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Unique tripodal chiral tertiary amine, 2,6-*trans*-1,2,6-trisubstituted piperidine with pyridine and bis(phenol) donor groups: Its stereoselective coordination to titanium(IV) ion

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Abstract

A new optically active functionalized tertiary amine, (2*R*,6*R*)-2,6-bis(2-hydroxyphenyl)-1-(2-pyridylmethyl)piperidine {(*R*,*R*)-**1**}, was synthesized and its complexation behavior as a tripodal ligand was elucidated with titanium(IV) ion. Protonolysis of Ti(OPr-*i*)$_4$ with (*R*,*R*)-**1** and H_2O in a stepwise manner led to the formation of C_3-symmetric tris(μ-oxo)trititanium(IV,IV,IV) complex [$Ti_3\mathbf{L}_3(\mu\text{-}O)_3$] {**L** = diphenolato anion of (*R*,*R*)-**1**} with unified chiralities induced at the metal center (*Λ*) and by the conformations of the N^O chelate loops (*λ*) as well as the six-membered non-planner chair-like (Ti-μ-O)$_3$ ring core as defined by X-ray crystallography. These stereochemical issues are principally regulated by the stereogenic centers on the ligand and a chair conformation of the piperidine skeleton, which settle an enantiotopos-differentiating *cis*($O_{phenolato}$–$O_{phenolato}$) binding mode by unequivocally locating one $O_{phenolato}$ in an axial position and the other $O_{phenolato}$ in an equatorial plane.

Keywords: Chiral tetradentate tripodal ligand; Chiral piperidine; Tris(μ-oxo)trititanium complex; Chirality-at-metal

1. Introduction

Tripodal ligands, which are characterized by a facial coordination to metal ions, have recently gained considerable attention and found applications in various fields of research such as bioinorganic chemistry [1] and catalytic olefin polymerization [2]. As among the most reliable tactics to construct tetradentate ligands with a tripodal nature, trialkyl amine platforms have been long utilized as represented by tris(2-pyridylmethyl)amine [3], *N*,*N*′-bis(2-hydroxybenzyl)-2-picolylamine [4], and tris{2-(*R*)-4-phenyl-1,3-oxazolinylmethyl}amine [5] (Fig. 1). When these compounds are coordinated to transition metal ions with an octahedral geometry, the arylmethyl side donor atoms are aligned facially on the coordination sphere to leave mutually *cis*-disposed two active sites, which are supposed to endow the metal complexes with unique catalytic properties. Thus, asymmetric catalyses of transition metal complexes coordinated with an optically active tripodal tertiary amine ligand should be of potential interest [6]. In fact, *cis*-β complexes possessing the same topological alignment of the ligating atoms but another connectivity for the chelate loops, have been demonstrated to catalyze a variety of characteristic asymmetric reactions in the past a few years [7,8]. In this context, we have been involved in the studies on asymmetric catalyses by octahedral metal complexes with tripodal ligands of {A^(N^B)^A}-type such as bis(2-hydroxybenzyl)-2-picolylamine, which are capable of adopting two different symmetries, either C_1 or C_s, upon coordination (Scheme 1) [9]. The C_1-isomer is of particular note because it is intrinsically chiral at the metal center (*Λ* or *Δ*) and the chirality (*λ* or *δ*) is also induced by the chelate-ring conformation [10], as in the case of *cis*-β complexes [7,8]. Since the isomers in Scheme 1 can be generally all accessible, an effective method to select an

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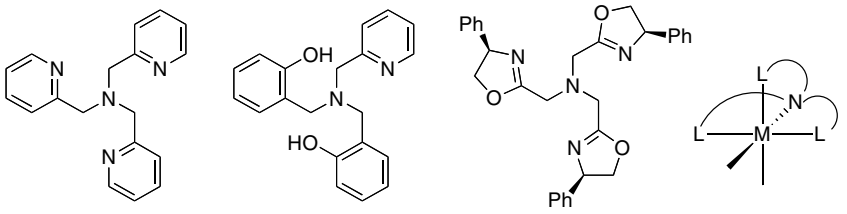
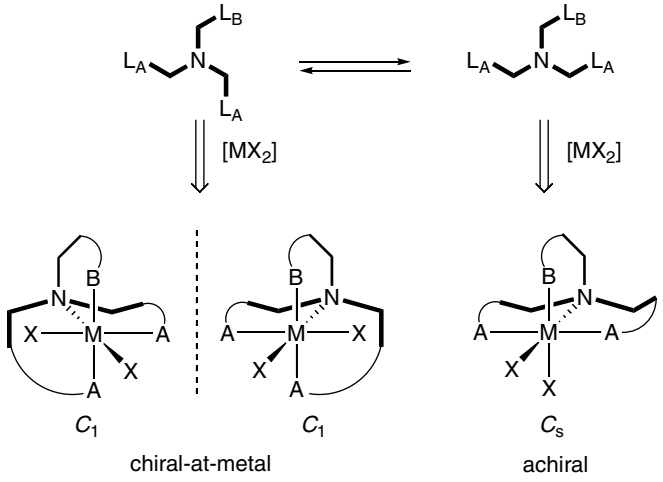


Fig. 1. Representative tetradentate tripodal ligands and an illustration for their facial coordination mode (L = donor group).

enantiomer with the desired C_1-symmetry is required. To this end, chiral 2,6-*trans*-1,2,6-trisubstituted piperidine derivatives should be promising because they should favor a chair-like ring conformation for the piperidine backbone to dispose the substituent at C2(6) in axial and the other one at C6(2) in equatorial positions, leading to the desired *cis*(O^O)- and enantio-selective binding to the metal center (Fig. 2). Hence, we set 2,6-*trans*-bis(2-hydroxyphenyl)-1-(2-pyridylmethyl)amine **1** as a prototypical ligand to meet the criteria described above [11]. It should be noted that the two phenol groups in **1** are homotopic in a dynamical sense owing to the rapid ring flipping of the piperidine and the inversion of the amine nitrogen atom so that **1** would bind to an octahedral metal center with a uniformed chirality and topicity. We were rather surprised to realize that optically active trialkyl amines of {A^(N^B)^A} type had not been sufficiently qualified as chiral tripodal ligands in metal-catalyzed asymmetric organic transformations in contrast to the recent investigations on the C_3-symmetric families [12,13].

To shed light on the structural feature of this unique chiral tripodal ligand **1** and its metal complex, we herein report our studies on its synthesis, characterization, and stereoselective coordination to titanium(IV) ion.



Scheme 1. Two possible symmetries of octahedral metal complex coordinated with tetradentate tripodal ligand of {A^(N^B)^A} type (the connectivity for the ligating atoms is symbolized by ^). Pre-coordinating groups in the ligand are denoted by $L_{A,B}$, their specific ligating atoms by A and B, and ancillary ligands by X.

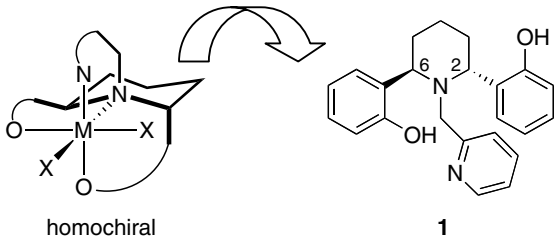
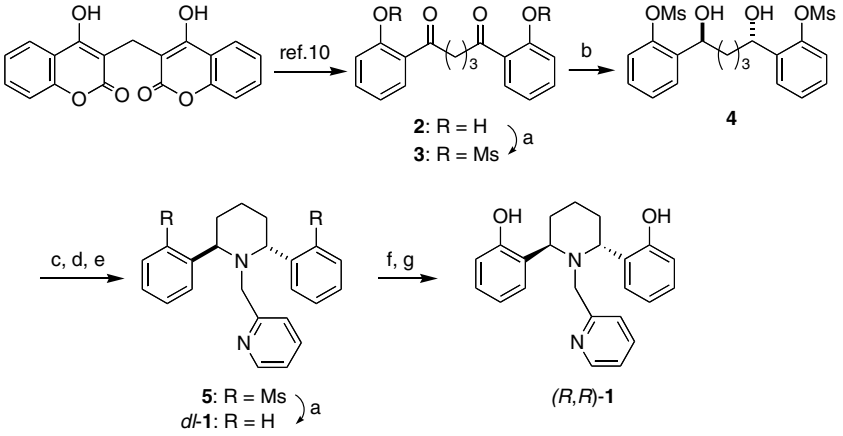


Fig. 2. Optically active tripodal ligand **1** based on 2,6-*trans*-1,2,6-trisubstituted piperidine platform for a *cis*(O^O)- and enantio-selective binding to the metal center.

2. Results and discussion

2.1. Synthesis of (*R*,*R*)-1

Commercially available dicoumarol was converted to 1,5-pentanedione **2** quantitatively by hydrolysis and subsequent decarboxylation according to the literature procedure (Scheme 2) [14]. After the phenol hydroxy groups of **2** were protected as the corresponding methanesulfonates, we first attempted various catalytic asymmetric reduction of **3** and found that (−)-$(Ipc)_2BCl$ gave optically active **4** with excellent enantio- and diastereo-selectivities, and good chemical yield (99% ee, *anti*/*syn* ⩾ 99:1, 68%) [15]. However, the methanesulfonylation of **4** followed by the treatment with 2-picolylamine led to a 1:2 mixture of *dl*- and *meso*-2,6-disubstituted piperidine derivative **5**. The loss of the stereochemistry in this ring formation was inevitably attributed to an S_N1-type displacement of the methanesulfonates at the benzylic positions, which are highly prone to generate a carbocation intermediate. Although this stereochemical problem has not been overcome, we found that the *dl*- and *meso*-forms of **1** were readily separable by column chromatography on silica gel. Thus, we performed $NaBH_4$ reduction of **3** to a *dl*- and *meso*-mixture of diol **4**, the former of which was separated by column chromatography and transformed to **5** as mentioned above followed by alkaline methanolysis of the methanesulfonyl groups to **1** [16]. The diastereomeric mixtures were separated to isolate *dl*-**1** in 66% yield from **3**. Recrystallization of *dl*-**1** from ethyl acetate afforded single crystals suitable for X-ray crystallography, which unambiguously determined its molecular structure (Fig. 3). Interestingly, the short O–N distances, 2.787 Å for the O(1)···N(1) and 2.662 Å for the O(2)···N(2), apparently indicated hydrogen



Scheme 2. Reaction conditions: (a) MsCl (2.1 equiv), Et_3N (2.1 equiv), CH_2Cl_2, rt, 1.5 h (99%); (b) $NaBH_4$ (2.1 equiv), EtOH, rt, then separation of the *dl*- and *meso*-forms by column chromatography on silica gel (50%); (c) MsCl (2.5 equiv), Et_3N (2.5 equiv), CH_2Cl_2, −20 °C, 2.5 h, then 2-picolylamine (9.5 equiv), rt, overnight (70%); (d) KOH, MeOH, 1,4-dioxane, 50 °C (94%); (e) separation of the diastereomers by column chromatography on silica gel; (f) (*R*,*R*)-*O*,*O*′-dibenzoyltartric acid (1 equiv), AcOEt, recrystallization; (g) satd. $NaHCO_3$, AcOEt (46% for two steps).

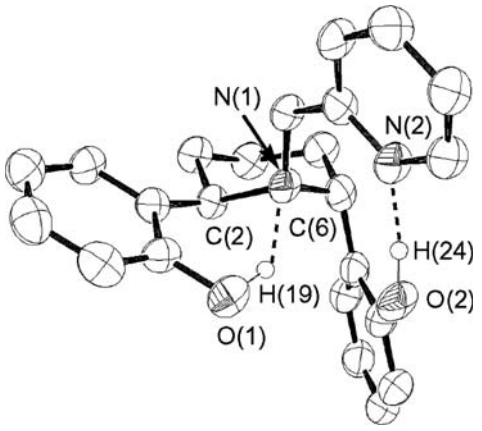
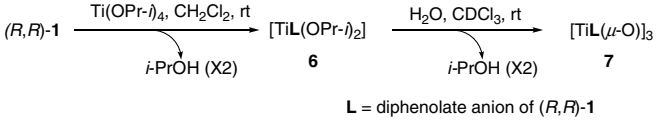


Fig. 3. An ORTEP diagram for the X-ray structure of *dl*-**1** with thermal ellipsoids at 50% probability. The hydrogen atoms except for those at O(1) and O(2) are omitted for clarity. The hydrogen bonding interactions between the phenolic hydroxyls and the amine nitrogen atoms are indicated by dashed lines.

bonding interaction between the phenolic hydroxyls and the amine nitrogen atoms to create a chiral concave sphere around the $N_{piperidine}$ [17]. Finally, the optical resolution of *dl*-**1** was performed by its derivation to a 1:1 salt with (*R*,*R*)-*O*,*O*′-dibenzoyltartaric acid and recrystallization of the diastereomeric salt from ethyl acetate. The absolute configuration of **1** thus obtained was determined to be (2*R*,6*R*) by refinement of the Flack parameter of its tris(μ-oxo)trititanium complex (*vide infra*).

2.2. Synthesis and structure of the titanium(IV) complexes of *1*

With (*R*,*R*)-**1** in hand, we next examined the synthesis and characterization of its titanium(IV) complex to gain some insights into the stereoselectivity in the complexation of (*R*,*R*)-**1** with transition metal ions. Protonolysis of Ti(OPr-*i*)$_4$ with (*R*,*R*)-**1** proceeded quantitatively in CH_2Cl_2 at room temperature to produce an octahedral titanium complex [Ti**L**(OPr-*i*)$_2$] {**L** = diphenolato anion of (*R*,*R*)-**1**} (**6**) as was evident by ^{1}H NMR analysis (Scheme 3). Interestingly, **6** was found to slowly undertake further protonolysis with H_2O in $CDCl_3$ to grow single crystals of tris(μ-oxo)trititanium(IV,IV,IV)complex [Ti_3**L**$_3$(μ-O)$_3$]·4$CDCl_3$ (**7**), whose virtually C_3-symmetric structure was unequivocally evaluated by X-ray crystallography as shown in Fig. 4a. Additionally, refinement of the flack parameter of **7** established its absolute configuration to be (2*R*,6*R*) for the ligand part. Each Ti(IV) center adopts a distorted octahedral geometry surrounded by the $N_{piperidine}$, the $N_{pyridine}$, and the two $O_{phenolato}$ of (*R*,*R*)-**1** and the two μ-O atoms (Fig. 5a, Table 1). One of the most striking aspects noted in the crystal structure of **7** is that (*R*,*R*)-**1** in fact adopts a *cis*($O_{phenolato}$^$O_{phenolato}$) coordination to render the metal center chiral (*A*, Fig. 5b). Furthermore, it was also indicated that the two N^O chelate rings in the ligand favored λ chiral conformation upon coordination (Fig. 5c). These stereochemical regulations are mainly attained by the fact that the piperidine backbone of (*R*,*R*)-**1** is fixed at a chair conformation to discreetly locate the *N*-pyridylmethyl and one of the phenolato groups in axial, and the other one in equatorial positions, which is supposed to strongly direct the $N_{piperidine}$ and one $O_{phenolato}$ in the equatorial coordination plane in a *cis*-fashion and the $N_{pyridine}$ and the other $O_{phenolato}$ in either apical site, respectively (Fig. 5a). The analogous achiral tripodal ligands to (*R*,*R*)-**1** have been demonstrated to adopt either C_1{*cis*($O_{phenolato}$–$O_{phenolato}$)}- [4g,19] or C_s{*trans*-($O_{phenolato}$–$O_{phenolto}$)}-symmetry [4a,4e,19c,19f,20] upon



Scheme 3. Successive protonolysis of Ti(OPr-*i*) with (*R*,*R*)-**1** and H_2O.

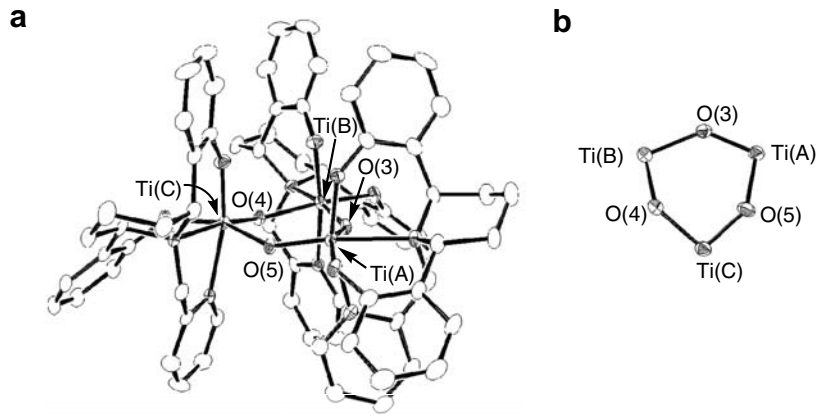


Fig. 4. (a) An ORTEP diagram for the X-ray structure of **7** and (b) its $[Ti_3(\mu\text{-}O)_3]$ ring core with thermal ellipsoids at 30% probability. Hydrogen atoms and the solvates ($CDCl_3$) are omitted for clarity.

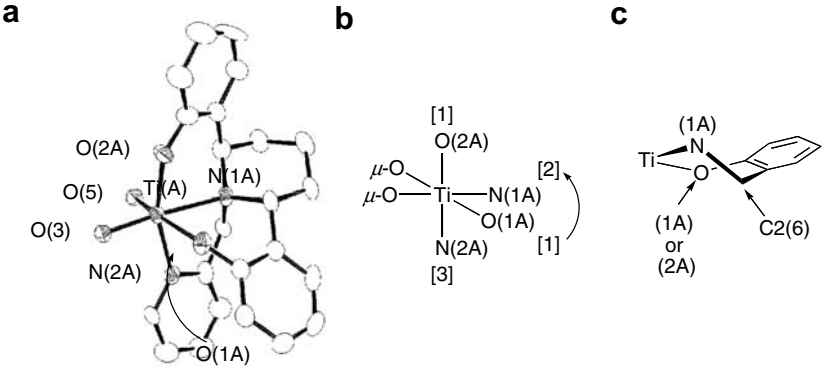


Fig. 5. (a) An ORTEP diagram for the mono nuclear unit of **7** with thermal ellipsoids at 50% probability, (b) a schematic representation for an anticlockwise (*A*) sense of the steering-wheel defined by the priority rankings of the ligating atoms in the equatorial plane viewed from the O(2A) side [10,18], and (c) an illustration for the chiral λ conformation induced at the Ti(N^O) chelate ring. The numbers in the bracket in (b) stand for the priority rankings of the ligating atoms.

Table 1
Selected bond lengths (Å) and angles (°) in **7**

$[Ti(A)\mathbf{L}(\mu\text{-}O_2)]$ part		$[Ti(B)\mathbf{L}(\mu\text{-}O_2)]$ part		$[Ti(C)\mathbf{L}(\mu\text{-}O_2)]$ part	
Ti(A)–N(1)	2.398(5)	Ti(B)–N(1B)	2.370(5)	Ti(C)–N(1C)	2.393(5)
Ti(A)–N(2)	2.187(5)	Ti(B)–N(2B)	2.209(5)	Ti(C)–N(2C)	2.171(5)
Ti(A)–O(1)	1.962(4)	Ti(B)–O(1B)	1.937(4)	Ti(C)–O(1C)	1.931(4)
Ti(A)–O(2)	1.854(4)	Ti(B)–O(2B)	1.875(4)	Ti(C)–O(2C)	1.859(4)
Ti(A)–O(3)	1.761(4)	Ti(B)–O(3)	1.758(4)	Ti(C)–O(4)	1.769(4)
Ti(A)–O(5)	1.916(4)	Ti(B)–O(4)	1.897(4)	Ti(C)–O(5)	1.945(4)
∠N(1)TiN(2)	76.52(19)	∠N(1)TiN(2)	93.55(19)	∠N(1)TiN(2)	74.61(19)
∠N(1)TiO(1)	81.68(18)	∠N(1)TiO(1)	83.26(18)	∠N(1)TiO(1)	80.9(2)
∠N(1)TiO(2)	83.71(19)	∠N(1)TiO(2)	83.11(19)	∠N(1)TiO(2)	85.8(2)
∠N(1)TiO(5)	80.99(18)	∠N(1)TiO(3)	80.83(18)	∠N(1)TiO(5)	82.29(18)
∠O(1)TiO(3)	99.73(19)	∠O(1)TiO(4)	97.44(19)	∠O(1)TiO(5)	96.4(2)
∠O(3)TiO(5)	97.64(18)	∠O(3)TiO(4)	96.75(19)	∠O(4)TiO(5)	98.12(19)
∠N(1)TiO(3)	172.86(18)	∠N(1)TiO(4)	172.73(19)	∠N(1)TiO(5)	168.85(19)
∠N(2)TiO(2)	160.2(2)	∠N(2)TiO(2)	159.1(2)	∠N(2)TiO(2)	160.4(2)
∠O(1)TiO(5)	156.13(19)	∠O(1)TiO(3)	159.56(18)	∠O(1)TiO(4)	160.0(2)

coordination to transition metal ions depending on natures of the central metals and the ancillary ligating atoms (Scheme 1). The survey on the X-ray structures in the Cambridge Structural Database (CSD) demonstrated that the former C_1-complexes possessed the same relative stereochemical relationship ($\lambda\delta$,*AC*) between the chiralities for the ligand conformation and at the metal center, respectively [4g,19]. However, to our best knowledge, (*R*,*R*)-**1** is

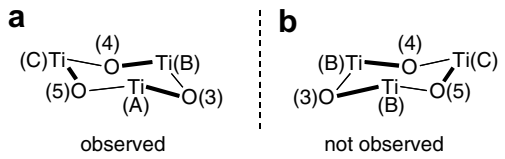


Fig. 6. (a) A schematic representation of the six-membered chair-like conformation of tris(μ-oxo)trititainium core structure with a C_3-symmetry in **7** and (b) a mirror image, which is not superimposable on the original one in (a). The longer Ti–O bond in *trans* to the $O_{phenolato}$ is shown in a bold line and the shorter one in *cis* to the $N_{piperidine}$ in a solid line.

the first enantio- and *cis*($O_{phenolato}$–$O_{phenolato}$)-selective chiral tripodal ligand of {A^(N^B)^A} type in the formation of an octahedral complex.

Another characteristic point of view in the crystal structure of **7** is the Ti and the μ-O atoms are deviated up and down by 0.46 Å and 0.37 Å on average, respectively, from the basal mean plane defined by the rest two Ti and two μ-O atoms to constitute a very shallow six-membered chair-like conformation for the (Ti-μ-O)$_3$ ring (Fig. 6). The analogous tris(μ-oxo)trititanium complexes have been synthesized before predominantly with cyclopentadienyl anions and its derivatives as supporting ligands [21]. However, it should be noted that, in contrast to these precedents, the two μ-O atoms are unequivalent and the Ti-μ-O bond in *trans* to the $O_{phenolato}$ atom is apparently longer than the one in *trans* to the $N_{piperidine}$ atom in a reflection of a stronger *trans* influence of the former ligating atom than the latter one on titanium(IV) ion [19e]. Accordingly, the two different Ti-μ-O bonds in length are alternately aligned in the (Ti-μ-O)$_3$ cycle in **7** to induce a chiral conformation with an almost C_3-symmetry (Fig. 6). This stereochemical outcome is also ascribed to the characteristic chiral topology of (*R*,*R*)-**1**.

In conjunction with great success in asymmetric oxidation of sulfides catalyzed by chiral Ti(salen) complex with a *cis*-β geometry [22], we examined the same reactions with mononuclear complex **6**. In a preliminary study, **6** (5 mol %) was demonstrated to catalyze asymmetric oxidation of methyl phenyl sulfide using hydrogen peroxide or its inclusion compound in urea (UHP) as a terminal oxidant, albeit with an insufficient level of chemo- and enantio-selectivities, and chemical yield (with H_2O_2: 53% yield, sulfoxide/sulfone = 6.9/1, 12% ee for sulfoxide; with UHP: 66% yield, sulfoxide/sulfone = 1.4/1, 40% ee for sulfoxide). Under the conditions, **6** underwent protonolysis to **7** that was proven to be catalytically inactive in a separate reaction, which should account for the low yielding in the sulfoxidation.

3. Conclusion

In summary, we synthesized a new chiral tetradentate tripodal ligand (*R*,*R*)-**1** of {O^(N^N)^O}-type characterized by 2,6-*trans*-1,2,6-trisubstituted piperidine scaffold appended with pyridine and phenol groups. Its X-ray crystallography disclosed that (*R*,*R*)-**1** formed a unique asymmetric concave site, which might show a unique organocatalysis [17]. It was demonstrated that (*R*,*R*)-**1** reacted with Ti(OPr-*i*)$_4$ to form primarily an octahedral monomeric complex [Ti**L**(OPr-*i*)$_2$] (**6**) quantitatively as evaluated by ^{1}H NMR analysis. In a preliminary study, **6** was demonstrated to catalyze asymmetric oxidation of methyl phenyl sulfide using hydrogen peroxide or its inclusion compound in urea (UHP) as a terminal oxidant, though the chemical yield and the enantioselectivity were both insufficient. The insufficient catalytic turnover number of **6** was in a large part attributed to its gradual protonolysis with H_2O to a tris(μ-oxo)trititanium(IV,IV,IV) complex [Ti$_3$**L**$_3$(μ-O)$_3$], which was shown to be catalytically inactive. The unique virtually C_3-symmetric trinuclear structure of **7**, where each titanium atom is coordinated with (*R*,*R*)-**1** in a tripodal fashion, was unambiguously determined by X-ray crystallography and its absolute configuration was defined by refinement of the flack parameter. Notably, (*R*,*R*)-**1** induced unified multiple chiralities at the metal center (*A*), the chelate N^O rings (*λ*), and the six-membered non-planner chair-like (Ti-μ-O)$_3$ cycle upon coordination. These configurations are principally regulated by the stereogenic centers on the ligand and a chair conformation of the piperidine skeleton, which unequivocally locates one phenolato group in axial and the other in equatorial positions. The difference in the *trans* influences of the tertiary amine nitrogen and the phenolato oxygen atoms, which unequally affect the Ti-μ-O bond lengths in *trans* to each atom, is also a key factor to render the six-membered chair-like conformation of the (Ti-μ-O)$_3$ cycle C_3-symmetric (chiral), biased from C_{3h}-symmetry (achiral) like cyclohexane. Further studies on asymmetric catalyses by transition metal complexes of (*R*,*R*)-**1** and its derivatives are currently under way in our laboratory.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded at 400 MHz on a JEOL JNM-AL-400 instrument. IR spectra were obtained with a SHIMADZU FTIR-8400 instrument. Optical rotations were measured with a JASCO P-1020 polarimeter. Column chromatography was conducted on silica gel 60N (spherical, neutral), 63–210 μm, available from Kanto Chemical Co. (Japan) and preparative thin-layer chromatography was performed on 0.5 nm × 20 cm × 20 cm E. Merck silica gel plate (60 F-254). Enantiomeric excesses were determined by HPLC (high performance liquid chromatography) analysis using SHIMADZU LC-10AT-VP equipped with an appropriate optically active column, as described in the footnotes of the corresponding tables. Anhydrous organic solvents were purchased from Kanto Chemical Co. (Japan) and used as received. Cyclic *meso* anhydrides **8** and **11** were available from Aldrich and **9** [23] and **10** [24] were prepared according to the literature procedures.

4.2. Synthesis of (*R,R*)-**1**

4.2.1. 1,5-Bis(2-hydroxyphenyl)-1,5-pentanedione (**2**) [14]

Commercially available dicoumarol (8.45 g, 25.1 mmol) was stirred with aq. KOH (20%, 200 mL) at reflux for 4 h. The reaction mixture was neutralized with conc. HCl (60 mL) and extracted with AcOEt (3 × 200 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated to dryness in vacuo to give **2** (7.0 g, 98%). The crude product was used in the next reaction without further purification. ^{1}H NMR (400 MHz): δ 12.27 (s, 2H), 7.80 (dd, $J = 1.5$ and 8.1 Hz, 2H), 7.47 (ddd, $J = 1.5$, 7.1, and 8.4 Hz, 2H), 6.99 (dd, $J = 1.0$ and 8.4 Hz, 2H), 6.91 (ddd, $J = 1.0$, 8.1, and 8.4 Hz, 2H), 3.16 (t, $J = 7.0$ Hz, 4H), 2.22 (qt, $J = 7.0$ Hz, 2H).

4.2.2. 1,5-Bis(2-methanesulfonyloxyphenyl)-1,5-pentanedione (**3**)

To a solution of **2** (70.0 g, 246 mmol) in anhydrous CH_2Cl_2 (600 mL) were added Et_3N (72.0 mL, 517 mmol) and MsCl (40.0 mL, 517 mmol) and the mixture was stirred at room temperature for 1.5 h under nitrogen atmosphere. The volatiles were evaporated and the resulting residue was partitioned into AcOEt (600 mL) and H_2O (300 mL). The two phases were separated and the aqueous layer was extracted with AcOEt (2 × 600 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and evaporated to give **3** as crystals (107 g, 98.7%). The product was used for the next reaction without further purification. The physical properties were collected for a sample purified by TLC (hexane/AcOEt 4:1). Mp 68–69 °C. ^{1}H NMR (400 MHz): δ 7.71 (dd, $J = 1.1$ and 7.7 Hz, 2H), 7.54 (ddd, $J = 1.1$, 8.3, and 8.8 Hz, 2H), 7.43 (d, $J = 8.8$ Hz, 2H), 7.40 (ddd, $J = 1.1$, 7.7, and 8.3 Hz, 2H), 3.24 (s, 6H), 3.08 (t, $J = 6.9$ Hz, 4H), 2.14 (qt, $J = 6.9$ Hz, 4H). IR (KBr): 3074, 3044, 3024, 3009, 2959, 2941, 2893, 2882, 2866, 1697, 1603, 1483, 1442, 1421, 1406, 1366, 1333, 1315, 1290, 1227, 1188, 1151, 1113, 1099, 991, 972, 881, 860, 800, 787, 748, 718, 698, 646, 604, 577, 536, 513 cm^{-1}. Anal. Calc. for $C_{19}H_{20}O_8S_2$: C, 51.81; H, 4.58. Found: C, 51.73; H, 4.59%.

4.2.3. (1RS,5SR)-1,5-Bis(2-methanesulfonyloxyphenyl)-1,5-pentanediol (**4**)

To a solution of **3** (107 g, 243 mmol) in dist. EtOH (1 L) at 0 °C was added $NaBH_4$ (20.0 g, 490 mmol) and the mixture was stirred for 2 h at room temperature. The reaction was quenched with conc. HCl (50 mL) followed by extraction with $CHCl_3$ (3 × 1 L). The combined organic layer was washed with brine, dried over Na_2SO_4, and evaporated to give the crude product with a 1:1 ratio of *dl*- and *meso*-forms. The residue was purified twice by column chromatography (SiO_2, hexane/AcOEt/acetic acid = 4/6/0.1) to obtain *dl*-**4** (53.6 g, 50%) as viscous oil. ^{1}H NMR (400 MHz): δ 7.61–7.54 (m, 2H), 7.39–7.24 (m, 6H), 5.04 (m, 2H), 3.24 (s, 6H), 2.43 (br s, 2H), 1.94 and 1.79 (ABm, 4H), 1.52 (m, 2H). IR (KBr): 3404, 3022, 2948, 2365, 1487, 1450, 1362, 1342, 1184, 1151, 1074, 1065, 976, 925, 878, 849, 785, 775, 525 cm^{-1}. Anal. Calc. for $C_{19}H_{24}O_8S_2$: C, 51.34; H, 5.44. Found: C, 51.36; H, 5.44%.

4.2.4. (−)-1,5-anti-Bis(2-methanesulfonyloxyphenyl)-1,5-pentanediol (**4**)

To a round bottomed flask containing $(Ipc)_2BCl$ (8.0 g, 25 mmol) and **2** (5.2 g, 12 mmol) immersed in a cooling bath at −78 °C (methanol–dry ice), was slowly added anhydrous THF (60 mL) under nitrogen atmosphere. The mixture was stirred at the temperature for 2 h and additional 15 h at room temperature. After cooled to 0 °C, the reaction mixture was treated with a suspension of bis(hydroxyethyl)amine (2.88 mL, 27.4 mmol) in anhydrous Et_2O (60 mL) and then allowed to warm to room temperature with stirring overnight. The resulting white precipitates were removed by filtration through a pad of Celite and the filtrate was evaporated. The residue (*anti*/*syn* ⩾ 99:1, >99% ee) was subjected to column chromatography on silica gel (hexane/AcOEt/acetic acid = 4/6/0.1) to obtain **4** (3.6 g, 69%). The enantiomeric excess was determined by HPLC analysis using an optically active column (DAICEL CHIRALCELL OD-H, hexane/2-propanol = 80/20, 0.5 mL/min). $[\alpha]_D^{23}$ −61.2 (*c* 0.1, EtOH). Mp 104–105 °C.

4.2.5. (2RS,6RS)-2,6-Bis(2-hydroxyphenyl)-1-pyridylmethylpiperadine (*dl*-**1**)

To a solution of MsCl (8.70 mL, 113 mmol) in CH_2Cl_2 (150 mL) at −20 °C was dropwise added a solution of **4** (20.0 g, 45 mmol) and Et_3N (15.7 mL, 113 mmol) in anhydrous CH_2Cl_2 (150 mL) under nitrogen atmosphere. The mixture had been stirred at the temperature for 2.5 h before 2-picolylamine (44.1 mL, 428 mmol) was loaded and then was allowed to warm to room temperature with stirring overnight. The solvent was evaporated in vacuo and the residue was partitioned into AcOEt (300 mL) and H_2O (200 mL). After phase separation, the aqueous layer was extracted with AcOEt (2 × 300 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel (hexane/AcOEt = 4/6) to give a 1:2 mixture of *dl*- and *meso*-**5** (16.3 g, 70.1%) as colorless oil. Further purification by column chromatography under the same conditions described above raised the ratio of *dl*- and *meso*-isomers up to 69:31 (8.0 g, 34%). During this procedure, *dl*- and *meso*-**5** were partially separated. ^{1}H NMR (400 MHz): *dl*-**5**: δ 8.37 (d, $J = 4.9$ Hz, 1H), 7.91–7.89 (m, 2H), 7.63 (ddd, $J = 1.7$, 7.5, and 7.6 Hz, 1H), 7.43 (br d, $J = 7.6$ Hz, 1H), 7.43–7.23 (m, 6H), 7.05 (dd, $J = 4.9$ and 7.5 Hz, 1H), 4.89 (dd, $J = 4.9$ and 6.4 Hz, 2H), 3.73 and 3.52 (ABq, $J = 6.2$ Hz, 2H), 2.93 (s, 6H), 2.16 and 1.86 (ABm, 4H), 1.73 (m, 2H). *meso*-**5**: δ 8.22 (br d, 1H), 7.83 (br d, $J = 6.8$ Hz, 2H), 7.40–7.25 (br dd, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 2.4$ Hz, 1H), 7.20–7.12 (m, 4H), 6.88 (br dd,

$J = 5.2$ and 7.6 Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 4.26 (br d, $J = 8.8$ Hz, 2H), 3.54 (s, 2H), 3.25 (s, 6H), 1.97 and 1.85 (ABm, 2H), 1.75-1.52 (m, 2H). To a solution of a 69:31 mixture of *dl*- and *meso*-**5** (8.00 g, 15.5 mmol)in MeOH (300 mL) and 1,4-dioxane (75 mL) was added aq. KOH (3 M, 300 mL) and the mixture was stirred at 50 °C overnight. The reaction mixture was neutralized with conc. HCl and extracted with AcOEt (3 × 600 mL). The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was chromatographed on silica gel with a 4:1 mixture of hexane and AcOEt as eluent to afford *dl*-**1** (3.6 g, 64%) as colorless crystals and *meso*-**1** (1.6 g, 30%) as white powder. Recrystallization of *dl*-**1** from AcOEt gave single crystals of suitable seize, one of which was submitted to X-ray analysis to define its relative stereochemistry. *dl*-**1**: Mp 205–206 °C.

4.2.6. (2*R*,6*R*)-2,6-Bis(2-hydroxyphenyl)-1-pyridylmethylpiperadine {(*R*,*R*)-**1**}

A mixture of *dl*-**1** (1.20 g, 3.30 mmol) and (*R*,*R*)-*O*,*O*′-dibenzoyltartaric acid (1.19 g, 3.30 mmol) was dissolved in AcOEt (600 mL) and the solution was allowed to stand at room temperature overnight. The salt precipitated was collected by suction filtration and dissolved in a two-phase mixture of AcOEt (300 mL) and satd. $NaHCO_3$ (200 mL). The organic layer was evaporated to afford an enantio-enriched free base of **1** (650 mg, 80% ee), which was recrystallized from AcOEt (200 mL) to obtain optically pure **1** (550 mg, 46%). $[\alpha]_D^{25}$ +78.8 (*c* 0.1, $CHCl_3$). Mp 205–206 °C. ^{1}H NMR (400 MHz): δ 8.62 (d, $J = 5.1$ Hz, 1H), 7.65 (ddd, $J = 1.7$, 7.6, and 7.8 Hz, 1H), 7.52–6.50 (br s, 6H) 7.23 (dd, $J = 5.2$ and 7.2 Hz, 1H), 7.05 (d, $J = 8.0$ Hz, 1H), 6.82 (dd, $J = 7.2$ and 8.6 Hz, 2H), 4.64–4.22 (br s, 2H), 4.28 and 3.96 (ABq, $J = 17.6$ Hz, 2H), 2.45–1.80 (br m, 6H). IR (KBr): 3038, 2941, 2868, 1599, 1578, 1585, 1487, 1375, 1354, 1277, 1236, 1204, 1184, 1153, 1097, 1082, 1045, 1011, 972, 926, 847, 752 cm^{-1}. Anal. Calc. for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77. Found: C, 76.46; H, 6.73; N, 7.74%.

4.3. Preparation of titanium(IV) complexes of (*R*,*R*)-**1**

4.3.1. [Ti**L**(O^iPr)$_2$] (**L** = diphenolato anion of (*R*,*R*)-**1**) (**6**)

To a solution of (*R*,*R*)-**1** (36 mg, 0.10 mmol) in anhydrous CH_2Cl_2 (1 mL) was added $Ti(O^iPr)_4$ (30 μL, 0.10 mmol) and the mixture was stirred at room temperature for 1 h under nitrogen atmosphere. The solvent was evaporated in vacuo to dryness to give **6** (52 mg, quantitative) as yellow solid. ^{1}H NMR (400 MHz): δ 9.29 (br d, $J = 8.0$ Hz, 1H), 7.77 (dd, $J = 7.6$ and 8.0 Hz, 1H), 7.43–7.32 (m, 2H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.16 (dd, $J = 7.2$ and 7.6 Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 1H), 7.03 (dd, $J = 6.8$ and 8.0 Hz, 1H), 6.76 (d, $J = 7.6$ Hz, 1H), 6.71–6.64 (m, 3H), 5.08 (br m, 1H), 4.62 and 4.34 (ABq, $J = 14.8$ Hz, 2H), 4.46 (d, $J = 9.9$ Hz, 1H), 3.82 (d, $J = 4.8$ Hz, 1H), 3.72 (br m, 1H), 2.56–2.27 (br m, 2H), 2.18–1.96 (br m, 2H), 182–1.52 (br m, 2H), 1.48 (d, $J = 6.0$ Hz, 3H), 1.45 (d, $J = 6.0$ Hz, 3H), 0.48 (d, $J = 6.0$ Hz, 3H), 0.38 (d, $J = 6.0$ Hz, 3H).

4.3.2. [Ti_3**L**$_3$(μ-O)$_3$]

Yellow single crystals of $[Ti_3\mathbf{L}_3(\mu\text{-}O)_3] \cdot 4CDCl_3$ (**7**) suitable for X-ray crystallography grew up from a solution of **6** in $CDCl_3$ upon standing at room temperature. IR (KBr): 3423, 3059, 2951, 2868, 1593, 1481, 1447, 1304, 1283, 1153, 1111, 1047, 1030, 922, 800, 770, 735, 660, 606 cm^{-1}. Anal. Calc. for $C_{69}H_{66}N_6O_9Ti_3 \cdot 0.6CDCl_3$: C, 62.42; H, 5.06; N, 6.28. Found: C, 62.40; H, 5.23; N, 6.47%. This compound was hardly dissolved in common organic solvents so that spectroscopic analyses conducted for the solution of **7** were not applied.

4.4. X-ray crystallographic data for *dl*-**1**

$C_{23}H_{24}N_2O_2$, $M = 360.45$, monoclinic, space group $P2_1/n$, $a = 14.2686(10)$ Å, $b = 7.8428(6)$ Å, $c = 16.4607(16)$ Å, $\beta = 94.007(4)°$, $V = 1837.5(3)$ Å^3, $T = -90$ °C, $Z = 4$, $D_c = 0.1303$ g/cm^3, μ(Mo-Kα) = 0.834 cm^{-1}, $R_1 = 0.0798$ [$I > 2\sigma I$], $Rw_2 = 0.2152$ (all data) for 4152 reflections and 247 variables, GOF = 0.928, residual electron density 0.30/−0.27 e Å^{-3}, programs: SIR97 [25] and SHELXL-97 [26] linked to CrystalStructure [27,28] crystallographic software package. The ORTEP diagram in Fig. 3 was drawn by Ortep-3 for Windows [29]. Full listings of the atomic coordinates, bond lengths and angles have been deposited with Cambridge Crystallographic Data as supplementary publication no. CCDC 603209.

4.5. X-ray crystallographic data for **7**

$C_{70}H_{66}D_4N_6O_9Ti_3Cl_{12}$, $M = 1928.26$, monoclinic, space group $P2_1$, $a = 13.2185(5)$ Å, $b = 21.5572(9)$ Å, $c = 13.7694(5)$ Å, $\beta = 94.3930(8)°$, $V = 3912.1(3)$ Å^3, $T = -90$ °C, $Z = 2$, $D_c = 1.450$ g/cm^3, μ(Mo-Kα) = 7.650 cm^{-1}, $R_1 = 0.0803$ [$I > 2\sigma I$], $Rw_2 = 0.1988$ (all data) for 17,153 reflections and 931 variables, GOF = 0.928, residual electron density 0.80/−0.72 e Å^{-3}, Flack parameter = 0.006, programs: SIR97 [25] and SHELXL-97 [26] linked to CrystalStructure [27,28] crystallographic software package. The ORTEP diagram in Fig. 3 was drawn by Ortep-3 for Windows [29]. Full listings of the atomic coordinates, bond lengths and angles have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 603208.

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[17] Accordingly, it is implied that a helical chirality (*C*, clockwise) [30] is induced around the piperidyl nitrogen atom of (*R*,*R*)-**1** and the tertiary amine site is set deep inside the chiral screw created by the three aromatic side arms. This structural feature has prompted us to examine the potentiality of (*R*,*R*)-**1** as a chiral base catalyst in asymmetric methanolytic desymmetrization of cyclic *meso*-anhydrides to hemiesters, demonstrating a good level of enantioselectivities (up to 78% ee) with catalyst loadings unprecedentedly as low as 1 mol% [31].

[18] The view is determined by the ligating atom with the highest priority ranking to the *trans*-ligating atom with a lower priority through the metal center. In order to avoid the inconvenience that the chirality description varies with the priority rankings of the ancillary ligating atoms irrespective to the absolute configuration, herein we take only the ligating atoms in the ligand into account and the μ-O atoms are not concerned to define the configuration at the metal center.

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