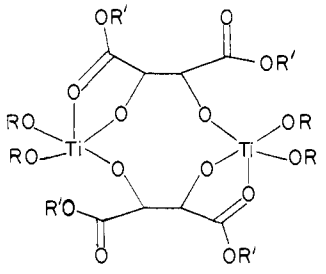
The enantioselective synthesis of organic compounds using chiral transition-metal complexes is an important, current topic in chemistry.[1] A recent contribution to this field has been the asymmetric epoxidation of allylic alcohols by alkyl hydroperoxides using titanium tartrate catalysts.[2] Previously, the structure of the binuclear titanium tartrate ester catalysts were presumed to be **1**,[3] on the basis of solid-state structural studies of binuclear



R = Pr$^i$
R' = Et, Pr$^i$

**1**

vanadyl tartrate complexes.[4] Since the vanadyl structures were unsatisfactory models for several reasons, we have been trying to crystallize actual binuclear titanium tartrate catalysts for X-ray structural investigation. As described in the present communication, these efforts have been successful. Here we report the crystal and molecular structures of **2** and **3**, two catalytically active

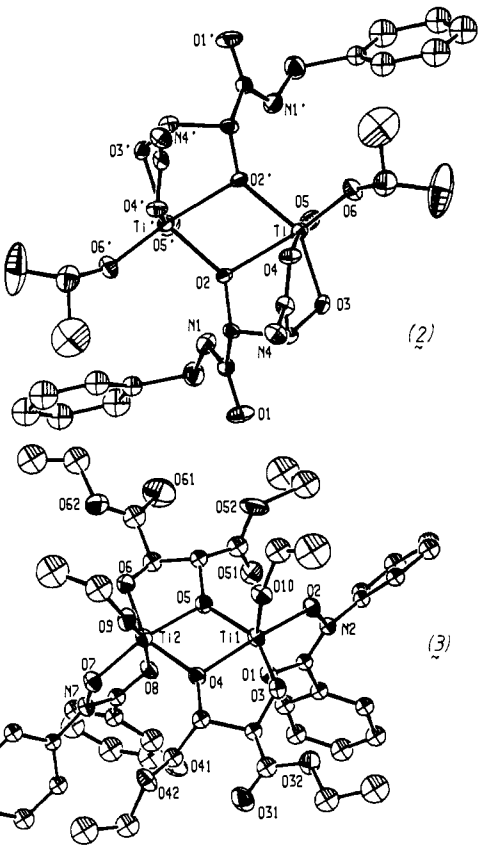
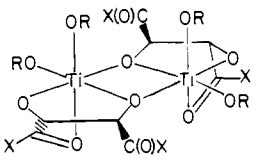
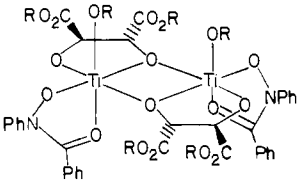


**Figure 1.** ORTEP drawings of **2** (top) and **3** (bottom) showing the atom labeling schemes and 40% probability thermal ellipsoids. For clarity, carbon atoms are not labeled and hydrogen atoms are omitted. In **2**, the benzyl groups on N4 and N4' and the isopropyl groups on O5 and O5' are also omitted for clarity.



R = Pr$^i$
**2** X = NHCH$_2$Ph



**3** R = Et

titanium tartrate complexes,[5] which should substantially aid mechanistic investigations of the asymmetric epoxidation reaction. To our knowledge, these are the first titanium "tartrate" structures to have been determined.

Compound **2** was synthesized by addition of 4.0 g (12.2 mmol) of (*R,R*)-*N,N'*-dibenzyltartramide to 80 mL of a stirring $CH_2Cl_2$ solution of Ti(O-*i*-Pr)$_4$ (3.64 g, 12.2 mmol). After 2.5 h the volatiles were removed in vacuo and the residue was dissolved in 30 mL of $CH_2Cl_2$. Removal of this solvent in vacuo[6] left a white foam, which was dissolved in 80 mL of ether with stirring. After 15 min, a white precipitate began to form at which point the reaction was placed in a −30 °C freezer. The precipitate was isolated by filtration, washed with 30 mL of ether, and dried in vacuo (yield, 61%). X-ray quality crystals were obtained from 8:1 toluene/$CH_2Cl_2$ over a 6-week period at −30 °C.[7,8] Compound

(1) Mosher, H. S.; Morrison, J. D. *Science (Washington, D.C.)* **1983**, *221*, 1013.
(2) For a review, see: Finn, M. G.; Sharpless, K. B. In "Asymmetric Synthesis"; Morrison, J. D., Ed.; Academic Press: New York, in press.
(3) Sharpless, K. B.; Woodard, S. S.; Finn, M. G. *Pure Appl. Chem.* **1983**, *55*, 1823.
(4) Ortega, R. B.; Tapscott, R. E.; Campana, C. F. *Inorg. Chem.* **1982**, *21*, 672 and references cited therein.
(5) The catalytic activity of **2** is reported in: Lu, L. D.; Johnson, R. A.; Finn, M. G.; Sharpless, K. B. *J. Org. Chem.* **1984**, *49*, 728. The catalytic activity of **3** has been observed with $\alpha$-phenylcinammyl alcohol (Ellman, J. A.; Pedersen, S. F., unpublished results).
(6) Dissolving the residue in additional solvent and then removing this solvent in vacuo helps remove most of the free alcohol released in the synthesis.

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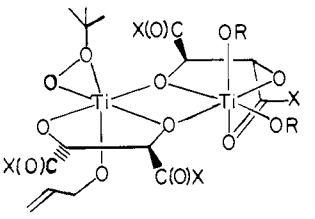
3 was prepared from 9.38 mmol each of $Ti(OEt)_4$, (*R,R*)-diethyl tartrate, and PhC(O)N(OH)Ph in $CH_2Cl_2$. Removal of solvent, dissolution in toluene, removal of toluene,[6] dissolution in 20 mL of ether, and filtration through dry Celite gave pale yellow plates after the filtrate was allowed to stand at room temperature overnight. The crystals were washed with ether (30 mL) and dried in vacuo (yield, 2.46 g, 51%).[9] Both compounds are very moisture sensitive and all manipulations were carried out in an atmosphere of dry nitrogen.

The structures of **2** and **3**, determined by X-ray diffraction,[10] are displayed in Figure 1. Although **2** is dimeric, its two halves being related by a crystallographically required twofold symmetry axis, one diolate oxygen atom of each tartramide ligand bridges two titanium atoms producing six-coordinate, pseudooctahedral coordination. Each titanium atom in **2** is facially coordinated by a tartramide ligand through the two diolate oxygen atoms, O(2) and O(3), and one of the carbonyl oxygen atoms, O(4). The two isopropoxide ligands are located trans to O(2) and O(4) and the coordination sphere of each metal is completed by the bridging oxygen atom. The Ti···Ti′ internuclear separation is 3.348 (3) Å. The planar $Ti_2O_2$ core is an asymmetric rhombus, with Ti–O(2) and Ti′–O(2) bond distances of 2.160 (9) and 1.973 (9) Å, respectively. The longer distance is the result of ring strain [O(2)–Ti–O(3) = 76.9 (4)°, O(2)–Ti–O(4) = 79.4 (4)°] and the influence of the good $\pi$-donor isopropoxide ligand [Ti–O(6) = 1.805 (9) Å] in the trans position [O(2)–Ti–O(6) = 159.1 (4)°].

Compound **3** also has a binuclear structure with the tartrate ester ligands bridging the two titanium atoms to form a $Ti_2O_2$ rhombus. A major difference between **2** and **3**, however, arises from the replacement of a terminal alkoxide by a chelating hydroxamate ligand, which has the additional effect of displacing the tartrate ester carbonyl functionality from the metal. This result is not surprising in view of the long Ti–O(4) bond, 2.204 (10) Å, found in **2**, which suggested that this link would be a weak one. In **3** the $Ti_2O_2$ core is nearly symmetric, probably because the trans influence and ring strain identified for **2** are not present. The two halves of **3** are related by a virtual, but not crystallographically required, *C*2 axis.

The weak coordination of the tartramide carbonyl oxygen atoms suggests that they will readily dissociate and recoordinate to the metal centers. This feature provides a means of exchanging the alkoxide ligands for the substrate molecules, *tert*-butyl hydroperoxide (TBHP) and allylic alcohol, via an intermediate in which one or both of the titanium atoms are pentacoordinate.

Although the structure found here is not the one employed in earlier discussions[3] of the mechanism for asymmetric epoxidation, it does have important features in common with the previous model. Exchange of two alkoxide ligands and dissociation of the carbonyl oxygen atom in **2**, or the equivalent loss of the hydroxamate and alkoxide ligands in **3**, exposes a meridional set of coordination positions on each titanium atom for binding the allylic alkoxide and potentially bidentate *tert*-butyl peroxide,[11] as shown in **4**. When this structure is viewed down the distal peroxide

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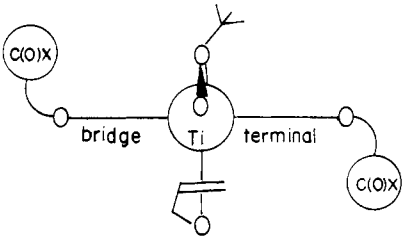
oxygen–Ti bond axis (**5**), the symmetry of the tartrate "windmill




5

arms" is apparent. A major difference, however, is that there is no longer a local twofold symmetry axis on each titanium atom, so the number of structures like **5** that must be considered as transition states has now doubled (eight vs. four). Thus the present structures reveal important features of dimeric titanium tartrate complexes which should provide valuable insight into the mechanism of the asymmetric epoxidation of allylic alcohols.

**Acknowledgment.** This work was supported by grants to S.J.L. from the National Science Foundation (CHE 83-40679) and to K.B.S. from the National Institutes of Health (GM 28384). S.F.P. thanks the National Institutes of Health for a National Research Service Award (GM 09812). We are also grateful to M. G. Finn for helpful discussions.

**Supplementary Material Available:** Atomic positional and thermal parameters for compounds **2** and **3** (4 pages). Ordering information is given on any current masthead page.

(7) Analytical data for **2**. Anal. Calcd for $TiC_{24}H_{32}N_2O_6$: C, 58.54; H, 6.55; N, 5.69; Ti, 9.73; $M_r$, 492.4. Found: C, 58.77; H, 6.47; N, 5.90; Ti, 9.87; $M_r$ (Signer method[8] in $CH_2Cl_2$), 997 (indicating a dimer).

(8) Clark, E. P. *Ind. Eng. Chem., Anal. Ed.* **1941**, *13*, 820.

(9) Analytical and spectroscopic data for **3**. Anal. Calcd for $TiC_{23}H_{27}NO_9$: C, 54.23; H, 5.34; N, 2.75; Ti, 9.40; $M_r$, 509.4. Found: C, 54.11; H, 5.44; N, 2.76; Ti, 9.35; $M_r$ (Signer method[8] in $CH_2Cl_2$), 908 (indicating a dimer). IR ($CH_2Cl_2$, $cm^{-1}$): 1740 ($\nu_{CO}$, tartrate); 1530 ($\nu_{CO}$, hydroxamate). Proton and $^{13}C$ NMR are complex and will be reported at a later date.

(10) X-ray crystallography. Compound **2** crystallizes as a 1:1 toluene adduct in the orthorhombic system, space group $C222_1$, with $a$ = 18.139 (3) Å, $b$ = 16.240 (4) Å, $c$ = 19.210 (3) Å, $V$ = 5659.0 Å$^3$, and $\rho_{calcd}$ = 1.264 g cm$^{-3}$ for $Z$ = 4. By use of 1823 unique, observed reflections collected at 225 K by diffractometry using Mo K$\bar{\alpha}$ ($\lambda$ = 0.7107 Å) radiation out to $2\theta$ = 50°, the structure was solved and refined by standard methods to a current value for the discrepancy index $R_1$ = 0.071. Compound **3** crystallizes in the monoclinic system, space group $P2_1$, with $a$ = 12.488 (2) Å, $b$ = 19.215 (4) Å, $c$ = 11.838 (1) Å, $\beta$ = 114.79 (1)°, $V$ = 2578.8 Å$^3$, and $\rho_{calcd}$ = 1.312 g cm$^{-3}$ for $Z$ = 2. The structure was refined by using 3179 reflections collected as above at 250 K to give $R_1$ = 0.067. Full details will be reported at a later date.

(11) Mimoun, H.; Chaumette, P.; Mignard, M.; Saussine, L.; Fischer, J.; Weiss, R. *Nouv. J. Chim.* **1983**, *7*, 467.

## Total Syntheses of the Amaryllidaceae Alkaloids (±)-Haemanthidine and (±)-Pretazettine

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Previous disclosures from these laboratories[2] have unveiled a general strategy for the synthesis of the alkaloids of the Amaryllidaceae family.[3] Interest in this class of alkaloids has been stimulated in part by reports of the potent anticancer and antiviral activity of the chemically labile base pretazettine (**2**).[4] Subsequent

(1) Recipient of a National Institutes of Health (National Cancer Institute) Research Career Development Award, 1980–1985.

(2) (a) Martin, S. F.; Puckette, T. A.; Colapret, J. A. *J. Org. Chem.* **1979**, *44*, 3391. (b) Martin, S. F.; Garrison, P. J. *J. Org. Chem.* **1982**, *47*, 1513.

(3) For reviews of the chemistry of the Amaryllidaceae alkaloids, see: (a) Fuganti, C. In "The Alkaloids"; Manske, R. H. F., Ed.; Academic Press: New York, 1975; Vol. 15, pp 83–164. (b) Grundon, M. F. In "Specialist Periodical Reports, The Alkaloids"; The Chemical Society: London, 1983; Vol. 13, pp 187–195, also Vol. 1–12. (c) Tsuda, Y. *Heterocycles* **1978**, *10*, 555.

(4) (a) Papas, T. S.; Sandhaus, L.; Chirigos, M. A.; Furusawa, E. *Biochem. Biophys. Res. Commun.* **1973**, *52*, 88. (b) Furusawa, E.; Suzuki, N.; Furusawa, S.; Lee, J. Y. B. *Proc. Soc. Exp. Biol. Med.* **1975**, *149*, 771. (c) Furusawa, E.; Furusawa, S.; Lee, J. Y. B.; Patanavanich, S. *Ibid.* **1976**, *152*, 186; *Chemotherapy (Basel)* **1978**, *24*, 259. (d) Furusawa, E.; Lockwood, R. H.; Furusawa, S.; Lum, M. K. M.; Lee, J. Y. B. *Ibid.* **1979**, *25*, 308. (e) Furusawa, E.; Irie, H.; Combs, D.; Wildman, W. C. *Ibid.* **1980**, *26*, 36. (f) Furusawa, E.; Lum, M. K. M.; Furusawa, S. *Ibid.* **1981**, *27*, 277. (g) Furusawa, E.; Lockwood, R. H. *Proc. West. Pharmacol. Soc.* **1981**, *24*, 45.

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