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Diastereoselective synthesis of C_2-symmetric hexacoordinated phosphate anions (HYPHATs) with predetermined chirality from 1,2-diaryl-ethane-1,2-diols

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Dedicated to Professor François Mathey

Abstract

C_2-symmetric HYPHAT anion (**5**) made of a central phosphorus(V) atom, one hydrobenzoin and two tetracholorocatechol ligands can be simply prepared in high yield as its dimethylammonium salt using a one pot-process and simple commercially available or easily prepared starting materials. The presence of the chiral hydrobenzoin ligands (e.g. *R*,*R*) leads to the formation of diastereomeric anions (Δ,*R*,*R*/Λ,*R*,*R*). A partial control over the configuration of the adduct by the chiral ligands is observed (diastereomeric ratio (d.r.) 75:25 in 5% DMSO–$CHCl_3$). This asymmetric induction can be improved (d.r. up to 90:10) by the introduction of *ortho* bromo substituents on the phenyl rings of the 1,2-diaryl-ethane-1,2-diol ligands.

Keywords: Predetermination of configuration; Hexacoordinated phosphorus; A(1,3) strain; Asymmetric induction

1. Introduction

The octahedral geometry of pentavalent hexacoordinated phosphorus allows the formation of chiral anions—Δ and Λ enantiomers—by complexation of the central phosphorus atom with three identical symmetric bidentate ligands [1,2]. Tris(benzenediolato)phosphate anion **1**, of particular interest for its easy preparation from catechol, PCl_5 and an amine, is unfortunately configurationally labile in solution as an ammonium salt due to an acid-induced racemization mechanism [3]. Recently, we reported that the introduction of electron-withdrawing groups (chlorine atoms) on the aromatic nuclei increases the configurational stability of the resulting tris(tetrachlorobenzenediolato)phosphate(V) derivative or TRISPHAT **2** [4]. This D_3-symmetric anion can be resolved by association with a chiral ammonium cation. It is an efficient nuclear magnetic resonance (NMR) chiral shift, resolving and asymmetric inducing reagent onto organic and organometallic derivatives—with a predilection for octahedral metallo-organic complexes [5].

However, with some chiral C_2-symmetric cations, low NMR shifts and asymmetric inducing properties were recently observed using anion **2** [6]. Assuming that its D_3-symmetry was not adapted for the chiral recognition of such cations, we decided to investigate the synthesis of C_2-symmetric hexacoordinated phosphate anions; our interest being motivated by the overall efficiency of such symmetry in asymmetric reactions or molecular recognition processes [7]. Furthermore, the introduction of a well-chosen C_2-symmetric chiral ligand could permit a diastereoselective synthesis of the resulting anion by predetermination of the configuration [8] around the phosphorus atom (Fig. 1).

However, chiral induction from ligands is, as a general rule, not very efficient for didentate ligands, whereas with ligands of higher denticity, especially those of four, five, and six donor atoms, a complete

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chiral induction can often be observed. In tris(didentate) octahedral complexes, most successful examples of predetermination of chirality have thus been made using three chiral didentate ligands [8,9]. When only one chiral ligand and two achiral didentate ligands are coordinated to a metal center, only sterically demanding ligands lead to measurable effects of chiral induction upon complex formation. Diastereoselectivity remains, however, low in most cases and often depends upon non-covalent interactions [10]. This was also observed in the only example known in the literature—prior to our own studies—of a hexacoordinated phosphate anion bearing a single chiral ligand. Anion **3**, containing (−)-mandelic acid along with two pyrocatechol rings, is configurationally labile and epimerizes in solution to give a 55:45 mixture of diastereomers [3c,11] (Fig. 2).

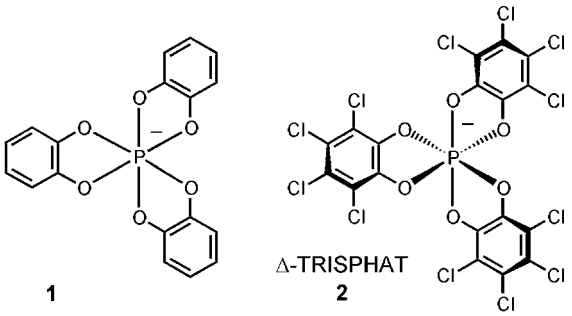


Fig. 1. D_3-symmetric hexacoordinated phosphate anions **1** and **2** (TRISPHAT).

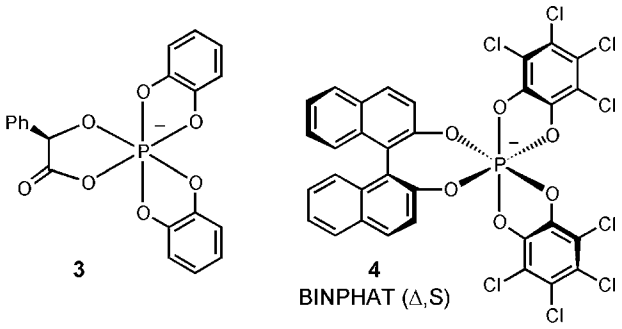


Fig. 2. Hexacoordinated phosphate anions **3** and **4** (BINPHAT) with predetermined configuration.

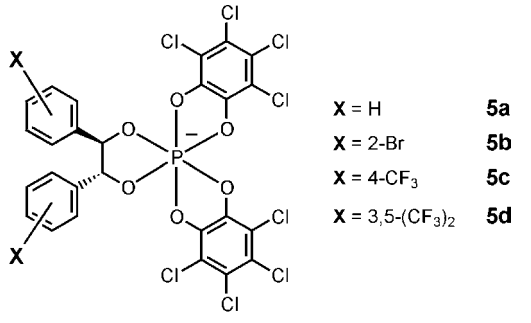


Fig. 3. Phosphate anions **5a**–**5d** containing 1,2-diaryl-ethane-1,2-diol **7a**–**7d** ligands.

Recently, we have shown that chiral C_2-symmetric ligand BINOL ([1,1′]binaphthalenyl-2,2′-diol) can control single-handedly the configuration of the resulting anion (BINPHAT **4**, diastereomeric ratio d.r. > 39:1) [6,12]. This successful example of high diastereoselectivity in the stereocontrolled synthesis of hexacoordinated phosphate anion **4** prompted us to test the generality of this chiral auxiliary approach with other chiral diols. Herein, we report on the synthesis of C_2-symmetric phosphate anions containing 1,2-diaryl-ethane-1,2-diols as chiral auxiliaries and on the resulting asymmetric induction (diastereoselectivity) from the chosen ligands. A modest selectivity was observed using 1,2-diphenyl-ethane-1,2-diol (anion **5a**, d.r. ≤ 75:25). It can be improved by the introduction of *ortho* bromo substituents on the phenyl rings (**5b**, d.r. ≤ 90:10).

2. Results and discussion

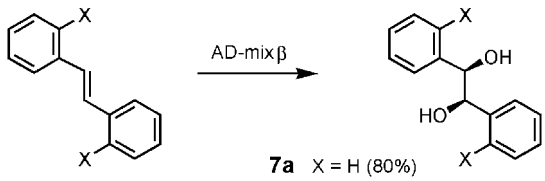
2.1. General considerations and choice of a class of chiral ligands

Our goal was thus to synthesize new C_2-symmetric hexacoordinated phosphate anions of configuration (Δ or Λ) controlled by a chiral ligand. Keeping in mind the overall efficiency of anion **2** in asymmetric applications [5], we chose to introduce two tetrachlorocatechol (**6**) moieties along with the chiral ligand. 1,2-Diphenyl-ethane-1,2-diol (**7a**) and its derivatives are chiral C_2-symmetric compounds which have been studied to a large extent in asymmetric chemistry as chiral ligands or auxiliaries [13]. Their general use is most probably due to their easy preparation in high enantiomeric purity by asymmetric dihydroxylation (AD) of (*E*)-stilbenes [14]. This AD procedure developed by Sharpless and coworkers is general and can be applied to a large variety of substituted stilbenes [15]. This gives a possibility of facile ligand optimization after the feedback from initial experiments. For these reasons, we selected 1,2-diaryl-ethane-1,2-diols as chiral ligands and decided to test their efficiency as chiral inducers for the determination of configuration of hexacoordinated phosphate anions.

However, the desired anions of general structure **5** (Fig. 3) were unknown in the literature. It was therefore necessary to develop an efficient and general synthetic procedure for their preparation. Several routes were considered before achieving this goal. They are described—along with the synthesis of the chiral ligands—in the following paragraphs.

2.2. Synthesis of the 1,2-diaryl-ethane-1,2-diols (7a–7d)

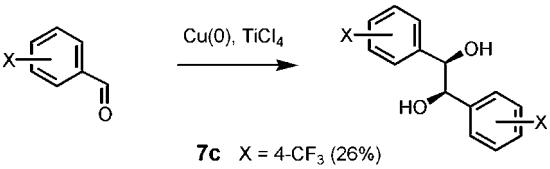
For the preparation of 1,2-diphenyl-ethane-1,2-diol **7a**, we reproduced the Sharpless procedure with commercially available AD-mix β and (*E*)-stilbene (Eq. (1)). (*R*,*R*)-**7a** was obtained in 80% yield in high enantiomeric purity (e.e. > 99%) [14].



(1)

7a X = H (80%)
7b X = Br (86 %)

For reasons that will be explained later (cf. Section 2.6), (*R*,*R*)-1,2-bis-(2-bromo-phenyl)-ethane-1,2-diol (**7b**), *rac*-1,2-bis-(4-trifluoromethyl-phenyl)-ethane-1,2-diol (**7c**) and *rac*-1,2-bis-(3,5-bis-trifluoromethyl-phenyl)-ethane-1,2-diol (**7d**) were also prepared for this project. Compound **7b** was synthesized in three steps: Wittig olefination of 2-bromo-benzaldehyde and (2-bromo-benzyl)-triphenyl-phosphonium under the conditions reported by Kelly et al. afforded a mixture of (*Z*)- and (*E*)-α,α′-dibromo-stilbene (77%) [16], which was treated with $TeCl_4$ at reflux in $CHCl_3$ to give pure (*E*) isomer in 84% yield [17]. Asymmetric dihydroxylation of this compound, following the conditions reported by Kagan and Girard, afforded **7b** (Eq. (1), 86% yield, e.e. > 98%) [18].



(2)

7c X = 4-CF_3 (26%)
7d X = 3,5-CF_3 (15%)

Racemic derivatives **7c** and **7d** were prepared following the procedure of Cuvinot and Alexakis by pinacol coupling of the corresponding aldehydes in one step albeit low yields (Eq. (2), 26 and 15%, respectively) [19]. With these 1,2-diaryl-ethane-1,2-diols in our hands, we turned our attention to the synthesis of the corresponding phosphate anions with a strong emphasis on the preparation of anion **5a** derived from diol **7a**.

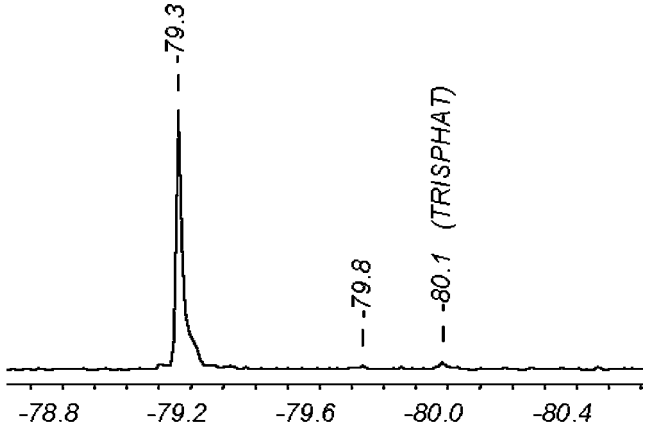
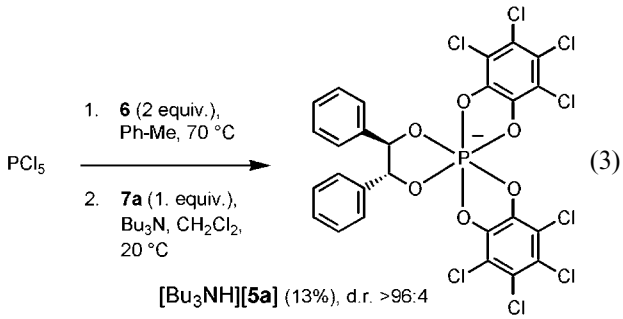


Fig. 4. ^{31}P-NMR spectrum (162 MHz, DMSO-d_6) of [^{n}Bu$_3$NH][**5a**].

2.3. Synthesis of phosphate anion 5a. Preliminary studies

For the synthesis of HYPHAT anion **5a**, we first attempted to adapt the synthetic procedure developed for TRISPHAT **2**—that is the one-time addition of three equivalents of tetrachlorocatechol **6** to one equivalent of PCl_5 followed by the addition of an amine. Ligands **6** (two equivalents) were added to a solution of PCl_5 in toluene at 70 °C. After 16–24 h, concentration in vacuo and additions of CH_2Cl_2, (*R*,*R*)-**7a** (one equivalent) and Bu_3N (two equivalents), the spontaneous formation of a precipitate was observed. This white powder corresponded to the desired salt [^{n}Bu$_3$NH][**5a**], albeit in low chemical yield (13%) along with minor amounts of [^{n}Bu$_3$NH][**2**] (Eq. (3)).



(3)

^{1}H- and ^{31}P-NMR analyses (DMSO-d_6, Fig. 4) revealed essentially one set of signals indicating the presence of one of the two diastereomeric ion pairs (Δ,*R*,*R* or Λ,*R*,*R*, d.r. ~96:4) [20]. Although, the high diastereoselectivity was satisfactory, the low yield was disappointing and many reactions were performed to improve this synthetic route. In all cases, selective precipitation of [ammonium][**5a**] salts without traces of [ammonium][**2**] was difficult. We also observed that prolonged reaction times were detrimental to the yield. Larger amounts of degradation products and of TRISPHAT **2** were isolated indicating possible recombinations of the ligands among the intermediates and products when enough time was given. We thus turned our attention to the design of a more efficient synthetic route.

2.4. Optimized syntheses of anion 5a

It was our analysis that the principal problem of the previous route was the presence of two different bidentate ligands, which could react simultaneously and lead

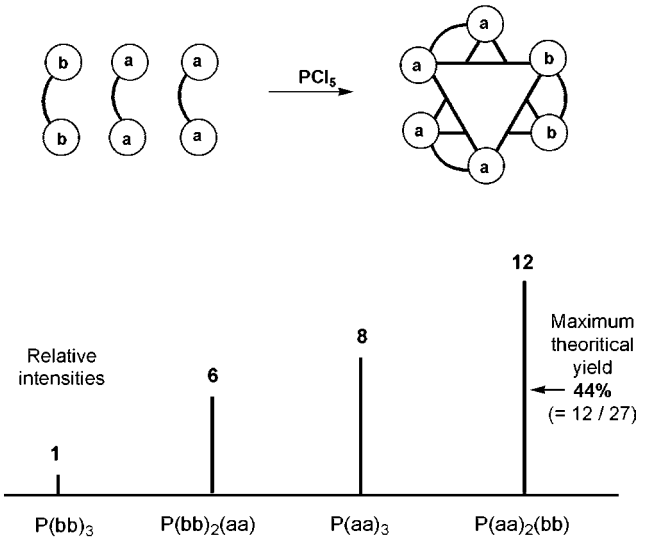


Fig. 5. Statistical distribution among possible phosphates from the reaction of two different ligands (aa and bb, 2:1 ratio) and PCl_5.

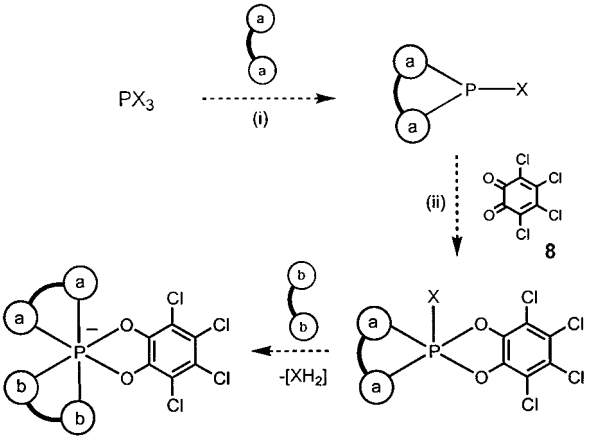


Fig. 6. Outline of the envisioned synthetic strategy for making of $[XH_2][P(aa)_2bb]$ salts.

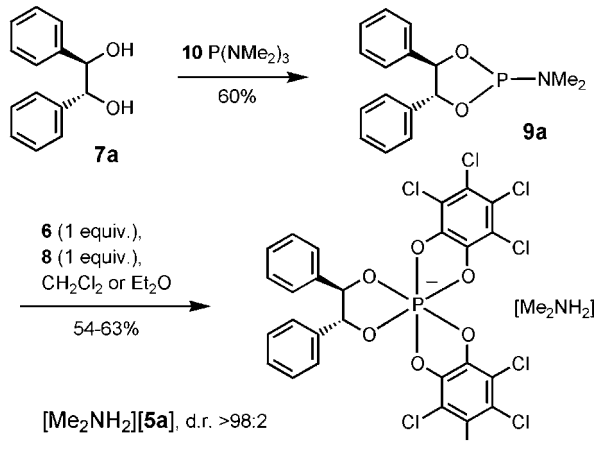


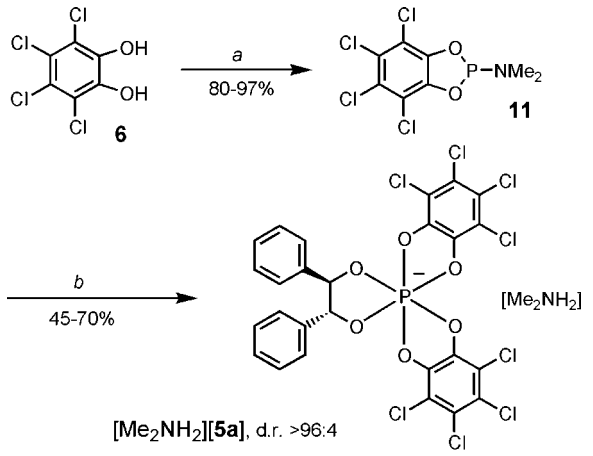
Fig. 7. Two-steps synthesis of $[Me_2NH_2]$[**5a**] via hydrobenzoin phosphoramidite **9a**.

to four different anionic compounds. This is represented in Fig. 5 considering the theoretical case of two different ligands aa and bb (2:1 ratio) which can bind to PCl_5. A statistical 1:6:8:12 repartition among the four possible products is then expected; the desired compound $[P(aa)_2bb]$ being synthesized with a maximum 44% theoretical yield.

To obtain a mixed $[P(aa)_2bb]$ adduct in high yield and in the exclusive of all others, we considered that the best synthetic route would be one allowing the sequential introduction of each of the three ligands in three different and orthogonal chemical steps [21]. Undeniably, if only one ligand was to be present at each chelation step, all chances of mutual competition between ligands would be nullified and the resulting mixture of compounds avoided. A synthetic route using three separate and high-yielding chelation steps should therefore lead to the formation of a single phosphate anion in high combined yield.

For the implementation of this approach, we considered the known facts that (i) PX_3 derivatives (X = halogens, OR, NR_2) can react with diols to form monochelated adducts [22] and (ii) monocyclized P (III) compounds are readily oxidized to bicyclic spirophosphoranes using *ortho*-chloranil **8** as an oxidant (Fig. 6) [23]. These two chelation steps were ideal for our projected route, as they could be performed sequentially in high yields. To perform the final chelation step and obtain the desired anion, it would then be sufficient to add a third diol ligand (ligand bb in Fig. 6) to the spirophosphorane intermediate. After displacement of the last substituent X, chelation would occur in the presence of a base forming the final ring. In a final set of beneficial twists, we realized that if substituent X were to be a base—such as an amino group—then the two protons delivered by the last diol would be directly scavenged in solution with no need to add an extra base. Salts $[XH_2][P(aa)_2bb]$ would directly result from the procedure. We also recognized that most diols are compatible with *ortho*-chloranil **8** and chelation steps 2 and 3 could therefore happen in a one-pot procedure.

In our initial attempts following these guidelines, chiral ligand **7a** was introduced at the start of the synthesis (as ligand aa in Fig. 6). We assumed that its early chelation around the phosphorus atom would maximize the chances of asymmetric induction at each of the following steps. Phosphoramidite **9a** was thus synthesized in a decent yield (60%) by reaction of (*R*,*R*)-**7a** with tris(dimethylamino)phosphine **10** [22c]. Then, reaction of **9a** with a 1:1 mixture of **6** and **8** afforded the desired $[Me_2NH_2]$[**5a**] as a single diastereomer (Fig. 7). Decent chemical yields—higher than those from the previous method—were obtained (54, 61 and 63% using CH_2Cl_2, CH_2Cl_2–hexane 4:1 or Et_2O as solvents respectively).



Scheme 1. (a) **6** (1.7 equivalents for 1.8 equivalents of **10**), NH_4Cl (2 mol%), toluene, reflux; (b) *o*-chloranil **8** (1.7 equivalents), **7a** (1.0 equivalents), solvent, 20 °C.

Table 1
Optimized syntheses of $[Me_2NH_2]$[**5a**] salts starting from tetrachlorocatechol **6**

Entry	Solvent	Time [a]	Yield	d.r. [b]	[**2**]% [f]
1 [c]	3:2 [e]	18	68	96:4	6
2 [c]	CH_2Cl_2	2	48–55	>96:4	6
3 [c]	Et_2O	2	45	>96:4	5
4 [c]	Et_2O	18	70	>96:4	5
5 [d]	4:1 [e]	4	70	>96:4	8

[a] Reaction time in hours.
[b] ^{31}P-NMR, DMSO-d_6, signals at δ −79.2 and −79.8 ppm, respectively.
[c] Using isolated **11**.
[d] One-pot protocol.
[e] CH_2Cl_2–hexane mixtures.
[f] Contamination of $[Me_2NH_2]$[**2**] in the precipitate.

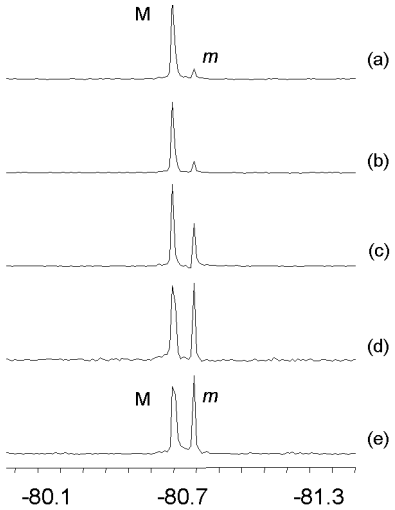


Fig. 8. Epimerization of $[Me_2NH_2]$[**5a**] as a function of time. ^{31}P-NMR (162 MHz, MeOH-d_4) (a) 1.5 h., d.r. 88:11; (b) 2.3 h.; d.r. 86:14; (c) 9.7 h, d.r. 67:32; (d) 17.8 h., 64:36; (e) 28.4 h., d.r. 61:39. Major (M) and minor (*m*) diastereomers.

This procedure was advantageous because phosphate salt $[Me_2NH_2]$[**5a**] precipitated as soon as it was formed giving no chances for the anion to decompose or equilibrate to other compounds. Most probably, the in-situ formation of $HNMe_2$ is favorable as it traps immediately the spirophosphorane intermediate to form the phosphate anion. However, although useful, this procedure was difficult to scale up due to the delicate synthesis of **9a**. We turned our attention to a final approach.

We considered that it would be more practical to start with phosphoramidite **11** derived from tetrachlorocatechol **6** and introduce the chiral ligand at the last step (as ligand bb in Fig. 6). This approach would be both economical in chiral ligand **7a** and elegant in terms of strategy as it could be generalized to all diols and not just hydrobenzoins [6]. Compound **11**, simply prepared by heating anhydrous **6** and freshly distilled **10** in refluxing toluene, was obtained in good to excellent yields (80–97%); purification being effected by sublimation of the crude product. Then, treatment of **11** with **8** and ligand **7a** in an appropriate solvent combination afforded the desired $[Me_2NH_2]$[**5a**] salt in decent to good yields (45–70%, Scheme 1, Table 1, entry 1–4).

The crude mixture from the first reaction containing essentially pure **11**, we realized that this synthetic sequence could be performed in a 'one-pot' procedure. This rendered the synthesis of salts $[Me_2NH_2]$[**5a**] even easier; reaction times were reduced from 18 to 4 h with no loss of chemical yield (Table 1, entry 5). In all these reactions using ligand **7a**, essentially a single diastereomer precipitated as observed in ^{1}H and ^{31}P-NMR (DMSO-d_6, d.r. $\geq$ 96:4).

With decent amounts of [ammonium][**5a**] salts in our hands, we turned our attention to the configurational stability of anion **5a**.

*2.5. Configurational stability of **5a** and asymmetric induction properties of ligand **7a***

As just mentioned, [ammonium][**5a**] salts were always obtained as precipitates in high diastereomeric ratios (d.r. $\geq$ 96.4). For the analyzes of the precipitates, care was taken to use DMSO-d_6 as a NMR solvent as Koenig and Klaebe had observed that this solvent promoted only little epimerization of the chiral hexacoordinated phosphate he had prepared [3c].

However, upon dissolution of the [ammonium][**5a**] salts in MeOH-d_4 a slow but definite equilibration between the two diastereomers was observed as the ratio changed from >96:4 to 61:39 after 29 h (Fig. 8). Using $CDCl_3$—with minor amounts of DMSO-d_6 to solubilize the substrate—the change was more dramatic as a 75:25 ratio was obtained immediately after dissolution (Fig. 9, spectrum c). All these results demonstrating a poor configurational stability in solution for anion **5a** in [ammonium][**5a**] salts.

The existence of an equilibrium between diastereomeric [ammonium][Δ-**5a**] and [ammonium][Λ-**5a**] salts was further proven while attempting the purification of salt [^{n}Bu$_3$NH][**5a**] (d.r. $>96{:}4$) from its [^{n}Bu$_3$NH][**2**] contaminant. Following a protocol developed in our group for the isolation and purification of TRISPHAT salts [24], a cation exchange of Bu_3NH^+ to the purple cation of crystal violet **12**—or [tris(para-dimethylaminophenyl)methylium][chloride]—was realized by chromatography (basic Al_2O_3, CH_2Cl_2) and resulted in the isolation of the desired ion pair [**12**][**5a**]. However, a 65:35 ratio of two diastereomeric salts (^{1}H- and ^{31}P-NMR, DMSO-d_6) was observed demonstrating that a partial epimerization had occurred during the chromatography. This diastereoselectivity (d.r. 65:35)—different from the one observed for [^{n}Bu$_3$NH][**5a**] in $CDCl_3$ (d.r. 75:25)—demonstrates that the cationic counter-ion plays also a role on the overall position of the thermodynamic equilibrium between the diastereomers.

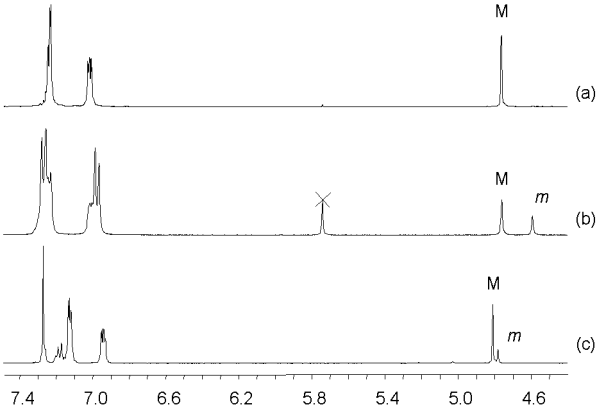


Fig. 9. ^{1}H-NMR (400 MHz) of (a) [Me_2NH_2][**5a**], DMSO-d_6, d.r. $>96{:}4$ and (b) [**12**][**5a**], DMSO-d_6, d.r. 65:35 and (c) [Me_2NH_2][**5a**], 15% DMSO-d_6–$CDCl_3$, d.r. 75:25. Major (M) and minor (*m*) diastereomers.

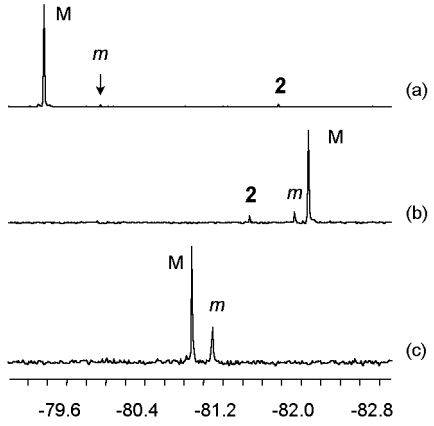
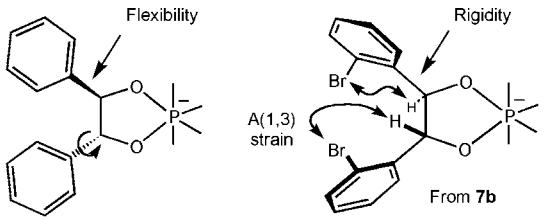


Fig. 10. ^{31}P-NMR (162 MHz) of [Me_2NH_2][**5b**] in (a) DMSO-d_6, 80 h., d.r. $>96{:}4$; (b) 15% DMSO-d_6–$CDCl_3$; 6 days, d.r. 90:10; (c) MeOH-d_4, 11 days, d.r. 68:32. Major (M) and minor (*m*) diastereomers. TRISPHAT is indicated by the number **2**.

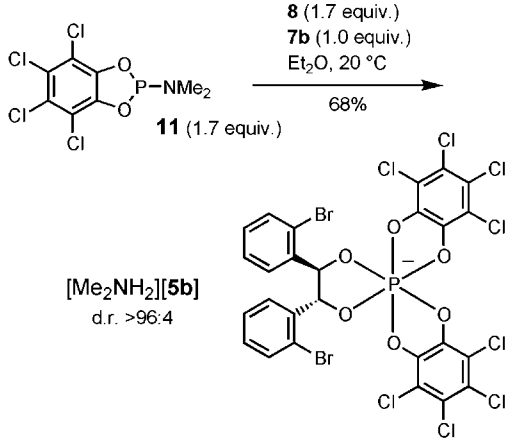
In conclusion, the high diastereoselectivity observed for the [ammonium][**5a**] salts isolated by precipitation was fortunate. When dissolved, an equilibration happened between the diastereomers; the rate and position of the equilibrium depend on the solvent and on the counter-ion. In all cases, a low diastereoselectivity (d.r. $<75{:}25$) resulted from the epimerization.

*2.6. Improved asymmetric induction and configuration stability from ligands **7b–7d***

We reasoned that the low diastereoselectivity might result from a lack of steric interactions between the phenyl groups of **7a** and the tetracatecholate ligands due, possibly, to the high conformational flexibility of the phenyl rings. In that case, introduction of *ortho* substituents on the phenyl rings would increase the size of the aromatic groups and rigidify the skeleton of the ligand by creation of allylic A(1,3) strains between the substituents and the stereogenic centers [25]. A higher diastereoselectivity should then result from the modification. Good literature precedents and ease of synthesis led us to consider and prepare ligand **7b** having *ortho*-bromo substituents.



Anion **5b** was then prepared—following the optimized procedure—by reaction of **11** and diol **7b** to give the [Me_2NH_2][**5b**] salt in 68% yield and—in the precipitate—a high diastereoselectivity (Eq. (4), d.r. $\sim 98{:}2$, Fig. 10, spectrum a). Dissolution of salt [Me_2NH_2][**5b**] led to an equilibration. In 15% DMSO-d_6–$CDCl_3$, a 90:10 diastereomeric ratio between the diastereomers of **5b** (Fig. 10, spectrum b) was obtained (vs. 75:25 for **5a**). In MeOH, only a 68:32 ratio (Fig. 10, spectrum c) was observed (vs. 61:39 for **5a**).



(4)

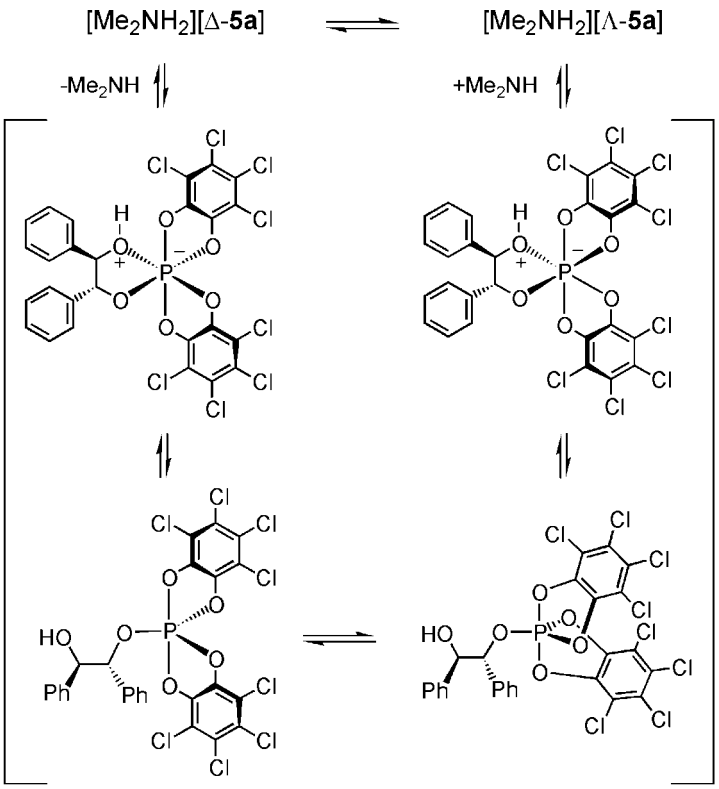


Fig. 11. Mechanistic rational for equilibration of the diastereomers of $[Me_2NH_2]$[**5a**] salt.

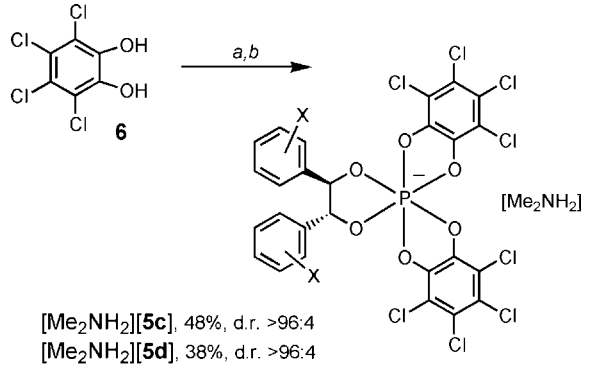
A definite increase in diastereoselectivity was obtained using ligand **7b**. However, it was not sufficient to lead to the preferred formation of a single diastereomer. This led us to try to stabilize configurationally the anions hopping that the good diastereomeric ratios obtained at the precipitation stage would then remain constant upon dissolution of isolated salts.

It was our analysis that the epimerization between Δ-**5a** and Λ-**5a** (or Δ-**5b**–Λ-**5b**) resulted from the electron-rich nature of the oxygen atoms of ligand **7a** (or **7b**). They can be protonated by the acidic $Me_2NH_2^+$ counter-ion. This labilize the P–O bonds and provokes a ring opening to a configurationally labile spirophosphorane (Fig. 11) [26].

If one considers that the opening of the ring carrying the protonated oxygen is the rate-determining step [4], then stopping the protonation of the electron-rich oxygen atoms would be sufficient to obtain a configurationally stable anion. The introduction of strong electron-withdrawing trifluoromethyl groups on the aromatic nuclei of the chiral ligands might thus help stabilize the phosphates. Ligands **7c** and **7d** were thus prepared for that goal [27].

Salts $[Me_2NH_2]$[**5c**] and $[Me_2NH_2]$[**5d**], derived from ligands **7c** and **7d** respectively, were prepared using the one-pot protocol in non-optimized 48 and 38% yields respectively (Scheme 2). ^{1}H-NMR analyses of the salts in DMSO-d_6 revealed—as usual—a high diastereomeric purity for the precipitates (d.r. $>$96:4 and 95:5 for **5c** and **5d**, respectively).

Upon dissolution in 5% DMSO-d_6–$CDCl_3$, a fast epimerization of salts $[Me_2NH_2]$[**5c**] and $[Me_2NH_2]$[**5d**] occurred. Equilibria were reached in less than 30 min and a 71:29 diastereomeric ratio was obtained for both salts. Clearly, the electron-poor aromatic nuclei of ligands **7c**–**7d**—not being directly connected to the oxygen atoms—have a reduced electron-withdrawing ability and do not exert any concrete influence on the rate of racemization.



Scheme 2. (a) **6** (1.7 equivalents for 1.8 equivalents of **10**), NH_4Cl (2 mol%), toluene, reflux; (b) *o*-chloranil **8** (1.7 equivalents), **7c** or **7d** (1.0 equivalents), solvent, 20 °C.

3. Conclusion

In this article, we have shown that C_2-symmetric hexacoordinated phosphate anions can be easily synthesized in a 'one-pot' process from simple-to-make or commercially available starting materials. These anions can be obtained as solids in high diastereomeric purity. However, once dissolved, they epimerize rapidly. Using 1,2-diphenyl-ethane-1,2-diol, a modest asymmetric induction is observed (d.r. 75:25 in 5% DMSO–$CHCl_3$), which can be improved (d.r. up to 90:10) by the introduction of *ortho* bromo substituents on the phenyl rings. Despite all our efforts, we have not been able to grow crystals suitable for X-ray analysis. The absolute configuration of salt (−)-[Me_2NH_2][**5a**] derived from (*R*,*R*)-**7a** remains so far unknown. Further studies are conducted in our group to find a chiral ligand, which would lead to high asymmetric induction and chemical stability in the resulting phosphate anion.

4. Experimental

4.1. General considerations

All reactions were carried out under an atmosphere of dry nitrogen or argon using an inert gas–vacuum double manifold and standard Schlenk techniques with magnetic stirring, unless otherwise stated. Solvents were dried and distilled prior to use. Chloroform (Fluka) and $CDCl_3$ (SDS) were filtered on basic alumina before use. Diethylether was distilled from sodium metal and benzophenone ketyl. Toluene was distilled from sodium metal. Methanol, hexane and dichloromethane were distilled from calcium hydride. Deionized water was used for aqueous solutions. Purifications of reaction products were carried out by chromatography using J.T. Baker silica gel (30–60 μm) or basic aluminum oxide (Fluka, type 5016A). Analytical thin layer chromatography was performed on Macherey–Nagel 0.25 mm silica gel plates. Visualization was accomplished with UV light. (*R*,*R*)-1,2-Diphenyl-ethane-1,2-diol (**7a**) and (*R*,*R*)-1,2-bis-(2-bromo-phenyl)-ethane-1,2-diol (**7b**) were synthesized according to literature procedures [14,18].

In all the phosphate salts syntheses, we define the stereoselectivity at the precipitation step by the NMR analysis of the precipitate in Me_2SO-d_6, because that this solvent seems to prevent fast epimerization between the diastereomers, thus giving us a good image of the real diastereomeric composition of the precipitate. Usually, only traces of a second diastereomer were observable in Me_2SO-d_6, whereas, both diastereomers were clearly seen upon dissolution of the precipitate in another solvent or solvent mixture. In such cases, both NMR interpretations are given.

NMR spectra are recorded at 295 K unless otherwise stated. ^{1}H-NMR spectra were recorded on Varian XL-200 (200 MHz) and Brüker AMX-400 (400 MHz) spectrometers. Chemical shifts are given in ppm relative to Me_4Si with the solvent resonance used as the internal standard. ^{31}P-NMR spectra were recorded on a Brüker AMX-400 (162 MHz). Chemical shifts are reported in ppm relative to H_3PO_4. ^{13}C-NMR spectra were recorded on Varian XL-200 (50 MHz), Brüker AMX-400 (100 MHz) spectrometers. Chemical shifts are given in ppm relative to Me_4Si, with the solvent resonance used as the internal standard ($CDCl_3$ 77.0 ppm, CD_3OD 49.0 ppm, Me_2SO-d_6 39.5 ppm, acetone-d_6 29.8 ppm). Assignments may have been achieved using COSY, HETCOR and/or NOESY experimental data. ^{19}F-NMR spectra were recorded on a Brüker AMX-400 (376 MHz) spectrometer. Chemical shifts are reported in ppm relative to C_6F_6. Optical rotations were measured on a Perkin Elmer 241 polarimeter in a thermostated (20 °C) 10 cm long microcell with high pressure sodium ($\lambda = 589$ nm) or mercury ($\lambda = 578$ nm) lamps and are reported as follows: $[\alpha]_D^{20}$ (*c* g/100 ml, solvent). Melting points (m.p.) were measured in open capillary tubes on a Stuart Scientific SMP3 melting point apparatus and are uncorrected. Electronspray mass spectra (ES-MS) were obtained on a Finnigan SSQ 7000 spectrometer by the Department of Mass Spectroscopy. Mass spectra (MS) were obtained on a Varian CH4 or SM1 spectrometer and relative intensities are given in parentheses (*m*/*z*, %). Elemental analyses were performed at the 'Institut de Chimie Pharmaceutique de l'Université de Genève' by Dr H.-J. Eder.

4.2. Preparation of [^{n}Bu$_3$NH][**5a**] by reaction with PCl_5

To a solution of PCl_5 (208 mg, 1.00 mmol) in toluene (4.0 ml) at 50 °C, tetrachlorocatechol **6** (496 mg, 2.00 mmol) was slowly added, and the mixture heated to 70 °C overnight. (*R*,*R*)-1,2-Diphenyl-ethane-1,2-diol (**7a**, 214 mg, 1.00 mmol) and tri-*n*-butylamine (476 ml, 2.00 mmol) were then added and the mixture was heated to 70 °C for a further 12 h. The precipitate was then filtered, washed with CH_2Cl_2, and dried to afford [^{n}Bu_3NH][**5a**] as a white solid (150 mg, ~13%) in ≥96:4 mixture of diastereomers. ^{31}P{^{1}H}-NMR (162 MHz, Me_2SO-d_6, major (M) and minor (*m*) diastereomers): δ −79.3 (M); −79.8 (*m*, trace). ^{1}H-NMR (400 MHz, Me_2SO-d_6, major diasteromer): δ 0.89 (t, $J = 7.5$ Hz, 9H), 1.30 (m, 6H), 1.55 (m, 6H), 2.99 (m, 6H), 4.76 (s, 2H), 7.02 (m, 4H), 7.23 (m, 6H), 8.84 (s broad, 1H); minor diastereomer not sufficiently visible in this solvent to be reliably described. ES–MS; *m*/*z*: (−) 735.0; (+) 186.1.

4.3. One-pot preparation of (−)-dimethylammonium bis(tetrachlorobenzenediolato)mono((R,R)-1,2-diphenyl-ethane-1,2-diolato)phosphate(V) or (−)-[Me_2NH_2][5a]

Tetrachlorocatechol **6** (211 mg, 0.85 mmol) and a catalytic amount of NH_4Cl (one crystal) were mixed together in dry toluene (2.0 ml). Freshly distilled tris-(dimethylamino)phosphine **10** (163 μl, 0.90 mmol) was then slowly added. Dimethylamine evolved and the mixture was refluxed for 15 min. The remaining solvent and excess of **10** were removed under reduced pressure and the residue carefully dried in vacuo. (*R*,*R*)-1,2-Diphenyl-ethane-1,2-diol **7a** (107 mg, 0.50 mmol) and *ortho*-chloranil **8** (209 mg, 0.85 mmol) were added and the mixture dissolved in a mixture of CH_2Cl_2–hexane 4:1 (5 ml). The dark red solution progressively lost its color within 4 h and a precipitate was formed. When the color did not change anymore, the precipitate was filtered, washed carefully successively with the CH_2Cl_2–hexane 4:1, toluene and CH_2Cl_2–hexane 4:1 again. It was then dried to afford [Me_2NH_2][**5**] as a single diastereomer (^1H,^{31}P-NMR) however along with 8% of inseparable [Me_2NH_2][**2**] salt (304 mg, 70%). The product could be further purified by trituration in CH_2Cl_2. $[\alpha]_D^{20} = -101$ (*c* 0.99; Me_2SO). M.p. > 210 °C (decomposition). $^{31}P\{^1H\}$-NMR (162 MHz, Me_2SO-d_6, major diastereomer): δ −79.3; ^1H-NMR (400 MHz, Me_2SO-d_6, major diastereomer): δ 2.53 (s, 6H, Me), 4.76 (s, 2H), 7.01 (m, 4H), 7.23 (s broad, 6H), 8.15 (s broad, 2H, NH_2). $^{13}C\{^1H\}$-NMR (100 MHz, Me_2SO-d_6, major diastereomer): δ 34.3 (NCH_3), 80.4 (CH), 111.9 (C_q, d, $J_{CP} = 19$ Hz), 112.1 (C_q, d, $J_{CP} = 18$ Hz), 119.8 (C_q), 119.9 (C_q), 126.7 (CH), 128.1 (CH), 128.2 (CH), 139.1 (C_q, d, $J_{CP} = 14$ Hz), 142.7 (C_q, d, $J_{CP} = 5.4$ Hz), 143.0 (C_q, d, $J_{CP} = 5.3$ Hz). ES-MS; *m*/*z*: (−) 735.0. Anal. Found: C, 41.72; H, 2.93; N, 1.85. Calc. for $C_{28}H_{20}Cl_8NO_6P$ (92%) and $C_{20}H_8Cl_{12}NO_6P$ (8%, [Me_2NH_2][TRISPHAT]): C, 41.97; H, 2.45; N, 1.78%.

In 15% Me_2SO-d_6–$CDCl_3$, both diastereomers can be observed after epimerization: $^{31}P\{^1H\}$-NMR (162 MHz, major (M) and minor (*m*) diastereomers): δ −82.1 (*m*), −82.3 (M). $^{13}C\{^1H\}$-NMR (100 MHz, major (M) and minor (*m*) diastereomers): δ 35.3 (NCH_3), 80.2 (CH, *m*), 81.2 (CH, M), 113.1 (C_q, d, $J_{CP} = 18$ Hz, M), 113.2 (C_q, d, $J_{CP} = 19$ Hz, *m*), 113.3 (C_q, d, $J_{CP} = 19$ Hz, M), 113.9 (C_q, d, $J_{CP} = 20$ Hz, *m*), 121.6 (C_q, *m*), 121.7 (C_q, M), 121.8 (C_q, M), 123.0 (C_q, *m*), 126.7 (CH, M), 127.6 (CH, *m*), 127.6 (CH, M), 127.9 (CH, M), 128.2 (CH, *m*), 128.3 (CH, *m*), 138.3 (C_q, d, $J_{CP} = 13$ Hz, M), 138.4 (C_q, d, $J_{CP} = 11$ Hz, *m*), 141.1 (C_q, d, $J_{CP} = 6.6$ Hz, *m*), 142.0 (C_q, d, $J_{CP} = 5.8$ Hz, M), 142.2 (C_q, d, $J_{CP} = 4.9$ Hz, M), 143.0 (C_q, d, $J_{CP} = 5.3$ Hz, *m*).

4.4. Preparation of [tris(para-dimethylamino-phenyl)methylium][5a] or [12][5a]

[$^nBu_3NH$][**5a**] (23.0 mg, 2.46 μmol) and crystal violet (10.2 mg, 2.50 μmol) were dissolved in CH_2Cl_2 (3.0 ml) and the resulting solution stirred for 5 min and then concentrated in vacuo. Purification by chromatography (basic Al_2O_3, 0.5 × 2 cm, CH_2Cl_2) afforded 7 mg (0.65 μmol, 25%) of [**12**][**5a**] as a dark purple solid containing a 65:35 mixture of diastereomers: $^{31}P\{^1H\}$-NMR (162 MHz, Me_2SO-d_6, major (M) and minor (*m*) diastereomers): δ −79.3 (M), −79.8 (*m*). ^1H-NMR (400 MHz, Me_2SO-d_6, major (M) and minor (*m*) diastereomers): δ 3.07 (s, 18H), 4.46 (s, 2H, *m*), 4.64 (s, 2H, M), 6.85 (m, 9H), 7.12 (m, 13H). ES–MS; *m*/*z*: (−) 735.0; (+) 372.2.

4.5. Preparation of tetrachlorobenzo〈1,3,2〉-dioxaphosphol-2-yl-dimethyl-amine (11)

In a sublimating flask and under a nitrogen atmosphere, tetrachlorocatechol (**6**, 1.24 g, 5.0 mmol) and a catalytic amount of NH_4Cl (∼10 mol%) were mixed together in dry toluene (5.0 ml). Freshly distilled tris-(dimethylamino)phosphine **10** (1.09 ml, 6.0 mmol) was slowly added. Dimethylamine evolved. The mixture was refluxed for 1 h and 30 min. The remaining solvent and excess of **10** were removed under reduced pressure. The gray residue was sublimated (170 °C, 0.06 mbar) to afford **11** (1.56 g, 97%) as a white crystalline solid. m.p. 125–130 °C. ^1H-NMR (400 MHz, C_6D_6): δ 1.85 (d, $J_{HP} = 9.2$ Hz, 6H). $^{13}C\{^1H\}$-NMR (100 MHz, C_6D_6): δ 35.0 (NCH_3), 115.3 (C_q), 125.0 (C_q), 143.5 (C_q, d, $J_{CP} = 8.0$ Hz). $^{31}P\{^1H\}$-NMR (162 MHz, C_6D_6): δ 156.9.

4.6. Preparation of dimethylammonium bis(tetrachlorobenzenediolato)mono((R,R)-1,2-bis(2-bromo-phenyl))-ethane-1,2-diolato)phosphate(V) or (−)-[Me_2NH_2][5b]

(−)-(*R*,*R*)-1,2-Bis-(2-bromo-phenyl)-ethane-1,2-diol (**7b**, 186 mg, 0.50 mmol), phosphoramidite **11** (161 mg, 0.50 mmol), and *ortho*-chloranil (123 mg, 0.50 mmol) were mixed together under a nitrogen atmosphere. The mixture was dissolved in Et_2O (5 ml). The dark red solution progressively lost its color within 2 h and a precipitate was formed. When the color did not change anymore, the precipitate was filtered, washed successively with Et_2O, toluene and Et_2O again, and dried to afford the desired dimethylammonium phosphate salt as a white solid (350 mg, 68%) a 98:2 mixture of diastereomers and 2% of inseparable [Me_2NH_2][**2**]. $^{31}P\{^1H\}$-NMR (162 MHz, Me_2SO-d_6, major diastereomer): δ −79.5. ^1H-NMR (400 MHz, Me_2SO-d_6, major diastereomer): δ 2.53 (s, 6H), 5.23 (s, d,

$J_{HP} = 0.8$ Hz, 2H), 7.16 (m, 2H), 7.34 (m, 4H), 7.41 (d, $J = 7.9$ Hz, 2H), 8.15 (s broad, 2H); minor diastereomer not sufficiently visible to be reliably described. $^{13}C\{^1H\}$-NMR (100 MHz, Me_2SO-d_6, major diastereomer): δ 34.3 (NCH_3), 78.3 (CH), 81.5 (C_q), 112.0 (C_q, d, $J_{CP} =$ 19 Hz), 112.3 (C_q, d, $J_{CP} = 18$ Hz), 120.1 (C_q), 120.2 (C_q), 122.1 (C_q), 128.0 (CH), 128.9 (CH), 129.8 (CH), 132.2 (CH), 137.9 (C_q, d, $J_{CP} = 14$ Hz), 142.6 (C_q, d, $J_{CP} = 28$ Hz). ES-MS; m/z: (−) 892.3. Anal. Found: C, 35.90; H, 2.21; N, 1.54. Calc. for $C_{28}H_{18}Br_2Cl_8NO_6P$: C, 35.82; H, 1.93; N, 1.49%.

In 15% Me_2SO-d_6–$CDCl_3$, both diastereomers can be observed after epimerization: $^{31}P\{^1H\}$-NMR (162 MHz, major (M) and minor (*m*) diastereomers): δ −82.1 (*m*), −82.3 (M). ^1H-NMR (400 MHz, major (M) and minor (*m*) diastereomers): δ 2.63 (s, 6H, Me), 5.33 (s, d, $J_{HP} = 1.7$ Hz, 2H, *m*), 5.38 (s, 2H, M), 7.03 (m, 2H, M), 7.06 (m, 2H, *m*), 7.28 (m, 4H, M), 7.32 (m, 4H, *m*), 7.43 (dd, $J = 8.0$, 1.3 Hz, 2H, M), 8.07 (d, $J = 6.6$ Hz, 2H, *m*), 8.23 (s broad, 2H, NH_2).

*4.7. Preparation of rac-1,2-bis(para-trifluoromethyl-phenyl)-ethane-1,2-diol] (**7c**)*

Preparation of the copper reagent: 7.5 g (30.0 mmol) of $CuSO_4{\cdot}5H_2O$ and 1.96 g (30.0 mmol) of Zn were stirred in 100 ml of water until complete precipitation of copper(0) was observed. The precipitate was filtered, washed with water, acetone, dry Et_2O, and dried in vacuo to yield 1.90 g of copper.

$TiCl_4$ (1.64 ml, 14.9 mmol) was added dropwise to a suspension of Cu (1.90 g, 30.0 mmol) in dry THF (25 ml) under a nitrogen atmosphere. The temperature of the reaction medium was regulated with a water bath. A brown precipitate was observed and the reaction mixture refluxed for 2 h. To the resulting green precipitate, *para*-trifluoromethylbenzaldehyde (683 μl, 5.0 mmol) was added dropwise and the mixture refluxed for another 2 h. It was left to cool overnight, then hydrolyzed by an aqueous solution of 4.50 g of trisodium citrate. The solid residue was filtered off and most of the solvent was removed under reduced pressure. The resulting oil was extracted with Et_2O, washed with brine, dried over anhydrous Na_2CO_3, filtered and concentrated in vacuo to afford 750 mg of a white solid. Purification by chromatography (SiO_2, hexane–AcOEt 70:30 up to 50:50) afforded 225 mg of **7c** (26%) with a DL-*meso* ratio of 93:7. M.p. 139–143 °C. ^1H-NMR (400 MHz, $CDCl_3$): δ 3.03 (s, 2H), 4.76 (s, 2H), 7.23 (d, $J = 8.3$ Hz,, 4H), 7.53 (d, $J = 8.3$ Hz, 4H). ^{19}F-NMR (376 MHz, $CDCl_3$): δ 101.1. $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ 78.4, 123.9 (q, $J = 259$ Hz), 125.3 (q, $J = 3.8$ Hz), 127.3, 130.5 (q, $J = 32$ Hz), 144.4.

*4.8. Dimethylammonium bis(tetrachlorobenzenediolato)-mono(1,2-bis(para-trifluoromethylphenyl))-ethane-1,2-diolato)phosphate(V) or [Me_2NH_2][**5c**]*

This compound was prepared from **7c** in a similar way to (−)-[Me_2NH_2][**5a**] using the one-pot protocol and **6** (126 mg, 0.51 mmol), **10** (98 μl, 0.54 mmol), **8** (125 mg, 0.51 mmol) and **7c** (105 mg, 0.30 mmol). CH_2Cl_2 was used as solvent and a reaction time of 3 h needed. [Me_2NH_2][**5c**] was obtained as a white solid (168 mg, ~48%) and contained 20% of inseparable [Me_2NH_2][**2**]. $^{31}P\{^1H\}$-NMR (162 MHz, Me_2SO-d_6, major diastereomer): δ −79.1. ^{19}F-NMR (376 MHz, Me_2SO-d_6, major diastereomer): δ 102.5. ^1H-NMR (400 MHz, Me_2SO-d_6, major diastereomer): δ 2.53 (s, 6H), 4.86 (d, $J = 0.8$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 4H), 7.65 (d, $J = 8.0$ Hz, 4H), 8.15 (s broad, 2H). ES-MS; m/z: (−) 870.4.

In 5% Me_2SO-d_6–$CDCl_3$, both diastereomers can be observed after epimerization: $^{31}P\{^1H\}$-NMR (162 MHz, major (M) and minor (*m*) diastereomers): δ −82.4 (M), −82.0 (*m*). ^{19}F-NMR (376 MHz, major (M) and minor (*m*) diastereomers): δ 101.2 (M), 101.3 (*m*). ^1H-NMR (400 MHz, major (M) and minor (*m*) diastereomers): δ 2.53 (s, 6H, Me), 4.86 (d, $J = 0.8$ Hz, 2H, *m*), 4.91 (m, 2H, M), 7.14 (d, $J = 8.0$ Hz, 4H, M + *m*), 7.50 (d, $J = 8.0$ Hz, 4H, M), 7.56 (d, $J = 7.8$ Hz, 4H, *m*), 8.25 (s broad, 2H, NH_2).

*4.9. Preparation of rac-1,2-bis(3,5-bistrifluoromethyl)-phenyl-ethane-1,2-diol (**7d**)*

Compound **7d** was prepared in a similar way as for **7c** using $TiCl_4$ (3.28 ml, 30.0 mmol), Cu (3.60 g, 60.0 mmol), 3,5-bis-trifluoromethyl-benzaldehyde (2.42 g, 10.0 mmol) to afford, after recrystallization (toluene) of the crude product, 379 mg of **7d** (15% yield). M.p. 135–137 °C. ^1H-NMR (400 MHz, $CDCl_3$): δ 3.06 (s, 2H), 4.87 (s, 2H), 7.52 (s, 4H), 7.82 (s, 2H). ^{19}F-NMR (376 MHz, $CDCl_3$): δ 100.6. $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): δ 77.7 (CH), 122.3 (CH, q, $J = 3.0$ Hz), 123.0 (C_q, q, $J = 273$ Hz), 127.0 (CH), 131.8 (C_q, q, $J = 33$ Hz), 141.5 (C_q). EI–MS; m/z: 467, 449, 243, 195, 145, 127, 69.

*4.10. Dimethylammonium bis(tetrachlorobenzene-diolato)mono(1,2-bis(3,5-trifluoromethylphenyl))-ethane-1,2-diolato)phosphate(V) or [Me_2NH_2][**5d**]*

This compound was prepared from **7d** in a similar way to (−)-[Me_2NH_2][**5a**] using the one-pot protocol and **6** (211 mg, 0.85 mmol), **10** (165 μl, 0.91 mmol), **8** (209 mg, 0.85 mmol) and **7d** (243 mg, 0.50 mmol). CH_2Cl_2 was used as solvent and a reaction time of 4.25 h needed. [Me_2NH_2][**5d**] was obtained as a white solid (200 mg, 38%) as essentially a single diastereomer.

$^{31}P\{^{1}H\}$-NMR (162 MHz, Me_2SO-d_6, major diastereomer): δ −79.8. ^{19}F-NMR (376 MHz, Me_2SO-d_6, major diastereomer): δ 101.8. ^{1}H-NMR (400 MHz, Me_2SO-d_6, major diastereomer): δ 2.53 (s, 6H), 5.02 (d, $J_{HP} = 2.8$ Hz, 2H), 7.67 (s, 2H), 8.01 (s, 4H), 8.15 (s broad, 2H). ES–MS; m/z: (−) 1006.4.

In 5% Me_2SO-d_6–$CDCl_3$, both diastereomers can be observed after epimerization: $^{31}P\{^{1}H\}$-NMR (162 MHz, major (M) and minor (m) diastereomers): δ −81.6 (m), −82.3 (M). ^{19}F-NMR (376 MHz, major (M) and minor (m) diastereomers): δ 100.6 (M), 100.9 (m). ^{1}H-NMR (400 MHz, major (M) and minor (m) diastereomers): δ 2.53 (s, 6H, Me), 4.85 (d, $J_{HP} = 2.4$ Hz, 2H, m), 4.94 (d, $J_{HP} = 1.5$ Hz, 2H, M), 7.46 (s, 4H, M + m), 7.83 (s, 2H, M), 8.00 (s, 4H, m), 8.14 (s broad, 2H, NH_2).

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