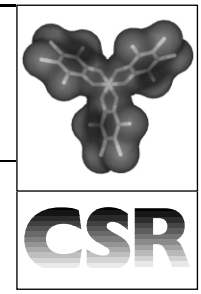
Recent developments in chiral anion mediated asymmetric chemistry



Jérôme Lacour* and Virginie Hebbe-Viton

Department of Organic Chemistry, University of Geneva, Quai Ernest Ansermet 30, CH-1211 Geneva 4, Switzerland. E-mail: jerome.lacour@chiorg.unige.ch; Fax: +41 22 328 7396

Received 28th February 2003
First published as an Advance Article on the web 16th July 2003

Chemical reactions and processes often involve cationic prostereogenic or racemic reagents, intermediates or products. To afford instead non-racemic or enantiopure compounds, an asymmetric ion pairing of the cations with chiral anionic counterions can be considered. This review presents recent examples of the synthesis and use of chiral anions for stereoselective purposes.

Jérôme Lacour was born in 1966 in Paris, France. He was educated at the Ecole Normale Supérieure (Ulm, Paris) and obtained in 1993 his PhD in Chemistry at the University of Texas at Austin under the supervision of Professor Philip D. Magnus. After post-doctoral studies in the laboratory of Professor David A. Evans at Harvard University, he joined the Organic Chemistry Department of the University of Geneva in 1995. He now holds an associate professor position financed by the Sandoz Family Foundation. In 2002, he received the Werner Prize of the Swiss Chemical Society. Since 2003 he has been a member of the Editorial Advisory Board of Chemical Communications. His main research interest is stereoselective chemistry in a wide sense. His contribution in this field is the development of new chiral hexacoordinated phosphorus anions and their use for the analysis, the resolution or the asymmetric synthesis of chiral cations.

Virginie Hebbe-Viton was born in 1976 in Chateau-Thierry, France. She received her Maîtrise and Diplôme d'Etudes Approfondies in Chemistry from Université Pierre et Marie Curie, Paris, in 1998 and 1999 respectively. She is now working as an assistant in the Organic Chemistry Department of the University of Geneva completing her studies toward a PhD.

1 Introduction

Many chemical reactions and processes involve cationic reagents, intermediates or products. Cations are frequent intermediates along reaction pathways that react with nucleophiles to produce interesting fragments and functional groups. Cations are often Lewis acidic and numerous applications have been developed using these reagents. A large range of important synthetic and biological processes are mediated by ammonium and imidazolium ions. Cations are also efficient templates for the construction of complex supramolecular arrays, such as the catenanes, knots, helicates and rotaxanes. Cations have also interesting physical properties being, for instance, among the first synthetic dyes to be developed.

For the purpose of this review, cations can also be *prostereogenic* or *chiral* and many of the above-mentioned applications, reactions or processes lead to *racemic* molecular or supramolecular assemblies. To afford instead non-racemic or enantiopure products, and benefit from possible new applications, an asymmetric ion pairing with chiral anions can be considered – the counterions behaving as asymmetric auxiliaries, ligands or reagents.[1]

In fact, the association of prostereogenic or chiral ionic species with enantiopure counterions results in the formation of diastereomeric salts. A wealth of evidence suggests that an ion electrostatically removed from its counterion is never formed in low-polarity solvents but, instead, an *ion pair* is produced. Ion pairing is an essential phenomenon, which has been extensively studied and reviewed.[2] The terms *contact*, *tight*, or *intimate ion pair* and *solvent-separated* or *loose ion pair* have become well known in the chemical world.[3] The notion of *penetrated ion pair* has also been introduced to explain the spectroscopic and photochemical properties of certain intricate associations.[4] The formation of tightly associated contact ion pairs between *prostereogenic* or *chiral* cations and chiral anions can therefore occur and lead, as a result, to large chemical and physical differences among the diastereomeric salts. A high level of asymmetric recognition between the chiral cations and anions can be achieved leading to efficient processes of resolution or asymmetry-induction. Stereoselectivity in reactions can be obtained by the preferred occurrence of one diastereomeric reactive ion pair containing a prostereogenic or chiral cation and its matched enantiopure counterion.

In early approaches, chiral anions issued or derived from the chiral pool have been essentially considered. Numerous applications, especially in the field of enantiomeric resolutions, have been developed.[5] Today, these anions are still used with much success and selected examples of applications will be presented. Recent developments in chiral anion mediated asymmetric chemistry have also made use of new synthetic anions. This review will thus survey the design, the properties and the synthesis of these novel chiral anionic auxiliaries and reagents. Applications of the anions as NMR chiral shift reagents, as

resolving agents for organic and inorganic cations and as chiral auxiliaries or ligands in stereoselective reactions will be presented.

2 "Guidelines" for the design of chiral anionic auxiliaries or reagents

To be efficient chiral auxiliaries or reagents, the chiral anions need, in our view, to fulfil some precise conditions and meet certain properties. They are outlined as a preamble in the following paragraphs.

2.1 Close spatial relationship between charge and chirality

The spatial relationship between the localisation of the charge and the chiral environment is obviously crucial for high stereoselectivity. The stereogenic element(s) should be in a position close to the charged atom/moiety as the separation of the charged centres from the asymmetric moieties will obviously disfavour selective interactions. The anions should also adopt a limited number of conformations to be better pre-organised for selective recognition phenomena. Rigid ions with chirality ordered around a central charged atom should thus be advantageous, since the negatively charged atom is the centre of the structure and the chiral environment extends from there toward the ionic partner.

2.2 Stability and properties

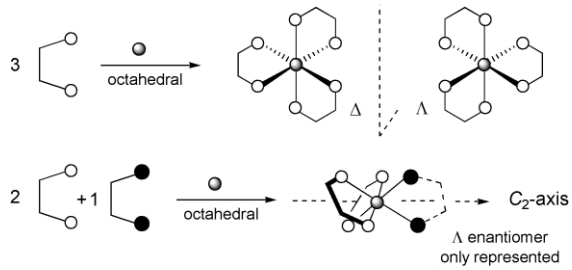
The anions should also possess a good overall chemical and configurational stability. The ions need to be large to favour interpenetration and rather lipophilic as a high solubility in low-polarity solvents is often crucial to maximise ion-pairing.[3]

2.3 Ease of synthesis and structural optimisation

The chiral ions should be easily accessible or prepared using simple synthetic procedures and – if possible – in an asymmetric manner. In this respect, main-group and coordination chemistry often presents the advantage of leading to rather complex molecular or supramolecular structures in a very few number of steps; the formation of the products being controlled by the self-assembly of the ligands around one or many template atoms. The structure of the self-assembled molecules can then be easily modified, according to need, by changing the nature of the ligands. This allows facile structural modifications.

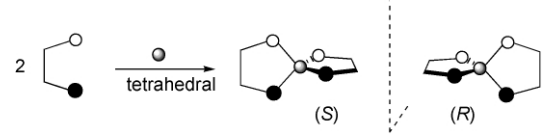
2.4 Symmetry and geometry

Although successful examples of asymmetric reactions using ligands/auxiliaries devoid of any particular symmetry are known, symmetrical structures (D_3, D_2, C_3, C_2) are often preferred as the presence of symmetry axes can simplify the design of the chiral reagents/catalysts and the understanding of the stereochemical outcome of the asymmetric processes.[6]



In this respect, the octahedral geometry is interesting as it suffices to coordinate to a central atom three identical symmetric bidentate ligands to form chiral D_3-symmetric helical molecules (*e.g.* $M(AA)_3$); such compounds existing either as Λ or Δ enantiomers of left- and right-handed propeller shape respectively. Coordination to the central octahedral atom of two different types of symmetrical bidentate ligand lead to structures of type $M(AA)_2(BB)$ which are this time C_2-symmetric.[7]

The pseudo-tetrahedral geometry of certain main-group or coordination metal atoms allows also the formation of chiral edifices of type $M(AB)_2$ by the complexation of a central M atom with two identical unsymmetrical bidentate AB ligands. "Spirane"-like chiral entities are formed of which configuration can assigned the *S* and *R* descriptors.[8]



These four "guidelines" outlined in this preamble constitute parameters that can be taken into account for the design of the chiral ions. However, as it is essentially impossible to predict, *a priori*, the efficiency of a chiral auxiliary, these "rules" only constitute a canvas, which allows a lot of degrees of freedom – just to prove them wrong if necessary.

3 Origin, structure and properties of useful chiral anions

3.1 Anions from the chiral pool

As mentioned, the chiral pool has been for many decades the major source of enantiomerically pure materials.[9] Among the natural compounds available, chiral carboxylic and sulfonic acids, like tartaric, mandelic, or 10-camphorsulfonic acids have provided over the years their conjugated bases as chiral anions (carboxylates and sulfonates, **1–3** respectively, Figure 1). These rather hydrophilic anions are usually available in large quantities in one enantiomeric form; the optical antipode being often accessible from commercial sources.[5] Simple derivatisation of some of these compounds provides further anionic structures: for instance, L-tartaric acid can be readily transformed into its disodium (−)-*O*,*O*′-dibenzoyl-L-tartrate (**4**) salt.[5a]

These anions however possess a rather large number of potential conformations. To reduce them, it is possible to coordinate the moieties to metal ions and the derived, more rigid, anionic complexes have proven their efficiency over the years in a large numbers of applications. The most characteristic of these compounds is the antimonyl (L or D)-tartrate anion **5**, which is commercially available as its sodium or potassium salt, Na_2Sb_2(L- or D-$C_4O_6H_2)_2{\cdot}5H_2O$ and K_2Sb_2(L- or D-$C_4O_6H_2)_2{\cdot}nH_2O$ respectively.[10]

Higher-order anionic lanthanide complexes made of chiral β-diketonate ligands have also been introduced as chiral anions; the ligands being most often derived from naturally occurring camphor. These charged derivatives, *e.g.* $Eu(tfc)_4^-$ **6** (Fig. 1) and $Eu(tfc)_3fod^-$, are formed by the reaction of chiral neutral, commercially available, lanthanide complex $Ln(tfc)_3$ and the potassium salt of the chiral tfc or fod ligands (tfc: 3-(trifluoromethylhydroxymethylene)camphorate; fod: 6,6,7,7,8,8,8-heptafluroro-2,2-dimethyl-3,5-octanedione).[11]

3.2 Intrinsically chiral metallo-organic complexes

The chirality of the described metal complexes **5** and **6** seems however to be more influenced by the asymmetric nature of the

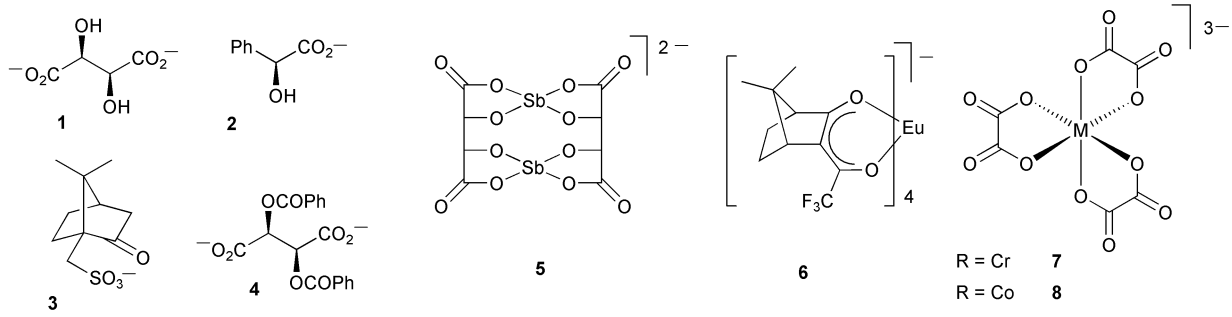


Fig. 1 Chiral anions **1–8**.

backbone of the ligands than by their spatial arrangement around the metal ions. This is not the case for the anionic chromium(III) and cobalt(III) tris(oxalato) octahedral complexes, **7** and **8**, which can be prepared as their potassium or ammonium salts in racemic form. These derivatives are configurationally stable and their resolution has been reported (Fig. 1).[12]

3.3 Tetrahedral borate anions

As previously mentioned (section 2.4), the tetrahedral geometry of the tetracoordinated atoms allows also the formation of intrinsically chiral structures by the complexation of the central atom with two identical unsymmetrical bidentate ligands. This was recognised for boron by Böeseken and Mijs who, as early as 1925, demonstrated that 4-chloro- and 3-nitro-catechols form chiral borate ions **9** and **10** (Fig. 2). These anions were partially resolved using the conjugated acids of brucine or strychnine.[13] Unfortunately, these bis(catecholato) anions **9** and **10** are configurationally labile. Their absolute configuration and enantiomeric purity in the alkaloid salts remains unknown. Recently, Hosseini *et al*. have synthesised a tetradentate bis(catecholato) ligand, which binds a boron atom in a tetrahedral coordination geometry to form chiral boracryptand **11**.[14] Nelson has investigated the configurational stability of borate anions **12** and **13** derived from 3-isopropyl-catechol and a tetraphenol ligand respectively.[15] At room temperature, Hosseini and Nelson have shown that the racemisation process of borates **11–13** is slow on the NMR time scale. For **12** and **13**, stereodynamics were detected by variable temperature (VT) NMR spectroscopy as coalescence of diastereotopic signals could be evidenced at higher temperatures. The free energies of racemisation were determined (85 and 79 kJ mol^{-1} for **12** and **13** respectively) and mechanistic rationales were proposed to explain their racemisation pathways.

In 1962, Torssell reported the synthesis and resolution of chiral tetraarylborate anions **14** and **15** (Figure 2). These configurationally stable compounds were initially developed to prove unambiguously the tetrahedral nature of borate ions. The separation of the optical antipodes was achieved by a selective crystallisation in the presence of enantiopure synthetic quaternary methyl-*n*-propylbenzylphenylammonium cation.[16] Such tetraarylborate anions can be characterised by their low nucleophilicity, high solubility in low-polarity solvents, large ionic radius, and ease of preparation from aryl-lithium or -Grignard reagents. All these properties make such tetraarylborate anions strong candidates for anion mediated asymmetric processes. This was recognised by Schuster *et al*. who reported in 1998 a general access to **15** and to structurally related derivative **16**;[17] these compounds being formed in 6 steps in racemic form and resolved following the procedure of Torssell.

Another approach to the formation of chiral borate anions is the coordination of the central boron atom by chiral ligands. Yamamoto and co-workers have synthesised the Brønsted acids of chiral borate anions **17** and **18** made or derived from enantiopure BINOL ([1,1′]binaphthalenyl-2,2′-diol).[18] Periasamy and co-workers have reported the resolution of **17** in the presence of (*R*)- or (*S*)-1-phenyl-ethylammonium cation.[19]

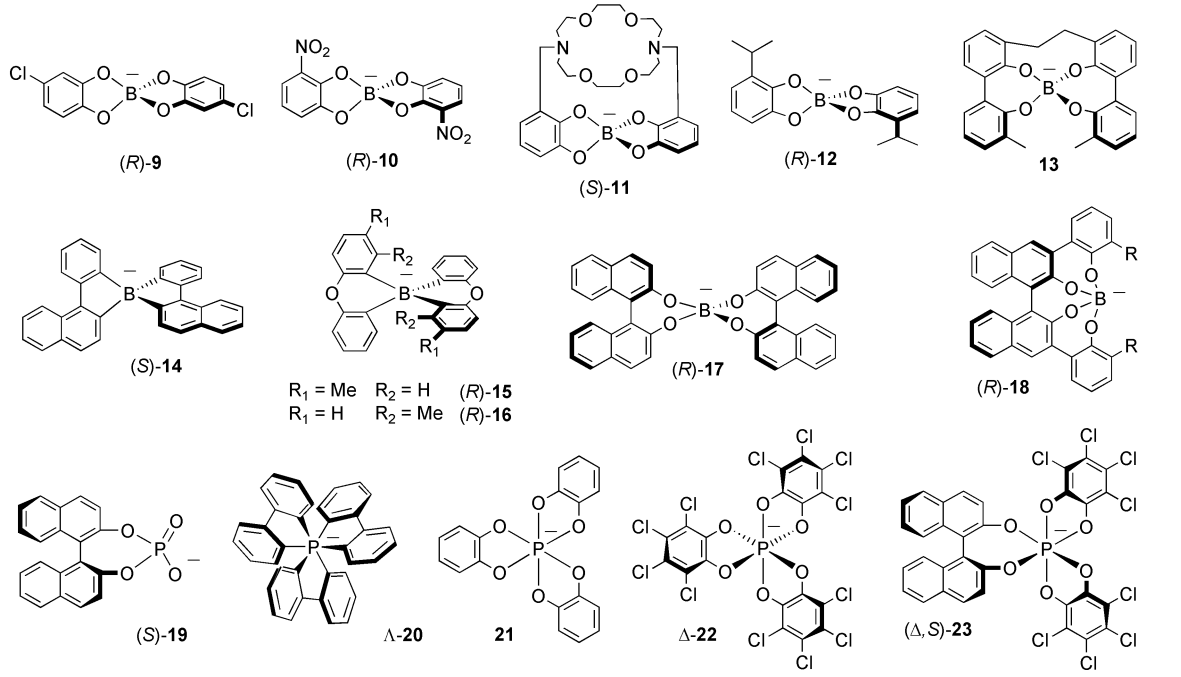


Fig. 2 Chiral anions **9–23**.

Arndtsen and co-workers have prepared silver(I) and copper(I) derivatives of enantiopure **17** in high yield and chemical purity.[20]

3.4 Phosphate anions

3.4.1 Tetracoordinated phosphorus anions. In section 3.1, we mentioned that carboxylic and sulfonic acids often provide their conjugated bases as chiral anions. This is also the case for phosphoric acid derivatives, and the (*S*)-(+)- or (*R*)-(−)-binaphthyl-2,2′-diyl hydrogen phosphate in particular;[21] its derived anion **19** being often used in asymmetric processes.

3.4.2 Hexacoordinated phosphorus anions. As previously described, the octahedral geometry allows the formation of chiral structures by complexation of a central atom with three identical bidentate ligands. Hexacoordinated phosphate **20**, prepared by Hellwinkel in 1965, is indeed chiral and both optical antipodes were obtained through resolution.[22]

Tris(benzenediolato)phosphate anion **21**, of particular interest for its simple preparation from catechol, PCl_5 and an amine, is unfortunately configurationally labile in solution as an ammonium salt. Mechanistic studies by Koenig *et al*. have shown that the racemisation of **21** is acid-catalysed and proposed an intramolecular one-ended dissociation mechanism to explain it.[23] Lacour *et al*. could then demonstrate that the introduction of electron-withdrawing chlorine atoms on the aromatic nuclei of the catecholate ligands increases the configurational stability of the resulting tris(tetrachlorobenzene diolato)phosphate(V) derivative.[24] This D_3-symmetric anion **22**, known as TRISPHAT, can be resolved by an association with a chiral ammonium cation (Fig. 2). The Λ enantiomer is isolated as the tri-*n*-butylammonium salt, [Bu_3NH][Λ-TRISPHAT], which is soluble in pure $CDCl_3$ and CD_2Cl_2. The Δ-enantiomer is prepared as the cinchonidinium derivative, which is only soluble in polar solvent mixtures (> 7.5% DMSO in $CDCl_3$). Interestingly, pseudo-enantiomeric cinchoninium cation is totally inefficient for the resolution of the hexacoordinated phosphate.

The synthesis of C_2-symmetric hexacoordinated phosphate anions was also reported by the same group. A general one-pot process was developed for the preparation of new classes of enantiopure C_2-symmetric anions – BINPHAT **23** (Fig. 2),[25] HYPHAT,[26] and TARPHAT[27] – containing BINOL, hydrobenzoin and tartrate ligands respectively; all these anions being isolated as their dimethylammonium salts in good yields and chemical purity.

With these naturally-occurring or synthetic anions, numerous asymmetric applications were developed. A selection of recent reports are detailed in the following paragraphs.

4 NMR determination of enantiomeric purity

As already mentioned, chiral cations are involved in many areas of chemistry and, unfortunately, only few simple methods are available to determine with precision their optical purity. In the last decades, NMR has evolved as one of the methods of choice for the measurement of the enantiomeric purity of chiral species.[28] Neutral chiral lanthanide shift reagents, which have been particularly efficient for most applications, are however rarely used with chiral cations due to an overall lack of interactions with these analytes that usually miss accessible electron donor sites. Furthermore, line broadening and distorted baselines are often observed upon addition of the paramagnetic reagents, limiting thus their efficiency.[29] A noticeable exception comes from the work of Green who showed that chiral tetrakis europate **6** and Eu(tfc)$_3$fod$^-$ derivative provoke a clean enantiodifferentiation (^{1}H-NMR) of alkylmethylphenylsulfonium cations, such as ethylmethyl-*p*-tolylsulfonium **24** (Fig. 3).[15]

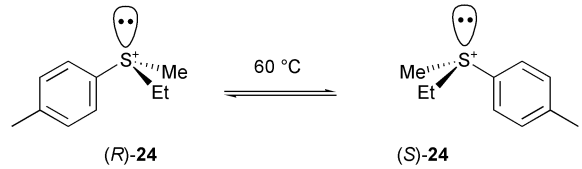
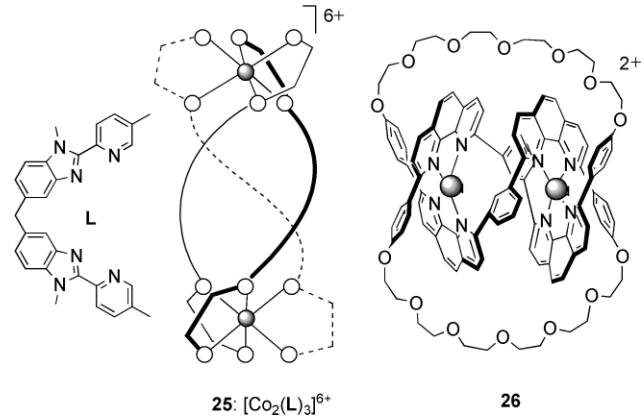


Fig. 3 Racemisation of ethylmethyl-*p*-tolylsulfonium **24**.

This has allowed the assignment of the *R* and *S* configurations of ethylmethylphenylsulfonium ions by comparison with an enantiomerically enriched sample of (*R*)-**24** as well as the visualisation of the racemisation of the cation at 60 °C.

Anionic substances have therefore an advantage over neutral reagents to behave as NMR chiral shift agents for chiral cations. They can form diastereomeric contact pairs directly and the short-range interactions that result can lead to clear differences in the NMR spectra of the two diastereoisomeric salts. For instance, anions **5** and **19** induce a differentiation in ^{1}H NMR for the enantiomers of chiral dinuclear Co(III) triple helicate **25**[30] and of dinuclear Cu(I) trefoil knot precursor **26**[31] respectively.



An overall efficiency of TRISPHAT **22** and BINPHAT **23** anions to behave as NMR chiral shift agents for chiral cations has been demonstrated over the last few years. Additions of [Bu_3NH][Λ-**22**],[32] [Bu_4N][Δ-**22**],[33] [Bu_4N][Λ- or Δ-**23**][34] and [Me_2NH_2][Λ- or Δ-**23**][35] to solutions of racemic or enantioenriched chiral cationic substrates have generally led to efficient NMR enantiodifferentiations. Well separated signals are usually observed on the spectra of the diastereomeric salts generated *in situ*. Sometimes, a direct ion-pairing of the chiral cations and anions **22** or **23** is necessary to maximise the NMR separation of the signals.[36] Cationic species as different as diquat **27**, quaternary ammonium **28**, phosphonium **29**, thiiranium ions **30**, ruthenium tris(diimine) **31** and (η^6-arene)-manganese **32** complexes have been analysed with success (Figs. 4 and 5).[37]

TRISPHAT anion **22** seems to be more particularly efficient with cationic metallo-organic and organometallic substrates. BINPHAT **23** often has superior chiral shift properties to **22** when associated with organic cations (Fig. 5). In all these examples, solvent polarity influences the quality of the separation since ion association is crucial. Solvent or solvent mixtures of low polarity are preferred for these experiments. Recently, Lacour, Sauvage and co-workers were able to show that the association of chiral $[CuL_2]^+$ complexes (L = 2-R-phen, 6-R-bpy and 2-iminopyridine) with TRISPHAT **22** leads to an NMR enantiodifferentiation, which can be used to determine the kinetics of racemisation of the complexes (bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline).[38]

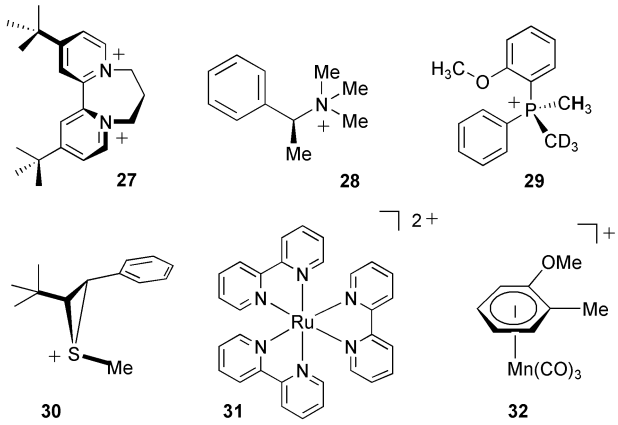


Fig. 4 Examples of chiral cations analysed with anions **22** or **23**.

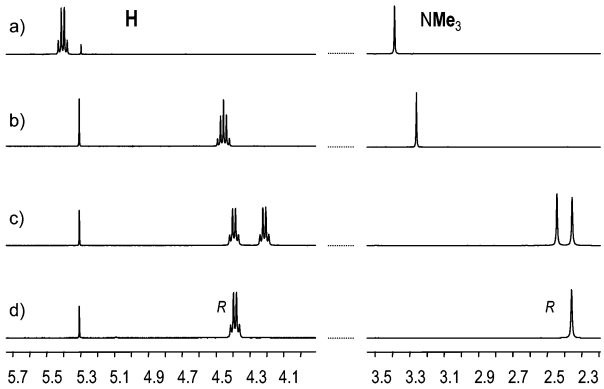


Fig. 5 ^{1}H NMR spectra (400 MHz, $CDCl_3$, parts) of a) [*rac*-**28**][I], b) [*rac*-**28**][Δ-**22**], c) [*rac*-**28**][(Δ,*S*)-**23**], d) [*R*-**28**][(Δ,*S*)-**23**].

Several reports independent from the Lacour's group have confirmed the efficiency of these chiral shift agents.[12b,39] Maury and Le Bozec have used the clear NMR separation of the enantiomers of ruthenium tris(diimine) complex **33** in the presence of Δ-**22** to demonstrate the preferred homochiral ion-pairing of the anion with the chiral cation (Figure 6). In this

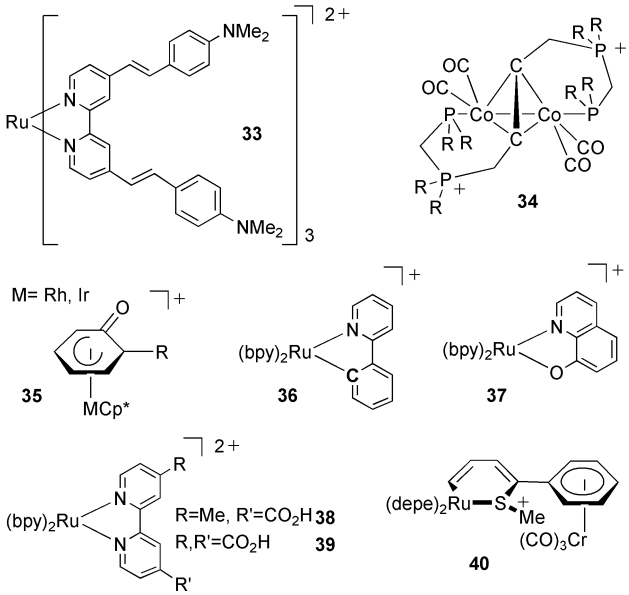
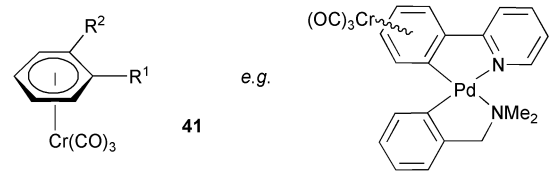


Fig. 6 Examples of chiral cations analysed with anion **22**.

example, as well as in other instances,[2,40] NMR spectroscopy was shown to be a particularly efficient technique for the determination of the nature of the interactions involved within the ion pairs.

Amouri, Gruselle, Thouvenot and co-workers have shown the capacity of **22** to differentiate the enantiomers of a unique propeller-like cobalt complex **34** [$(Co_2(CO)_4)$)μ,η^2,η^2-(–H_2CC≡CCH_2–)(–dppm)$_2$], of planar chiral [(Cp*)M(2-alkylphenoxo)] rhodium and iridium complexes **35** and of cationic [Ru(bpy)$_2$(LL′)] derivatives; ligand LL′ being ppy (phenylpyridine, **36**), quo (8-quinolate, **37**), cmbpy (4-methyl-2,2′-bipyridine-4-carboxylic acid, **38**) and dcbpy (2,2′-bipyridine-4,4′-dicarboxylic acid, **39**) (Fig. 6). In the latter cases, the homochiral or heterochiral ion pairing of the D_3-symmetric TRISPHAT **22** and the C_1- or C_2-symmetric coordination complexes **38** and **39** was studied in details.[39d] Rose-Munch *et al.* also studied the interaction of **22** with novel cationic chiral heterobimetallic chromium–ruthenium complex **40**.[39e]

Finally, Lacour, Kündig and co-workers were able to show that TRISPHAT can be used to determine the enantiomeric purity of (η^6-arene)chromium complexes of general structure **41**.[33] This was used recently by Djukic and Pfeffer to demonstrate the enantiomeric purity of planar chiral cyclopalladated (η^6-arene)Cr(CO)$_3$ complexes.[41] These results broaden the field of application of **22** to chiral neutral, and not just cationic, species.



Interesting chiral NMR effects were also observed by Hosseini and co-workers using borocryptand **11**. This receptor binds cationic metal and ammonium ions in a 1:1 ratio. An enantiomeric differentiation of resulting chiral borocryptates using NMR spectroscopy in a chiral liquid crystalline medium was then achieved using different NMR probes localised both on the receptor **11** and on the substrate (Cs^+, NH_4^+); the observed chirality at the substrate was described as being induced by the spiroborate junction and mediated by the peristatic chirality of the cavity.[14]

5 Resolution of chiral cations

Many chemical reactions and processes yield cationic racemic products and either a resolution or a stereoselective synthesis must be envisaged to obtain the chiral cations in an enantioenriched or enantiopure form. Resolution – that is the physical separation of the enantiomers of a chiral racemic substance – has been intensively studied and selected representative examples of such processes mediated by chiral anions are presented.

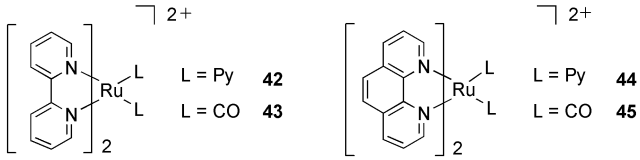
The largest number of resolutions are effected by the conversion of a racemate into a mixture of diastereomers. In this type of reaction, the substrates to be resolved are treated with one enantiomer of a chiral substance (the resolving agent). The diastereomeric pairs can be ionic and the vast majority of the resolutions are based on solubility differences of solids. Other methods (chromatography, extraction) are possible and will be presented.

5.1 By solubility differences of solids

Dicationic ruthenium(II) complexes [Ru(bpy)$_2$(py)$_2$]$^{2+}$ **42**, [Ru(bpy)$_2$(CO)$_2$]$^{2+}$ **43**, [Ru(phen)$_2$(py)$_2$]$^{2+}$ **44** and [Ru(phen)$_2$(CO)$_2$]$^{2+}$ **45**, which are important chiral building blocks

in the growing field of stereoselective or stereospecific complex synthesis, can be for instance resolved with chiral anions as resolving agents. *O*,*O*′-Dibenzoyl-L-tartrate **4** is selective for complex **42**, while antimonyltartrate **5** allows the resolution of **43** and **45**; compound **44** is resolved by enantiopure arsenyltartrate.[39d,42] (*S*)-(+)-Binaphthyl-2,2′-diyl phosphate **19** anion was used by Sauvage *et al*. to separate the enantiomers of chiral dicopper(I) trefoil knot precursor **26** by crystallisation.[31] Gruselle and co-workers have used tris(oxalato) cobalt(III) octahedral complex **8** to partially resolve, in the presence of Mn^{2+} cations, monocationic derivatives **36** and **37**;[12b] this group later used TRISPHAT Δ-**22** to perform the same task with cation **36**.[43]

Although efficient, resolution procedures based on the selective crystallisation of one diastereomeric salt can be sometimes hard to elaborate. It is for instance difficult to rationalise why anions **4** and **5** are most efficient for the resolution of **42**, and **43** or **45**, respectively – and not reciprocally. Furthermore, development of these procedures can be often – not always – time-consuming and beset with irreproducibility.



5.2 By chromatography

Preparative chromatographic resolution procedures have overall freed chemists from the constraint of dependency on crystallisation. They are most often performed with covalent diastereomer mixtures but ionic salts can also be separated. Although, in principle, preformed ionic diastereomer mixtures are separable by chromatography (see below), in practice most ion-pair chromatographic resolutions have involved the addition of non-racemic counterions to the mobile phase.[10]

Williams *et al*. have, for instance, reported the resolution of a dinuclear cobalt(III) helicate **25** by ion-pair chromatography with a concentrated solution of enantiopure sodium (+)-antimonyltartrate **5** as the eluent.[30] Similarly Sauvage and Keene resolved iron(II) dinuclear double helicate **46** by chromatography (Fig. 7).[44] To realise the resolution, a racemic mixture of

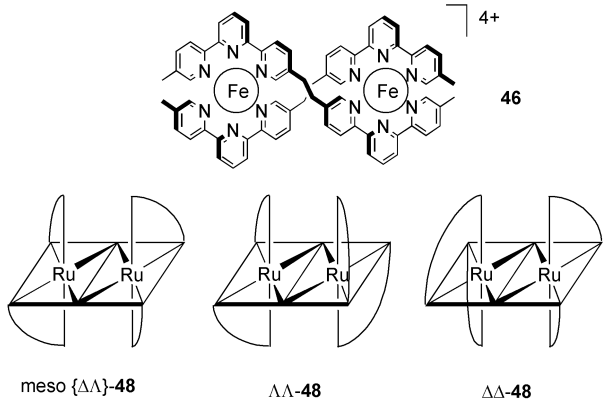
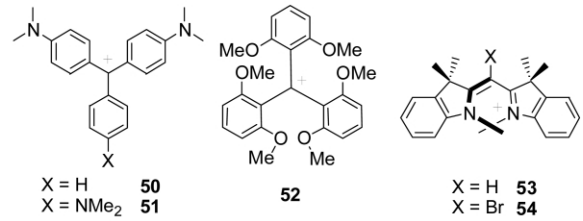


Fig. 7 Double helicate **46** and schematic representation of the isomers of **48**.

the sulfate salt of **46** was absorbed onto a column of SP Sephadex C-25 cation exchanger and eluted with the aqueous sodium salt of *O*,*O*′-di-4-toluyl-L-tartrate **47**, parent derivative of anion **4**. After an 'effective column length' of *ca.* 6 m (achieved by recycling using a peristaltic pump), two separate bands were collected affording, after methathesis, the enantiomers of the helicate in pure *M* and *P* forms.

One study that shows the extreme efficiency of chromatography to separate optical (and other) isomers of chiral cationic complexes was recently reported by Keene and co-workers.[45] The dinuclear ligand-bridged complex systems $[\{Ru(bpy)_2\}(\mu\text{-}bpm)\{Ru(Me_2bpy)_2\}]^{4+}$ **48** and $[\{Ru(bpy)(Me_2bpy)\}_2(\mu\text{-}bpm)]^{4+}$ **49** (bpm = 2,2′-bipyrimidine; Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine) exhibit a range of stereoisomers – diastereoisomers, enantiomers and geometric isomers (Fig. 7). From synthetic procedures producing mixtures of all possible forms of the respective complexes, the four stereoisomeric forms of **48** (*viz.* ΔΛ, ΛΔ, ΔΔ and ΛΛ) and the six stereoisomeric forms of **49** (*viz.* ΔΛ-*trans*, ΔΛ-*cis*, ΔΔ-*trans*, ΔΔ-*cis*, ΛΛ-*trans*, and ΛΛ-*cis*) have been isolated using chromatographic techniques on SP Sephadex C-25 cation exchanger and anions **4** and **47** in the mobile phase in particular. This is the first reported separation of the stereoisomers for a system of the type $[\{Ru(pp)_2\}(\mu\text{-bpm})\{Ru(pp')_2\}]^{4+}$ (pp and pp′ = bidentate polypyridyl ligands; pp ≠ pp′).

As mentioned at the beginning of section 5.2, chromatographic resolution of chiral cations can nevertheless be realised with preformed ionic diastereomer mixtures. Recently, it was found that the lipophilicity of TRISPHAT anion **22** modifies profoundly the chromatographic properties of the cations associated with it and the resulting ion pairs are usually poorly retained on polar chromatographic phases (SiO_2, Al_2O_3). This is exemplified on Fig. 8 by the comparison of the chromatographic



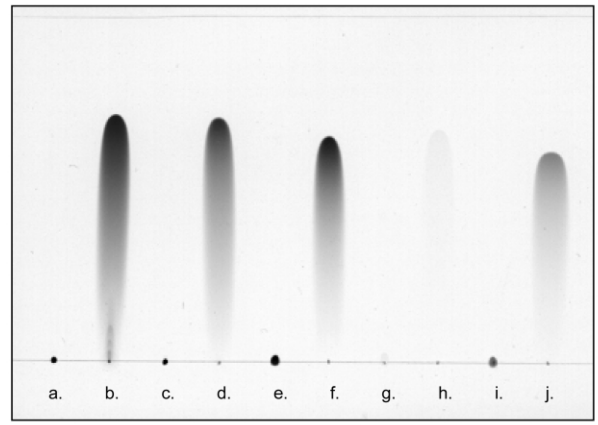
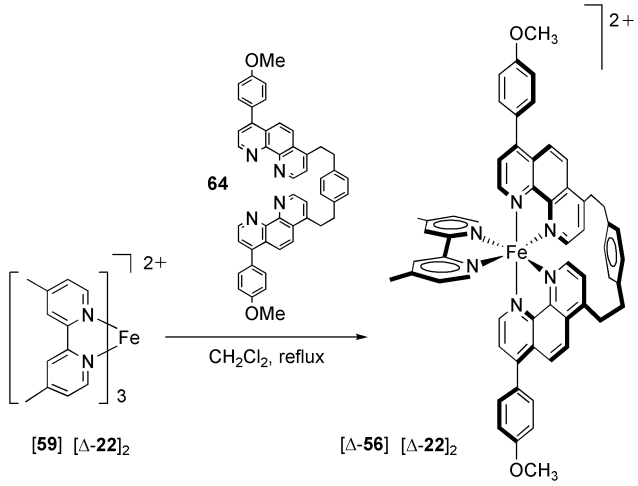


Fig. 8 Chromatographic behaviour on analytical TLC (SiO_2, CH_2Cl_2) of a) [**50**]Cl, b) [**50**][**22**], c) [**51**][oxalate], d) [**51**][**22**], e) [**52**][BF_4], f) [**52**][**22**], g) [**53**][BF_4], h) [**53**][**22**], i) [**54**][BF_4], j) [**54**][**22**].

behaviour of classical achiral (chloride, oxalate, tetrafluoroborate) and TRISPHAT salts of dyes **50**–**54**; the migrating aptitude of salts [**50**–**54**][**22**] depending upon the concentration of the analyte.[46]

Using enantiopure TRISPHAT anion, accessible from [cinchonidinium][Δ-**22**] or [Bu_3NH][Λ-**22**] salts, the chromatographic resolution of chiral cations is feasible as the diastereomeric ion pairs often possess rather different retardation factors. For instance, $[Ru(bpy)_3]^{2+}$ **31** (Fig. 4) and $[Ru(Me_2bpy)_3]^{2+}$ **55** complexes were separated into diastereomeric homochiral [Δ-RuL_3][Δ-**22**]$_2$ and heterochiral [Λ-RuL_3][Δ-

22]$_2$ salts by column chromatography over silica gel (eluent CH_2Cl_2).[47] Rather large differences in retardation factors were observed (ΔR_f 0.10–0.23). The resolution can be also performed on preparative thin-layer chromatographic (TLC) plates. The protocol was extended to monocationic cyclometallated ruthenium complexes of type **36** and to a configurationally stable mononuclear iron(II) complex **56** (Scheme 1).[48]



Scheme 1 Diastereoselective synthesis of configurationally stable iron(II) tris(bisimine) complex **56**.

5.3 By asymmetric extraction

The lipophilicity of the TRISPHAT anion **22** also confers on its salts an affinity for organic solvents and, once dissolved, the ion pairs do not partition in aqueous layers. This rather uncommon property was used by Lacour's group to develop a simple and practical resolution procedure of chiral cationic coordination complexes by asymmetric extraction. The resolution of racemic substrates by preferential extraction of one enantiomer from water into immiscible organic solvents has been well studied.[5] The extraction and the resulting selectivity arise from the preferential binding in the organic phase of one enantiomer of the substrate with a chiral lipophilic selector. Anion **22** was thus considered for the asymmetric extraction in organic layers of chiral cations, and coordination complexes in particular.

[Ru(Me$_2$bpy)$_3$]$^{2+}$ **55** and [Ru(Me$_2$phen)$_3$]$^{2+}$ **57** were selected for their ease of synthesis and high water solubility as chloride salts (Me$_2$phen = 4,7-dimethyl-1,10-phenanthroline). Solutions of salts [Bu$_3$NH][Λ-**22**] in $CHCl_3$ or [cinchonidinium][Δ-**22**] in 7.5–10% DMSO/$CHCl_3$ were prepared (1 equiv.) and added to orange-coloured solutions of racemic [**55**]Cl_2 or [**57**]Cl_2 in water (1 equiv.). Upon vigorous stirring of the biphasic mixtures, a partial transfer of coloration occurred from the aqueous layers to the organic ones (Fig. 9). Selectivity ratios as high as 35:1 were measured for the enantiomers of the cations in the organic and aqueous layers, demonstrating without ambiguity the efficiency of the resolution procedure. An extension of this protocol was further developed for a diiron(II) triple helicate and afforded in separate phases the *P* or *M* enantiomers of the $[Fe_2L_3]^{4+}$ helix.[49]

6 Stereoselective chemistry induced by chiral anions

6.1 Asymmetry-induction onto configurationally labile derivatives

Chiral compounds are sometimes configurationally stable as solids and configurationally labile in solution. When optically

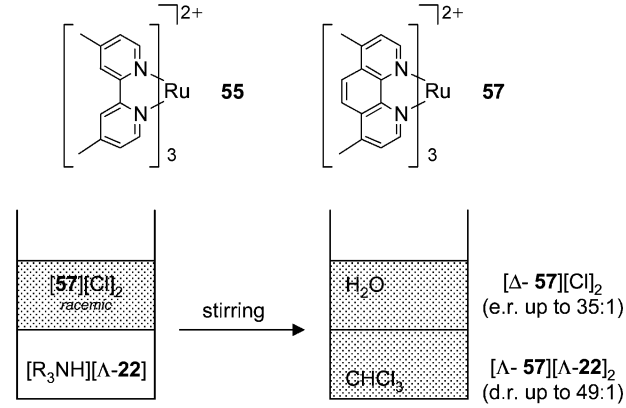


Fig. 9 Schematic representation of the asymmetric resolution of salt [**57**]Cl_2; e.r. and d.r. indicate enantiomeric and diastereomeric ratios.

active samples of these derivatives are solubilised, a racemisation occurs due to the free interconversion of the enantiomers in solution. To obtain these compounds in one predominant configuration over time, a possible strategy is to add stereogenic elements to their backbone; intramolecular diastereoselective interactions occur and favour one of the equilibrating diastereomers. If the chiral compounds are charged, an alternative strategy to control their configuration is to consider their asymmetric ion pairing with chiral counter-ions; intermolecular – rather than intramolecular – diastereoselective interactions then control the stereoselectivity (Pfeiffer Effect, Fig. 10).

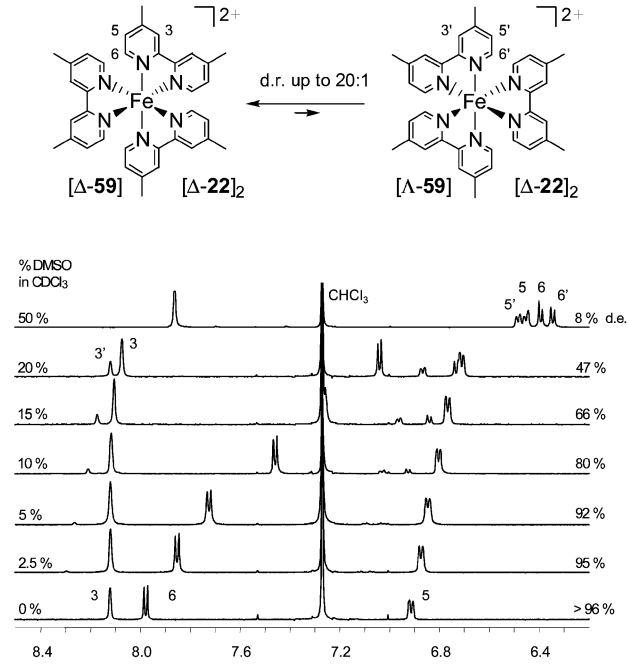
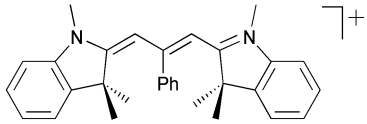


Fig. 10 ^{1}H NMR spectra (parts) of equilibrating salts [Δ-**59**][Δ-**22**]$_2$ and [Λ-**59**][Δ-**22**]$_2$ in [D_6]DMSO/$CDCl_3$ and resulting diastereoselectivity.

The induction of optical activity by chiral anions onto cationic racemic substrates has been previously considered. The interactions of chiral anions with transition metal complexes have been studied in particular.[50] Of most relevance to the review is the observation by Schuster[17] and co-workers that chiral borate anions **15** and **16** forms penetrated ion pairs with configurationally labile chiral cationic dye **58** leading to an asymmetry-induction that was monitored by CD.

Unfortunately, in most of these and other previous examples, the extent of the asymmetry-induction was determined by chiroptical measurements (ORD, CD) that gave qualitative and not quantitative information. The NMR chiral shift efficiency of



58

TRISPHAT **22** and other hexacoordinated phosphate anions was therefore considered as an excellent analytical tool to provide accurate measurement of the induced selectivity by NMR spectroscopy.

Configurationally labile cations, as varied as [Fe(Me_2bpy)$_3$]$^{2+}$ **59** and [Co(Me_2bpy)$_3$]$^{2+}$ **60** complexes, dicobalt(II) triple helicate **61**, monomethine dyes **53** and **54**, diquat **62** and quaternary ammonium **63**, were paired with enantiopure anions **22** and/or **23** (Figs. 8, 10 and 11). In all cases, an

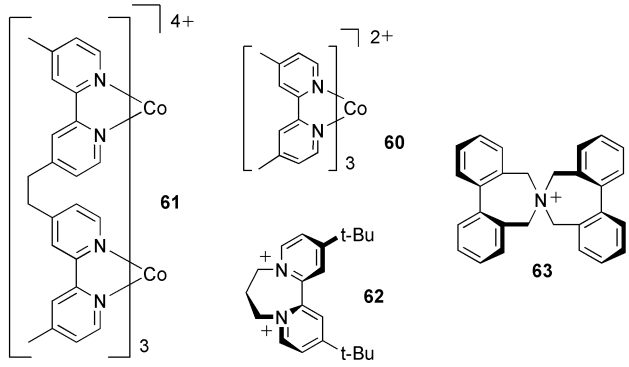


Fig. 11 Examples of configurationally labile chiral cations **60–63**.

enantiodifferentiation of the interconverting enantiomers of the chiral cations was observed in ^{1}H NMR spectroscopy.[25,51] In most cases, the analyses could be performed at room temperature as the interconversion was slow on the NMR time scale, *e.g.* **54** and **59–62**.

For cations **53** and **63**, low temperature NMR experiments were necessary to reveal stereodynamical behaviours and allow the observation of split signals for the enantiomers. Stereoselective recognition between the chiral cations and anions was observed in essentially all cases as integration of the split signals revealed the preferential occurrence of one diastereomeric salt over the other. Diastereomeric ratios as high as 20:1 can be observed for some of the substrates, *e.g.* salt [**59**][Δ-**22**] and [**60**][Δ-**22**] (Fig. 10). The selectivity strongly depends upon the polarity of the solvent medium. An increase in the diastereoselectivity is usually observed upon the decrease of solvent polarity. This is interpreted as the result of closer interactions between the ions.[3] In most cases, induced CD spectra could also be measured allowing the determination of the preferred configuration of the chiral cations.

Finally, asymmetry-inductions by chiral anions onto chiral cations are not limited to molecular associations. Recently, Huc and Oda have reported one of the first examples of the Pfeiffer effect expressed at the nanometer or micrometer supramolecular scale. Non chiral dicationic amphiphiles were associated with tartrate anions **2** and the resulting membranes were chirally twisted upon interacting with the counterions. They could also demonstrate that the mechanism of the asymmetry-induction involves specific anion–cation recognition and the induction of conformationally labile chirality in the cations.[52]

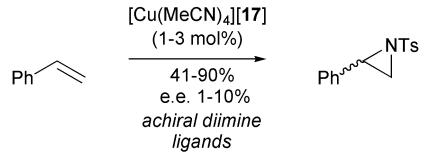
6.2 Stereoselective synthesis of configurationally stable edifices

As described in the previous paragraph, chiral mononuclear divalent tris(diimine) complexes of first row transition metals are notoriously known for their high chemical but low configurational stability. Recently, the synthesis of a bis 1,10-phenanthroline ligand (**64**) leading to octahedral complexes containing a well-defined axis was reported: simple treatment of [Fe(Me_2bpy)$_3$][PF_6]$_2$ with **64** at reflux in 1,2-dichloroethane affording the [Fe(**64**)(Me_2bpy)][PF_6]$_2$ or [**56**][PF_6]$_2$ salt in high chemical yield and purity. Using the chromatographic properties of anion **22**, the Lacour and Sauvage groups were able to resolve complex **56** by simple preparative thin-layer chromatography and report on the unusual configurational stability of **56**.[48b] More interestingly, they could show that the treatment of configurationally labile, yet diastereomerically enriched, [Fe(Me_2bpy)$_3$][Δ-**22**]$_2$ precursor with **64** led to the asymmetric synthesis of **56** as essentially a single diastereomer (d.r. > 20:1). The selectivity of the reaction results from the preferred homochiral association of anion **22** and iron(II) complex **56**. Studies have indicated that the selectivity arises from a thermodynamic control as an asymmetric equilibration of the diastereomers happens at an elevated temperature.

Bimetallic networks coordinated with oxalate bridges of general formula $\{[M^{II}M^{III}(ox)_3]^-C^+]\}_n$ (ox = $C_2O_4^{2-}$, C^+ = monocation) form an important family of molecular magnets.[12] In these compounds, the anionic sub-network $[M^{II}M^{III}(ox)_3]^-$ which results from a linking of D_3-symmetric monomeric species $M(ox)_{3/2}]^n$ presents two different structures following the relative configurations of these hexacoordinated subunits (Δ,Λ): a) two-dimensional and organised in honeycomb stitch if this linking is heterochiral (Δ/Λ); b) three-dimensional and helicoidal if it is homochiral (ΔΔ or ΛΛ). Recently, using optically active anion **7**, Andres and co-workers showed that the formation of these polymers is highly stereospecific.[53]

6.3 Enantioselective catalysis

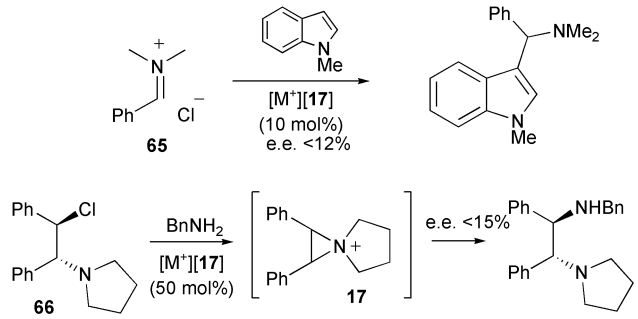
The influence of chiral anionic counterions on the stereochemical outcome of reactions which involve cationic intermediates or reagents have been investigated recently. Arndtsen and co-workers have used chiral borate anion **17** to achieve an enantioselective formation of aziridines by the reaction of prostereogenic olefins and PhINTs in presence of [Cu(MeCN)$_4$][(*R*)-**17**] or [Cu(MeCN)$_4$][(*R*)-**17**] salts and achiral diimine ligands (Scheme 2).[20] Decent to good chemical



Scheme 2 Enantioselective synthesis of aziridines.

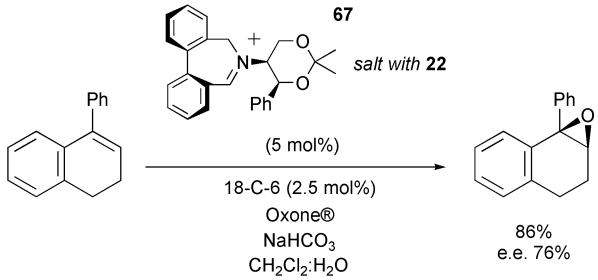
yields (41–90%) were obtained demonstrating that anion **17** had no negative effect on the reaction. However, low enantiomeric excesses (1–10%) were measured. It indicates nevertheless that a chiral counterion can influence the reactivity of an achiral cationic catalyst. Examples of aziridination and cyclopropanation reactions using both chiral ligands and chiral counterions have shown a significant influence of the anionic moiety and the existence of "matched" and "mis-matched" diastereomeric pairs.

Anion **17** was also considered by Nelson and co-workers to induce asymmetry in the reactions of prostereogenic cations.[54] Acidic ($Et_2NH_2^+$, Et_3NH^+, (*R*)-$PhCHMeNH_3^+$) ammonium and metallic (Na^+, Ag^+) salts of (*R*)-**17** and (*S*)-**17** were prepared. The reaction of iminium ion **65** and indole was studied in the presence of catalytic amounts of these compounds (Scheme 3). A modulation of the reactivity of the Mannich reaction could be observed. But the enantiomeric excesses were low (0–11%). Better results were observed in the reaction of chloroamine **66** with benzylamine that involves the asymmetric ring-opening of the *meso*-aziridinium cation (e.e. < *ca.* 15%).



Scheme 3 Enantioselective Mannich and ring-opening of aziridinium ion reactions.

Finally, the influence of chiral TRISPHAT anion **22** on the enantioselective oxaziridinium-catalysed epoxidation reaction was studied recently by Lacour and co-workers. They could show that the ion pairing of iminium cation **67** with TRISPHAT anion allows the use of strict biphasic conditions CH_2Cl_2:H_2O which, in combination with 18-crown-6, can improve the enantioselectivity of the oxone-mediated epoxidation (e.e. up to 76%) (Scheme 4). However, the chirality of anion **22** (Δ, Λ or *rac*) was shown to have no influence over the stereochemical outcome of the epoxidation.[55]



Scheme 4 Enantioselective oxaziridinium catalysed epoxidation reaction.

7 Conclusion

In this review, we hope that we have been able to show that, by the imaginative use of "old" chiral anions or by the design and synthesis of new ones, novel asymmetric applications, reactions and processes were made possible. We believe that there is much to gain from this supramolecular approach to stereoselective synthesis as, for instance, both configurations of a chiral cationic complex or of a chiral product from a reaction can be generated with no need to prepare two sets of enantiomeric ligands or reagents. It is *a priori* sufficient to form the cationic complex or reagent with achiral ligands and exchange the traditional achiral anions (PF_6^-, BF_4^-, *etc*.) for chiral anionic counterions. However, as has been described in this review, there is still much ground to be covered and, no doubt, new and more selective anions or techniques need to be prepared to achieve some of the desired goals.

Finally, most of the selected examples have used chiral anions in enantiomerically enriched or pure forms. Applications of chiral counterions in their racemic form are also feasible. For instance, Marks and co-workers have shown that racemic tris(2,2′,2″-nonafluorobiphenyl)fluoroaluminate, of which chirality arises from partially restricted internal C_6F_4–C_6F_5 rotation, can influence the ion pairing of cationic polymerisation catalysts. Maury, Le Bozec, Ledoux and co-workers have used the lipophilicity of racemic TRISPHAT to enhance the solubility of polymer or dendrimer containing cationic, octupolar nonlinear optically active, ruthenium trisbipyridyl subunits.[56]

8 Addendum

Several papers regarding chiral anion mediated chemistry have appeared since the submission of this manuscript. Kubik and co-workers have shown that C_3-symmetric cyclic hexapeptides containing alternating L-proline and 3-aminobenzoic acid derivatives as subunits possess different affinities towards the two enantiomers of the *N*,*N*,*N*-trimethyl-1-phenylethyl ammonium cation. Ion pairing of this cation with racemic **22** improves the binding affinity in $CHCl_3$ by a factor of ~3 over picrate.[57] Fontecave and co-workers have been able to resolve the *cis*-[Ru(dmp)$_2$(CH3CN)$_2$] complex (dmp = 2,9-dimethyl-1,10-phenanthroline) using Δ-**22** as counterions. This "chiral-at-metal" ruthenium derivative was then used as a catalyst for the oxidation of sulfides to sulfoxides by hydrogen peroxide. The reactions displayed a low but significant level of enantioselectivity (18% ee in the case of 4-bromophenyl methyl sulfide).[58] Laursen, Lacour *et al*. have used BINPHAT anion **23** as a resolving and NMR chiral shift agent for the isolation of enantiopure highly configurationally stable [4]heterohelicenium cations.[59] Finally, Lacour and co-workers have shown that a novel chiral hexacoordinated phosphate anion can be prepared in two steps from methyl-α-D-mannopyranoside. The ease of its stereoselective synthesis (d.e. > 96%), its chemical robustness and its broad efficiency with both organic and metallo-organic substrates should ensure its general use in asymmetric anion mediated processes.[60]

9 Acknowledgements

We would like to thank Professor F. R. Keene and Drs H. Amouri and A. Nelson for sharing unpublished reports and preprints as well as Professors B. Arndtsen, F. R. Keene, A. Macchioni and Drs J.-P. Djukic, J. J. Jodry, D. Monchaud and A. Nelson who have kindly proof-read this manuscript. I am much indebted to the enthusiastic efforts of all the former and present members of the group who have contributed to the success of our projects. We are grateful for financial support of this work from the Swiss National Science Foundation, the Federal Office for Education and Science (COST D11), the Société Académique de Genève, the Schmidheiny Foundation as well as the Sandoz Family Foundation.

10 References

1 To limit the scope of the review, only examples of asymmetric chemistry involving "unreactive" chiral anions will be presented. Chiral organolithiums or Grignard reagents, which can be considered as chiral anions, will therefore not be covered in this article. For a recent review on this topic, see: A. Basu and S. Thayumanavan, *Angew. Chem. Int. Ed.*, 2002, **41**, 716.

2 A. Macchioni, *Eur. J. Inorg. Chem.*, 2003, 195 and references therein.

3 A. Loupy and B. Tchoubar, *Salt Effects in Organic and Organometallic Chemistry*, 1st ed., VCH, Weinheim, Germany, 1992; C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 3rd ed., VCH, Weinheim, Germany, 2002.

4 G. Boche, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 731 and references therein.

5 (*a*) E. L. Eliel and S. H. Wilen, *Stereochemistry of Organic Compounds*, 1st ed., John Wiley & Sons, New York, USA, 1994; (*b*) J. Jacques, A.

Collet and S. H. Wilen, *Enantiomers, Racemates, and Resolutions*, 2nd ed., Krieger, Melbourne, USA, 1994.
6 J. K. Whitesell, *Chem. Rev.*, 1989, **89**, 1581; A. Alexakis and P. Mangeney, *Tetrahedron: Asymmetry*, 1990, **1**, 477; C. Moberg, *Angew. Chem. Int. Ed.*, 1998, **37**, 248.
7 A. Von Zelewsky, *Stereochemistry of Coordination Compounds*, 1st ed., John Wiley & Sons, Chichester, UK, 1996.
8 R. S. Cahn, C. Ingold and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 385.
9 H. Blaser, *Chem. Rev.*, 1992, **92**, 935.
10 Y. Yoshikawa and K. Yamasaki, *Coord. Chem. Rev.*, 1979, **28**, 205.
11 T. K. Green, J. R. Whetstine and E. J. R. Son, *Tetrahedron: Asymmetry*, 1997, **8**, 3175.
12 (*a*) R. Andres, M. Brissard, M. Gruselle, C. Train, J. Vaissermann, B. Malezieux, J. P. Jamet and M. Verdaguer, *Inorg. Chem.*, 2001, **40**, 4633; (*b*) M. Brissard, H. Amouri, M. Gruselle and R. Thouvenot, *C. R. Chim.*, 2002, **5**, 53and references therein.
13 J. Böeseken and J. A. Mijs, *Recl. Trav. Chim. Pays-Bas*, 1925, **44**, 758.
14 E. Graf, R. Graff, M. W. Hosseini, C. Huguenard and F. Taulelle, *Chem. Commun.*, 1997, 1459.
15 S. Green, A. Nelson, S. Warriner and B. Whittaker, *J. Chem. Soc., Perkin Trans. 1*, 2000, 4403.
16 K. Torssell, *Acta Chem. Scand.*, 1962, **16**, 87.
17 D. J. Owen, D. VanDerveer and G. B. Schuster, *J. Am. Chem. Soc.*, 1998, **120**, 1705.
18 K. Ishihara, M. Miyata, K. Hattori, T. Tada and H. Yamamoto, *J. Am. Chem. Soc.*, 1994, **116**, 10520; K. Ishihara, H. Kurihara, M. Matsumoto and H. Yamamoto, *J. Am. Chem. Soc.*, 1998, **120**, 6920.
19 M. Periasamy, L. Venkatraman, S. Sivakumar, N. Sampathkumar and C. R. Ramanathan, *J. Org. Chem.*, 1999, **64**, 7643.
20 D. B. Llewellyn, D. Adamson and B. A. Arndtsen, *Org. Lett.*, 2000, **2**, 4165.
21 J. Jacques and C. Fouquey, *Org. Synth.*, 1989, **67**, 1.
22 D. Hellwinkel, *Angew. Chem.*, 1965, 378.
23 J. Cavezzan, G. Etemad-Moghadam, M. Koenig and A. Klaebe, *Tetrahedron Lett.*, 1979, 795 and references therein.
24 I. V. Shevchenko, A. Fischer, P. G. Jones and R. Schmutzler, *Chem. Ber.*, 1992, **125**, 1325; J. Lacour, C. Ginglinger, C. Grivet and G. Bernardinelli, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 608; J. Lacour, C. Ginglinger and F. Favarger, *Tetrahedron Lett.*, 1998, 4825.
25 J. Lacour, A. Londez, C. Goujon-Ginglinger, V. Buß and G. Bernardinelli, *Org. Lett.*, 2000, **2**, 4185.
26 J. Lacour and A. Londez, *J. Organomet. Chem.*, 2002, **643–644**, 392.
27 J. Lacour, A. Londez, D.-H. Tran, V. Desvergnes-Breuil, S. Constant and G. Bernardinelli, *Helv. Chim. Acta*, 2002, **85**, 1364.
28 D. Parker, *Chem. Rev.*, 1991, **91**, 1441; T. J. Wenzel and J. D. Wilcox, *Chirality*, 2003, **15**, 256.
29 G. Bruylants, C. Bresson, A. Boisdenghien, F. Pierard, A. Kirsch-De Mesmaeker, J. Lacour and K. Bartik, *New J. Chem.*, 2003, **27**, 748and references therein.
30 L. J. Charbonniere, G. Bernardinelli, C. Piguet, A. M. Sargeson and A. F. Williams, *J. Chem. Soc., Chem. Commun.*, 1994, 1419.
31 C. Dietrich-Buchecker, G. Rapenne, J. P. Sauvage, A. De Cian and J. Fischer, *Chem. Eur. J.*, 1999, **5**, 1432.
32 J. Lacour, C. Ginglinger, F. Favarger and S. Torche-Haldimann, *Chem. Commun.*, 1997, 2285.
33 H. Ratni, J. J. Jodry, J. Lacour and E. P. Kündig, *Organometallics*, 2000, **19**, 3997.
34 J. Lacour, L. Vial and C. Herse, *Org. Lett.*, 2002, **4**, 1351.
35 L. Pasquato, C. Herse and J. Lacour, *Tetrahedron Lett.*, 2002, **43**, 5517.
36 J. Giner Planas, D. Prim, F. Rose-Munch, E. Rose, D. Monchaud and J. Lacour, *Organometallics*, 2001, **20**, 4107.
37 J. Lacour, *Chimia*, 2002, **56**, 672.
38 V. Desvergnes-Breuil, V. Hebbe, C. Dietrich-Buchecker, J.-P. Sauvage and J. Lacour, *Inorg. Chem.*, 2003, **42**, 255.
39 (*a*) O. Maury, J. Lacour and H. Le Bozec, *Eur. J. Inorg. Chem.*, 2001, 201; (*b*) H. Amouri, R. Thouvenot, M. Gruselle, B. Malezieux and J. Vaissermann, *Organometallics*, 2001, **20**, 1904; (*c*) H. Amouri, R. Thouvenot and M. Gruselle, *C. R. Chim.*, 2002, **5**, 257; (*d*) R. Caspar, H. Amouri, M. Gruselle, C. Cordier, B. Malézieux, R. Duval and H. Leveque, *Eur. J. Inorg. Chem.*, 2003, 499; (*e*) J. G. Planas, D. Prim, F. Rose-Munch and E. Rose, *Organometallics*, 2002, **21**, 4385; H. Mesnil, M. C. Schanne-Klein, F. Hache, M. Alexandre, G. Lemercier and C. Andraud, *Chem. Phys. Lett.*, 2001, **338**, 269.
40 F. R. Keene, *Chem. Soc. Rev.*, 1998, **27**, 185; N. C. Fletcher and F. R. Keene, *J. Chem. Soc., Dalton Trans.*, 1999, 683.
41 A. Berger, J.-P. Djukic, M. Pfeffer, A. de Cian, N. Kyritsakas-Gruber, J. Lacour and L. Vial, *Chem. Commun.*, 2003, 658.
42 X. Hua and A. Von Zelewsky, *Inorg. Chem.*, 1995, **34**, 5791; B. Bosnich and F. P. Dwyer, *Aust. J. Chem.*, 1966, **19**, 2229; T. J. Rutherford, P. A. Pellegrini, J. Aldrich-Wright, P. C. Junk and F. R. Keene, *Eur. J. Inorg. Chem.*, 1998, 1677.
43 M. Brissard, M. Gruselle, B. Malezieux, R. Thouvenot, C. Guyard-Duhayon and O. Convert, *Eur. J. Inorg. Chem.*, 2001, 1745.
44 G. Rapenne, B. T. Patterson, J. P. Sauvage and F. R. Keene, *Chem. Commun.*, 1999, 1853.
45 B. T. Patterson, F. M. Foley, D. Richards and F. R. Keene, *Dalton Trans.*, 2003, 709.
46 J. Lacour, S. Barchéchath, J. J. Jodry and C. Ginglinger, *Tetrahedron Lett.*, 1998, **39**, 567.
47 J. Lacour, S. Torche-Haldimann, J. J. Jodry, C. Ginglinger and F. Favarger, *Chem. Commun.*, 1998, 1733.
48 (*a*) D. Monchaud, J. Lacour, C. Coudret and S. Fraysse, *J. Organomet. Chem.*, 2001, **624**, 388; (*b*) D. Monchaud, J. J. Jodry, D. Pomeranc, V. Heitz, J.-C. Chambron, J.-P. Sauvage and J. Lacour, *Angew. Chem. Int. Ed.*, 2002, **43**, 2317.
49 J. Lacour, C. Goujon-Ginglinger, S. Torche-Haldimann and J. J. Jodry, *Angew. Chem. Int. Ed.*, 2000, **39**, 3695; J. J. Jodry and J. Lacour, *Chem. Eur. J.*, 2000, **6**, 4297.
50 P. Pfeiffer and K. Quehl, *Chem. Ber.*, 1931, **64**, 2667; B. Norden and F. Tjerneld, *FEBS Lett.*, 1976, **67**, 368; S. Kirschner, N. Ahmad, C. Munir and R. J. Pollock, *Pure Appl. Chem.*, 1979, **51**, 913.
51 J. Lacour, J. J. Jodry, C. Ginglinger and S. Torche-Haldimann, *Angew. Chem. Int. Ed.*, 1998, **37**, 2379; J. Lacour, J. J. Jodry and D. Monchaud, *Chem. Commun.*, 2001, 2302; C. Pasquini, V. Desvergnes-Breuil, J. J. Jodry, A. Dalla Cort and J. Lacour, *Tetrahedron Lett.*, 2002, **43**, 423; L. Vial and J. Lacour, *Org. Lett.*, 2002, **4**, 3939.
52 D. Berthier, T. Buffeteau, J. M. Leger, R. Oda and I. Huc, *J. Am. Chem. Soc.*, 2002, **124**, 13486.
53 R. Andres, M. Gruselle, B. Malezieux, M. Verdaguer and J. Vaissermann, *Inorg. Chem.*, 1999, **38**, 4637.
54 C. Carter, S. Fletcher and A. Nelson, 2003, private communication.
55 J. Lacour, D. Monchaud and C. Marsol, *Tetrahedron Lett.*, 2002, **43**, 8257.
56 Y. X. Chen, M. V. Metz, L. T. Li, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1998, **120**, 6287; T. Le Bouder, O. Maury, H. Le Bozec, I. Ledoux and J. Zyss, *Chem. Commun.*, 2001, 2430; H. Le Bozec, T. Le Bouder, O. Maury, A. Bondon, I. Ledoux, S. Deveau and J. Zyss, *Adv. Mater.*, 2001, **13**, 1677.
57 G. Heinrichs, L. Vial, J. Lacour and S. Kubik, *Chem. Commun.*, 2003, 1252.
58 M. Chavarot, S. Menage, O. Hamelin, F. Charnay, J. Pecaut and M. Fontecave, *Inorg. Chem.*, 2003, in press.
59 C. Herse, D. Bas, F. C. Krebs, T. Bürgi, J. Weber, T. Wesolowski, T. Wesolowski, B. W. Laursen and J. Lacour, *Angew. Chem. Int. Ed.*, 2003, in press.
60 C. Pérollier, S Constant, J. J. Jodry, G. Bernardinelli and J. Lacour, *Chem. Commun.*, 2003, 2014.