Diversity Oriented Synthesis of Chiral Hexacoordinated Phosphate Anions

Jérôme Lacour,*[a] Samuel Constant,[a] and Virginie Hebbe[a]

Dedicated to Professor Marc Julia on the occasion of his 80th birthday

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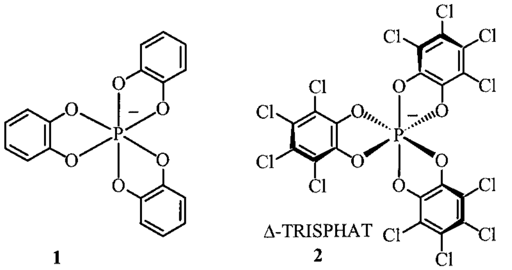
Novel hexacoordinated phosphate anions consisting of a central phosphorus(v) atom and at least one tetrachloropyrocatechol ligand can be simply prepared in modest to decent yields (37–71%) as their dimethylammonium salts following a one-pot process and with simple, usually commercially available, starting materials. A variety of symmetrical diones (α-diketones or *ortho*-quinones) can be used in this protocol and the structurally-diverse products are chemically stable when two tetrachloropyrocatechol ligands surround the P atom.

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 bidentate ligands.[1−10] The 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 (Figure 1).[11−14] Previously, the introduction of electron-withdrawing chlorine atoms on the aromatic nuclei was reported to increase the configurational stability of the resulting tris(tetrachlorobenzenediolato)phosphate(v) derivative.[15] This D_3-symmetric anion, known as TRISPHAT (**2**), can be resolved by association with a chiral ammonium cation.[16] It is an efficient NMR chiral shift,[17−23] resolving[24−27] and asymmetry-inducing[27−29] reagent for organic and organometallic derivatives − with a predilection for organometallic complexes.

However, with some organic chiral cations, small NMR shifts and asymmetry-inducing properties were recently observed using anion **2** (Figure 1). Assuming that its D_3-symmetry is not adapted for the chiral recognition of such cations, the synthesis of C_2-symmetric hexacoordinated phosphate anions was investigated, our interest being motivated by the overall efficiency of such a symmetry in asymmetric reactions or molecular recognition processes.[30,31] An efficient and general one-pot process was then developed for the preparation of new classes of enantiopure C_2-symmetric hexacoordinated phosphate anions − BINPHAT (**3**),[32] HYPHAT (**4**)[33] and TARPHAT (**5**)[34] − containing BINOL, hydrobenzoin and tartrate ligands, respectively. All these anions were isolated as their dimethylammonium salts in good yields and chemical purity. They show − in particular BINPHAT − higher selectivity than TRISPHAT in some chiral recognition processes and NMR chiral shift applications.[32,35−37]



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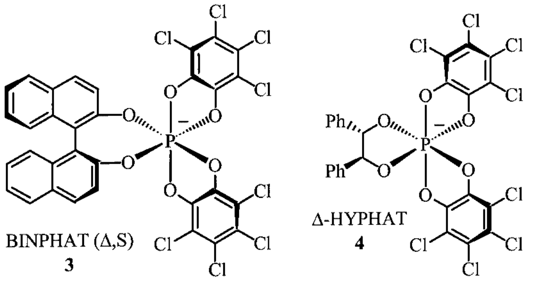

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Figure 1. Known hexacoordinated phosphate anions: **1**, **2** (TRISPHAT), **3** (BINPHAT) and **4** (HYPHAT)

Due to the synthetic pathway that was developed (see below), these C_2-symmetric anions always contain two tetrachloropyrocatecholate ligands along with the chiral moiety. Although this feature was initially a deliberate choice, as we did not know whether the anions would be stable without the two electron-withdrawing ligands, it later

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[a] Université de Genève, département de chimie organique, Quai Ernest Ansermet 30, 1211 Genève 4, Switzerland
Fax: (internat.) + 41-22/328-7396
E-mail: jerome.lacour@chiorg.unige.ch

became a liability as it limits the possibility of structural diversity in the backbone of the phosphate anionic auxiliaries. It was therefore debatable whether the one-pot synthetic pathway that had been developed could be adapted to accommodate the synthesis of hexacoordinated phosphate anions with three different bidentate ligands (C_1-symmetry) and whether the resulting products would be chemically stable. Herein, we report that additional structural diversity can be brought about by the careful choice of α-dicarbonyl or *ortho*-quinone reagents, and that two tetrachloropyrocatecholates seem to be necessary for the formation of highly chemically stable hexacoordinated phosphate anions.

Results and Discussion

Synthetic Strategy

Our goal was to develop a synthetic pathway that would allow a controlled and efficient preparation of hexacoordinated phosphate anions with three different bidentate ligands around the phosphorus atom. However, previous studies in our group on the synthesis of hexacoordinated phosphate anions had shown several pitfalls, which indicated that such a goal might be a synthetic challenge.

For instance, if one tries to adapt the synthetic protocol developed for the TRISPHAT anion **2**, that is the one-time addition of three equivalents of bidentate ligands to one equivalent of PCl_5 and one equivalent of trialkylamine, then a "library" of 10 compounds is likely to be generated. This is represented in Figure 2 considering the theoretical case of three different ligands (aa), (bb) and (cc) (1:1:1 ratio) which react simultaneously with PCl_5 and subsequent derivatives. A statistical 1:1:1:3:3:3:3:3:3:6 repartition among 10 possible products is expected; the desired compound [P(aa)(bb)(cc)] being synthesized with a maximum 22% (6:27) theoretical yield.

This problem of the random distribution of the ligands around the phosphorus atom was already considered when preparing anions **3**−**5**. To obtain the desired $[P(aa)_2(bb)]$ products in high yields and with 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. 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 would be avoided. A synthetic route using three separate and high-yielding chelation steps would 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, NR_2) react with diols to form monochelated adducts, and ii) monocyclized P(III) compounds are readily oxidized to bicyclic spirophosphoranes using α-diketones or *ortho*-quinones as oxidants, and *o*-chloranil **6** in particular (Scheme 1).[38] These two chelation steps were ideal for our projected route, as they can be performed sequentially in high yields. To perform the final chelation step and obtain the desired anion, it was sufficient to add a third diol ligand (ligand cc, Scheme 1) to the spirophosphorane intermediate. After displacement of the last substituent X, chelation should 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 would be directly scavenged in solution with no need to add an extra base; salts $[XH_2]$[P(aa)(cc)(*o*-chloranil)] would result directly from the procedure. We also recognized that most diols are compatible with *ortho*-quinones and chelation steps 2 and 3 could therefore happen in a one-pot procedure. Li-

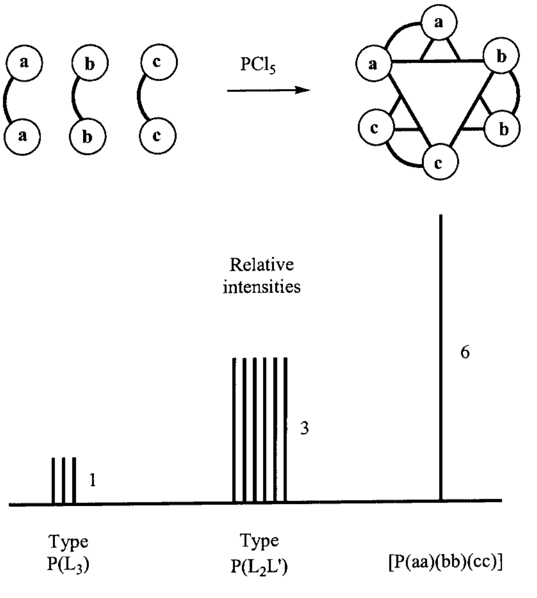
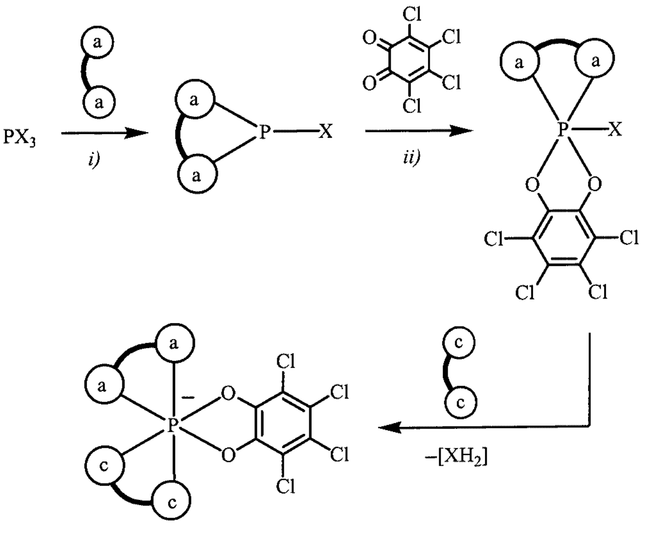


Figure 2. Statistical distribution among possible hexacoordinated phosphates from the reaction of three different ligands (aa, bb and cc, 1:1:1 ratio) and PCl_5; L, L′ = (aa), or (bb), or (cc)



Scheme 1. Outline of the successful synthetic strategy used for the synthesis of $[XH_2]$[P(aa)(cc)(*o*-chloranil)] salts; for i) and ii) see text

gands (aa) and (cc) could be either tetrachloropyrocatechol (**7**) or the projected chiral diols.

However, this synthetic strategy was successful for the preparation of anions **3−5** only after realizing that tetrachloropyrocatechol (**7**) has to be introduced in the first chelation step (as ligand aa, Scheme 1) and the chiral ligands in the last (as ligands cc). Otherwise, starting from hydrobenzoin and tartrate diols, only low yields of pure phosphoramidites were obtained.[33,34] In the case of BINOL, clean preparation of the derived phosphoramidite was achieved,[39] but its very slow oxidation by **6** made the overall process inefficient.[40] It is only when using **7** as ligand aa that both the phosphoramidite (**8**) synthesis and the subsequent oxidation can be achieved in high yield and purity. In these previous examples, *o*-chloranil (**6**) was used as the oxidant to introduce the second tetrachloropyrocatecholate ligand. The three steps could then be combined in a one-pot process making this protocol simple to run on a large scale.

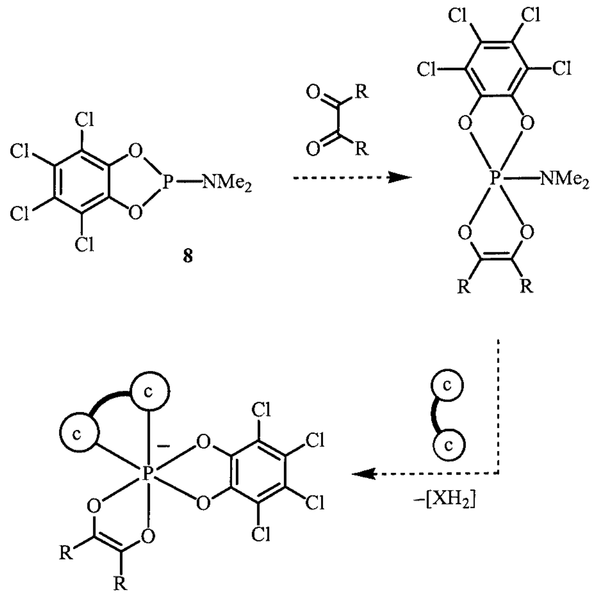
For the synthesis of hexacoordinated anions of C_1-symmetry, it was thus decided to use and modify this previously described protocol rather than develop a new one. Since previous experience (see above) had shown that the introduction of tetrachloropyrocatechol in the first step is mandatory, no change was made to this first part of the protocol. As the syntheses of anions **3−5** had shown that various ligands can be added in the third chelation step, confidence was high that it would also happen for the synthesis of the targeted compounds. Finally, if structural diversity was to be achieved, it meant the use of oxidants different from *o*-chloranil for the second chelation step. This analysis is represented in Scheme 2 starting from phosphoramidite **8**. A selection of α-diketones or *ortho*-quinones was thus made and used following this procedure.

Choice and Preparation of the α-Dicarbonyl and ortho-Quinone Oxidants

Care was taken to choose a rather large diversity of diones (α-diketones or *ortho*-quinones)[38] to test the extent of the feasibility of this approach. We expected that the nature (cyclic/acyclic, flexible/rigid, planar/non-planar, aromatic/non-aromatic, heterocyclic/non-heterocyclic) of the reagents could influence the efficiency of the oxidation/chelation step as well as the stability of the products. A selection of three *ortho*-quinones, 9,10-phenanthrenequinone (**9**),[41−47] acenaphthene-1,2-dione (**10**)[48] and [1,10]phenanthroline-5,6-dione (**11**)[49] was made (Figure 3). Compounds **9** and **10** are commercially available and the heterocyclic derivative **11** can be prepared in one step from [1,10]phenanthroline following the procedure of Yamada et al.[50] The rigidity, aromaticity and planarity of the reduction products of compounds **9−11** were foreseen to be positive factors for the chemical stability of the derived phosphate anions. We had, however, some initial reservations about compound **11**, as an undesired participation of the nitrogen atoms could be envisioned from previously reported studies,[43] which could lead to unwanted side-reactions. As mentioned, α-diketones were also selected. Benzil (**12**)[41,51,52] and butanedione (**13**)[41] are commercially available. (+)-(1*S*,4*R*)-Camphorquinone (**14**),[53] prepared in high yield by SeO_2 oxidation of (1*S*,4*R*)-camphor, was also used.[54−56] In this case, our interest was motivated by the possibility of an asymmetric induction from the chiral skeleton of the dione onto the backbone of the derived phosphate anion.

Synthesis and Characterization of Novel Bis(tetrachlorocatecholato) Phosphates

Keeping in mind that the chemical stability of the targeted phosphate anions was unknown, the novel procedure was tested using tetrachloropyrocatechol (**7**) as the third added diol (as ligand cc in Scheme 2). Although C_2-symmetric



Scheme 2. Outline of the synthetic strategy used for the synthesis of mixed salts $[XH_2][P(aa)(bb)(cc)]$

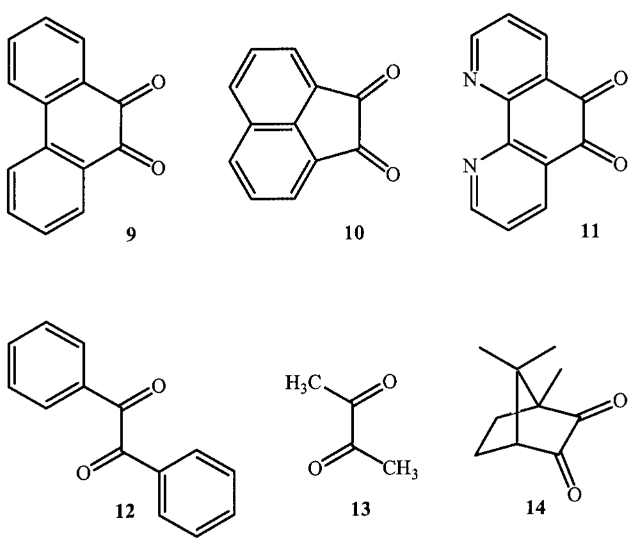
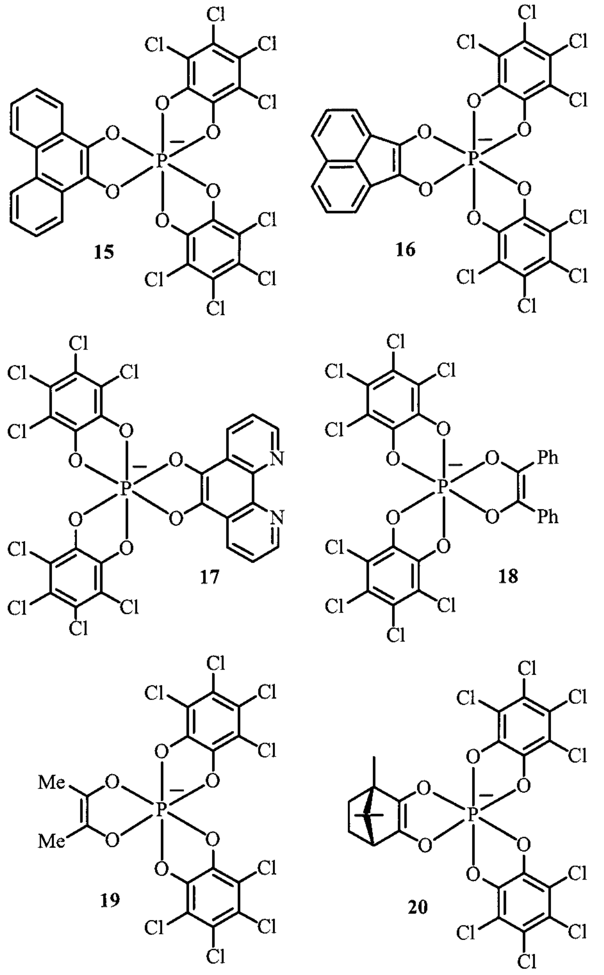


Figure 3. Selected quinones **9−11** and α-diketones **12−14**



15 16 17 18 19 20

Figure 4. Projected hexacoordinated phosphate anions **15**−**20** derived from diones **9**−**14**

phosphate anions (**15**−**19**, Figure 4) containing two tetrapyrocatecholate ligands would again usually result from the process, it provided a "safer" framework for the study as the derived phosphate anions would have a better chance of being stable and isolable.

Phosphoramidite **8** was prepared in situ by the reaction of tetrachloropyrocatechol (**7**) with tris(dimethylamino)phosphane. As shown previously,[32−34] this first reaction was virtually quantitative and the crude reaction mixture could be used without further purification. Treatment of **8** with diones **9**, **11**−**13**, and tetrachloropyrocatechol (**7**) afforded in one-pot the desired salts [Me_2NH_2][**15**], [Me_2NH_2][**17**], [Me_2NH_2][**18**] and [Me_2NH_2][**19**] in moderate to decent yields (37−71%, Table 1).

Contrary to the previous studies,[32−34] in which better yields and higher purity were obtained with larger amounts of **8** and *o*-chloranil (1.7 equivalents each), we observed that a more balanced 1:1.2:1:1 stoichiometry between reagents **7**(as ligand aa):$P(NMe_2)_3$:dione:**7**(as ligand cc) can be used to afford equally good results (Table 1, entries 1−2, 7−8). In most cases, a rapid evolution of the coloration of the crude mixtures was noticed upon the addition of the colored diones providing an efficient visual test for the progression of the reactions. With acenaphthene-1,2-dione (**10**) and camphorquinone (**14**), the crude mixtures remained red- and orange-colored, respectively, during the whole duration of the experiments, despite many attempts to induce the reactions (time, temperature, solvent, stoichiometry); spectral analysis of the crude mixtures revealed a total lack of reactivity.

Careful choice of the solvent medium was also required. In too-polar solvents or solvent combinations, salts [Me_2NH_2][**15**] and [Me_2NH_2][**17**−**19**] were rather soluble and did not precipitate completely. In too-nonpolar conditions, precipitation of by-products and contaminants − such as [Me_2NH_2][**2**] − occurred along with the desired ion pairs. It was therefore necessary to optimize the solvent conditions for each dione **9**, **11**−**13** as we noticed strong solubility differences for the derived anions (Table 1). Nevertheless, the polarity of the solvent medium was easily adjusted from one reaction to the next by controlling the amount of *n*-hexane in the medium. This solvent was added dropwise after three hours of reaction until the appearance of a precipitate in the crude mixture.

Table 1. Synthesis of hexacoordinated phosphate anions **15**−**20**

Entry	Dione	Method	Solvent	Product	Yield [%]	^{31}P NMR[a]	Purity [%]
1	9	A[b]	CH_2Cl_2/Hex 5:1	[Me_2NH_2][**15**]	46	−77.7	85
2	9	B[c]	CH_2Cl_2/Hex 1:1	[Me_2NH_2][**15**]	68	−78.2	80
3	10	A	CH_2Cl_2/Hex 3:2	[Me_2NH_2][**16**]	0		
4	10	A	Et_2O	[Me_2NH_2][**16**]	0		
5	10	A	CH_2Cl_2	[Me_2NH_2][**16**]	0		
6	11	A	CH_2Cl_2 only	[Me_2NH_2][**17**]	71	−77.3	94
7	12	A	CH_2Cl_2/Hex 1:1	[Me_2NH_2][**18**]	37	−81.9	100
8	12	B	CH_2Cl_2/Hex 1:1	[Me_2NH_2][**18**]	35	−81.9	100
9	13	B	CH_2Cl_2/Hex 1:1	[Me_2NH_2][**19**]	60	−80.3	49
10	13	B[d]	CH_2Cl_2/Hex 1:1	[Me_2NH_2][**19**]	51	−80.2	83
11	14	A	CH_2Cl_2/Hex 1:1	[Me_2NH_2][**20**]	0		
12	14	A	Et_2O/Hex 5:2	[Me_2NH_2][**20**]	0		
13	14	B	CH_2Cl_2/Hex 1:1	[Me_2NH_2][**20**]	0		

[a] Performed in [D$_6$]DMSO. [b] Method A: a 1.0:1.2:1.0:1.0 ratio of reagents aa (**7**):$P(NMe_2)_3$:dione:cc(**7**) was used. See the Exp. Sect. [c] Method B: a 1.7:1.8:1.7:1.0 ratio of reagents aa (**7**):$P(NMe_2)_3$:dione:cc(**7**) was used. See the Exp. Sect. [d] 20 equivalents of dione **13** was used in procedure B.

As mentioned, the most successful results were obtained with diones **9**, **11** and **12** to form salts [Me_2NH_2][**15**], [Me_2NH_2][**17**] and [Me_2NH_2][**18**], respectively (35−71%, Table 1, entries 1, 6 and 7). Variable amounts of impurities (0−15%, Exp. Sect.) were observed in the isolated products. ^{31}P NMR analysis revealed minor signals in the $\delta = -80$ ppm region, indicating the presence of other hexacoordinated phosphate anions, which, with the exception of the TRISPHAT anion **2**, could not be identified with precision. In the case of butadione **13**, the presence of a second phosphate ($\delta = -90.3$ ppm, [D_6]DMSO) was detected along with the desired anion **19** ($\delta = -80.2$ ppm, [D_6]DMSO). When the reaction was performed under classical conditions, an approximately 1:1 ratio was found between these adducts in the ^{31}P NMR spectrum (procedure B, Figure 5 spectrum a, Exp. Sect.). When a large excess of α-diketone (20 equivalents) was used, an 83:17 ratio was obtained in favor of the desired anionic derivative **19**, which could not be separated from the contaminant at this stage.

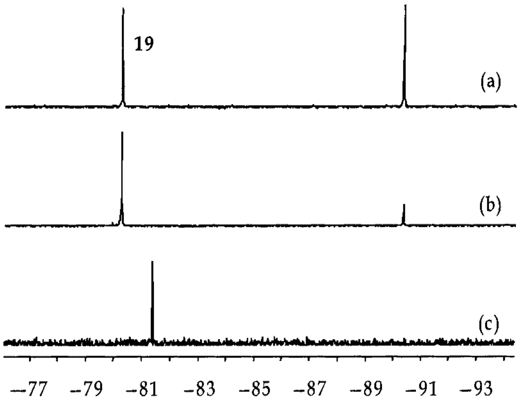


Figure 5. ^{31}P NMR spectra (162 MHz, parts, [D_6]DMSO) of [Me_2NH_2][**19**] isolated from the classical (a) and the modified (b) procedure B and of [**CV**+][**19**] (c)

We believe that the lack of reactivity observed with acenaphthene-1,2-dione (**10**) and camphorquinone (**14**) is not the result of electronic factors since compound **10** (redox potential, $E_{1/2}$ = 0.780 V) is a better oxidant than both 9,10-phenanthrenequinone (**9**; $E_{1/2}$ = 0.458 V) and *o*-chloranil (**6**; $E_{1/2}$ = 0.712 V).[57] A correlation between the lack of reactivity and the O···O distance between the oxygen atoms for the α-dicarbonyl groups can, however, be proposed. An analysis of the structure of diones **9**,[58] **10**,[59] **11**,[60] **12**,[61] **13**[62] and **14**[63] was performed using known X-ray crystallographic data (Cambridge database). It revealed that longer O···O distances occur in the unreactive diones **10** (2.859 Å) and **14** (2.920 Å, mean value), whereas much shorter values are observed for the reactive *ortho*-quinones **9** (2.691 Å, mean value) and **11** (2.709 Å), as well as α-diketones **12** (2.636 Å, mean value) and **13** (2.720 Å).[64] This longer distance between the oxygen atoms of **10** and **14** probably means an increase in strain in the transition states that lead to the spirophosphorane intermediates and thus their lack of formation.

To test the chemical stability of the novel phosphate anions and obtain pure samples of each, ion-exchange reactions were performed between the dimethylammonium salts and crystal violet − [tris(dimethylaminophenyl)methinium][chloride] or [**CV**$^+$][Cl]. The salts [**CV**$^+$][**15**], [**CV**$^+$][**17**], [**CV**$^+$][**18**] and [**CV**$^+$][**19**] were isolated by chromatography (SiO_2 or basic Al_2O_3, CH_2Cl_2) using previously reported conditions.[65] In all cases, the impurities were removed and the triarylcarbenium salts were stable over time in most solvents and solvent combinations (Table 2).

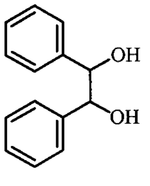
Table 2. Purification of hexacoordinated phosphate anions **15**, **17**−**19**.

Salt	Product	Yield [%]	Purity [%]
[Me_2NH_2][**15**]	[**CV**$^+$][**15**]	54	100
[Me_2NH_2][**17**]	[**CV**$^+$][**17**]	32	100
[Me_2NH_2][**18**]	[**CV**$^+$][**18**]	100	100
[Me_2NH_2][**19**]	[**CV**$^+$][**19**]	28	100

Overall, this novel procedure is efficient and modular, and we felt that it could be adapted for the synthesis of C_1-symmetric phosphate anions.

Synthesis and Characterization of C$_1$*-Symmetric Phosphates*

Commercially available 9,10-phenanthrenequinone (**9**) and benzil (**12**) were selected among the tested diones, as these quinones give chemically stable adducts (**15** and **18**) in decent and reproducible yields. In this study, as in the previous ones,[32−34] enantiopure ligands were considered as the third diols since they permit the predetermination of the configuration of the P atom and a diastereoselective synthesis of the phosphate anions.[66−68] Hydrobenzoin (**21**) and BINOL (**22**) were then chosen due to the rather high chemical stability of their C_2-symmetric HYPHAT (**4**) and BINPHAT (**3**) adducts.



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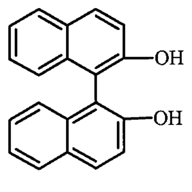

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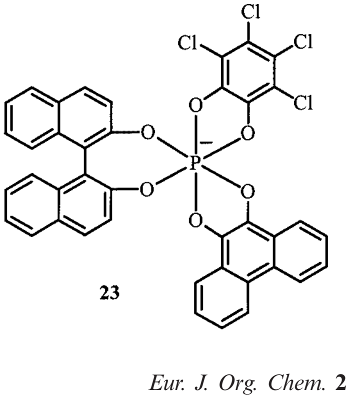

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In-situ generated phosphoramidite **8** was treated with diones **9** or **12** in the presence of ligands **21** or **22**. ^{31}P NMR analyses revealed, to our surprise, a very large number of signals in the $\delta = -80$ ppm region indicating the presence of many phosphate derivatives in the crude mixtures, in particular in the reaction of **8** with dione **12** and **22** (19 signals, Table 3 entry 4, Figure 6 spectrum a).[69,70] Even if one considers that the presence of the enantiopure BINOL ligand can double the number of signals, many more resonances than one would initially expect were observed in almost all the spectra. With ligand **21**, no stable derivatives could be isolated from the crude reaction mixtures. Only in the reaction of **8** with **9** and **22** was a major compound (**23**) dominant; this could be isolated as its [Me_2NH_2][**23**] salt by selective precipitation from CH_2Cl_2 (26%, Table 3 entry 3, Figure 6 spectra b and c). The presence of a single set of signals in the NMR spectra indicates that anion **23** is most probably obtained as a sole diastereoisomer demonstrating again the efficiency of the BINOL skeleton for the asymmetric synthesis of phosphate anions.[32] The results of the four possible combinations are summarized in Table 3. Unfortunately, a very poor chemical stability was observed for salt [Me_2NH_2][**23**] in solution: it decomposes within minutes in all the NMR solvents studied.

Table 3. Synthesis of C_1-symmetric phosphate anions

Entry	Ligand	Dione	Product	Signals[a]
1	21	9	–	10
2	21	12	–	9
3	22	9	[Me_2NH_2][**23**]	12
4	22	12	–	19

[a] ^{31}P NMR (162 MHz, [D_6]DMSO or [D_6]acetone): number of signals observed in the crude mixture ($\delta = -80$ ppm region).

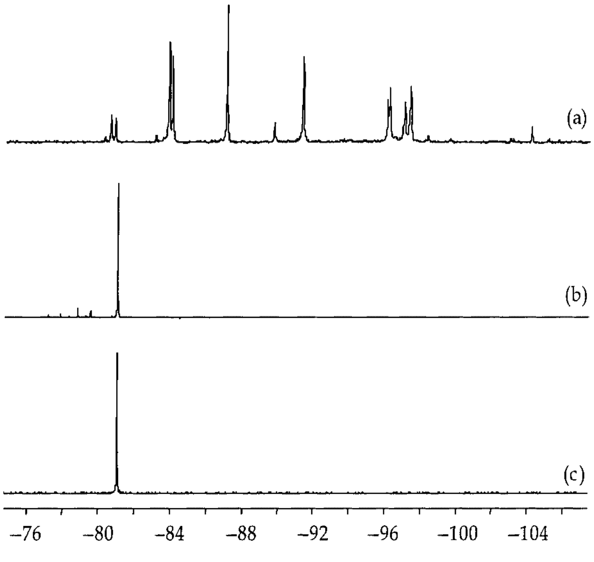

Figure 6. ^{31}P NMR spectra (162 MHz, parts) of: (a) the crude reaction of **8**, **12** and **22** ([D_6]DMSO), (b) crude and (c) purified [Me_2NH_2][**23**] ([D_6]acetone)

Conclusion

We have shown that various diones (α-diketones or *ortho*-quinones) can be used in a one-pot process for the synthesis of novel hexacoordinated phosphate anions. The dione is introduced around the phosphorus atom as a bidentate dioxo moiety bringing a valuable diversity to the backbone of the phosphate anions. These experiments seem to indicate that the resulting products are chemically stable only when two electron-withdrawing tetrachloropyrocatecholate ligands surround the P atom. Studies directed towards the use of anion **17** in coordination chemistry are being pursued.

Experimental Section

General Remarks: All reactions were carried out under dry N_2 or Ar by means of an inert gas/vacuum double manifold line and standard Schlenk techniques with magnetic stirring, unless otherwise stated. Solvents were dried and distilled prior to use: Toluene was freshly distilled from over Na metal, and CH_2Cl_2 and hexane from over CaH_2. $CDCl_3$ (SDS) was filtered through basic alumina. Commercially available tetrachloropyrocatechol is monohydrated and had to be thoroughly dried by azeotropic distillation (toluene) prior to use. Tris(dimethylamino)phosphane was freshly distilled for every use. Diones **9**, **10**, **12** and **13** were purchased from Acros and used without any prior purification. NMR spectra were recorded on Bruker AMX-300 or Bruker AMX-400 spectrometers at room temperature unless stated otherwise. ^{1}H NMR: chemical shifts are given in ppm relative to Me_4Si with the solvent resonance used as the internal standard. ^{31}P NMR: chemical shifts are reported in ppm relative to H_3PO_4. ^{13}C NMR: chemical shifts are given in ppm relative to Me_4Si, with the solvent resonance used as the internal standard ($CDCl_3$: $\delta = 77.0$ ppm; [D]$_6$DMSO: $\delta = 39.5$ ppm). Some assignments were performed with the help of COSY, HETCOR and/or NOESY experiments. IR spectra were recorded with a Perkin–Elmer 1650 FT-IR spectrometer using a diamond ATR Golden Gate sampling. Melting points 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 Spectrometry of the University of Geneva. UV/Visible spectra were recorded on a CARY-1E apparatus.

Synthesis of Dimethylammonium Phosphate Salts

General Procedure A: Anhydrous tetrachloropyrocatechol (**7**; 250 mg, 1.01 mmol, 1.0 equiv.) and a catalytic amount of NH_4Cl (1 crystal) were mixed together in dry toluene (5.0 mL). Tris(dimethylamino)phosphane (221 µL, 1.21 mmol, 1.2 equiv.) was then slowly added. Dimethylamine evolved and the mixture was refluxed for 15 min. The remaining solvent and excess of tris(dimethylamino)phosphane were removed under reduced pressure and the residue (**8**) was carefully dried in vacuo. Then, solutions of tetrachloropyrocatechol (250 mg, 1.01 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL, degassed) and of one of the selected diones (1.01 mmol, 1.0 equiv.) in CH_2Cl_2 (3 mL, degassed) were added sequentially to **8**. After 3 hours, hexane was added to induce a trace of precipitation. After 16 hours, the precipitate was filtered, washed with cold CH_2Cl_2/hexane (4 °C, 10 mL) and dried in vacuo to afford the desired [Me_2NH_2][phosphate] salts.

General Procedure B: This procedure is essentially identical to procedure A but with larger amounts of reagents: anhydrous tetrachloropyrocatechol (**7**; 250 mg, 1.01 mmol, 1.7 equiv.), tris(dimethylamino)phosphane (195 µL, 1.07 mmol, 1.8 equiv.) in dry toluene (5.0 mL). Then, solutions of tetrachloropyrocatechol (149 mg, 0.6 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL, degassed) and of one of the selected diones (1.01 mmol, 1.7 equiv.) in CH_2Cl_2 (3 mL, degassed).

Salt [Me_2NH_2][15]: Prepared as described in procedure A using dione **9** (210 mg, 1.01 mmol) and hexane (1 mL) to induce a trace of precipitation. Cold CH_2Cl_2/hexane (5:1; 15 mL) was used to wash the precipitate. [NH_2Me_2][**15**] was collected as a brown solid (362 mg, 46%). M.p. 241 °C (decomposition). IR: $\tilde{\nu}$ = 2351, 165, 1605, 1446, 1372, 990, 819 cm^{-1}. ^1H NMR ([D_6]DMSO, 400 MHz): δ = 8.82 [d, ^3J = 8.3 Hz, 2 H, *H*(4 and 5)], 8.17 (s broad, 2 H, NH_2), 7.85 [dd, ^3J = 8.1, ^4J = 1.0 Hz, 2 H, *H*(1 and 8)], 7.61 [ddd, ^3J = 7.6, ^3J = 7.6, ^4J = 0.8 Hz, 2 H, *H*(2 and 7)], 7.63 [ddd, ^3J = 8.3, ^3J = 8.3, ^4J = 1.5 Hz, 2 H, *H*(3 and 6)], 2.54 (s, 6 H, CH_3) ppm. ^{13}C NMR ([D_6]DMSO, 100 MHz): δ = 142.5 (d, $^2J_{C,P}$ = 5.6 Hz), 142.4 (d, $^2J_{C,P}$ = 5.6 Hz), 132.3 (d, $^2J_{C,P}$ = 5.6 Hz), 127.3, 126.1, 124.7, 123.9, 122.6, 122.4, 121.7 (d, $^3J_{C,P}$ = 3.2 Hz), 120.7 [C(3)], 113.3 (d, $^3J_{C,P}$ = 2.4 Hz), 113.1 (d, $^3J_{C,P}$ = 2.4 Hz), 34.8 ppm. ^{31}P NMR ([D_6]DMSO, 162 MHz): δ = −76.2 (10%), −77.7 (85%, **15**), −79.9 (5%, **2**) ppm. UV/Vis (MeOH, 1.10 × 10^{-5} M): λ_{max} (ε) = 216 (1.4 × 10^5), 257 (5.5 × 10^4), 302 (1.5 × 10^4). ES-MS (−): *m/z* (%) = 730.9 (46), 245.2 (31).

Using procedure B, salt [NH_2Me_2][**15**] (δ = −78.2 ppm, 80%) was isolated as a brown solid (316 mg, 68%) which contained three other signals in the δ = −80 ppm region (−76.7, 7%; −77.8, 8%; −80.2; 5%) along with minor amounts of a degradation product around δ = 0 ppm.

Salt [Me_2NH_2][17]: Prepared as described in procedure A using dione **11** (110 mg, 0.476 mmol) and CH_2Cl_2 as the only solvent. Cold CH_2Cl_2 (10 mL) was used to wash the precipitate. [NH_2Me_2][**17**] was obtained as a brown solid (257 mg, 71%). M.p. 230 °C (decomposition). IR: $\tilde{\nu}$ = 1449, 1376, 1069, 990, 821 cm^{-1}. ^1H NMR ([D_6]DMSO, 400 MHz): δ = 8.98 [dd, $^3J_{H,H}$ = 4.3, $^4J_{H,H}$ = 1.8 Hz, 2 H, *H*(2 and 9)], 8.35 [dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.8 Hz, 2 H, *H*(4 and 7)], 8.26 (s, 2 H, NH_2), 7.72 [dd, $^3J_{H,H}$ = 8.1, $^3J_{H,H}$ = 4.3 Hz, 2 H, *H*(3 and 8)], 2.56 (s, 6 H, CH_3) ppm. ^{13}C NMR ([D_6]DMSO, 100 MHz): δ = 147.7, 142.3 (d, $^2J_{C,P}$ = 6.4 Hz), 142.2 (d, $^2J_{C,P}$ = 6.4 Hz), 136.1, 133.7 (d, $^2J_{C,P}$ = 5.6 Hz), 129.0, 123.6, 121.8, 121.9, 119.3 (d, $^3J_{C,P}$ = 15.2 Hz), 113.4 (d, $^3J_{C,P}$ = 3.2 Hz), 113.2 (d, $^3J_{C,P}$ = 3.2 Hz), 34.8 ppm. ^{31}P NMR ([D_6]DMSO, 162 MHz): δ = −75.1 (4), −77.3 (94, **17**), −79.7 (2, **2**) ppm. UV/Vis (MeOH, 1.13 × 10^{-5} M): λ_{max} (ε) = 216 (7.6 × 10^4), 252 (2.7 × 10^4), 282 (1.5 × 10^4). ES-MS (−): *m/z* (%) = 732.8 (36), 244.9 (6).

Salt [Me_2NH_2][18]: Prepared as described in procedure A using dione **12** (212.1 mg, 1.01 mmol) and hexane (5 mL) to induce a trace of precipitation. Cold CH_2Cl_2/hexane (1:1, 15 mL) was used to wash the precipitate. [NH_2Me_2][**18**] was collected as a white solid (284 mg, 37%). M.p. 192 °C (decomposition). IR: $\tilde{\nu}$ = 1445, 1389, 1237, 1066, 989, 952, 817 cm^{-1}. ^1H NMR ([D_6]DMSO, 400 MHz): δ = 8.18 (br. s, 2 H, NH_2), 7.32−7.21 (m, 10 H, H_{Arom}), 2.55(s, 6 H, CH_3) ppm. ^{13}C NMR ([D_6]DMSO, 100 MHz): δ = 142.8 (d, $^2J_{C,P}$ = 5.6 Hz), 142.7 (d, $^2J_{C,P}$ = 6.4 Hz), 132.5 (d, $^2J_{C,P}$ = 2.4 Hz), 132.0 (d, $^3J_{C,P}$ = 15.2 Hz), 128.8, 127.9, 126.8, 121.2, 121.0, 112.9 (d, $^3J_{C,P}$ = 16.0 Hz), 112.8 (d, $^3J_{C,P}$ = 16.0 Hz), 34.8 ppm. ^{31}P NMR([D_6]DMSO, 162 MHz): δ = −81.9 ppm. UV/Vis (MeOH, 1.04 × 10^{-5} M): λ_{max} (ε) = 217 (1.1 × 10^5), 301 (1.3 × 10^4). ES-MS (−): *m/z* (%) = 733.0 (25%).

Using procedure B, salt [NH_2Me_2][**18**] was isolated as a white solid (165 mg, 35%) which contained only the desired phosphate anion **18**.

Salt [Me_2NH_2][19]: Prepared as described in procedure B using 20 equivalents of dione **13** (1.02 g, 1.9 mmol, 20 equiv.) and hexane (5 mL) to induce a trace of precipitation. Cold CH_2Cl_2/hexane (1:1, 15 mL) was used to wash the precipitate. [NH_2Me_2][**19**] was collected as a white solid (202 mg, 51%) containing an impurity at δ = −90.3 ppm (^{31}P NMR, 17%), which could not be separated from the desired anion at this stage. M.p. 174 °C (decomposition). IR: $\tilde{\nu}$ = 3120, 1600, 1448, 1388, 1231, 1144, 988, 951, 817 cm^{-1}. ^1H NMR ([D_6]DMSO, 400 MHz): δ = 8.17 (br. s, 2 H, NH_2), 2.55 (s, 6 H, NH_2CH_3), 1.68 (s, 6 H, CH_3) ppm. ^{13}C NMR ([D_6]DMSO, 100 MHz): δ = 142.8 (d, $^2J_{C,P}$ = 5.8 Hz), 142.7 (d, $^2J_{C,P}$ = 5.8 Hz), 126.84, 126.82, 120.2 (d, $^2J_{C,P}$ = 16.5 Hz), 112.2 (d, $^3J_{C,P}$ = 18.9 Hz), 112.0 (d, $^3J_{C,P}$ = 19.8 Hz), 34.3, 11.2 (d, $^2J_{C,P}$ = 14 Hz) ppm. ^{31}P NMR([D_6]DMSO, 162 MHz): δ = −80.2 (83%), −90.3 (17%). UV/Vis (MeOH, 3.93 × 10^{-5} M): λ_{max} (ε) = 217 (8 × 10^4), 301 (6.6 × 10^3). ES-MS (−): *m/z* (%) = 608.8 (100), 246.9 (51).

Using classical procedure B, salt [NH_2Me_2][**19**] was isolated as a white solid (408 mg, 60%) which contained only 49% of the desired phosphate anion **18** (δ = −80.3 ppm) along with the impurity at δ = −90.4 ppm (51%).

Salt [Me_2NH_2][23]: Anhydrous tetrachloropyrocatechol **7** (250 mg, 1.01 mmol, 1.0 equiv.) and a catalytic amount of NH_4Cl (1 crystal) were mixed together in dry toluene (5.0 mL). Tris(dimethylamino)phosphane (221 µL, 1.21 mmol, 1.2 equiv.) was then slowly added. Dimethylamine evolved and the mixture was refluxed for 15 min. The remaining solvent and excess of tris(dimethylamino)phosphane were removed under reduced pressure and the residue (**8**) was carefully dried in vacuo. Then, solutions of **9** (210 mg, 1.01 mmol, 1.0 equiv.) in CH_2Cl_2 (2 mL, degassed) and of (*S*)-BINOL (289 mg, 1.01 mmol, 1.0 equiv.) in CH_2Cl_2 (3 mL, degassed) were added sequentially to **8**. After 3 hours, hexane (5 mL) was added to induce a trace of precipitation. After 16 hours, the precipitate was filtered, washed with cold CH_2Cl_2 (4 °C, 10 mL) and was dried in vacuo. [NH_2Me_2][**23**] was collected as a brown solid (210 mg, 26%). M.p. 146 °C (decomposition). IR: $\tilde{\nu}$ = 1591w, 1450s, 1372m, 1333m, 1235m, 1163s, 1058m, 1000s, 950s, 820s cm^{-1}.^1H NMR ([D_6]acetone, 300 MHz): δ = 8.12−8.06 (m, 2 H), 7.26−7.19 (m, 2 H), 7.14−7.10 (m, 2 H), 6.83−6.62 (m, 10 H), 6.54−6.47 (m, 2 H), 6.08 (dd, ^3J = 8.9, ^4J = 1.1 Hz, 1 H), 5.82 (dd, ^3J = 8.9, ^4J = 0.9 Hz, 1 H), 2.05(s, 6 H) ppm. ^{31}P NMR ([D_6]acetone, 121 MHz): δ = −81.0 ppm. UV/Vis (MeOH, 1.0 × 10^{-5} M): λ_{max} (ε) = 221 (11.3 × 10^4); 254 (4.4 × 10^4). ES-MS (−): *m/z* (%) = 769.2 (18).

Tris(dimethylaminophenyl)methinium Phosphate Salts. General Procedure: Salts [Me_2NH_2][**15**], [Me_2NH_2][**17**], [Me_2NH_2][**18**] or [Me_2NH_2][**19**] (26 µmol, 1.0 equiv.) were dissolved in acetone (5 mL) and crystal violet (26 µmol, 13 mg, 1.2 equiv.) was added. The resulting solutions were stirred for 30 min and concentrated in vacuo. Purification by chromatography over SiO_2 (CH_2Cl_2) or basic Al_2O_3 (CH_2Cl_2/EtOH) afforded the desired salts in chemically pure form as dark purple solids.

Salt [CV^+][15]: Chromatography (SiO_2, CH_2Cl_2, 10 × 2 cm) afforded a dark purple oil (15.4 mg, 54%). R_f = 0.51 (CH_2Cl_2). IR: $\tilde{\nu}$ = 2976, 1576, 1449, 1351, 1160, 816 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.53 [d, $^3J_{H,H}$ = 8.3 Hz, 2 H, *H*(4 and 5)], 7.99 [d, $^3J_{H,H}$ = 4.0 Hz, 2 H, *H*(1 and 8)], 7.42−7.36 [m, 4 H, *H*(2, 3, 6 and 7)], 7.15 (d, $^3J_{H,H}$ = 9.1 Hz, 6 H, C*H*CHCNMe$_2$), 6.63 (d, $^3J_{H,H}$ = 9.1 Hz, 6 H, CHC*H*CNMe$_2$), 3.04 (s, 18 H, NCH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 178.0, 155.3, 142.8 (d, $^2J_{C,P}$ =

6.4 Hz), 142.6 (d, $^{2}J_{C,P}$ = 6.4 Hz), 139.6, 135.0, 126.5, 125.9, 125.8, 123.3, 122.5, 121.5, 121.4, 113.5 (d, $^{3}J_{C,P}$ = 13.5 Hz), 113.1 (d, $^{3}J_{C,P}$ = 13.5 Hz), 112.1, 40.3 ppm. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = −78 ppm. UV/Vis (MeOH, 0.90 × 10^{-5} M): λ_{max} (ε) = 215 (2.9 × 10^{4}), 251 (1.1 × 10^{4}), 303 (6.5 × 10^{3}), 585 (2.0 × 10^{4}). ES-MS (−): *m/z* (%) = 730.9 (100), 522.9 (4); (+) 372.4 (100).

Salt [CV$^+$][17]: Chromatography [Al_2O_3 (pH > 9.5), CH_2Cl_2/EtOH (95:5), 7 × 2 cm] afforded a dark purple oil (9.2 mg, 32%). R_f = 0.51 (CH_2Cl_2/EtOH, 95:5). IR: $\tilde{\nu}$ = 1577, 1450, 1352, 1163, 817 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 8.97 [dd, $^{3}J_{H,H}$ = 4.1, $^{4}J_{H,H}$ = 1.6 Hz, 2 H, *H*(2 and 9)], 8.32 [dd, $^{3}J_{H,H}$ = 8.3, $^{4}J_{H,H}$ = 1.6 Hz, 2 H, *H*(4 and 7)], 7.70 [dd, $^{3}J_{H,H}$ = 8.3, $^{3}J_{H,H}$ = 4.3 Hz, 2 H, *H*(3 and 8)], 7.29 (d, $^{3}J_{H,H}$ = 9.3 Hz, 6 H, C*H*CHCNMe$_2$), 7.00 (d, $^{3}J_{H,H}$ = 9.3 Hz, 6 H, CHC*H*CNMe$_2$), 3.22 (s, 18 H, NC*H*$_3$) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ = 176.2, 155.2, 147.3, 141.8 (d, $^{2}J_{C,P}$ = 5.8 Hz), 141.7 (d, $^{2}J_{C,P}$ = 6.6 Hz), 141.1, 139.1, 133.2 (d, $^{2}J_{C,P}$ = 5.6 Hz), 128.3, 125.7, 123.0, 121.42, 121.38, 118.9, 112.9 (d, $^{3}J_{C,P}$ = 2.5 Hz), 112.7 (d, $^{3}J_{C,P}$ = 3.3 Hz), 112.5, 40.0 ppm. ^{31}P NMR ([D$_6$]DMSO, 162 MHz): δ = −78.4 ppm. UV/Vis (MeOH, 1.08 × 10^{-6} M): λ_{max} (ε) = 215 (96 × 10^{4}), 252 (35 × 10^{4}), 287 (19 × 10^{4}), 301 (19 × 10^{4}), 586 (53 × 10^{4}). ES-MS (−): *m/z* (%) = 732.9 (23); (+) 372.5 (100).

Salt [CV$^+$][18]: Chromatography (SiO_2, CH_2Cl_2, 10 × 2 cm) afforded a dark purple oil (28.7 mg, 100%). R_f = 0.37 (CH_2Cl_2). IR: $\tilde{\nu}$ = 2362, 1577, 1354, 1163, 819 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 400 MHz): δ = 7.32−7.20 (m, 16 H, H_{arom}), 6.97 (d, $^{3}J_{H,H}$ = 9.4 Hz, 6 H, C*H*CNMe$_2$), 3.20 (s, 18 H, C*H*$_3$) ppm. ^{13}C NMR ([D$_6$]DMSO, 100 MHz): δ = 176.2, 155.2, 142.3 (d, $^{2}J_{C,P}$ = 6.6 Hz), 142.2 (d, $^{2}J_{C,P}$ = 5.8 Hz), 139.1, 132.0 (d, $^{2}J_{C,P}$ = 2.5 Hz), 131.5 (d, $^{3}J_{C,P}$ = 14.0 Hz), 128.2, 127.4, 126.3, 125.8, 120.7, 120.5, 112.5, 112.4 (d, $^{3}J_{C,P}$ = 16.5 Hz), 112.3 (d, $^{3}J_{C,P}$ = 16.0 Hz), 40.0 ppm. ^{31}P NMR ([D$_6$]DMSO, 162 MHz): δ = −83.0 ppm. UV/Vis (MeOH, 1.4 × 10^{-5} M): λ_{max} (ε) = 213 (7.8 × 10^{3}), 250 (2.2 × 10^{3}), 302 (1.6 × 10^{3}), 585 (6.4 × 10^{3}). ES-MS (−): *m/z* (%) = 732.9 (25), 521.1 (50); 247.0 (100); (+) 372.2 (100).

Salt [CV$^+$][19]: Chromatography [Al_2O_3 (pH > 9.5), CH_2Cl_2/EtOH (95:5), 7 × 2 cm] afforded a dark purple oil (12.6 mg, 28%). R_f = 0.92 (CH_2Cl_2/EtOH, 95:5). IR: $\tilde{\nu}$ = 2916, 1576, 1454, 1352, 1163, 814 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 7.3 (d, ^{3}J = 9.1 Hz, 6 H, C*H*CHCNMe$_2$), 7.00 (d, ^{3}J = 9.1 Hz, 6 H, CHC*H*CNMe$_2$), 3.22 (s, 18 H, NC*H*$_3$), 1.67 (s, 6 H, CC*H*$_3$) ppm. ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 176.2, 155.2, 142.5 (d, $^{2}J_{C,P}$ = 5.5 Hz), 142.4 (d, $^{2}J_{C,P}$ = 6.1 Hz), 139.1, 126.86, 126.82, 125.8, 120.1 (d, $^{2}J_{C,P}$ = 12.9 Hz), 112.2 (d, $^{3}J_{C,P}$ = 15.4 Hz), 112.0 (d, $^{3}J_{C,P}$ = 16.0 Hz), 112.5, 40.0, 11.3 (d, $^{2}J_{C,P}$ = 14.8 Hz) ppm. ^{31}P NMR ([D$_6$]DMSO, 121 MHz): δ = −81.4 ppm. UV/Vis (MeOH, 1.55 × 10^{-5} M): λ_{max} (ε) = 223 (18 × 10^{4}), 248 (14 × 10^{4}), 303 (18 × 10^{3}), 587 (62 × 10^{3}). ES-MS (−): *m/z* (%) = 608.8 (54), 247.1 (18); (+) 372.3 (100).

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[62] CCD refcodes: CABBIQ; CABBIQ01.

[63] CCD refcode: CAMPQU.

[64] For **12** and **13**, a rotation around the central C-C bond is necessary to align the carbonyl groups (dihedral angle O-C-C-O = 0°); The measurement of the minimal O···O distance did not, however, involve any change of the bond lengths.

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[68] The chiral ligands need to be C_2-symmetric as a lower symmetry will usually double the number of stereoisomers in the derived hexacoordinated phosphate anions.

[69] One cannot exclude the possibility of a reaction of phosphoramidite **8** with diols **7** or **22** prior to the oxidation. Such a reaction would form phosphite or tautomeric spirophosphorane derivatives, which would then react with the diones to form the hexacoordinated anions.

[70] Up to 19 compounds were observed in the NMR spectrum, which is close to the number of signals that can come from the statistical distribution, multiplied by two by the presence of the chiral BINOL. Obviously, many rearrangements occur which, unfortunately, could not be studied due to the rapid decomposition of the adducts.

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