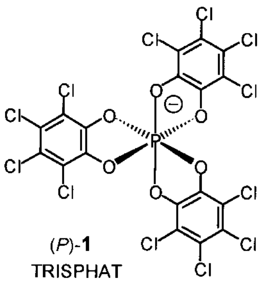
# Diastereoselective Ion Pairing of TRISPHAT Anions and Tris(4,4′-dimethyl-2,2′-bipyridine)iron(II)**

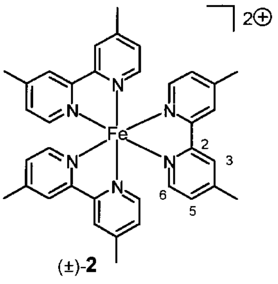
Jérôme Lacour,* Jonathan J. Jodry, Catherine Ginglinger, and Sonya Torche-Haldimann

The induction of optical activity on configurationally labile racemic molecules by a chiral environment is an essential phenomenon that has been studied on several systems.[1] For instance, optically active anions can induce optical activity onto cationic organic molecules or coordination complexes.[2] The extent of the asymmetric induction was determined in these examples by chiroptical measurements, which gave qualitative but not quantitative information. The magnitude of the induction (diastereoselectivity) is not known, and the efficiency of the chiral inducers is difficult to appreciate. Herein we report that the asymmetric induction from chiral anions onto a chiral cation can indeed be an extremely efficient process.

Recently we showed that the anion TRISPHAT (**1**), which is easily prepared and resolved, is configurationally stable as an ammonium salt in solution.[3] We decided to study its asymmetric ion pairing with a cation of similar shape and geometry, namely, the easily prepared $D_3$-symmetric $[Fe(4,4'\text{-}Me_2bpy)_3]^{2+}$ (**2**; bpy = 2,2′-bipyridine). Complexes **3** are made up of two host anions **1** (racemic, *M* or *P*) and one configurationally labile[4] guest cation **2**, and were synthesized in a single step: Treatment of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ with 4,4′-dimethyl-2,2′-bipyridine (3 equiv) in hot water and extraction of the resulting purple solution with TRISPHAT[5] (2 equiv) afforded the desired complexes **3** as the major products along with minor amounts of bipyridine ligand in the organic layer ($CH_2Cl_2$/acetone 25/1).[6] Further purification by recrystallization gave pure complexes **3** in decent yields (56–71%).[7] Racemic **3**, (**2**)(rac-**1**)$_2$, is insoluble in $CH_2Cl_2$ or $CHCl_3$, as opposed to the corresponding salts with *M* or *P* anions.



(*P*)-**1**
TRISPHAT



(±)-**2**

The highly asymmetric ion pairing of anions **1** (*P* or *M*) and cation **2** was simply demonstrated: $^1H$ NMR spectra of (**2**)(*P*-**1**)$_2$ and (**2**)(*M*-**1**)$_2$ in $[D_6]$DMSO (0–50%)/$CDCl_3$ (1.0 mM) showed partial or complete resolution in the region containing signals of the cation (Figure 1).[8] We were able to distinguish between the diastereomeric pairs $(P\text{-}\mathbf{2})(P\text{-}\mathbf{1})_2 \equiv \mathbf{3}_P$ and $(M\text{-}\mathbf{2})(P\text{-}\mathbf{1})_2 \equiv \mathbf{3}_M$ for compound (**2**)(*P*-**1**)$_2$, and $(M\text{-}\mathbf{2})(M\text{-}\mathbf{1})_2 \equiv \text{ent-}\mathbf{3}_P$ and $(P\text{-}\mathbf{2})(M\text{-}\mathbf{1})_2 \equiv \text{ent-}\mathbf{3}_M$ for compound (**2**)(*M*-**1**)$_2$. The diastereoselectivity of the asymmetric ion pairing between $[\mathbf{3}_P, \mathbf{3}_M]$ and $[\text{ent-}\mathbf{3}_P, \text{ent-}\mathbf{3}_M]$ was then directly calculated by integration of the respective signals (Table 1).

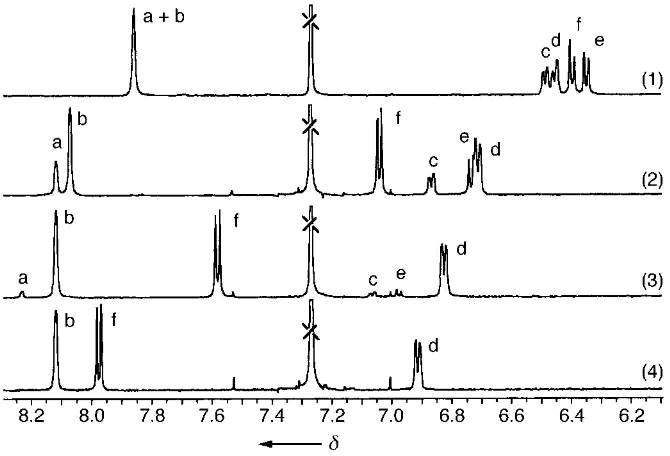


Figure 1. Sections of $^1H$ NMR spectra of (**2**)(*P*-**1**)$_2$ in $[D_6]$DMSO/$CDCl_3$ as a function of the percentage of $[D_6]$DMSO: 1) 50%, 8% *ds*; 2) 20%, 47% *ds*; 3) 7.5%, 87% *ds*; 4) 0%, >96% *ds*. The signals a, c, e and b, d, f correspond to the hydrogen atoms 3, 5, 6 in $\mathbf{3}_M$ and $\mathbf{3}_P$, respectively.

Table 1. Diastereoselectivity for (**2**)(*P*-**1**)$_2$ and (**2**)(*M*-**1**)$_2$ as a function of the percentage of $[D_6]$DMSO in $CDCl_3$.

| % $[D_6]$DMSO | (**2**)(**1**)$_2$[a] | |
|---|---|---|
| | *de* [%] | *dr*[b] |
| 0 | >96 | >50:1 |
| 1.0 | 96 | 50:1 |
| 2.5 | 95 | 40:1 |
| 5.0 | 92 | 23:1 |
| 7.5 | 87 | 14:1 |
| 10 | 80 | 9.3:1 |
| 12.5 | 73 | 6.5:1 |
| 15 | 66 | 4.9:1 |
| 20 | 47 | 2.8:1 |
| 25 | 19 | 1.9:1 |
| 50 | 8 | 1.2:1 |

[a] Compound **1** of *P* or *M* configuration. [b] Diastereomeric ratio.

Upon decreasing the solvent polarity (by lowering the portion of DMSO), one diastereomer became predominant; a diastereoselectivity (*ds*) of up to 96% was achieved in pure $CDCl_3$ (Figure 1, Table 1). The circular dichroism (CD) spectrum of a solution of (**2**)(*P*-**1**)$_2$ (0.1% DMSO in $CHCl_3$, $4.6 \times 10^{-6}$ M) revealed strong exciton coupling in the π–π* region ($\Delta\varepsilon_{288} = +168$, $\Delta\varepsilon_{305} = -260\,\text{M}^{-1}\text{cm}^{-1}$), and the metal-to-ligand charge transfer (MLCT) transitions in the visible range showed opposite Cotton effects ($\Delta\varepsilon_{491} = -17$, $\Delta\varepsilon_{592} =$

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[*] Dr. J. Lacour, J. J. Jodry, C. Ginglinger, S. Torche-Haldimann
Département de Chimie Organique
Université de Genève
quai Ernest Ansermet 30, CH-1211 Genève 4 (Switzerland)
Fax: (+41) 22-328-73-96
E-mail: lacour@sc2a.unige.ch

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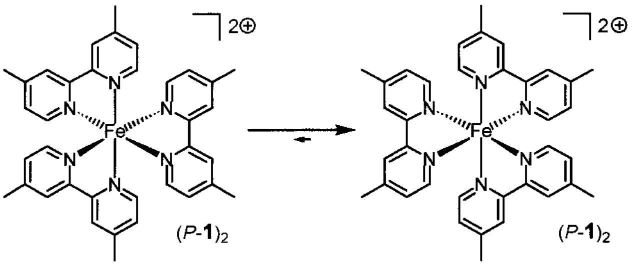
$+19\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$). The CD spectrum of (**2**)($M$-**1**)$_2$ is the mirror image of that of (**2**)($P$-**1**)$_2$. These spectra can be assigned to the $P$ and $M$ configurations of the cationic complexes, demonstrating that $\mathbf{3}_P$ and ent-$\mathbf{3}_P$ are the major diastereomers.[9] Therefore, with the decrease of the polarity of solvent, a highly asymmetric induction has taken place in solution favoring the diastereomeric ion pairs $\mathbf{3}_P$ and ent-$\mathbf{3}_p$. As a consequence, the equilibria $\mathbf{3}_P \rightleftharpoons \mathbf{3}_M$ and ent-$\mathbf{3}_P \rightleftharpoons$ ent-$\mathbf{3}_M$ have been shifted towards these two preferred complexes (Scheme 1). The increase in diastereoselectivity with decreasing polarity is interpreted as the result of closer interactions between the ions.[10]



*heterochiral*
($M$-**2**)($P$-**1**)$_2 \equiv \mathbf{3}_M$

*homochiral*
($P$-**2**)($P$-**1**)$_2 \equiv \mathbf{3}_P$

Scheme 1. Shift of the equilibrium in favor of the homochiral diastereomeric ion pair ($P$-**2**)($P$-**1**)$_2 \equiv \mathbf{3}_P$ rather than the heterochiral ($M$-**2**)($P$-**1**)$_2 \equiv \mathbf{3}_M$.

The derivatives $\mathbf{3}_p$ and ent-$\mathbf{3}_p$ correspond to the homochiral association of the chiral, helical ions: Octahedral tris-bidendate complexes such as **1** and **2** adopt propellerlike structures and exist as enantiomers, $P$ ($\Delta$) or $M$ ($\Lambda$) (right- or left-handed propellers), which can combine in either a homochiral ($\Delta-\Delta$, $\Lambda-\Lambda$) or a heterochiral relationship ($\Delta-\Lambda$). Prior to our study, it had been shown that the packing of molecular propellers depends on many parameters and particularly on their relative stereochemistry.[11] Experimental and computer modeling studies on monolayers of tris(bisimine)ruthenium(II) complexes have shown that either homochiral or heterochiral association could be preferred depending upon the spatial arrangement of the propellers.[11d, e, 12] Enantioselective quenching experiments on excited states and ion-association reactions recently demonstrated that both homochiral or heterochiral "encounter" pairs can be favored in solution depending upon the solvent and the structure of the molecular propellers involved: Low to good selectivities were obtained in those studies performed in polar protic media.[13]

Herein we have shown that for the two particular molecular propellers **1** and **2**, the homochiral mode of association is favored in a solvent of low polarity and proceeds with high selectivity. Further studies are being conducted to determine the nature of the supramolecular assembly of the ions[14] and the geometric parameters favoring the high diastereoselectivity.

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