

Enantiomerically pure zinc phosphonates based on mixed phosphonic acid–phosphine oxide chiral building blocks

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Received 28th September 2000, Accepted 19th January 2001

First published as an Advance Article on the web 27th February 2001

The coordination chemistry of enantiomerically pure phosphonic acids $\text{H}_2\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)(\text{R})$ [$\text{R} = \text{CH}_3$ and C_2H_5] with zinc is described. The structures of two new optically active layered zinc phosphonates (*R*)- α - $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)(\text{CH}_3))$ and (*R*)- α - $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)(\text{C}_2\text{H}_5))\cdot\text{H}_2\text{O}$ were determined, in which the phosphine oxide is coordinated to zinc. This coordination can be avoided when the synthesis is performed in a slightly acidic medium, as evidenced by the structure of (*R*)- β - $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)(\text{CH}_3))\cdot\text{H}_2\text{O}$.

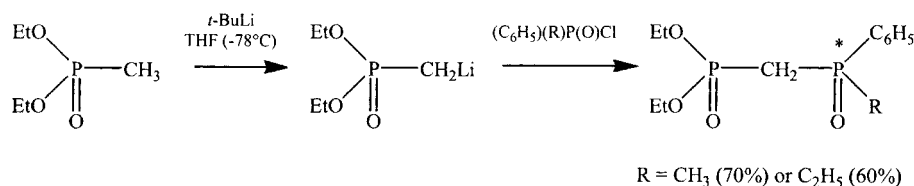
Introduction

The field of metal phosphonates has grown very large,¹ with various examples of applications,² among which catalysis has retained a particular interest for our group.³ Moreover, for a given metal, we and others have shown that the structure and dimensionality of these supramolecular assemblies are strongly dependent on the organic precursor, according to its size and the number and nature of its functional groups.⁴ In a recent communication, we described the first enantiomerically pure phosphonate, showing that even the optical purity of the phosphonic acid precursor can induce changes in the metal/ PO_3 coordination mode in the resulting phosphonates.⁵ In this paper, we fully report the coordination chemistry of phosphonic acids functionalized by enantiomerically pure phosphine oxide groups [$\text{H}_2\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{R})(\text{C}_6\text{H}_5)$; $\text{R} = \text{CH}_3$ (**1**-*R*) or C_2H_5 (**2**-*R*) and **2**-*S*)] and show how the inorganic framework adapts itself to the main features of the organic units. The use of phosphine oxides as crystallization aids is well known and stems from their ability to form strong hydrogen bonds with proton donor organic substrates.⁶ Thus, the preparation of materials incorporating this kind of functional block could potentially lead to liquid chromatography chiral stationary phases⁷ for the resolution of enantiomers of chiral alcohols, amines or α -amino acids. In this context, the coordination of the phosphine oxide must be avoided, and we were interested to know if this was possible in the case of metal phosphonates.

Results

The phosphonic acid $\text{H}_2\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{R})(\text{C}_6\text{H}_5)$ racemates (**1** [$\text{R} = \text{CH}_3$]-**2** [$\text{R} = \text{C}_2\text{H}_5$]) were prepared according to a

modified version of the procedure described by Collignon *et al.*⁸ The key reaction is the condensation of the lithiated anion of diethyl methylphosphonate with the corresponding alkyl-phenylphosphinyl chloride (Scheme 1). The optical resolution of **1** and **2** was performed using quinine or quinidine to give **1**-*R* in 81% yield (based on one of the enantiomers), **2**-*R* in 84% yield and **2**-*S* in 76% yield. These compounds were then reacted with zinc nitrate in water, in Teflon sealed autoclaves at 110 °C under neutral-pH conditions, to yield enantiomerically pure layered phosphonates having similar structures: (*R* or *S*)- α - $\text{Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{R})(\text{C}_6\text{H}_5))\cdot\text{H}_2\text{O}$ [$\text{R} = \text{CH}_3$: α - Zn1 -*R*) (85% yield); $\text{R} = \text{C}_2\text{H}_5$: α - Zn2 -*R*) (87% yield) and α - Zn2 -*S*) (78% yield)]. The structure of α - Zn2 -*R*) was solved by single crystal X-ray diffraction showing a metal/ PO_3 arrangement within the slabs similar to that observed in the previously reported α - Zn1 -*R*)⁵ (*ab* plane; Fig. 1); the zinc atoms are tetrahedrally coordinated with three oxygen atoms from the phosphonate groups and one oxygen atom from the phosphine oxide moiety. In each layer, the zinc atoms are arranged in 12-membered rings, constructed by corner-sharing of alternating ZnO_4 and PO_3C tetrahedra. The phenyl groups are oriented toward the interlayer space, with a basal spacing ($c/2 = 12.65 \text{ \AA}$ [$\text{R} = \text{CH}_3$] and $c = 13.30 \text{ \AA}$ [$\text{R} = \text{C}_2\text{H}_5$]) shorter than the 15–16 Å value generally observed for layered metal phenylphosphonates. This is due to a close-packing of the sheets caused by an unusual interdigitation of the aromatic rings from neighboring slabs (Fig. 2), with probable π - π interactions that contribute to a good stabilization of this two-dimensional arrangement. The lattice water molecules are present between the layers, weakly hydrogen-bonded to phosphonate oxygen atoms, thus explaining the low temperature (55 °C) at which the dehydration takes place. The configuration of the chiral phosphorus atom of the



Scheme 1

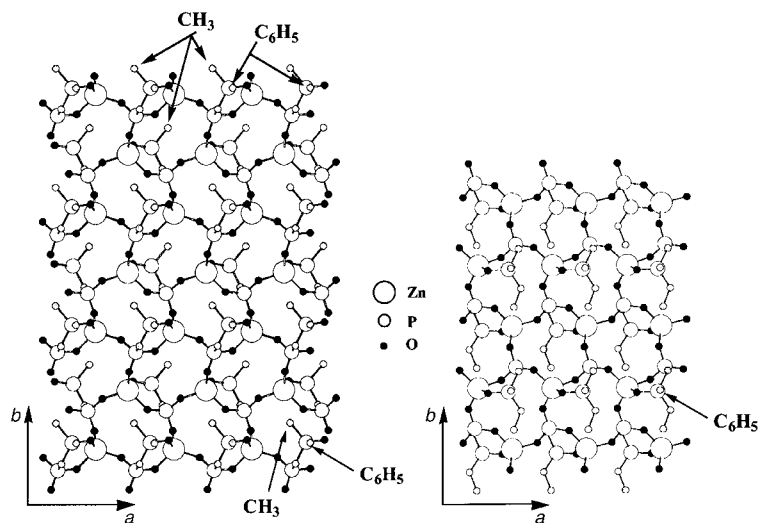


Fig. 1 Schematic representation of a $(R)\text{-}\alpha\text{-Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{R})(\text{C}_6\text{H}_5))\cdot\text{H}_2\text{O}$ [$\text{R}=\text{CH}_3$ (according to ref. 5; left), $\text{R}=\text{C}_2\text{H}_5$ (right)] layer viewed down the c axis.

phosphine oxide group was unambiguously determined to be R (see Fig. 2) by refining the inversion twin ratio, showing that no racemization occurred during the self-assembly of the phosphonate network. In addition, the spectroscopic data of compounds $\alpha\text{-Zn2-(R)}$ and $\alpha\text{-Zn2-(S)}$ were found to be identical (FTIR spectra, ^{31}P CP-MAS NMR spectra, X-ray powder diffraction patterns, TGA curves) and the values of the specific rotation measured for the two compounds were found to be the same with opposite signs ($[\alpha]_{\text{D}}^{20} = \pm 5$ ($c=1$ in 1 M HCl)), thus giving evidence that the two compounds are enantiomers.

It is worthwhile noting that a triclinic space group was found for compound $\alpha\text{-Zn2-(R)}$ whereas $\alpha\text{-Zn1-(R)}$ is an orthorhombic phase; this is probably due to the replacement of the methyl substituent bound to the phosphine oxide by an ethyl chain. This lower symmetry results in the presence of two sets of positions for the $\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5)$ blocks in the unit cell, in agreement with solid state ^{31}P CP-MAS NMR measurements showing four signals for this phase: 7.9 and

10.6 ppm (PO_3), 57.2 and 57.6 (PO). The two P–C–P blocks were easily indexed, using rotational resonance conditions. These experiments have been developed to recover homonuclear dipolar coupling constants from high-resolution NMR experiments conducted with MAS, in systems containing isolated spin pairs. The line shape of the ^{31}P signals changes if the spinning speed is adjusted such that an integer multiple of the spinning speed matches the chemical shift difference between the two coupled phosphorus nuclei (homonuclear coupling due to the short distance between the P atoms in the P–C–P linkage).⁹ Thus two signal pairs were identified: (57.6, 7.9 ppm) and (57.2, 10.6 ppm) (Fig. 3). Moreover, the dehydration of the $(R$ or $S)\text{-}\alpha\text{-Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{R})(\text{C}_6\text{H}_5))\cdot\text{H}_2\text{O}$ series was found to be non-reversible; the structure of the anhydrous form of $\alpha\text{-Zn1-(R)}$, $(R)\text{-}\alpha\text{-Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5))$, solved by single crystal X-ray diffraction, reveals a decrease of the interlayer distance (close to 2 Å), consistent

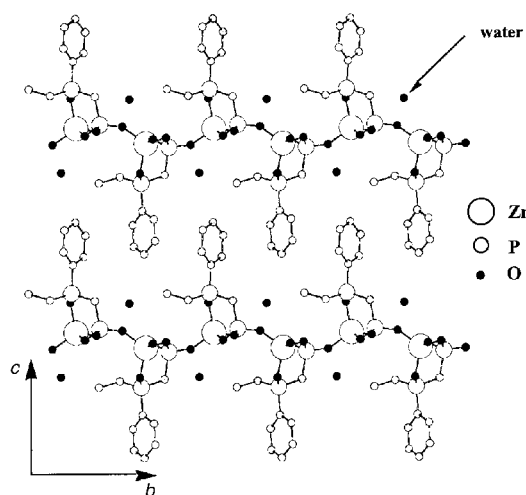


Fig. 2 Schematic representation of the layered arrangement of $(R)\text{-}\alpha\text{-Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5))\cdot\text{H}_2\text{O}$ as seen perpendicular to the a axis. Selected interatomic distances (Å): Zn–O: 1.891(7), 1.898(7), 1.925(7), 1.979(7) Å for Zn(1) and 1.904(7), 1.906(6), 1.928(8), 1.998(7) Å for Zn(2); (phosphonate group) P–O: 1.510(7), 1.516(7), 1.521(8) Å for P(1) and 1.516(7), 1.518(7), 1.508(8) Å for P(2); (phosphine oxide group) P–O: 1.514(8) Å for P(3) and 1.531(8) Å for P(4).

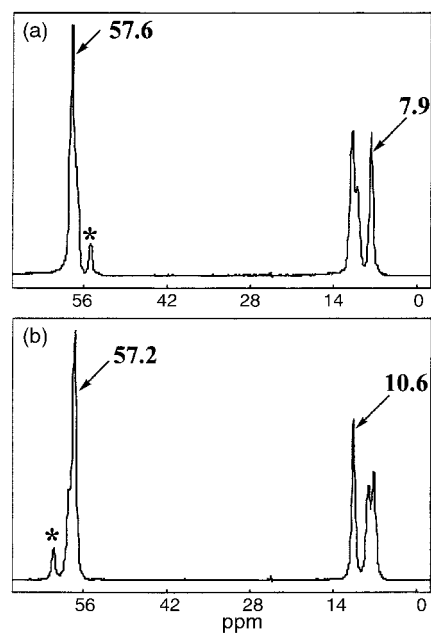


Fig. 3 Experimental ^{31}P MAS NMR spectra of $(R)\text{-}\alpha\text{-Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{C}_2\text{H}_5)(\text{C}_6\text{H}_5))\cdot\text{H}_2\text{O}$, spinning at 7.6 kHz (a) and 8.1 kHz (b), under the condition of rotational resonance ($n=1$) for the signal pairs: [57.2 and 10.6 ppm] (a) and [57.6 and 7.9 ppm] (b). The asterisks denote spinning side bands.

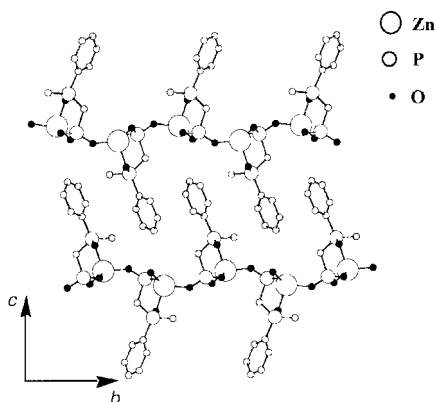


Fig. 4 Schematic representation of the layered arrangement of $(R)\text{-}\alpha\text{-Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5))$ as seen perpendicular to the a axis.

with a markedly higher interdigitation of the phenyl rings (Fig. 4). This leads to a very efficient space filling arrangement, with strong interactions between the aromatic rings that probably tightly hold the layers together. This effect is responsible for a stabilization of the dehydrated form of $\alpha\text{-ZnI-(R)}$, that consequently does not absorb water. As expected, the removal of the non-coordinated water molecule does not modify the metal/ PO_3 arrangement within the layers (Fig. 5).

We have previously shown that the coordinating properties of functional groups (CO_2H , NH_2) present on the phosphonic acid precursor are sensitive to the pH value of the reaction medium: *i.e.*, when the pH is acidic enough, the coordination of these groups to the metal atoms can be avoided.¹⁰ We have checked that this was also true in the case of precursor I-(R) since $(R)\text{-}\beta\text{-Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5))\cdot\text{H}_2\text{O}$ [$\beta\text{-ZnI-(R)}$] was isolated when the synthesis was performed at pH 4. The structure of this compound was solved by single-crystal X-ray diffraction and confirms that the phosphine oxide is not bonded to zinc and is expanding towards the interlayer space (Fig. 6). The metal atoms within the sheets (ab -plane) are octahedrally coordinated by four phosphonate oxygen atoms (leading to a (112) connectivity for the PO_3 groups) and two water molecules that are bridging two different zinc atoms. The structure can thus be described as infinite chains of edge-

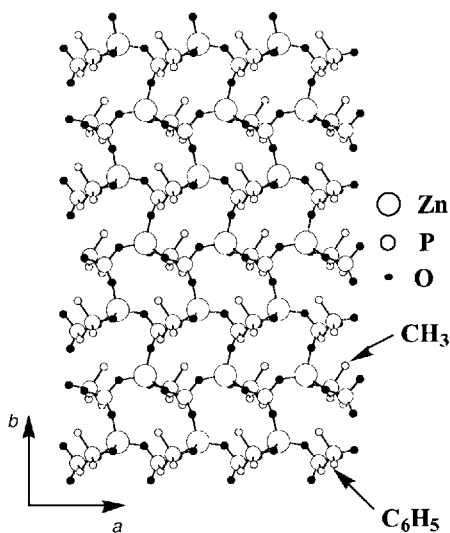


Fig. 5 Schematic representation of a $(R)\text{-}\alpha\text{-Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5))$ layer viewed down the c axis. Selected interatomic distances (\AA): Zn–O: 1.892(2), 1.914(2), 1.939(2), 2.007(2) \AA ; (phosphonate group) P–O: 1.504(2), 1.513(2), 1.517(2) \AA ; (phosphine oxide group) P–O: 1.513(2) \AA .

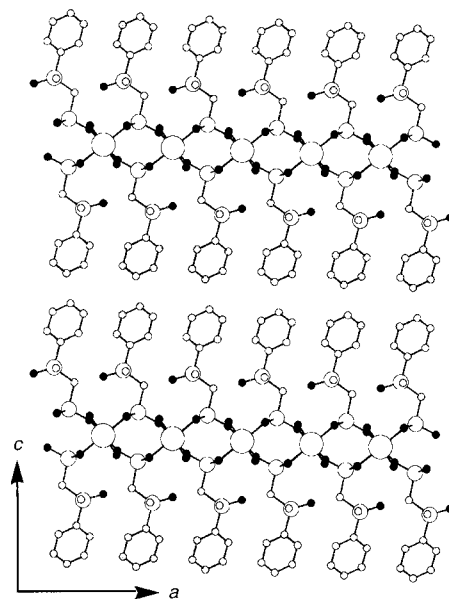


Fig. 6 Schematic representation of the layered arrangement of $(R)\text{-}\beta\text{-Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5))\cdot\text{H}_2\text{O}$ as seen perpendicular to the b axis.

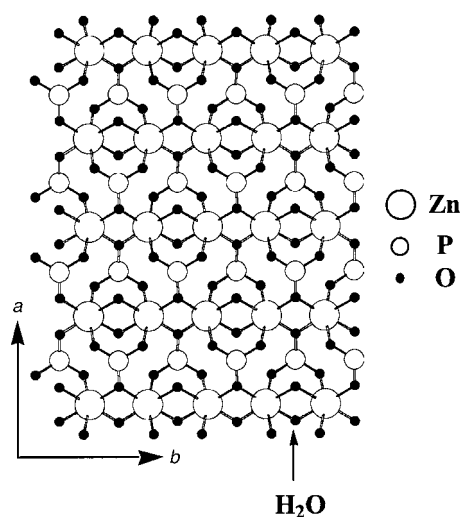


Fig. 7 Schematic representation of a $(R)\text{-}\beta\text{-Zn}(\text{O}_3\text{PCH}_2\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5))\cdot\text{H}_2\text{O}$ layer as seen perpendicular to the c axis. Selected interatomic distances (\AA): Zn–O: 2.025(4) [$\times 2$], 2.051(6) [$\times 2$], 2.229(6) [$\times 2$] \AA for Zn(1) and 2.036(4) [$\times 2$], 2.074(6) [$\times 2$], 2.236(6) [$\times 2$] \AA for Zn(2); (phosphonate group) P–O: 1.511(6), 1.518(7), 1.544(3) \AA ; (phosphine oxide group) P–O: 1.499(4) \AA .

sharing ZnO_6 octahedra running parallel to the b -axis, connected together by the PO_3 moieties to form the 2D inorganic network (Fig. 7). The configuration of the chiral phosphorus center was (R). As the water molecule is coordinated to zinc, the water loss is observed at a higher temperature (150°C) than that observed for $\alpha\text{-ZnI-(R)}$. While the $\text{P}(\text{O})(\text{CH}_3)(\text{C}_6\text{H}_5)$ group is not coordinated, it should be noted however that the metal/ PO_3 arrangement does not correspond to that usually observed in $\text{M}^{\text{II}}(\text{RPO}_3)\cdot\text{H}_2\text{O}$ alkyl- or arylphosphonates;¹¹ this is due to the size of the phosphine oxide moiety that cannot fit this latter structural model, in which the PO_3R groups are closely packed. This gives again evidence of the structure directing role of the organic moiety in the coordination chemistry of phosphonic acids. In addition, these results clearly demonstrate that the two optical antipodes of a chiral metal phosphonate can be selectively prepared. However, if the synthesis is performed at higher temperature

(180 °C), a racemization of the phosphonic acid occurs, leading to racemic phosphonates identical to that obtained when the preparation is carried out using the racemic phosphonic acid as starting material.⁴

Experimental

Materials and methods

All starting materials were purchased from Aldrich Chemical Co. and were used as received. The chemical analyses were performed by the C.N.R.S. Analysis Laboratory (Vernaison). FTIR spectra were obtained on a Bruker Vector22 FT-IR spectrometer with the usual KBr pellet technique. A Perkin-Elmer TGS2 thermogravimetric analyzer was used to obtain TGA thermograms, that were run in an air atmosphere from room temperature to 250 °C at a scan rate of 5 °C min⁻¹. The ¹H and ³¹P NMR spectra recorded in solution were taken on an AC 200 Bruker spectrometer, with tetramethylsilane (trimethylphosphite) as reference. Solid state ³¹P NMR spectra were acquired on a Bruker DSX400 spectrometer operating at 9.4 T, using CP-MAS {¹H}-³¹P excitation, as previously described,¹² with a typical contact time of 1.5 ms and 1 s recycle time. Spectra were simulated using a modified version of the Bruker Winfit program.¹³

Structure determination of α -Zn2-(R)

Data collection was carried out at room temperature with a single crystal approximately 0.3 × 0.08 × 0.08 mm in size on a STOE Imaging Plate Diffraction System,¹⁴ using graphite-monochromatized MoK-L_{2,3} radiation ($\lambda = 0.71073$ Å). Data intensities were corrected for Lorentz-polarization and absorption (Gaussian analytical correction). *P1* was found to be the correct space group, both at the residue factor and the structure coherence level. A starting model was found with the SHELXTL V5.0 direct method program¹⁵ and refined (*F*², all reflections included) with the Jana2000 program.¹⁶ All subsequent calculations were carried out with the JANA2000 program package. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were kept at fixed positions with a common fixed isotropic displacement parameter. At the last stage of the refinement, a secondary extinction coefficient¹⁷ was introduced and the residue factor smoothly converged with *R/R_w* = 0.0365/0.0685 for 2644 reflections with *I* σ (*I*) > 2 [from 3597 collected reflections: *R*(int)_{all} = 0.049] and 305 parameters. The absolute configuration was unambiguously determined by refining the inversion twin fraction *t*(inv) = -0.009(17), which was subsequently fixed to 0.

Crystal data. (*R*)- α -Zn(O₃PCH₂P(O)(C₂H₅)(C₆H₅))·H₂O, triclinic, *P1*; *a* = 5.5106(7), *b* = 8.922(1), *c* = 13.306(2) Å, α = 90.43(2), β = 100.70(2), γ = 90.16(2)°, *V* = 642.8(2) Å³, *Z* = 2, *M* = 329.54, μ = 21.6 cm⁻¹.

Structure determination of the anhydrous form of α -Zn1-(R)

Data collection was carried out as above at room temperature, with a single crystal approximately 0.32 × 0.14 × 0.14 mm in size. *P2₁2₁2₁* was found to be the correct space group. At the last stage of the refinement (same conditions as above), the residue factor smoothly converged with *R/R_w* = 0.0224/0.0418 for 2197 reflections with *I* σ (*I*) > 2 [from 2466 collected reflections: *R*(int)_{all} = 0.040] and 176 parameters. The absolute configuration was unambiguously determined by refining the inversion twin fraction *t*(inv) = -0.006(9), which was subsequently fixed to 0.

Crystal data. (*R*)- α -Zn(O₃PCH₂P(O)(CH₃)(C₆H₅)), orthorhombic, *P2₁2₁2₁*; *a* = 5.5038(3), *b* = 8.9927(6), *c* = 21.187(1) Å, *V* = 1048.6(1) Å³, *Z* = 4; *M* = 297.50; μ = 26.4 cm⁻¹.

Structure determination of β -Zn1-(R)

Data collection was carried out as above (but at 120 K), with a single crystal approximately 0.52 × 0.11 × 0.008 mm in size. *C2* was found to be the correct space group. At the last stage of the refinement (same conditions as above), a secondary extinction coefficient¹⁷ was introduced and the residue factor smoothly converged with *R/R_w* = 0.0356/0.0632 for 1851 independent reflections with *I* σ (*I*) > 2 [from 2553 collected reflections: *R*(int)_{all} = 0.074] and 112 parameters. A disorder in the position of the phenyl rings was observed, according to two main orientations tilted one to another by 90°. The occupation ratio was refined to 0.51 and 0.49 for the two sets of aromatic carbon atoms respectively. The absolute configuration was unambiguously determined by refining the inversion twin fraction *t*(inv) = -0.05(3), which was subsequently fixed to 0.

Crystal data. (*R*)- β -Zn(O₃PCH₂P(O)(CH₃)(C₆H₅))·H₂O, monoclinic, *C2*; *a* = 9.293(2), *b* = 6.2124(7), *c* = 19.321(3) Å, β = 92.68(2), *V* = 1114.2(3) Å³, *Z* = 4; *M* = 315.52, μ = 24.8 cm⁻¹.

CCDC reference numbers 149558–149560. See <http://www.rsc.org/suppdata/jm/b0/b007868i/> for crystallographic data in .cif or other electronic format.

Synthesis of H₂O₃PCH₂P(O)(C₂H₅)(C₆H₅), 2

Ethylphenylphosphinyl chloride was prepared according to the literature by reaction of the sodium salt of ethyl phenylphosphinate with ethyl iodide (73% yield).¹⁸ The resulting ethyl ethylphenylphosphinate was refluxed in thionyl chloride to give the desired product in 85% yield. Then, to a solution of diethyl methylphosphonate¹⁹ (64 mmol) in dry THF (120 mL) under nitrogen at -78 °C was added dropwise 62.5 mmol of *t*-BuLi in hexane. After 15 min ethylphenylphosphinyl chloride was added dropwise, and the solution was slowly allowed to warm to -35 °C in 3 h. Water was then added, and the mixture was extracted with CH₂Cl₂. The extract was dried (MgSO₄) and concentrated under vacuum. The excess of diethyl methylphosphonate was removed under vacuum, using a Kugelrohr apparatus. The remaining oil (the diethyl ester form of **2**) was purified by chromatography on silica gel and an ethanol/ethyl acetate (40 : 60) mixture was used as eluent (70% yield). ¹H-NMR (200 MHz, CDCl₃) δ 1.13 (dt, 3H, PCH₂CH₃, *J*³P-H = 19 Hz, *J*³H-H = 7.5 Hz), 1.16 (t, 3H, OCH₂CH₃, *J*³H-H = 7 Hz), 1.32 (t, 3H, OCH₂CH₃, *J*³H-H = 7 Hz), 2.20 (m, 2H, P-CH₂-CH₃), 2.60 (dd, 2H, P-CH₂-P, *J*²P-H = 14.5 Hz, *J*²P-H = 20.5 Hz), 3.96 (quint., 2H, OCH₂, *J*³P-H = *J*³H-H = 7 Hz), 4.16 (quint., 2H, OCH₂, *J*³P-H = *J*³H-H = 7 Hz), 7.52 (m, 3H, C₆H₅), 7.80 (m, 2H, C₆H₅). ³¹P-NMR (81 MHz, CDCl₃) δ 20.2 (PO₃), 34.9 (PO). This oil was then refluxed in concentrated hydrochloric acid for 2 days. After evaporation of the mixture under reduced pressure, water was added. The aqueous phase was washed twice with ethyl acetate, and then evaporated to give compound **2** in quantitative yield. ¹H-NMR (200 MHz, DMSO) δ 0.85 (dt, 3H, PCH₂CH₃, *J*³P-H = 19 Hz, *J*³H-H = 7.5 Hz), 2.10 (m, 2H, P-CH₂-CH₃), 2.60 (m, 2H, P-CH₂-P), 7.45 (m, 3H, C₆H₅), 7.58 (m, 2H, C₆H₅). ³¹P-NMR (81 MHz, DMSO) δ 14.4 (PO₃), 32.7 (PO).

Resolution of H₂O₃PCH₂P(O)(C₂H₅)(C₆H₅), 2

A solution of racemic H₂O₃PCH₂P(O)(C₂H₅)(C₆H₅) [2 mmol] in 30 ml of hot ethanol was added to the desired chiral base [quinine or quinidine, 3 mmol] dissolved in 15 ml of hot ethanol. The mixture was allowed to stand for 5 days at room temperature, after which the crystals that gradually appeared

were isolated by filtration, corresponding in all cases to a 1 : 1 acid/base complex. Two compounds were thus obtained: **2-(R)**: quinine [84% yield; elemental analysis: Found: P 10.90, C 60.91, H 6.82, N 4.80; calc. for $C_{29}P_2O_6N_2H_{38}$: P 10.82, C 60.83, H 6.69, N 4.89%; $[\alpha]_D^{20} = -149$ ($c = 1$ in 1 M HCl)], **2-(S)**: quinidine [76% yield; elemental analysis: Found: P 10.80, C 60.96, H 6.70, N 4.87; calc. for $C_{29}P_2O_6N_2H_{38}$: P 10.82, C 60.83, H 6.69, N 4.89%; $[\alpha]_D^{20} = +173$ ($c = 1$ in 1 M HCl)]. The complexes (150 mg) were then suspended in 45 ml of water; 2 equivalents of sodium hydroxide were then added and the mixture was stirred for 1 hour. The reaction medium was then extracted twice using dichloromethane, allowing recovery of the chiral base in the organic phase. The pure enantiomeric *R*-form of **2** ($[\alpha]_D^{20} = -5$ ($c = 1$ in 1 M HCl)) from **2-(R)**: quinine and *S*-form of **2** ($[\alpha]_D^{20} = +5$ ($c = 1$ in 1 M HCl)) from **2-(S)**: quinidine respectively were then quantitatively recovered by passing the aqueous phase through DOWEX-50 (H^+ form, eluted with water until neutral) and evaporation. The pure enantiomeric *R*-form of **1** and α -Zn**1-(R)** were prepared as previously described⁵ ($[\alpha]_D^{20} = -18$ ($c = 1$ in 1 M HCl)). The anhydrous form of α -Zn**1-(R)** was obtained by slow heating until 70 °C (1 °C h⁻¹).

Synthesis of (*R*) and (*S*)- α -Zn(O₃PCH₂P(O)(C₂H₅)(C₆H₅))·H₂O [α -Zn**2-(R)** and α -Zn**2-(S)**]

A mixture of zinc nitrate (0.3 mmol), the resolved phosphonic acid **2-(R)** [or **2-(S)**] (0.2 mmol) and 1 M sodium hydroxide (0.4 mmol) in 20 mL water was placed in the PTFE cell of an autoclave that was sealed and kept at 110 °C in a drying oven for 3 days. α -Zn**2-(R)** [or α -Zn**2-(S)**] was obtained as white crystals in 87% yield [or 78%]. Identical spectroscopic data were obtained for the two compounds: IR (KBr, cm⁻¹) 3529 (m), 3482 (m), 1165 (m), 1156 (m), 1126 (s), 1103 (s), 1092 (vs), 1073 (m), 1035 (m), 1027 (m), 1017 (m), 995 (m); TGA room temperature to 300 °C, 5.7% around 55 °C [-H₂O, calculated 5.5%]; $[\alpha]_D^{20} = -5$ ($c = 1$ in 1 M HCl) for α -Zn**2-(R)** and +5 ($c = 1$ in 1 M HCl) for α -Zn**2-(S)**. Elemental analysis for α -Zn**2-(R)**: Found: P 18.92, C 32.90, H 4.24; calc. for $ZnC_9P_2O_4H_{12}$: P 18.79, C 32.80, H 4.28%.

Synthesis of (*R*)- β -Zn(O₃PCH₂P(O)(CH₃)(C₆H₅)) [β -Zn**1-(R)**]

Same procedure as above, except that **1-(R)** (0.2 mmol) and 1 M sodium hydroxide (0.2 mmol) were used instead (yield: 38%). IR (KBr, cm⁻¹) 3300 (br, m), 1162 (s), 1148 (vs), 1127 (s), 1114 (vs), 1077 (s), 1053 (s), 990 (s); TGA room temperature to 300 °C, 5.9% around 55 °C [-H₂O, calculated 5.7%]; $[\alpha]_D^{20} = -18$ ($c = 1$ in 1 M HCl).

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