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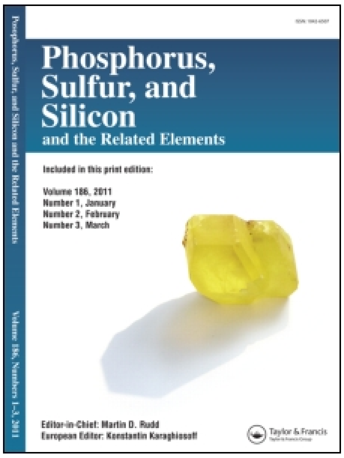

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Chiral Hexacoordinated Phosphorus Anions : Effective Auxiliaries for Anion Mediated Asymmetric Processes

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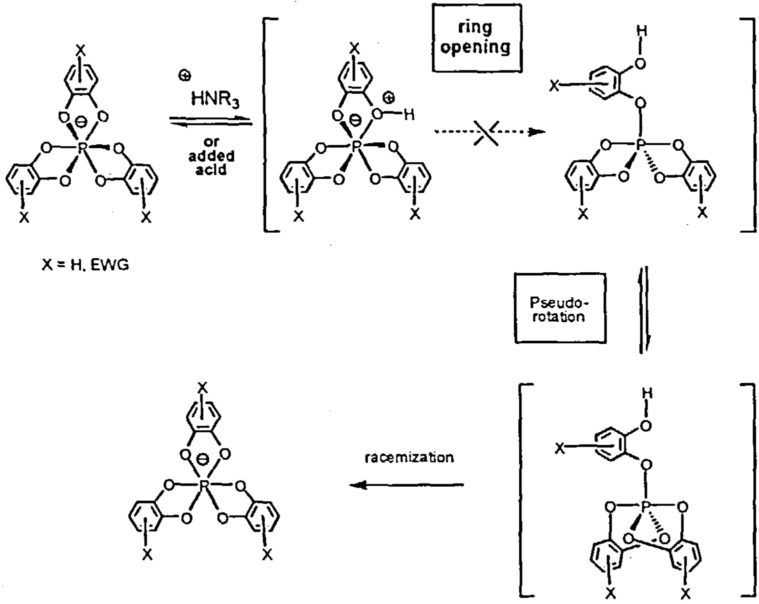
Easily synthesized and resolved TRISPHAT anion is an efficient chiral auxiliary for asymmetric processes with chiral cations.

Keywords: Hexacoordinated Phosphorus; Chiral Anions; Asymmetric Induction; Supramolecular Chemistry

INTRODUCTION

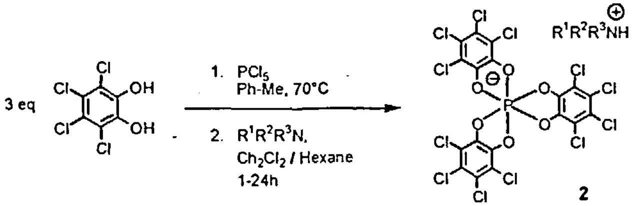
One objective of our research is to develop the synthesis of non nucleophilic chiral anions of original structure and geometry, and to use them as chiral auxiliaries in asymmetric chemistry. We are more particularly interested in studying the nature of the discriminating interactions that occur within the intimate or penetrated ion pairs of these species and, chiral or prochiral, cations.

The octahedral geometry of pentavalent hexacoordinated phosphorus allows the formation of chiral phosphate anions by complexation of the phosphorus with three identical bidentate ligands.[1] The tris(benzenediolato)phosphate(V) anion **1**, easily prepared as an ammonium salt in a single step from catechol, PCl_5 and an amine, was known to be configurationally labile in solution *via* an acid catalyzed one-ended dissociation racemization mechanism (Scheme1, X = H).[2] Recently, we suggested that the rate determining step was the ring opening and shown that the use of catechols substituted with electron-withdrawing groups (EWG) leads to more *configurationally stable* anions: EWG decrease the basicity of the oxygens of the catechols, avoid their protonation, stop the opening of the phosphate anion to the phosphorane intermediate and thus avert the racemization (Scheme1, X = EWG).[3]



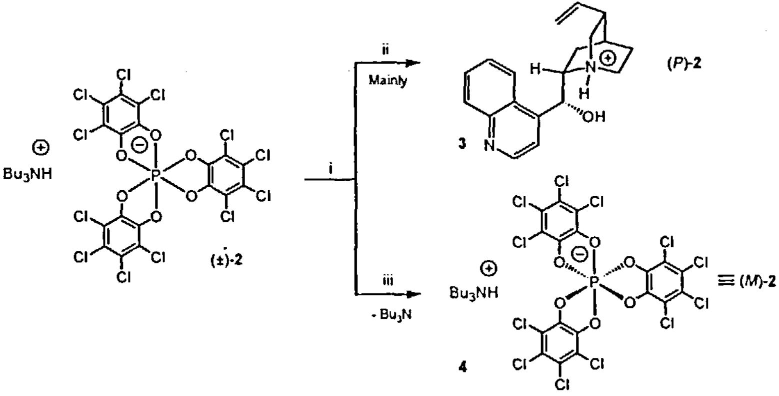
SCHEME 1 Possible racemization mechanism of hexacoordinated phosphate anions

The tris(tetrachlorobenzenediolato)phosphate(V) anion 2 (or TRISPHAT), easily synthesized from electron-poor, readily available, tetrachlorocatechol is thus *configurationally stable* as an ammonium salt in solution.[4] Treatment of PCl_5 with 3 equivalents of tetrachlorocatechol in hot toluene, followed by addition of an amine in dichloromethane / hexane affords its ammonium salts as precipitates in good yields (70-90%, Eq 1).



(1)

For the resolution of TRISPHAT, we have developed a short and efficient procedure (Scheme 2):[5] Addition of 0.5 equiv. of cinchonidine to a solution of racemic tri-*n*-butylammonium TRISPHAT salt [(Bu$_3$NH$^+$)(±-**2**)] in CH$_2$Cl$_2$ leads, after proton exchange, to the diastereoselective precipitation of a solid **3** containing essentially the [cinchonidinium-(*P*-**2**)] salt (70% de in CH$_2$Cl$_2$). Filtration and concentration of the mother liquor *in vacuo* afford a white solid **4** containing essentially optically enriched [(Bu$_3$NH$^+$)(*M*-**2**)] (70% ee). Recrystallisation of **3** in EtOAc-acetone affords as colorless plates optically pure [cinchonidinium-(*P*-**2**)]•EtOAc. Near perfect octahedral structure, as well as absolute *P* or Δ configuration of the TRISPHAT anion in this salt were unambiguously confirmed by X-ray structure analysis. Recrystallisations of solid **4** in CHCl$_3$ then CH$_2$Cl$_2$ afford in the mother liquors, chemically and optically purified, [^{n}Bu$_3$NH$^+$-(*M*-**2**)] (96% ee).[6]



Reagents and conditions: i, 0.5 equiv. of cinchonidine, CH$_2$Cl$_2$, 20°C, 6 h; ii, filtration, **3** (49%); iii, concentration of the mother liquor *in vacuo* (60°C, 10^{-4} bar, 12 h), **4** (56%, 70% ee).

SCHEME 2 Resolution of TRISPHAT anion **2**

We have been able to demonstrate that anion **2** is an efficient NMR chiral shift agent for chiral cations. Enantiomers of tris(diimine)ruthenium (II) and iron (II) complexes, phosphonium salts and monomethine cations can be observed in ^{1}H, ^{13}C (and ^{31}P)

NMR upon addition of [(Bu_3NH^+)(*M*-**2**)] salt.[7] TRISPHAT anions **2** are also very efficient chiral auxiliaries. For instance, two chiral TRISPHAT anions can behave as efficient hosts for chiral cationic tris(diimine)iron(ii)guests: In a low polarity solvent ($CHCl_3$), a highly diastereoselective homochiral ion pairing can take place as the two anions control effectively the configuration of the labile chiral cation (up to d.e. > 96%).

Acknowledgements

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