

# Chiral Anion Mediated Asymmetric Chemistry: Advantages and Perspectives

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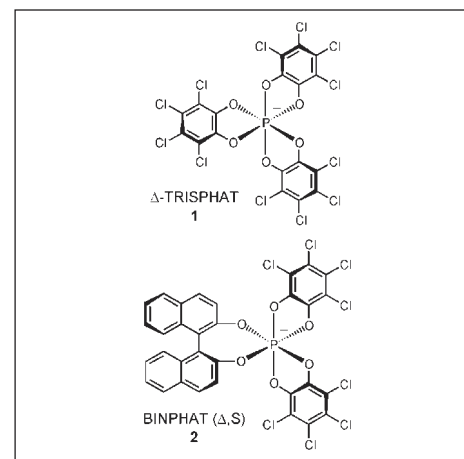
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In most of these examples, the chiral discriminating interactions responsible for the making of the complexes in high selectivity have been intramolecular diastereoselective interactions as the enantiopure ligands lead, by self-assembly, to the preferred formation of one diastereomer.

The research that we are performing in Geneva is based on purely non-covalent interactions between the chiral cationic complexes and enantiopure anions. It places itself in a complementary position, as diastereoselective interactions are intermolecular rather than intramolecular. We believe that there is much to gain from this supramolecular approach as, for instance, both configurations of a chiral cationic complex can be generated with no need to prepare two sets of enantiomeric ligands. It is sufficient to form the complex with achiral ligands and exchange, at the end of the synthesis, the traditional achiral anions ( $\text{PF}_6^-$ ,  $\text{BF}_4^-$ , etc.) for chiral anionic counterions. This can render the asymmetric synthesis of coordination complexes very simple.

Over the last few years, we could show that hexacoordinated phosphorus anions, such as TRISPHAT (1) and BINPHAT (2) (Fig.), are indeed efficient anionic auxili-

aries. They form tightly associated diastereomeric ion pairs with chiral cations. The resulting short-range interactions often lead to an efficient NMR enantiodifferentiation. These lipophilic anions are also efficient resolving and asymmetry-inducing agents leading to effective procedures of resolution (asymmetric extraction, chromatography) or stereoselective synthesis. These results were recently reviewed in this journal [2].



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Efficient asymmetric synthesis and catalysis are in constant demand from academic and industrial laboratories due to the importance of obtaining chiral compounds in enantioenriched or enantiopure forms for biological, pharmaceutical, physical or theoretical applications.

In the fields of asymmetric chemistry, inorganic and supramolecular syntheses are still very new topics. Recent progress in the design of enantiopure ligands has allowed chemists to gain much control over the configuration of chiral molecular and supramolecular transition metal complexes, and elegant asymmetric syntheses of such compounds have appeared in the literature [1].

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