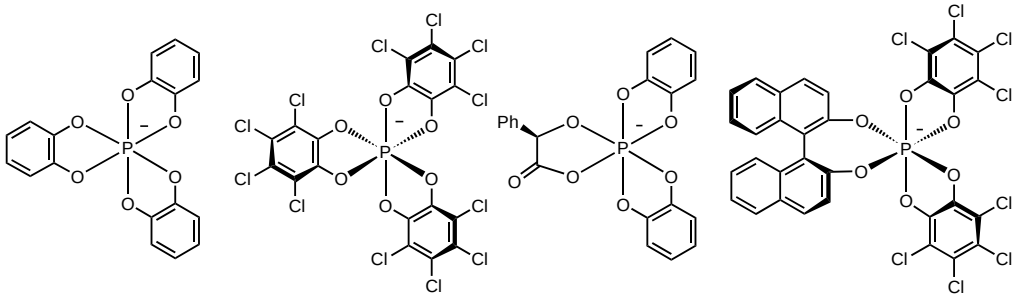
Asymmetric Synthesis and Configurational Stability of C_2-Symmetric Hexacoordinated Phosphate Anions (TARPHATs) with Predetermined Chirality from Tartrate Esters

by **Jérôme Lacour***[a]), **Anne Londez**[a]), **Duy-Hien Tran**[a]), **Valérie Desvergnes-Breuil**[a]), **Samuel Constant**[a]), and **Gérald Bernardinelli**[b])

[a]) Département de Chimie Organique, Université de Genève, quai Ernest-Ansermet 30, CH-1211 Geneva 4
[b]) Laboratoire de Cristallographie, Université de Genève, quai Ernest-Ansermet 24, CH-1211 Geneva 4

C_2-Symmetric TARPHAT anions **5** made of a central P^V atom, one tartrato (= dialkyl 2,3-di(hydroxy-κO)butanedioato(2−)), and two tetrachloropyrocatecholato (= 3,4,5,6-tetrachlorobenzene-1,2-diolato(2−)-$\kappa O,\kappa O'$) ligands can be easily prepared in decent to high yields (50–86%) as their dimethylammonium salt by using a one-pot process and simple commercially available starting materials. The presence of the chiral tartrato ligands (usually (2*R*,3*R*)) leads to the formation of diastereoisomeric anions ((*Δ*,2*R*,3*R*)/(*Λ*,2*R*,3*R*)). Decent to good control by the chiral ligands – under equilibration conditions – over the *Λ* or *Δ* configuration of the adducts was observed (d.r. 84:16 in $CHCl_3$ for the di(*tert*-butyl) tartrate derivative), the selectivity depending on the nature of the ester chains as well as on the solvent.

Introduction. – The octahedral geometry of the pentavalent hexacoordinated P-atom allows the formation of chiral anions – Δ and Λ enantiomers – by complexation of the central P-atom with three identical symmetric bidentate ligands [1][2]. Tris(benzenediolato)phosphate anion **1**, of particular interest for its easy preparation from pyrocatechol (= benzene-1,2-diol), PCl_5, and an amine, is unfortunately configurationally labile in solution as an ammonium salt, due to an acid-induced racemization mechanism [3]. Previously, we reported that the introduction of electron-withdrawing Cl-atoms at 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



1 **2** **3** **4**

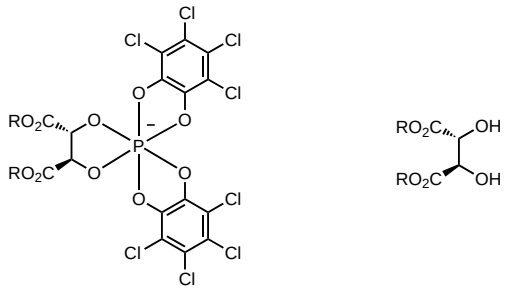
Fig. 1. *Known hexacoordinated phosphate anions:* **1**, **2** (TRISPHAT), **3**, *and* **4** (BINPHAT)

efficient NMR chiral shift, resolving, and asymmetry-inducing reagent for organic and organometallic derivatives – with a predilection for metalloorganic complexes [5].

However, with some chiral C_2-symmetric cations, low NMR shifts and asymmetry-inducing properties were recently observed with 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 a symmetry in asymmetric reactions or molecular recognition processes [6][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 around the P-atom [8].

However, chiral induction is, as a general rule, not very efficient for bidentate ligands. In tris(bidentate) octahedral complexes, most successful examples of predetermination of chirality have thus been made with three chiral bidentate ligands [8][9]. When only one chiral ligand and two achiral bidentate ligands are coordinated to a metal center, only sterically demanding ligands lead to measurable effects of chiral induction upon complex formation. But diastereoselectivity remains low in most cases and often depends upon noncovalent 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 diastereoisomers [3c][11].

Recently, we have shown that the chiral C_2-symmetric ligand binol (= [1,1′-binaphthalene]-2,2′-diolato(2−)) can control single-handedly the configuration of the resulting anion BINPHAT **4** (diastereoisomer ratio (d.r.) > 39:1) [6][1]). 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



5a R = Me
b R = Et
c R = i-Pr
d R = *t*-Bu

6a R = Me
b R = Et
c R = i-Pr
d R = *t*-Bu

Fig. 2. *Phosphate anions* **5a**–**d** *containing tartrate esters* **6a**–**d** *as ligands.* Ligands **6** are represented with their natural (2*R*,3*R*) configuration.

[1]) BINPHAT **4** – synthesized in a one-pot process and good yield – is, however, sensitive to acids and decomposes rapidly in $CHCl_3$ or CH_2Cl_2 when associated with acidic ammonium counterions.

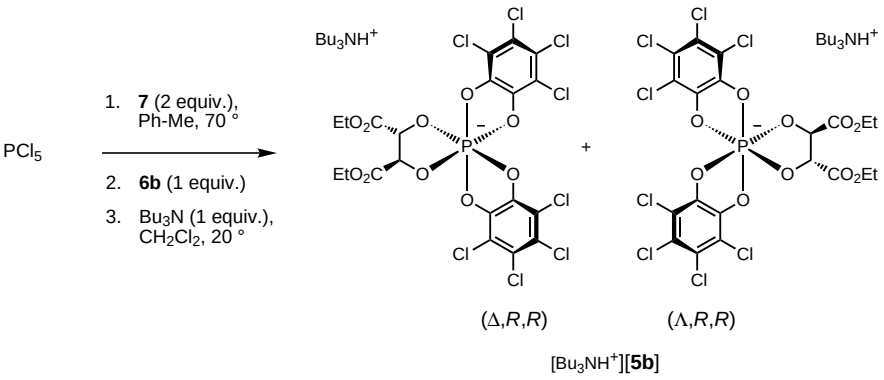
approach with other chiral diols. Herein, we report on the synthesis of C_2-symmetric phosphate anions **5** containing tartrate esters as chiral auxiliaries and on the resulting asymmetric induction (diastereoselectivity) from the ligands.

2. Results and Discussion. – 2.1. *General Considerations.* Our goal was, thus, to synthesize new C_2-symmetric hexacoordinated phosphate anions of configuration Δ or Λ controlled by a chiral ligand. Dialkyl tartrates **6** are chiral C_2-symmetric diols, which have been used to a large extent in asymmetric syntheses as ligands/auxiliaries [12] or as starting materials from the chiral pool to prepare more elaborate substrates or ligands [13]. The ester substituent can be easily modified, and this gives a possibility of facile ligand optimization. Furthermore, many derivatives are cheaply available from commercial sources in both the natural L ((2*R*,3*R*)) and the unnatural D ((2*S*,3*S*)) series. For these reasons, we selected tartrate esters as chiral ligands and decided to test their efficiency as chiral inducers for the determination of configuration of hexacoordinated phosphate anions. Commercially available dialkyl L-tartrates **6a** (R=Me), **6b** (R=Et), **6c** (R = i-Pr), and **6d** (R = *t*-Bu) were chosen for these studies (*Fig. 2*). The enantiomeric D-**6a** was also used routinely.

Keeping in mind the overall efficiency of anion **2** in asymmetric applications [5], we chose to introduce two tetrachloropyrocatechol (**7**) moieties along with the chiral ligand. However, the desired anions of general structure **5** (*Fig. 2*) were unknown in the literature. Thus, an efficient and general synthetic procedure was developed for their preparation. Several routes were considered before achieving this goal. They are described in the following paragraphs.

2.2. *Synthesis of Phosphate Anions* **5a**–**d**: *Preliminary Studies.* For the synthesis of anions **5**, we first attempted to adapt the synthetic procedure developed for TRISPHAT **2** [4]. Diol **7** (2 equiv.) was thus added to a solution of PCl_5 in toluene at 70° and heated for 15 min to 16 h. Then, ligands D-**6a**, **6b**, or **6c** were added, and after four more hours, concentration *in vacuo* and successive additions of CH_2Cl_2 and Bu_3N (1.0 equiv.) resulted in the formation of complex crude mixtures containing – as minor products – the desired salts [Bu_3NH][**5a**], [Bu_3NH][**5b**], or [Bu_3NH][**5c**] (see *Scheme 1* for ligand **6b**).

Scheme 1. *Direct Synthesis of [Bu_3NH][**5b**] from PCl_5, Tetrachloropyrocatechol* (**7**), *and Ligand* **6b**



The best result was obtained with ligand **6b**. ^{31}P-NMR Analysis ((D$_6$)DMSO) of the crude reaction mixture revealed two signals in the -80 ppm region indicating the presence of two diastereoisomeric anions ((*Δ*,2*R*,3*R*) or (*Λ*,2*R*,3*R*)) and this with a high diastereoselectivity (d.r. $> 90:10$). ^{1}H-NMR Analysis confirmed the high selectivity and revealed, for the major diastereoisomer, a large ^3J(H,P) coupling constant (21 Hz) between the H-atoms of the tartrate backbone and the central P-atom, whereas a much smaller coupling (8 Hz) was observed for the minor diastereoisomer (*vide infra*, *Sect. 2.6*)[2]). Fortunately, spontaneous crystallization of the predominant diastereoisomer of [Bu$_3$NH][**5b**] occurred from the crude oil and – after a week – several crystals suitable for X-ray analysis could be picked up by hand with pliers[3]). Low-temperature X-ray structural analysis revealed the presence of two cations and two anions in the asymmetric unit, the anions having the same Λ configuration and differing only by the s-*cis* or s-*trans* conformations of the ethyl chains of the esters groups. Enantiomerically and diastereoisomerically pure [Bu$_3$NH][**5b**] of (*Λ*,2*R*,3*R*) configuration was, therefore, isolated. Near-perfect octahedral structures were obtained for the anions. The largest deviation from octahedral angles at the P-atom is 5.3°. The P–O bond lengths of the O-atoms linked to the tartrate ligands (P–O(tartrate) 1.67 Å) are shorter than the

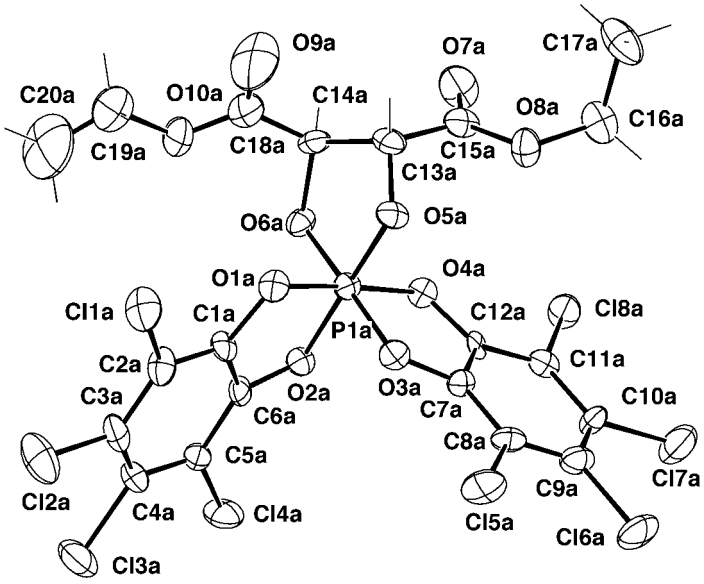


Fig. 3. *Perspective view of anion* **a** *of [Bu$_3$NH][**5b**$_L$]*. The Bu$_3$NH$^+$ cation is omitted for clarity; ellipsoids are represented with 40% probability level. Selected bond lengths [Å]: P(1a)–O(1a) 1.721(8), P(1a)–O(2a) 1.722(7), P(1a)–O (3a) 1.727(7), P(1a)–O(4a) 1.743(8), P(1a)–O(5a) 1.656(7), P(1a)–O(6a) 1.682(7), P(1b)–O(1b) 1.706(8), P(1b)–O(2b) 1.722(8), P(1b)–O(3b) 1.739(8), P(1b)–O(4b) 1.707(8), P(1b)–O(5b) 1.668(8), P(1b)–O(6b) 1.669(8)

---

[2]) The absence of ^3J(H,H) coupling constants between the H-atoms is probably due *i*) to a fast exchange between the available conformations (*λ* and *δ*) of the 5-membered ring and *ii*) to the H–C–C–H torsional angles (86.4 and 91°, as determined by X-ray structural analysis, *vide infra*) which are close to a 90° value.

[3]) Several picked up crystals were dissolved in (D$_6$)DMSO and analyzed by ^{1}H-NMR to confirm their chemical nature.

others (P–O(pyrocatechol) 1.72 Å) [2e]. This can be considered as the result of an electronic interaction of the σ(P–O(tartrate)) with the σ^*(P–O(pyrocatechol)) orbitals [2e][14].

However, purification of salts [Bu_3NH][**5a**], [Bu_3NH][**5b**], or [Bu_3NH][**5c**] by selective precipitation or crystallization could never be realized in a controlled manner. Reactions with D-**6a** led to complex mixtures of products (6 different signals were observed in ^{31}P-NMR) from which pure [Bu_3NH][D-**5a**] salt could not be isolated. A similar observation was made with ligand **6c**. Usually, precipitation of [Bu_3NH][**2**] occurred along with desired [Bu_3NH][**5a**–**c**] salts, the TRISPHAT salt being sometimes the major component of the crude mixture. Many reactions were performed to improve this synthetic route without any success. We, thus, turned our attention to the design of a more efficient synthetic route.

2.3. *Optimized Synthesis of Anions* **5a**–**d**: *Synthetic Strategy.* We supposed that the principal problem of the route outlined in *Sect. 2.2* was the presence of different bidentate ligands, which could react simultaneously and lead to four different anionic compounds. This is represented in *Fig. 4* 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 distribution among the four possible products is then expected, the desired compound [$P(aa)_2(bb)$] being synthesized in a maximum 44% theoretical yield.

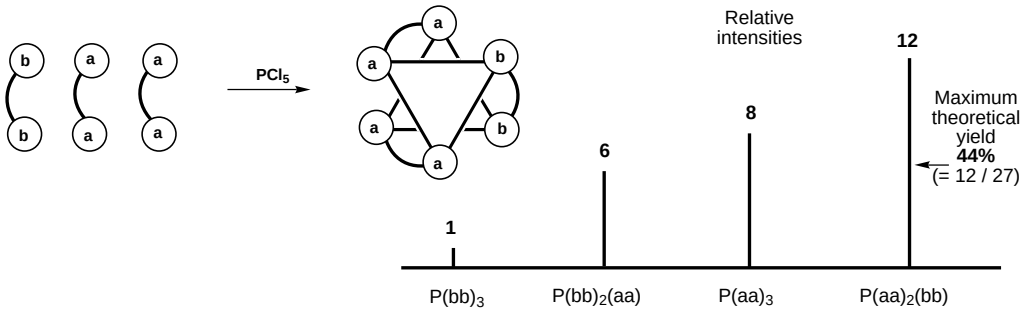
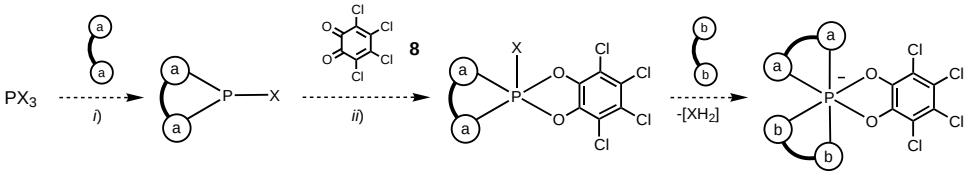


Fig. 4. *Statistical distribution among possible phosphates from the reaction of two different ligands* ((aa) and (bb), 2:1 ratio) *and* PCl_5

To obtain a mixed [$P(aa)_2(bb)$] adduct in high yield and to the exclusion 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 [15]. Undeniably, if only one ligand were present at each chelation step, all chances of mutual competition between ligands would be nullified and the resulting mixture of compounds be avoided. A synthetic route of 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, RO, R_2N) can react with the OH groups of tartrate to form monochelated adducts [16], and *ii*) monocyclized P^{III} compounds are readily oxidized to bicyclic spirophosphoranes with *ortho*-chloranil (= 3,4,5,6-tetrachlorocyclohexa-3,5-diene-1,2-dione; **8**) as an oxidant (*Scheme 2*) [2d][17]. These two chelation steps were

Scheme 2. *Synthetic Strategy for the Preparation of [XH_2][$P(aa)_2(bb)$] Salts*

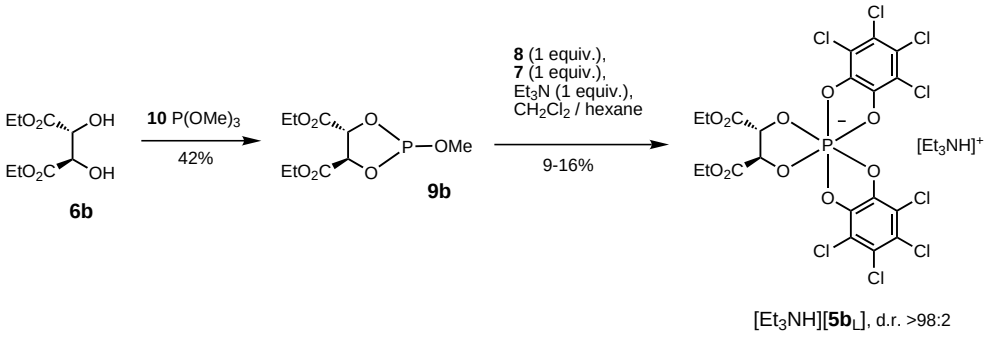


i) *ii*) See text.

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 *Scheme 2*) 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 a base – such as an amino group – then the two protons delivered by the last diol (bb) would be directly scavenged in solution with no need to add an extra base. Salts [XH_2][$P(aa)_2(bb)$] would directly result from the procedure. We also recognized that most diols are compatible with *ortho*-chloranil (**8**), and thus the last two chelation steps could be performed in a one-pot procedure.

2.4. *Optimized Synthesis of Anions* **5a**–**d**: *First Approach*. In our initial attempts to synthesize anions **5a**–**d** following the guidelines of *Scheme 2*, we decided to introduce chiral ligands **6a**–**d** at the beginning of the synthesis (as ligand (aa)). We assumed that an early chelation of the chiral ligands around the P-atom would maximize the chances of asymmetric induction at each of the following steps. However, making the starting P^{III} adducts of tartrate esters **6a**–**d** turned out to be more challenging than initially foreseen, reported yields and/or purity being difficult to reproduce in our hands[4]). Only phosphite **9b**, obtained by the direct reaction of **6b** and trimethyl phosphite ($P(OMe)_3$; **10**), could be once isolated in decent yield (42%) and high chemical purity [18] (*Scheme 3*).

Scheme 3. *Two-Step Synthesis of [Me_2NH_2][***5b***]* via *Phosphite* **9b**



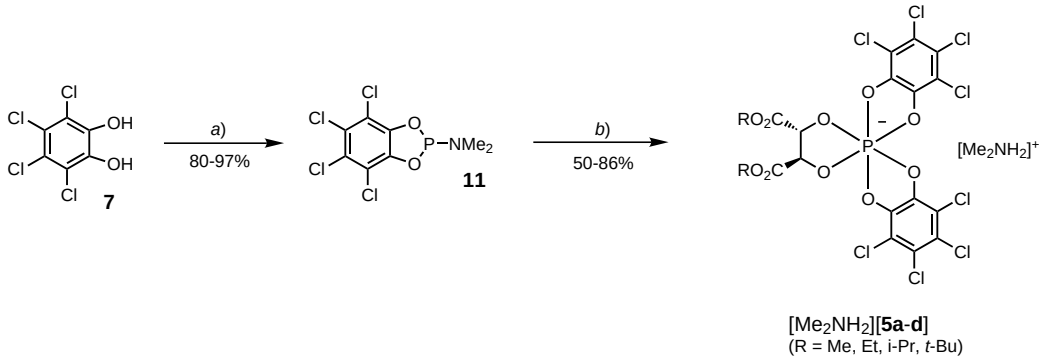
[4]) High sensitivity of the adducts to O_2 as well as difficult separation of the products – when ammonium halide salts were involved as by-products – are probably responsible for the low yields or lack of reproducibility.

Successive treatment of a solution of **9b** in CH_2Cl_2 with **8** (1.0 equiv., 85°), **7** (1.0 equiv.), and Et_3N (1.0 equiv.) afforded – after the addition of hexane – the desired $[Et_3NH][\mathbf{5b}]$ salt as a white solid albeit in low yield (9%). The precipitate contained only one diastereoisomer ($^3J(H,P) = 21$ Hz) and no trace of TRISPHAT anion. Performing the reaction at 50° instead of 85° improved slightly the yield from 9 to 16%, but not enough to make this protocol useful. We thus turned our attention to a second and final approach.

2.5. *Optimized Synthesis of Anions* **5a**–**d**: *Second Approach*. We considered starting with phosphoramidite **11** derived from tetrachloropyrocatechol **7** and introducing the chiral ligands **6a**–**d** in the last step (as ligands (bb) in *Scheme 2*); this approach being more practical and elegant in terms of strategy as it could be generalized to all the tartrate esters. Compound **11**, simply prepared by heating anhydrous **7** and freshly distilled $P(NMe_2)_3$ (**12**) in refluxing toluene, was obtained in good to excellent yields (80–97%) after purification by sublimation (*Scheme 4*). Then, treatment of **11** (1.7 equiv.) with **8** (1.7 equiv.) and ligands **6a**–**d** (1.0 equiv.) in an appropriate solvent combination afforded the desired $[Me_2NH_2][\mathbf{5a}–\mathbf{d}]$ salts in moderate to good yields. The crude mixture obtained 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 $[Me_2NH_2][\mathbf{5a}–\mathbf{d}]$ even easier, and the desired salts were obtained in moderate to good yields (30–86%, *Table 1*).

This procedure is the result of many attempts to optimize yields and purity of the salts $[Me_2NH_2][\mathbf{5a}–\mathbf{d}]$. We noticed, *e.g.*, that the best yields are obtained with 1.7 equiv. of **8** and **11**[5]), lower or larger amounts of these reagents leading to diminished outputs. Time is also a crucial factor as yields are always much lower after 4 h of reaction than after 16 h (*Table 1*). Careful choice of the solvent medium is also required. In too polar solvents or solvent combinations, salts $[Me_2NH_2][\mathbf{5a}–\mathbf{d}]$ are rather soluble and do not precipitate quantitatively. Under too low polar conditions, precipitation of by-products and contaminants – such as $[Me_2NH_2][\mathbf{2}]$ – occurs along

Scheme 4. *Optimized Synthesis of* $[Me_2NH_2][\mathbf{5a}–\mathbf{d}]$



a) **7** (1.7 equiv. for 1.8 equiv. of $P(NMe_2)_3$ (**12**)), NH_4Cl (2 mol-%), toluene, reflux. *b*) *o*-chloranil (**8**; 1.7 equiv.), **6a** (1.0 equiv.), solvent, 20°.

---

[5]) In the one-pot protocol, 1.8 equiv. of **12** and 1.7 equiv. of **7** are used.

Table 1. *One-Pot Syntheses of Salt [Me_2NH_2][**5a**–**d**]*

Anion	Ester	Solvent	Time	Yield [%]	d.r.[a])		[Me_2NH_2][**2**]
					$\mathbf{5}_L$	$\mathbf{5}_S$	
5a	Me	Et_2O	16 h	83	75	25	10%
	Me	Et_2O	4 h	61	98	2	–
	Me	CH_2Cl_2/hexane 1 : 1	16 h	58	73	27	–
5b	Et	CH_2Cl_2/hexane 1 : 1	64 h	86	44	56	6%
	Et	CH_2Cl_2/hexane 4 : 1	4 h	30	94	6	< 2%
5c	i-Pr	CH_2Cl_2/hexane 3 : 1	16 h	72	14	86	4%
5d	*t*-Bu	CH_2Cl_2/hexane 1 : 1	16 h	71	51	49	2%
	t-Bu	CH_2Cl_2/hexane 1 : 1	4 h	50	51	49	4%

[a]) In the precipitate ((D$_6$)DMSO): The ratios may vary from one reaction to the next.

with the desired [Me_2NH_2][**5a**–**d**] ion pairs. Therefore, it was necessary to optimize the solvent conditions for each ligand **6a**–**d** as we noticed strong solubility differences for the derived anions (*Table 1*).

The diastereoisomer purity of salts [Me_2NH_2][**5a**–**d**] was determined by ^{1}H- and ^{31}P-NMR, and care was taken to use (D$_6$)DMSO as the NMR solvent as *Koenig* and *Klaebe* had shown that only little epimerization occurred for chiral hexacoordinated phosphate **3** in this medium [3c]. In the ^{1}H-NMR spectra, we could usually observe two different sets of signals corresponding to the two possible diastereoisomers (*e.g.*, (*Λ*,*R*,*R*) and (*Δ*,*R*,*R*) from L-tartrate esters), and the diastereoisomer purity was then determined by integration of the respective signals. In all cases, we noticed that the signals of the H-atoms of the tartrate backbone appeared as *d*s due to a coupling to the central P-atom. This was confirmed by the ^{31}P-NMR spectra measured under non-decoupled conditions (*Figs. 5* and *6*[2])). Comparing the spectroscopic data, we observed that the spectrum of one diastereoisomer of each anion **5a** to **5d** showed always a larger value for its ^3J(H,P) coupling constant than of the other (*Fig. 5*, *Table 2*)[6]).

During the course of this study (*vide infra*, *Sect. 2.6* and *2.7*), we came to realize that this difference in the value of the coupling constants is an important analytical parameter for the determination of the relative and absolute configuration ((*Δ*,*R*,*R*) or (*Λ*,*R*,*R*)) of the diastereoisomers. For this reason, we chose to label the diastereoisomers of anions **5a**–**d** with the letters L ($\mathbf{5a}_L$–$\mathbf{d}_L$) and S ($\mathbf{5a}_S$–$\mathbf{d}_S$) to indicate the large or small nature of their ^3J(H,P) coupling constant. Detailed analysis of the spectroscopic data then revealed that the ^{1}H- and ^{31}P-NMR signals of diastereoisomers $\mathbf{5a}_L$–$\mathbf{d}_L$ were always downfield compared to those of $\mathbf{5a}_S$–$\mathbf{d}_S$. We also observed – for each of the diastereoisomer series $\mathbf{5a}_L$–$\mathbf{d}_L$ and $\mathbf{5a}_S$–$\mathbf{d}_S$ – a decrease in the magnitude of the ^3J(H,P) coupling constant – 23 to 9.7 Hz and 16 to 2.9 Hz, respectively – with an increase in size of the ester side chains (from Me to *t*-Bu, *Table 2*).

Although it was necessary to find optimal solvent conditions for each of the chiral ligand used, this strategic route turned out to be the best as we could repeatedly prepare

---

6) The *Karplus*-like relationship for the hexacoordinated P-atom has not yet been fully recognized (see [2e] and ref. cit. therein). Therefore, it is difficult to extrapolate structural information from the values of the ^3J(H,P) coupling constants.

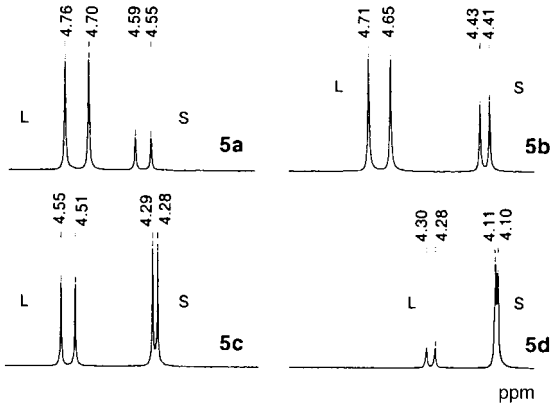


Fig. 5. *^{1}H-NMR Spectra* (400 MHz, (D_6)DMSO, parts) *of the H-atoms of the tartrate backbone of salts [Me_2NH_2][**5a**–**d**]*. L and S indicate the nature $\mathbf{5a}_L$–$\mathbf{d}_L$ or $\mathbf{5a}_S$–$\mathbf{d}_S$ of the diastereoisomers (see text). δ values in ppm.

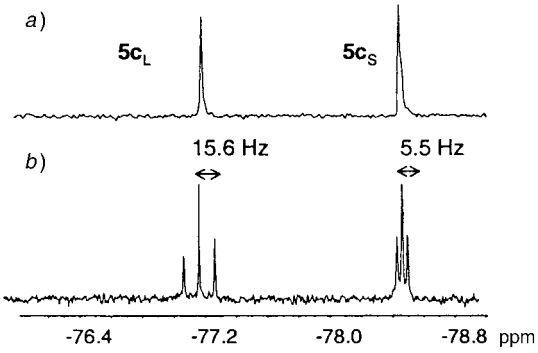


Fig. 6. *a) $^{31}P\{^1H\}$- and* b) *^{31}P-NMR Spectra* (162 MHz, (D_6)DMSO) *of [Me_2NH_2][**5c**]*. For subscripts L and S, see text.

Table 2. *^{3}J(H,P) Coupling Constants* [Hz], *^{31}P-NMR Chemical Shifts* δ [ppm], *and Absolute Configurations of Diastereoisomers* $\mathbf{5a}_L$–$\mathbf{5d}_L$ *and* $\mathbf{5a}_S$–$\mathbf{5d}_S$. Solvent (D_6)DMSO.

Anion	Ester	$\mathbf{5a}_L$–$\mathbf{d}_L$			$\mathbf{5a}_S$–$\mathbf{d}_S$			Major diastereoisomer[b])
		^3J(H,P)	δ (P)	isomer[a])	^3J(H,P)	δ (P)	isomer[a])	
5a	Me	23	– 76.4	*A*	16	– 77.3	*A*	$\mathbf{5a}_L$
5b	Et	21	– 76.4	*A*	9.2	– 77.7	*A*	$\mathbf{5b}_L$
5c	i-Pr	15.6	– 76.6	*A*	5.5	– 77.9	*A*	$\mathbf{5c}_S$
5d	*t*-Bu	9.7	– 77.2	*A*	2.9	– 78.8	*A*	$\mathbf{5d}_S$

[a]) Configuration of the anion obtained from ligands **6a**–**d** of (2*R*,3*R*) configuration (*vide infra*, *Sect. 2.7*). [b]) On average in the precipitate ((D_6)DMSO).

the desired anions. While these reactions were reproducible in terms of yields (*Table 1*), we found that the diastereoselectivity strongly varied from one reaction to the next without being able to pinpoint which factor was determinant. With decent

amounts of salts $[Me_2NH_2][\mathbf{5a}-\mathbf{d}]$ in hand, we turned our attention to the initial question, that is the efficiency – or not – of the tartrate ester ligands **6a**–**d** to control – under equilibration conditions – the configuration at the P stereogenic center.

2.6. *Predetermination of Configuration of* **5a**–**d** *by Ligands* **6a**–**d**: *Solvent and Substituent Effects.* Upon dissolution of $[Me_2NH_2][\mathbf{5a}-\mathbf{d}]$ in (D_4)MeOH, we could observe a slow but definite equilibration between diastereoisomers $\mathbf{5a}_L-\mathbf{d}_L$ and $\mathbf{5a}_S-\mathbf{d}_S$. The diastereoisomer ratios changed from their initial values to a *ca.* 75 : 25 ratio after *ca.* 250 h of equilibration, and this always in favor of diastereoisomers $\mathbf{5a}_L-\mathbf{d}_L$ (*Fig. 7*); little influence on the diastereoselectivity of the nature of the ester chains was observed.

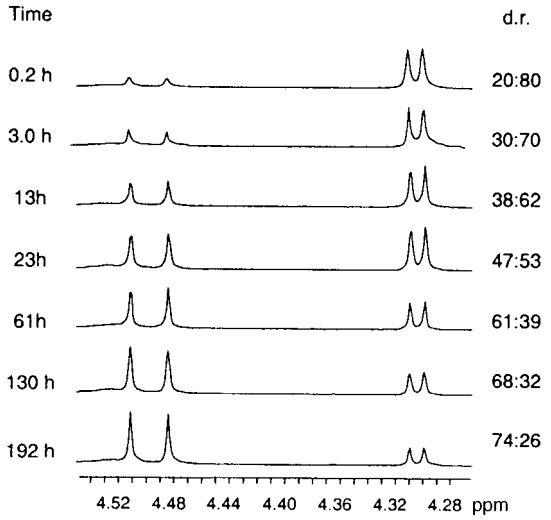


Fig. 7. *Epimerization of* $[Me_2NH_2][\mathbf{5a}]$ *as a function of time, as established by* ^{1}*H-NMR* (400 MHz, (D_4)MeOH)

However, with $CDCl_3$ – or $CDCl_3/(D_6)$DMSO mixtures – as solvent, the changes were more dramatic as the equilibrium positions could be reached after dissolution in much shorter periods of time (*ca.* 5–10 h). Diastereoisomers $\mathbf{5a}_S-\mathbf{d}_S$ were always favored, and a strong influence on the diastereoselectivity of the nature of the ester ligands was found as an increase in the diastereoisomer ratios while progressing in the ester series from Me to *t*-Bu, from 65 : 35 (**5a**) to 70 : 30 (**5b**), 80 : 20 (**5c**), and 84 : 16 (**5d**) (*Fig. 8*). All these results demonstrated a rather poor configurational stability in solution for anions **5a**–**d** in [ammonium][**5a**–**d**] salts. However, we were pleased to see that at least one of the ligands, namely **6d**, could provoke in $CDCl_3$ a decent amount of asymmetric induction. Solvent effects were further documented as we observed a slightly reduced diastereoselectivity upon equilibration of salt $[Me_2NH_2][\mathbf{5d}]$ in CD_2Cl_2 (80 : 20, resp., in favor diastereoisomer $\mathbf{5d}_S$ instead of 84 : 16 in $CDCl_3$).

In conclusion, the high diastereoselectivity sometimes observed for the $[Me_2NH_2][\mathbf{5a}-\mathbf{d}]$ salts isolated by precipitation was fortunate. When dissolved, an equilibration between the diastereoisomers occurred, the rate and position of the equilibrium depending on the solvent and the ester substituents. Only in the case of phosphate anion **5d** (*t*-Bu) and with $CDCl_3$ as solvent, a rather high diastereoselectivity

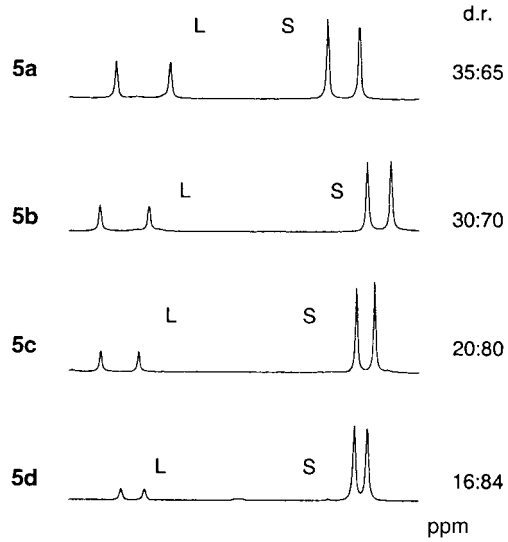
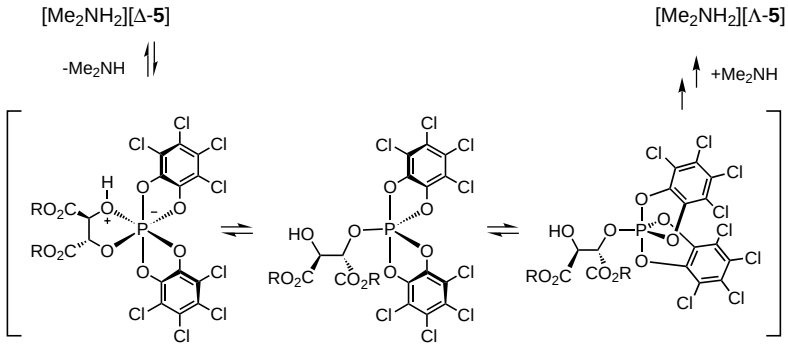


Fig. 8. *Asymmetric induction by the ester ligands of [Me_2NH_2][**5a**–**d**] in 10% (D_6)DMSO/$CDCl_3$, as established by ^{1}H-NMR* (400 MHz, $\Delta\delta$ 0.4 ppm) *after equilibration*

(d.r. 84:16) could be observed after epimerization. We concluded that the epimerization between $\mathbf{5a}_L$–$\mathbf{d}_L$ and $\mathbf{5a}_S$–$\mathbf{d}_S$ results from the electron-rich nature of the O-atoms of ligands **6a**–**d**. They can be protonated by the acidic $Me_2NH_2^+$ counter ion. This labilizes the P–O bonds and provokes a ring opening to a configurationally labile spirophosphorane (*Scheme 5*) [4a][7]).

Scheme 5. *Mechanistic Rational for the Equilibration of Diastereoisomers* $\mathbf{5a}_L$–$\mathbf{d}_L$ *and* $\mathbf{5a}_S$–$\mathbf{d}_S$



2.7. *Relative and Absolute Configurations of Anions* **5a**–**d**. In *Sect. 2.6*, several trends concerning the equilibration in solution of diastereoisomers $\mathbf{5a}_L$–$\mathbf{d}_L$ and $\mathbf{5a}_S$–$\mathbf{d}_S$, were demonstrated, but the configuration of these diastereoisomers was not established yet. Thus, all the previous epimerization experiments were performed again and

---

7) There was no direct observation of phosphorane intermediates. They can be bipyramidal, square-planar pyramidal, or any structure in-between. See [1f].

monitored by circular dichroism (CD). MeOH Solutions of salts $[Me_2NH_2][\mathbf{5a}-\mathbf{d}]$, obtained from ligands D-**6a** (2*S*,3*S*) and **6b**–**d** ((2*R*,3*R*)), were prepared and allowed to equilibrate. The starting solutions contained different diastereoisomeric compositions – essentially $\mathbf{5a}_L$, $\mathbf{5b}_S/\mathbf{5b}_L$ (*ca.* 1:1), $\mathbf{5c}_S$, and $\mathbf{5d}_S$, respectively – and equilibrated to give very similar spectra (*Fig. 9*). This indicated – by correlation of these results with those of the ^{1}H- and ^{31}P-NMR experiments (*vide supra*, *Sect. 2.6*) – that diastereoisomers $\mathbf{5a}_L-\mathbf{d}_L$ (predominant after equilibration in MeOH) are all of identical relative configurations. As it can be expected, the CD spectrum of $[Me_2NH_2]$[D-**5a**] obtained from D-**6a** (*Fig. 9*,*d*) has *Cotton* effects opposite to those of $[Me_2NH_2][\mathbf{5b}-\mathbf{d}]$, obtained from **6b**–**d** ($\Delta\varepsilon_{221}=+50$, $\Delta\varepsilon_{211}=-50$ M^{-1} cm^{-1}, *Fig. 9*,*a*–*c*). Importantly, we also noticed that the CD spectra of solutions of $[Me_2NH_2]$[**5c**] and $[Me_2NH_2]$[**5d**] (containing essentially diastereoisomers $\mathbf{5c}_S$ and $\mathbf{5d}_S$ at the beginning) revealed immediately after dissolution (*Fig. 10*,*a*) *Cotton* effects opposite to those observed after equilibration (*Fig. 10*, *b*), demonstrating without ambiguity that diastereoisomers $\mathbf{5a}_L-\mathbf{d}_L$ and $\mathbf{5a}_S-\mathbf{d}_S$ have opposite relative configurations at the P-atom. Assignment of the relative and absolute configurations of diastereoisomers $\mathbf{5a}_L-\mathbf{d}_L$ – obtained from ligands **6a**–**d** ((2*R*,3*R*)) – was then easy as anion $\mathbf{5b}_L$ had already been characterized as having a (*Λ*,*R*,*R*) configuration by X-ray analysis. Assignment of the (*Δ*,*R*,*R*) configuration to diastereoisomers $\mathbf{5a}_S-\mathbf{d}_S$ – although it could be deduced – was carried out experimentally by X-ray diffraction analysis of crystals of pure $[Me_2NH_2][\mathbf{5d}_S]$ obtained from **6d** (*Fig. 11*).

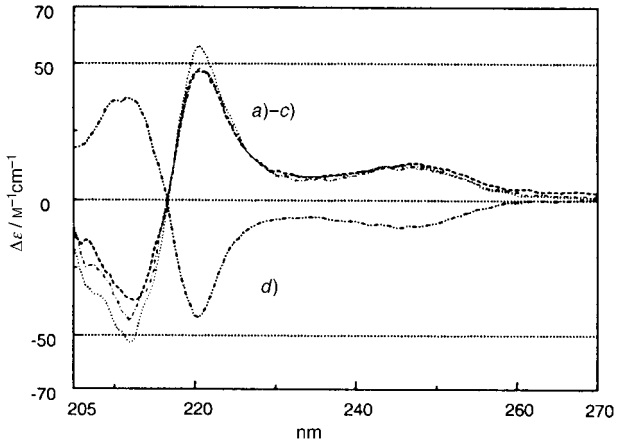


Fig. 9. *CD Spectra* (MeOH, $1.3\cdot10^{-5}$ M) *after a prolonged period of time* a)–c) *of* $[Me_2NH_2][\mathbf{5b}-\mathbf{d}]$, *obtained from* **6b**–**d** ((2*R*,3*R*)), *and* d) *of* $[Me_2NH_2]$[D-**5a**], *obtained from* D-**6a** ((2*S*,3*S*))

3. Conclusions. – We have shown that C_2-symmetric hexacoordinated phosphate anions can be easily synthesized in a 'one-pot' process from easy-to-make or commercially available starting materials. These anions could be sometimes obtained as solids in high diastereoisomer purity. However, once dissolved, they epimerized rather rapidly. In $CHCl_3$, modest to good selectivities were observed starting with (2*R*,3*R*)-tartrate esters (d.r. 65:35 (Me) to 84:16 (*t*-Bu), *Δ* isomer), the asymmetric induction improving with the increase in size of the ester substituent. Interestingly, with

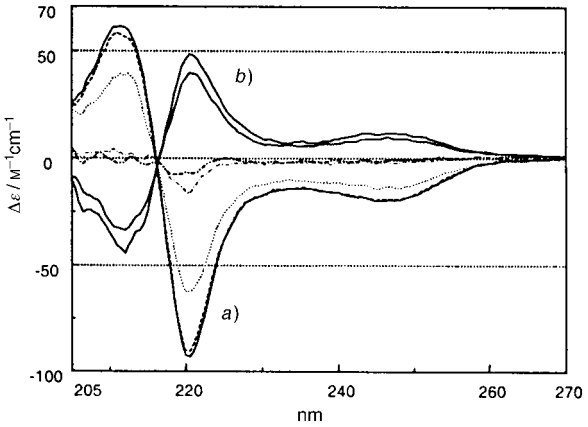


Fig. 10. *CD Spectra of [Me_2NH_2][**5d**], obtained from* **6d** ((2*R*,3*R*)), *as a function of time* (MeOH, $1.3 \cdot 10^{-5}$ M): a) *initial time,* $\mathbf{5d}_S/\mathbf{5d}_L$ *80:20 and* b) *after 170 h*

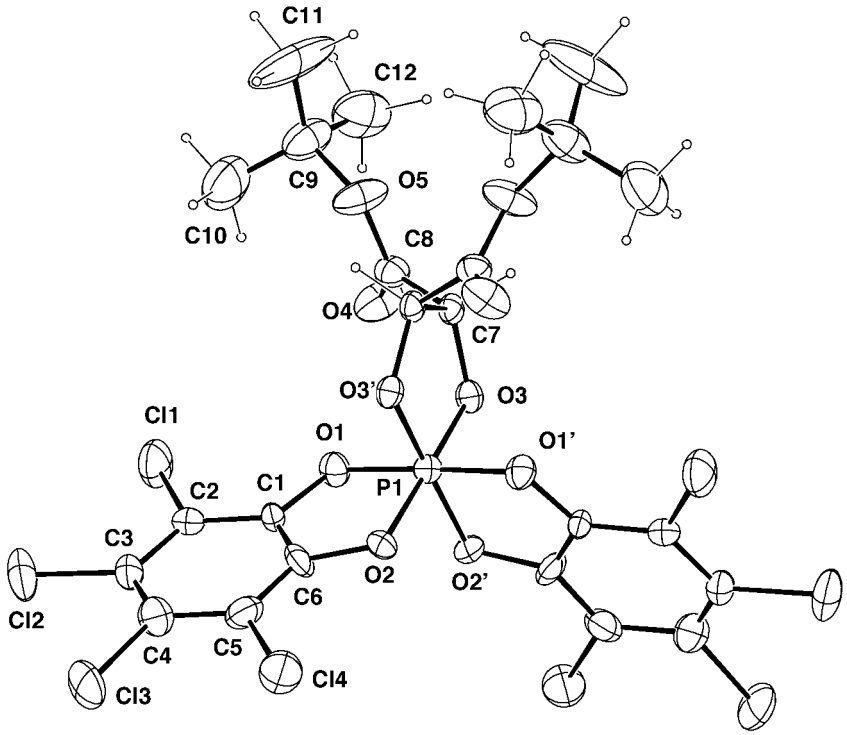


Fig. 11. *Perspective view of the anion of [Me_2NH_2][**5d**$_S$] · MeOH*. The cation $Me_2NH_2^+$ and MeOH are omitted for clarity; ellipsoids are represented with 40% probability level.

MeOH as solvent, the configuration of the preferred diastereoisomer was different as the (2*R*,3*R*) backbone of the tartrate esters induced as *Λ* configuration for the anions (d.r. *ca.* 75:25, independent of the ester substituent). Application of these anions as

chiral auxiliaries and/or ligands for asymmetric reactions and processes are currently studied in our group.

We thank the *Swiss National Science Foundation*, the *Federal Office for Education and Science* (COST D11), and the '*Société Académique de Genève*' for financial support, as well as the *Fondation de Famille Sandoz* for professor (*J. L.*) and post-doctoral (*V. D. B.*) fellowships.

Experimental Part

General. All reactions were carried out under dry N_2 or Ar by means of an inert gas/vacuum double manifold and standard *Schlenk* techniques with magnetic stirring, unless otherwise stated. Solvents were dried and distilled prior to use. $CHCl_3$ (*Fluka*) and $CDCl_3$ (*SDS*) were filtered over basic alumina before use. Et_2O was distilled from Na metal and benzophenone ketyl. Toluene was distilled from Na metal. MeOH, hexane, and CH_2Cl_2 were distilled from CaH_2. Deionized H_2O was used for aq. solns. Commercially available tetrachloropyrocatechol (**7**) is monohydrated and needs to be thoroughly dried by azeotropic distillation (toluene) prior to any use. Commercially available ligands **6a** (*Aldrich* or *Fluka*), **6b** (*Fluka*), **6c** (*Fluka*), and **6d** (*Fluka*) were used without further purification. In all the phosphate-salt syntheses, the stereoselectivity was determined at the precipitation step by NMR analysis of the precipitate in (D_6)DMSO since this solvent seems to prevent fast epimerization between the diastereoisomers, thus giving a good image of the real diastereoisomer composition of the precipitate. Depending on the tartrate esters and reaction conditions, low to good diastereoselectivity was observed. When the two diastereoisomers were present, both NMR interpretations are given when possible. The diastereoisomers are distinguished by the small (S) or large (L) nature of the ^3J(H,P) coupling constants and are labeled accordingly as $\mathbf{5}_S$ or $\mathbf{5}_L$. M.p.: open capillary tubes, *Stuart-Scientific SMP3* melting-point apparatus; uncorrected. $[\alpha]^{20}$: *Perkin-Elmer 241* polarimeter, thermostated (20°) 10-cm-long microcell, high-pressure sodium (λ 589 nm) or mercury lamps; *c* in g/100 ml.

UV/VIS Spectra: λ_{max} (ε) in nm. CD Spectra: $\lambda(\Delta\varepsilon)$ in nm. IR Spectra: in cm^{-1}. NMR Spectra: at r.t. unless otherwise stated; *Bruker AMX-400* (^{1}H at 400, ^{13}C at 100, and ^{31}P at 162 MHz) and *Varian XL-200* (^{13}C at 50 MHz) spectrometers; chemical shifts δ(H) and δ(C) in ppm rel. to Me_4Si with the solvent resonance used as the internal standard (^{13}C: $CDCl_3$ 77.0 ppm, CD_3OD 49.0 ppm, (D_6)DMSO 39.5 ppm, (D_6)acetone 29.8 ppm), and δ(P) rel. to H_3PO_4, *J* in Hz; assignments by COSY, HETCOR, and/or NOESY data; C_q = quaternary center; most ^{13}C-NMR spectra were complicate due to the presence of two diastereoisomers, only spectra without ambiguity are reported. MS: *Varian CH$_4$* or *SM1* spectrometer electron-spray mass spectra (ES-MS) were obtained on a *Finnigan SSQ-7000* spectrometer by the Department of Mass Spectroscopy. Elemental analyses were performed at the 'Institut de Chimie Pharmaceutique de l'Université de Genève' by Dr. *H.-J. Eder*.

*Crystal-Structure Determination of [Bu$_3$NH][**5b**$_L$] and [Me$_2$NH$_2$][**5b**$_S$]·MeOH* (*Table 3*). Cell dimensions and intensities were measured by means of a *Nonius CAD4* and *Stoe STADI4* diffractometer with graphite-monochromated CuK_α radiation (λ = 1.5418 Å). Data were corrected for *Lorentz* and polarization effects and for absorption [19]. The structures were solved by direct methods with MULTAN 87 [20], all other calculations used XTAL [21] system and ORTEP [22] programs.

Both compounds show large disorders for the cationic moieties leading to relatively large uncertainties in the final geometrical parameters. [Bu_3NH][**5b**$_L$]: both anions (**a** and **b**) of the asymmetric unit have the same absolute configuration and differ only by the orientation of their Et substituent C(19)–C(20). One (Bu_3NH) cation **c** exhibits disorders, but only the N-atom is refined on two sites with population parameters of 0.80 and 0.20, resp. The other cation, **d**, shows much larger disorders and is refined on two distinct positions for all atomic sites with population parameters of 0.60 and 0.40, resp. Both cations are refined with restraints on bond lengths and bond angles. [Me_2NH_2][**5d**$_S$]·MeOH: the anionic moiety is located on a twofold axis with the P-atom on special position *3b*. The Me_2NH^+ and MeOH moieties are disordered and located approximately at the same sites, on both sides of the C_2 axis. A refinement in the space group $P3_1$ (without the C_2 axis) leads to the observation of the same disorders. These molecules are refined with restraints on bond lengths and bond angles and population parameters of 0.5 (equality of charges).

Crystallographic data (excluding structure factors) have been deposited with the *Cambridge Crystallographic Data Centre* (deposition No. 173668 and 173669 for [Bu_3NH][**5b**$_L$] and [Me_2NH_2][**5d**$_S$]·MeOH resp.). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. +44(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 3. *Crystal Data, Intensity Measurement, and Structure Refinement for [Bu_3NH][**5b**$_L$] and [Me_2NH_2][**5d**$_S$] · MeOH*

	[Bu_3NH][**5b**$_L$]	[Me_2NH_2][**5d**$_S$] · MeOH
Formula	$[P(C_6O_2Cl_4)_2\ (C_8H_{12}O_6)]^-$ $[NH(C_4H_9)_3]^+$	$[P(C_6O_2Cl_4)_2\ (C_{12}H_{20}O_6)]^-$ $[NH_2(CH_3)_2]^+\ (CH_3OH)$
M_r	913.3	861.1
Crystal system	monoclinic	trigonal
Space group	$P2_1$	$P3_121$
a [Å]	13.449(3)	10.809(1)
b [Å]	19.453(2)	10.809(1)
c [Å]	16.550(3)	28.391(3)
α [°]	90	90
β [°]	108.843(6)	90
γ [°]	90	120
V [Å^3]	4098(1)	2872.6(6)
Z	4	3
Dc [g · cm^{-3}]	1.480	1.493
μ(CuK_α) [mm^{-1}]	5.849	6.242
T_{min}, T_{max}	0.18029, 0.42569	0.31336, 0.62358
$((\sin\theta)/\lambda)_{max}$ [Å^{-1}]	0.52	0.53
Temperature [K]	170	200
No. measured refl.	10461	4771
No. observed refl.	8479	1745
Criterion for observed	$\lvert F_o\rvert > 4\sigma(F_o)$	$\lvert F_o\rvert > 4\sigma(F_o)$
Refinement (on F)	full-matrix	full-matrix
No. parameters	984	217
Restraints	60	4
Weighting scheme	$\omega = 1/[\sigma^2(F_o) + 0.001\ (F_o^2)]$	$\omega = 1/[\sigma^2(F_o) + 0.0004\ (F_o^2)]$
Max. and average Δ/σ	0.014, $0.11 \cdot 10^{-4}$	$0.39 \cdot 10^{-2}$, $0.23 \cdot 10^{-3}$
Max. and min. $\Delta\rho$ [e · Å^{-3}]	0.47, −0.37	0.51, −0.51
Flack parameter [23] x	0.02(2)	0.03(7)
S	1.94(2)	1.70(5)
R[a]), ωR[b])	0.053, 0.063	0.056, 0.056

[a]) $R = \Sigma\,|\,|F_o| - |F_c|\,|/\Sigma\,|F_o|$. [b]) $\omega R = [\Sigma\,(\omega\,|F_o| - |F_c|)^2/\Sigma\,\omega\,|F_o|^2]^{1/2}$ $S = [\Sigma\,\{((F_o - F_c)/\sigma(F_o))^2\}/(N_{ref} - N_{var})]^{1/2}$

1. *Tributylammonium (Λ)-Bis[3,4,5,6-tetrachlorobenzene-1,2-diolato(2−)-κO,κO′][diethyl (2*R*,3*R*)-2,3-di(hydroxy-κO)butanedioato(2−)]phosphate(1−)* ([Bu_3NH][(Λ-**5b**) = [Bu_3NH][**5b**$_L$]). To a soln. of PCl_5 (200.4 mg, 0.96 mmol) in toluene (2.0 ml) at 50°, anh. tetrachloropyrocatechol (**7**; 477.1 mg, 1.92 mmol) was slowly added and the mixture heated to 70°. After 15 min, **6b** ((2*R*,3*R*); 164.7 µl, 0.96 mmol) was added and the mixture stirred further for 22 h. Then, the mixture was allowed to cool to 20° and evaporated. After the addition of CH_2Cl_2 (8 ml) and Bu_3N (229.6 µl, 0.96 mmol), the mixture was stirred for 30 min and evaporated. No precipitate was formed, and a complex product mixture was analyzed by ^{1}H- and ^{31}P-NMR. However, upon standing for a few weeks at 20°, colorless crystals of pure [Bu_3NH][**5b**$_L$] appeared in the crude oil that were picked up by hand and analyzed by X-ray diffraction. Only partial spectral characterization was realized due to lack of material. M.p. 213°. ^{1}H-NMR (400 MHz, (D_6)DMSO): 0.88 (*t*, *J* = 7.2, 9 H); 1.01 (*t*, *J* = 7.2, 6 H); 1.30 (*sext.*, *J* = 7.2, 6 H); 1.55 (*m*, 6 H); 2.96 (br. *s*, 1 H); 3.00 (*m*, 6 H); 4.02 (*m*, 4 H); 4.67 (*d*, *J*(H,P) = 21, 2 H). ^{31}P-NMR (162 MHz, (D_6)DMSO): −77.1.

2. *(4*R*,5*R*)-2-Methoxy-1,3,2-dioxaphospholane-4,5-dicarboxylic Acid Diethyl Ester* (**9b**). Procedure adapted from [18]: Trimethyl phosphite (**10**; 1.77 ml, 15.0 mmol) and **6b** (2.60 ml, 15.0 mmol) were mixed under N_2 in a distillation apparatus. The mixture was heated to 100° until MeOH began to distil, then to 120° until the distillation stopped. The desired product was then obtained by distillation at 100°/0.05 mbar: **9b** (1.70 g, 42%). Colorless oil, which had to be kept under N_2. All spectroscopic data corresponded to literature data [16b].

^{1}H-NMR (400 MHz, (D_6)DMSO): 1.21 (*t*, *J* = 7.1, 3 H); 1.22 (*t*, *J* = 7.1, 3 H); 3.41 (*d*, *J*(H,P) = 11, 3 H); 4.18 (*m*, 4 H); 5.01 (*dd*, *J* = 5.8, 5.3, 1 H); 5.18 (*dd*, *J* = 5.3, 0.9, 1 H). ^{31}P-NMR (162 MHz, (D_6)DMSO): 110.8.

3. *Triethylammonium (Λ)-Bis[3,4,5,6-tetrachlorobenzene-1,2-diolato(2−)-κO,κO′][diethyl (2R,3R)-2,3-di(hydroxy-κO)butanedioato(2−)]phosphate(1−)* ([Et_3NH][**5b**$_L$]). To soln. of **9b** (266 mg, 1.00 mmol) in toluene (5.0 ml) at 85° was added *ortho*-chloranil (**8**; 246 mg, 1.00 mmol) in small portions. The resulting soln. was then heated at 85° until the intense red color disappeared (*ca.* 1 h), and the mixture was allowed to cool to r.t. Tetrachloropyrocatechol (**7**; 248 mg, 1.00 mmol) and Et_3N (136 µl, 1.00 mmol) were added. The mixture was then stirred at r.t. for 3 days, and some precipitate appeared, which was filtered, washed (toluene), and dried: [Et_3NH][**5b**$_L$] (75.0 mg, 9%). White solid. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.01 (*m*, 15 H); 3.08 (*m*, 6 H); 4.05 (*m*, 4 H); 4.67 (*d*, *J*(H,P) = 21, 2 H); 9.23 (br. *s*, 1 H). ^{13}C-NMR (50 MHz, (D_6)DMSO): 8.7 (Me); 13.6 (Me); 45.7 (CH_2); 61.1 (CH_2); 70.2 (*d*, *J* = 2.6, CH); 111.1 (*d*, *J*(C,P) = 19, C_q); 112.5 (*d*, *J*(C,P) = 18, C_q); 120.1 (C_q); 120.2 (C_q); 142.4 (*d*, *J*(C,P) = 5.7, C_q); 143.0 (*d*, *J*(C,P) = 5.9, C_q); 170.3 (*d*, *J*(C,P) = 4.6, C=O). ^{31}P-NMR (162 MHz, (D_6)DMSO): −77.1. ES-MS (neg.): 727.1.

4. *Dimethylammonium Bis[3,4,5,6-tetrachlorobenzene-1,2-diolato(2−)-κO,κO′][dimethyl (2S,3S)-2,3-di(hydroxy-κO)butanedioato(2−)]phosphate(1−)* ([Me_2NH_2][D-**5a**]). As described for [Me_2NH_2][**5b**] (*Exper. 5*), with **7** (500 mg, 2.02 mmol), $P(NMe_2)_3$ (**12**; 440 µl, 2.42 mmol), and an Et_2O soln. (12 ml) of D-**6a** (216 mg, 1.21 mmol) and **8** (497 mg, 2.02 mmol). The reaction was performed in Et_2O for 16 h, and [Me_2NH_2][D-**5a**] was collected as a white precipitate (750 mg, 83%), which was washed with cold Et_2O (12 ml, 4°). ^{1}H- and ^{31}P-NMR: D-**5a**$_L$/D-**5a**$_S$ 75:25, besides 10% of [Me_2NH_2][**2**]. M.p. 172° (dec.). UV/VIS (MeOH, $1.3 \cdot 10^{-5}$ M): 217 ($8.7 \cdot 10^4$), 301 ($7.8 \cdot 10^3$). IR (KBr): 3175*s*, 2947*m*, 2459*w*, 1737*s*, 1597*m*, 1451*s*, 1384*m*, 1296*m*, 1275*m*, 1238*m*, 1119*m*, 995*s*, 823*s*, 761*m*, 688*m*, 637*m*, 585*w*, 481*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 2.50 (*s*, 6 H); 3.53 (*s*, 6 H, D-**5a**$_L$); 3.69 (*s*, 6 H, D-**5a**$_S$); 4.54 (*d*, *J*(H,P) = 16, 2 H, D-**5a**$_S$); 4.70 (*d*, *J*(H,P) = 23, 2 H, D-**5a**$_L$); 8.19 (br. *s*, 2 H). ^{31}P-NMR (162 MHz, (D_6)DMSO): −76.4 (D-**5a**$_L$); −77.3 (D-**5a**$_S$). ES-MS (neg.): 698.8.

Dimethylammonium Bis[3,4,5,6-tetrachlorobenzene-1,2-diolato(2−)-κO,κO′][dimethyl (2R,3R)-2,3-di(hydroxy-κO)butanedioato(2−)]phosphate(1−) ([Me_2NH_2][**5a**]). As described for [Me_2NH_2][**5b**] (*Exper. 5*), from **6a** (89 mg, 0.50 mmol) and a soln. of **7** (211 mg, 0.85 mmol) and **8** (210 mg, 0.85 mmol) in Et_2O (10 ml). The reaction was performed in Et_2O for 4 h, and [Me_2NH_2][**5a**] was collected as a white precipitate (227 mg, 61%), which was washed with cold Et_2O (10 ml). ^{1}H- and ^{31}P-NMR: **5a**$_L$/**5a**$_S$ *ca.* 98:2. M.p. 172° (dec.). $[\alpha]_D^{20}$ = +144.5; $[\alpha]_{578}^{20}$ = +152.3; $[\alpha]_{546}^{20}$ = +176.5; $[\alpha]_{436}^{20}$ = +331.7; $[\alpha]_{365}^{20}$ = +628.5 (*c* = 0.103, DMSO). UV/VIS (MeOH, $1.35 \cdot 10^{-5}$ M): 217 ($14.4 \cdot 10^4$); 301 ($11.2 \cdot 10^3$); 350 ($1.8 \cdot 10^3$). IR (KBr): 3175*s*, 2947*m*, 2459*w*, 1737*s*, 1597*m*, 1451*s*, 1384*m*, 1296*m*, 1275*m*, 1238*m*, 1119*m*, 995*s*, 823*s*, 761*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 2.53 (*s*, 6 H); 3.57 (*s*, 6 H, **5a**$_L$); 3.69 (*s*, 6 H, **5a**$_S$); 4.57 (*d*, *J*(H,P) = 15, 2 H, **5a**$_S$); 4.75 (*d*, *J*(H,P) = 23, 2 H, **5a**$_L$); 8.44 (br. *s*, 2 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 34.2 (MeN); 52.1 (Me, **5a**$_L$); 70.2 (*d*, *J*(C,P) = 2.5, CH, **5a**$_L$); 112.1 (*d*, *J*(C,P) = 19.8, C_q, **5a**$_L$); 112.4 (*d*, *J*(C,P) = 18.1, C_q, **5a**$_L$); 120.1 (*d*, *J*(C,P) = 13.2, C_q, **5a**$_L$); 137.3 (C_q, **5a**$_L$); 142.3 (*d*, *J*(C,P) = 5.8, C_q, **5a**$_L$); 142.9 (*d*, *J*(C,P) = 5.8, C_q, **5a**$_L$); 170.7 (*d*, *J*(C,P) = 4.4, C_q, **5a**$_L$). ^{31}P-NMR (162 MHz, (D_6)DMSO): −76.4 (**5a**$_L$). ES-MS (neg.): 698.8.

Under modified conditions (16 h in CH_2Cl_2/hexane 1:1 (10 ml)), salt [Me_2NH_2][**5a**] could be isolated in a decent yield (58%, **5a**$_L$/**5a**$_S$ 73:27). No trace of [Me_2NH_2][**2**] was observed.

5. *One-Pot Preparation of Dimethylammonium Bis[3,4,5,6-tetrachlorobenzene-1,2-diolato(2−)-κO,κO′][dimethyl (2R,3R)-di(hydroxy-κO)butanedioato(2−)]phosphate(1−)* ([Me_2NH_2][**5b**]). *General Procedure.* Anh. **7** (500 mg, 2.02 mmol; recrystallized several times from toluene) and a cat. amount of NH_4Cl (1 crystal) were mixed in dry toluene (5.0 ml). Freshly distilled $(Me_2N)_3PO$ (**12**; 440 µl, 2.42 mmol) was then slowly added. Me_2NH evolved, and the mixture was refluxed for 15 min. The remaining solvent and excess **12** were evaporated and the residue (**11**) was carefully dried *in vacuo*. Then, **6b** (207 µl, 1.21 mmol) and *ortho*-chloranil (**8**; 497 mg, 2.02 mmol) were dissolved in CH_2Cl_2 (10 ml, degassed), and the resulting soln. was added to crude **11**. Hexane (10 ml) was then added until a trace of precipitation occurred, the CH_2Cl_2/hexane ratio being in this case 1:1. The dark red soln. progressively lost its color. After 64 h, the precipitate was filtered, washed carefully with cold CH_2Cl_2/hexane 1:1 (4°, 10 ml), and dried: [Me_2NH_2][**5b**] (816 mg, 86%), **5b**$_L$/**5b**$_S$ 44:56 mixture of diastereoisomers (^{1}H- and ^{31}P-NMR). M.p. >250° (dec.). UV/VIS (MeOH, $1.10 \cdot 10^{-6}$ M): 216 ($1.7 \cdot 10^5$), 201 ($1.4 \cdot 10^5$). IR (KBr): 3173*s*, 2981*m*, 1734*s*, 1653*m*, 1456*s*, 1390*m*, 1274*m*, 1237*m*, 1123*m*, 991*s*, 822*s*, 746*m*, 695*m*, 635*m*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 0.98 (*t*, J = 7.2, 6 H, **5b**$_S$); 1.17 (*t*, *J* = 7.2, 6 H, **5b**$_L$); 2.49 (*s*, 6 H); 3.94 (*m*, 4 H, **5b**$_S$); 4.12 (*m*, 4 H, **5b**$_L$); 4.41 (*d*, *J* = 9.2, 2 H, **5b**$_L$); 4.65 (*d*, *J* = 21, 2 H, **5b**$_S$); 8.33 (br. *s*, 2 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 13.5 (Me, **5b**$_L$); 13.9 (Me, **5b**$_S$); 34.2 (Me); 61.0 (CH_2, **5b**$_S$/**5b**$_L$); 70.2 (CH, **5b**$_S$); 70.7 (CH, **5b**$_L$); 111.9 (*d*, *J*(C,P) = 20, C_q, **5b**$_S$), 112.1 (*d*, *J*(C,P) = 20, C_q, **5b**$_L$); 112.3 (*d*, *J*(C,P) = 18, C_q, **5b**$_S$); 112.5 (*d*, *J*(C,P) = 19, C_q, **5b**$_L$); 119.9 (C_q, **5b**$_S$); 120.1 (C_q, **5b**$_S$); 120.3 (C_q, **5b**$_L$); 120.4 (C_q, **5b**$_L$); 142.2 (*d*, *J*(C,P) = 6.8, C_q, **5b**$_S$); 142.3 (*d*, *J*(C,P) = 5.8, C_q, **5b**$_L$); 142.7 (*d*, *J*(C,P) = 5.7, C_q, **5b**$_L$); 142.9 (*d*, *J*(C,P) = 5.7, C_q, **5b**$_S$); 169.0

(*d*, *J*(C,P) = 12.5, C_q, **5b**$_L$), 170.1 (*d*, *J*(C,P) = 4.6, C_q, **5b**$_S$). ^{31}P-NMR (162 MHz, (D_6)DMSO): −76.4 (**5b**$_L$); −77.7 (**5b**$_S$). ES-MS (neg.): 727.0.

Under slightly modified conditions (**8** (1.7 equiv.) added as a solid and reaction for 4 h), [Me_2NH_2][**5b**] could once be isolated in 82% yield, but contaminated with 7% of [Me_2NH_2][**2**]. Anal. calc. for $C_{22}H_{20}Cl_8NO_{10}P$ (93%) + $C_{20}H_8Cl_{12}NO_6P$ (7%): C 33.85, H 2.50, N 1.80; found: C 33.81, H 3.00, N 1.73.

6. *Dimethylammonium Bis[3,4,5,6-tetrachlorobenzene-1,2-diolato(2−)-*κ*O,*κ*O′][diisopropyl (2*R*,3*R*)-di(hydroxy-*κ*O)butanedioato(2−)]phosphate(1−)* ([Me_2NH_2][**5c**]). As described for [Me_2NH_2][**5b**] (*Exper. 5*) with **7** (500 mg, 2.02 mmol), **12** (440 µl, 2.42 mmol), and a soln. of **6c** (283 mg, 1.21 mmol) and **8** (497 mg, 2.02 mmol) in CH_2Cl_2 (10 ml). The reaction was performed in CH_2Cl_2/hexane 3:1 for 16 h, and [Me_2NH_2][**5c**] was collected as a white precipitate (702 mg, 72%), which was washed with cold CH_2Cl_2/hexane 3:1 (10 ml). ^{1}H- and ^{31}P-NMR: **5c**$_L$/**5c**$_S$ 14:86, besides 4% of [Me_2NH_2][**2**]. M.p. 242° (dec.). UV/VIS (MeOH, $1.07 \cdot 10^{-6}$ M): 218 ($1.8 \cdot 10^5$), 203 ($1.8 \cdot 10^5$), 201 ($1.8 \cdot 10^5$). CD (MeOH, $1.07 \cdot 10^{-6}$ M, 20°): 222 (−105), 248 (−20). IR (KBr): 3460*m*(br.), 3178*s*(br.), 2982*s*, 2934*m*, 2828*m*, 2462*w*, 1738*s*, 1593*m*, 1450*s*(br.), 1388*s*, 1302*m*, 1237*s*, 1122*m*, 1103*m*, 1007*s*, 992*s*, 756*m*, 706*m*, 674*m*, 635*m*, 582*w*, 500*w*, 483*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.14 (*m*, 6 H, **5c**$_S$); 1.20 (*m*, 6 H, **5c**$_L$); 2.54 (*s*, 6 H); 4.29 (*d*, *J*(H,P) = 5.5, 2 H, **5c**$_S$); 4.54 (*d*, *J*(H,P) = 15.6, 2 H, **5c**$_L$); 4.85 (*m*, 2 H, **5c**$_L$); 4.96 (*m*, 2 H, **5c**$_S$); 8.15 (br. *s*, 2 H). ^{31}P-NMR (162 MHz, (D_6)DMSO): −76.6 (**5c**$_L$); −77.9 (**5c**$_S$). ES-MS (neg.): 754.4.

7. *Dimethylammonium Bis[3,4,5,6-tetrachlorobenzene-1,2-diolato(2−)-*κ*O,*κ*O′][di(*tert*-butyl) (2*R*,3*R*)-di(hydroxy-*κ*O)butanedioato(2−)]phosphate(1−)* ([Me_2NH_2][**5d**]). As described for [Me_2NH_2][**5b**] (*Exper. 5*), with **7** (500 mg, 2.02 mmol), **12** (440 µl, 2.42 mmol), and a CH_2Cl_2 (10 ml) soln. of **6d** (318 mg, 1.21 mmol) and **8** (497 mg, 2.02 mmol). The reaction was performed in CH_2Cl_2/hexane 1:1 (20 ml) for 16 h, and [Me_2NH_2][**5d**] was collected as a white precipitate (707 mg, 71%), which was washed with cold CH_2Cl_2/hexane 1:1 (15 ml, 4°). ^{1}H- and ^{31}P-NMR: **5d**$_L$/**5d**$_S$ 51:49, besides < 2% of [Me_2NH_2][**2**]. Recrystallization of an anal. sample in MeOH afforded colorless crystals of anal. pure [Me_2NH_2][**5d**$_S$], used for X-ray diffraction analysis and [α]$_D$ and CD measurements. M.p. 182° (dec.). $[\alpha]_D^{20} = -205$ (*c* = 0.30, DMSO: [Me_2NH_2][**5d**$_S$]). UV/VIS (MeOH, $1.06 \cdot 10^{-5}$ M): 218 ($1.2 \cdot 10^5$), 301 ($8.8 \cdot 10^3$). CD (MeOH, $2.1 \cdot 10^{-6}$ M, 20°; [Me_2NH_2][**5d**$_S$]): 213 (18), 219 (−117), 245 (−46), 307 (−27). IR (KBr): 3164*w*(br.), 2980*w*, 1743*m*, 1592*w*, 1454*s*, 1390*m*, 1369*m*, 1302*w*, 1251*m*, 1237*m*, 1163*w*, 1124*m*, 994*m*, 824*s*, 780*w*, 729*m*, 696*m*, 674*m*, 653*m*, 576*w*, 484*w*. ^{1}H-NMR (400 MHz, (D_6)DMSO): 1.33 (*s*, 18 H, **5d**$_L$); 1.41 (*s*, 18 H, **5d**$_S$); 2.53 (*s*, 6 H); 4.10 (*d*, *J*(H,P) = 2.9, 2 H, **5d**$_S$); 4.33 (*d*, *J*(H,P) = 9.7, 2 H, **5d**$_L$); 8.15 (br. *s*, 2 H). ^{13}C-NMR (100 MHz, (D_6)DMSO): 27.9 (Me, **5d**$_S$); 28.0 (Me); 34.7 (MeN); 71.7 (*d*, *J* = 1.7, CH); 72.3 (*d*, *J* = 2.3, CH, **5d**$_S$); 81.6 (C_q); 82.0 (C_q, **5d**$_S$); 112.2 (*d*, *J*(C,P) = 23, C_q); 112.3 (*d*, *J*(C,P) = 19, C_q); 112.5 (*d*, *J*(C,P) = 20, C_q, **5d**$_S$); 112.6 (*d*, *J*(C,P) = 19, C_q, **5d**$_S$); 120.3 (C_q); 120.5 (C_q, **5d**$_S$); 120.7 (C_q); 120.8 (C_q, **5d**$_S$); 142.6 (*d*, *J*(C,P) = 5.3, C_q); 142.7 (*d*, *J*(C,P) = 5.3, C_q); 142.7 (*d*, *J*(C,P) = 5.3, C_q), **5d**$_S$); 143.3 (*d*, *J*(C,P) = 5.3, C_q, **5d**$_S$); 168.0 (*d*, *J*(C,P) = 17, C_q, **5d**$_S$); 169.0 (*d*, *J*(C,P) = 12, C_q). ^{31}P-NMR (162 MHz, (D_6)DMSO): −77.2 (**5d**$_L$); −78.8 (**5d**$_S$). ES-MS (neg.): 782.5.

Under slightly modified conditions, [Me_2NH_2][**5d**] was isolated in 87% yield, but contaminated with 8% of [Me_2NH_2][**2**]. Anal. calc. for $C_{26}H_{28}Cl_8NO_{10}P$ (92%) and $C_{20}H_8Cl_{12}NO_6P$ (8%): C 37.01, H 3.21, N 1.69; found: C 36.52, H 3.40, N 1.57.

REFERENCES

[1] a) M. J. Gallagher, I. D. Jenkins, in 'Topics in Stereochemistry', Eds. E. L. Eliel and S. H. Wilen, John Wiley & Sons, New York, 1968, Vol. 3, p. 76; b) D. Hellwinkel, in 'Organic Phosphorus Compounds', Eds. G. M. Kosolapoff and L. Maier, John Wiley & Sons, 1972, Vol. 3, p. 251; c) R. Luckenbach, in 'Methoden der Organischen Chemie', Ed. M. Regitz, Georg Thieme Verlag, Stuttgart, 1982, Vol. E2, p. 897; d) R. A. Cherkasov, N. A. Polezhaeva, *Russ. Chem. Rev.* **1987**, *56*, 163; e) R. Burgada, R. Setton, in 'The Chemistry of Organophosphorus Compounds', Ed. F. R. Hartley, John Wiley & Sons, New York, 1994, Vol. 3, p. 185; f) R. R. Holmes, *Chem. Rev.* **1996**, *96*, 927; g) R. R. Holmes, *Acc. Chem. Res.* **1998**, *31*, 535.

[2] a) D. Hellwinkel, *Angew. Chem.* **1965**, 378; b) D. Hellwinkel, S. F. Mason, *J. Chem. Soc. B* **1970**, 640; c) D. Hellwinkel, W. Krapp, *Phosphorus* **1976**, *6*, 91; d) I. V. Shevchenko, A. Fischer, P. G. Jones, R. Schmutzler, *Chem. Ber.* **1992**, *125*, 1325; e) A. Skowronska, J. Kowara, R. Kaminski, G. Bujacz, M. W. Wieczorek, *J. Org. Chem.* **2000**, *65*, 304.

[3] a) M. Koenig, A. Klaebe, A. Munoz, R. Wolf, *J. Chem. Soc., Perkin Trans. 2* **1979**, 40; b) A. Klaebe, M. Koenig, R. Wolf, P. Ahlberg, *J. Chem. Soc., Dalton Trans.* **1977**, 570; c) J. Cavezzan, G. Etemad-Moghadam, M. Koenig, A. Klaebe, *Tetrahedron Lett.* **1979**, 795.

[4] a) J. Lacour, C. Ginglinger, C. Grivet, G. Bernardinelli, *Angew. Chem., Int. Ed.* **1997**, *36*, 608; b) J. Lacour, C. Ginglinger, F. Favarger, *Tetrahedron Lett*. **1998**, 4825.
[5] J. Lacour, J. J. Jodry, C. Ginglinger, S. Torche-Haldimann, *Angew. Chem., Int. Ed*. **1998**, *37*, 2379; J. Lacour, C. Goujon-Ginglinger, S. Torche-Haldimann, J. J. Jodry, *Angew. Chem., Int. Ed*. **2000**, *39*, 3695; J. J. Jodry, J. Lacour, *Chem.–Eur. J.* **2000**, *6*, 4297; D. Monchaud, J. Lacour, C. Coudret, S. Fraysse, *J. Organomet. Chem.* **2001**, *624*, 388; J. Lacour, J. J. Jodry, D. Monchaud, *Chem. Commun*. **2001**, 2302.
[6] J. Lacour, A. Londez, C. Goujon-Ginglinger, V. Buss, G. Bernardinelli, *Org. Lett*. **2000**, *2*, 4185.
[7] J. K. Whitesell, *Chem. Rev.* **1989**, *89*, 1581; A. Alexakis, P. Mangeney, *Tetrahedron: Asymmetry* **1990**, *1*, 477; C. Rosini, L. Franzini, A. Raffaelli, P. Salvadori, *Synthesis* **1992**, 503.
[8] A. von Zelewsky, 'Stereochemistry of Coordination Compounds', John Wiley & Sons, Chichester, 1996; U. Knof, A. von Zelewsky, *Angew. Chem., Int. Ed*. **1999**, *38*, 302.
[9] J. L. Pierre, *Coord. Chem. Rev*. **1998**, *178–180*, 1183.
[10] M. Yashiro, T. Murata, S. Yoshikawa, S. Yano, *J. Chem. Soc., Dalton Trans.* **1994**, 1073; M. Yashiro, T. Murata, M. Sato, M. Kosaka, K. Kobayashi, T. Sakurai, S. Yoshikawa, M. Komiyama, S. Yano, *J. Chem. Soc., Dalton Trans.* **1994**, 1511; A. Tatehata, *Inorg. Chem*. **1982**, *21*, 2496; R. S. Vagg, P. A. Williams, *Inorg. Chim. Acta* **1981**, *51*, 61; T. J. Goodwin, P. A. Williams, R. S. Vagg, *Inorg. Chim. Acta* **1982**, *63*, 133.
[11] A. Munoz, G. Gence, M. Koenig, R. Wolf, *Bull. Soc. Chim. Fr*. **1975**, 1433; M. Koenig, A. Klaebe, A. Munoz, R. Wolf, *J. Chem. Soc., Perkin Trans. 2* **1976**, 955.
[12] T. Katsuki, K. B. Sharpless, *J. Am. Chem. Soc*. **1980**, *102*, 5974; V. S. Martin, S. S. Woodard, T. Katsuki, Y. Yamada, M. Ikeda, K. B. Sharpless, *J. Am. Chem. Soc*. **1981**, *103*, 6237; W. R. Roush, A. E. Walts, L. K. Hoong, *J. Am. Chem. Soc*. **1985**, *107*, 8186; W. R. Roush, R. L. Halterman, *J. Am. Chem. Soc.* **1986**, *108*, 294; W. R. Roush, A. M. Ratz, J. A. Jablonowski, *J. Org. Chem*. **1992**, *57*, 2047.
[13] H. Blaser, *Chem. Rev*. **1992**, *92*, 935; D. Seebach, A. K. Beck, A. Heckel, *Angew. Chem., Int. Ed.* **2001**, *40*, 92.
[14] K.-Y. Akiba, (Wasada University, Tokyo), personal communication.
[15] R. B. Merrifield, G. Barany, W. L. Cosand, M. Engelhard, S. Mojsov, *Pept., Proc. Am. Pept. Symp., 5th* **1977**, 488.
[16] For examples of P^{III} derivatives of tartrate esters, see a) H. J. Lucas, F. W. J. Mitchell, C. N. Scully, *J. Am. Chem. Soc*. **1950**, *72*, 5491; b) A. E. Arbuvov, V. M. Zoroastrova, T. N. Myasoedova, *Izv. Akad. Nauk SSSR, Ser. Khim.* **1960**, 2127; c) A. Zwierzak, *Can. J. Chem*. **1967**, *45*, 2501; d) Y. Y. Samitov, A. A. Musina, L. I. Guracil, E. T. Mukmenev, B. A. Arbusov, *Bull. Acad. Sci. USSR, Div. Chem. Sci*. **1975**, *7*, 1407; e) I. Hoppe, U. Schöllkopf, M. Nieger, E. Egert, *Angew. Chem., Int. Ed.* **1985**, *24*, 1067; f) I. F. Pickersgill, P. G. Devitt, T. P. Kee, *Synth. Commun.* **1993**, 1643; g) Y. Huang, A. E. Sopchik, A. M. Arif, W. G. Bentrude, *J. Am. Chem. Soc*. **1993**, *115*, 4031; h) N. A. Makarova, L. I. Guracil, E. T. Mukmenev, B. A. Arbusov, *Bull. Acad. Sci. USSR, Div. Chem. Sci*. **1973**, *3*, 627; i) H. Nöth, H.-J. Vetter, *Chem. Ber*. **1961**, 1505; j) R. A. Mitsch, *J. Am. Chem. Soc*. **1967**, *89*, 6297; k) J. A. Mosbo, J. G. Verkade, *J. Am. Chem. Soc*. **1973**, *95*, 4659; l) W. G. Bentrude, W. N. Setzer, A. E. Sopchik, S. Chandrasekaran, M. T. Ashby, *J. Am. Chem. Soc*. **1988**, *110*, 7119.;
[17] J. Krill, I. V. Shevchenko, A. Fischer, P. G. Jones, R. Schmutzler, *Chem. Ber*. **1997**, *130*, 1479; I. V. Shevchenko, P. G. Jones, A. Fischer, R. Schmutzler, *Heteroatom. Chem*. **1992**, *3*, 177.
[18] D. W. White, R. D. Bertrand, G. K. McEwen, J. G. Verkade, *J. Am. Chem. Soc*. **1970**, *92*, 7125.
[19] E. Blanc, D. Schwarzenbach, H. D. Flack, *J. Appl. Crystallogr*. **1991**, *24*, 1035.
[20] P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, M. M. Woolfson, 'System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data', Universities of York, England, and Louvain-la-Neuve, Belgium, 1987.
[21] S. R. Hall, H. D. Flack, J. M. Stewart, 'Eds XTAL3.2 User's Manual', Universities of Western Australia and Maryland, 1992.
[22] C. K. Johnson, 'ORTEP II', Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
[23] H. D. Flack, G. Bernardinelli, *Acta Crystallogr., Sect. A* **1999**, *55*, 908; H. D. Flack, G. Bernardinelli, *J. Appl. Crystallogr.* **2000**, *33*, 1143.

Received November 22, 2001