Chiral Resolution

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Fluorinated TRISPHAT Anions: Spectroscopic Probes for Detailed Asymmetric Ion Pairing Studies**

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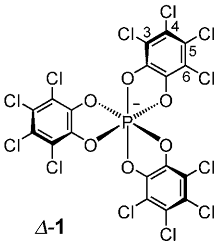
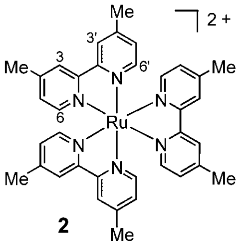
Ion pairing is an important phenomenon, which strongly affects the chemistry of organic, metallo-organic, and organometallic compounds.[1] Many reactions performed with homogeneous cationic transition-metal catalysts are directly influenced by the negative counterion, as the anion plays a critical role for the reaction rate and (enantio)selectivity.[2,3] Recently, detailed structural analyses of ion pairs, experimental[4] and theoretical,[5] have shed new light on the precise nature of salt effects. Much progress has been made using NMR spectroscopy: Homonuclear ^{1}H,^{1}H-NOESY and heteronuclear ^{1}H,^{19}F-HOESY experiments have allowed qualitative and quantitative structural investigations on the interactions of cationic moieties and their counterions,[6] and diffusion data from pulse-field gradient spin echo (PGSE) experiments have provided useful information on the average dimensions of salt aggregates in solution.[7]

Many different cationic moieties have been analyzed. In comparison, a relatively limited number of anionic substances have been studied. Only a dozen derivatives possess both NMR-sensitive atoms in their core or periphery as well as the requisite reactivity when associated to a given cation. Typical examples are BF_4^-, BPh_4^-, BArF$^-$,[8] and PF_6^-; this collection of anions is varied enough to allow most ion pairing studies. However, many of the cationic moieties that were studied are chiral and little information regarding asymmetry has been obtained from their interactions with the above-mentioned achiral anions. Here we report on the synthesis and resolution of two novel fluorine-containing, enantiopure, hexacoordinate phosphate anions, named TRISPHAT-F3 and TRISPHAT-F4, which can be used to demonstrate the exact geometry within ion pairs of chiral cations and anions.

Recently, the chemistry of chiral hexacoordinate phosphate anions has been rejuvenated,[9] as anions such as tris(tetrachlorobenzenediolato)phosphate(v) (**1**, TRISPHAT, Λ or Δ enantiomers) have been shown to be valuable chiral NMR solvating, resolving, and asymmetry-inducing reagents.[10] Effective resolution protocols involving configurationally stable Ru^{II} complexes, in particular [Ru(4,4′-Me$_2$bpy)$_3$]$^{2+}$ (**2**, bpy = 2,2′-bipyridine), have been developed using anion **1**.[9]



Δ-**1**



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Although a high level of chiral recognition was achieved with salts of **1** and **2**, the exact topography within the preferred ion pairs remained uncertain. Monitoring of the addition of enantiopure TRISPHAT salts to racemic D_3-symmetric [Ru(LL)$_3$]$^{2+}$ complexes by ^{1}H NMR spectroscopy has shown the following: 1) Anions Δ-**1** have a stronger influence on homochiral cationic moieties ($\Delta\Delta$ versus $\Delta\Lambda$), and 2) the protons of the cation along the C_3 axis are more strongly perturbed, indicating a preferred approach of the anion in that direction.[11] However, no such qualitative information has been gathered for the chiral anion since the chlorine atoms at the periphery of phosphate **1** are "silent" in NMR spectroscopy. The precise structural geometry within the ion pairs in solution was, overall, a mystery.

To obtain a complete and conclusive image of the situation, we decided to replace the chlorine by fluorine atoms, as these NMR-sensitive atoms are possible probes for selective approaches within the ion pairs. If one considers the D_3 symmetry of **1**, halogen atoms positioned at C3 and C6 ought to be sensitive to approaches along the C_3 axis of the anion, and those at the C4 and C5 positions to the approach of cations along the three C_2 axes (Figure 1). Selective replace-

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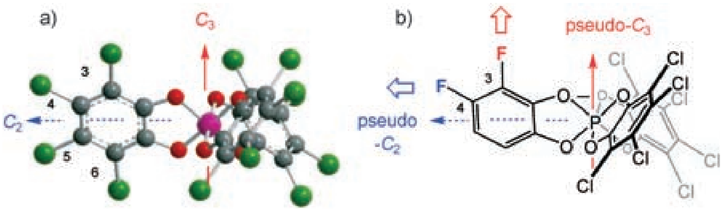
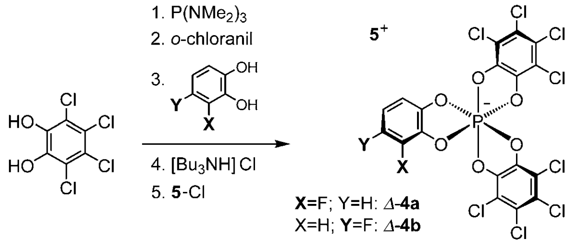


Figure 1. a) Lateral view of Δ-**1** and the axes of symmetry. b) Sensing of pseudo-C_3 or pseudo-C_2 approaches by selective positioning of fluorine atoms.

ment of chlorine by fluorine at the C3 and C4 positions would thus generate anions biased towards recognition along the pseudo-C_3 and pseudo-C_2 axes of the derived phosphates, respectively.

To minimize the structural modifications of TRISPHAT, only one of the three tetrachlorocatecholate ligands was exchanged by a fluorine-containing diol. 3-Fluorocatechol (**3a**) and 4-fluorocatechol (**3b**) were selected for their commercial availability. The phosphate anions **4a** and **4b**, namely TRISPHAT-F3 and TRISPHAT-F4, were prepared on a 5-g scale following reported guidelines (Scheme 1):[12]



Scheme 1. Synthesis of phosphate anions **4a** and **4b** and their subsequent resolution using **5**-Cl.

Anhydrous tetrachlorocatechol and $P(NMe_2)_3$ were allowed to react in toluene at reflux. After concentration in vacuo, successive addition in CH_2Cl_2 of *o*-chloranil (3,4,5,6-tetrachloro-3,5-cyclohexadiene-1,2-dione), **3a** or **3b**, and then $[Bu_3NH]Cl$ yielded the desired tri-*n*-butylammonium salts of racemic phosphates **4a** and **4b**. Analytically pure compounds $[Bu_3NH]$[**4a**] or $[Bu_3NH]$[**4b**] were obtained after chromatography (yield 85%, four consecutive steps).

The resolution of the anions was achieved by the addition of *N*-benzyl-cinchonidinium chloride salt (**5**-Cl, 1.0 equiv) to solutions of $[Bu_3NH]$[*rac*-**4a**] or $[Bu_3NH]$[*rac*-**4b**] in $CHCl_3$. The diastereomerically pure (−)-[**5**][Δ-**4a**] and (−)-[**5**][Δ-**4b**] salts were selectively precipitated with good yields (> 45%). X-ray structure determination with the cinchonidinium derivatives (e.g. (−)-[**5**][Δ-**4a**], Figure 2) showed an absolute Δ configuration for **4a** and **4b**.[13,14] The P–O bond lengths and O-P-O bond angles are virtually identical to those measured for TRISPHAT **1**. The nonracemic anions **4a** and **4b** displayed good chemical and configurational stability, as no evidence of a racemization could be found, for instance, during the ion-exchange metathesis of cation **5** by Bu_4N^+.

The ability of anions **4a** and **4b** to behave as effective chiral auxiliaries for cation **2** was first tested in ^1H NMR titration experiments. Various amounts of (−)-$[Bu_4N]$[Δ-**4a**]

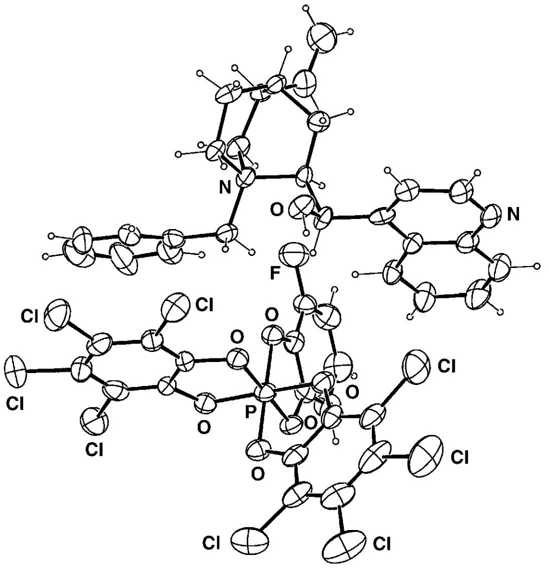


Figure 2. X-ray crystal structure of (−)-[**5**][Δ-**4a**]. Ellipsoids represent the 50% probability level.

or (−)-$[Bu_4N]$[Δ-**4b**] (0.5–10 equiv) were added to solutions of [*rac*-**2**]$(PF_6)_2$ in CD_2Cl_2 (see the Supporting Information). In all these experiments, a strong NMR enantiodifferentiation was observed upon addition of the anions (Figure 3 a,b);

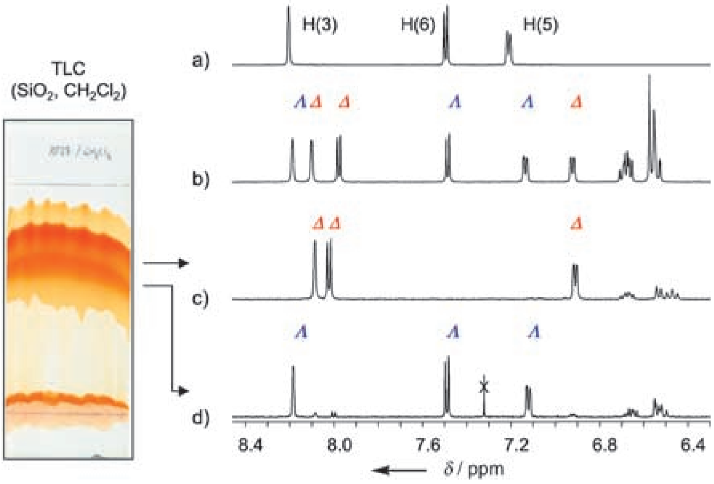


Figure 3. Left: View of the TLC plate in the separation of the complexes. Right: The corresponding ^1H NMR spectra (400 MHz, CD_2Cl_2): a) [*rac*-**2**]$(PF_6)_2$; b) [*rac*-**2**]$(PF_6)_2$ + 5.0 equiv of $[Bu_4N]$[Δ-**4a**]; c) [Δ-**2**][Δ-**4a**]$_2$, d.r. > 48:1; d) [Λ-**2**][Δ-**4a**]$_2$, d.r. 13.5:1. X = trace of $CHCl_3$.

TRISPHAT-F3 and TRISPHAT-F4 behaved similarly to the original anion **1**. To determine precisely 1) the nature of the preferred association, 2) the effect of the position of the fluorine atom, and 3) the exact topography within the preferred ion pairs, we decided to obtain the enantio- and diastereomerically pure salts [Δ-**2**][Δ-**4a**]$_2$, [Λ-**2**][Δ-**4a**]$_2$, [Δ-**2**][Δ-**4b**]$_2$, and [Λ-**2**][Δ-**4b**]$_2$.

Chromatographic separation of these complexes was therefore performed.[10c,15] The salts [*rac*-**2**]$(PF_6)_2$ and [**5**][Δ-

4a] or [**5**][Δ-**4b**] (2.2 equiv) were mixed, dissolved, and adsorbed on preparative thin-layer chromatographic plates. In each case, elution with CH_2Cl_2 resulted in two well-separated bands (Figure 3, left), which were scraped off the glass surface and stirred in CH_2Cl_2. The resulting suspensions were filtered and concentrated in vacuo. ^1H NMR spectroscopy revealed sets of signals corresponding to the separated Δ and Λ enantiomers of cation **2** (Figure 3 c,d). The circular dichroism analysis indicated that the first and second eluted fractions contained predominantly the cationic complex with absolute Δ and Λ configurations, respectively (see the Supporting Information).[16] The diastereomeric salts [Δ-**2**][Δ-**4a**]$_2$/[Λ-**2**][Δ-**4a**]$_2$ and [Δ-**2**][Δ-**4b**]$_2$/[Λ-**2**][Δ-**4b**]$_2$ were thus obtained in decent chemical yields (30–40 %, Table 1).

The NMR spectra of the homochiral and heterochiral salts [Δ-**2**][Δ-**4**]$_2$ and [Λ-**2**][Δ-**4**]$_2$, respectively, were then compared with those of the PF_6^- and Δ-**1** salts. The chemical shifts for the cationic protons of all these compounds are reported in Table 1. Several trends can be observed. Only the Δ enantiomer of **2** is strongly perturbed by the presence of the homochiral anions Δ-**4a** and Δ-**4b**; the Λ enantiomer shows a much smaller influence of the anions ($\Delta\delta_{max} = -0.14$ versus 0.53). In the homochiral series, protons H(6,6′) along the C_3 axis are the most efficiently split with a drift towards higher frequencies. For all other signals, upfield shifts result with a decreased influence along the C_2 axes. It had previously been shown that classical anions have preferred contacts with methyl and H(3,3′) protons of cationic 4,4′-Me_2bpy transition-metal complexes.[17] Interestingly, this is not the case with the TRISPHAT family. Anions Δ-**4a**, Δ-**4b**, and Δ-**1** all behave in favor of homochiral associations along the C_3 axis of the cation (Table 1, entries 3, 5, and 7).[11,18]

Nonetheless, detailed quantitative analysis revealed some nuances. Anion Δ-**4b** induces weaker variations of proton chemical shifts than do anions Δ-**1** and Δ-**4a** (e.g., protons H(6,6′): $\Delta\delta = 0.32$, 0.51 and 0.53, respectively). The chemical shifts of the fluorine atom of anion Δ-**4b** within its Δ-**2** and Λ-**2** salts are identical, whereas a difference can be noted for Δ-**4a**. Anion Δ-**4b** also displays a reduced chromatographic separation of the enantiomers of **2** as compared to Δ-**1** and Δ-**4a** ($\Delta R_f = 0.19$, 0.27, and 0.30, respectively). The lack of halogen substituent at the C3 or C6 positions of one of the

Table 1: Data on the diastereomeric ion pairs [Δ^+][Δ^-]$_2$ and [Λ^+][Δ^-]$_2$ of cation **2** and anions **4a**, **4b**, and **1**. The solvent for ^1H NMR spectroscopy was CD_2Cl_2.

Entry	Compound	Yield [%]	R_f[a]	d.r.[b]	$[\alpha]_D^{20}$	H(6) δ	H(6) $\Delta\delta$[c]	H(5) δ	H(5) $\Delta\delta$[c]	CH_3 δ	CH_3 $\Delta\delta$[c]	H(3) δ	H(3) $\Delta\delta$[c]	F δ	F $\Delta\delta$[d]
1	[*rac*-**2**](PF_6)$_2$	–	0	–	–	7.50	–	7.21	–	2.57	–	8.20	–	−72.90	–
2	[Λ-**2**][Δ-**4b**]$_2$	40	0.36	15:1	+17	7.42	−0.08	7.15	−0.06	2.45	−0.12	8.17	−0.03	−122.90	−0.50
3	[Δ-**2**][Δ-**4b**]$_2$	36	0.55	>48:1	−839	7.82	+0.32	6.97	−0.24	2.34	−0.23	8.12	−0.08	−122.90	−0.50
4	[Λ-**2**][Δ-**4a**]$_2$	30	0.31	13.5:1	+46	7.56	+0.06	7.11	−0.10	2.43	−0.14	8.19	−0.01	−139.40	−1.17
5	[Δ-**2**][Δ-**4a**]$_2$	30	0.61	>48:1	−734	8.03	+0.53	6.92	−0.29	2.27	−0.30	8.09	−0.11	−139.65	−1.42
6	[Λ-**2**][Δ-**1**]$_2$	30	0.55	26:1	+36	7.46	−0.04	7.18	−0.03	2.48	−0.09	8.18	−0.02	–	–
7	[Δ-**2**][Δ-**1**]$_2$	35	0.82	>48:1	−882	8.01	+0.51	6.95	−0.26	2.31	−0.24	8.11	−0.09	–	–

[a] CH_2Cl_2 was used as eluent. [b] The diastereomeric purity was determined by ^1H NMR spectroscopy. [c] The difference in chemical shift for the protons of **2** as compared to those of the [*rac*-**2**](PF_6)$_2$ salts. [d] The difference in chemical shift for the fluorine atom as compared to those of the [Bu_4N][Δ-**4**] salts.

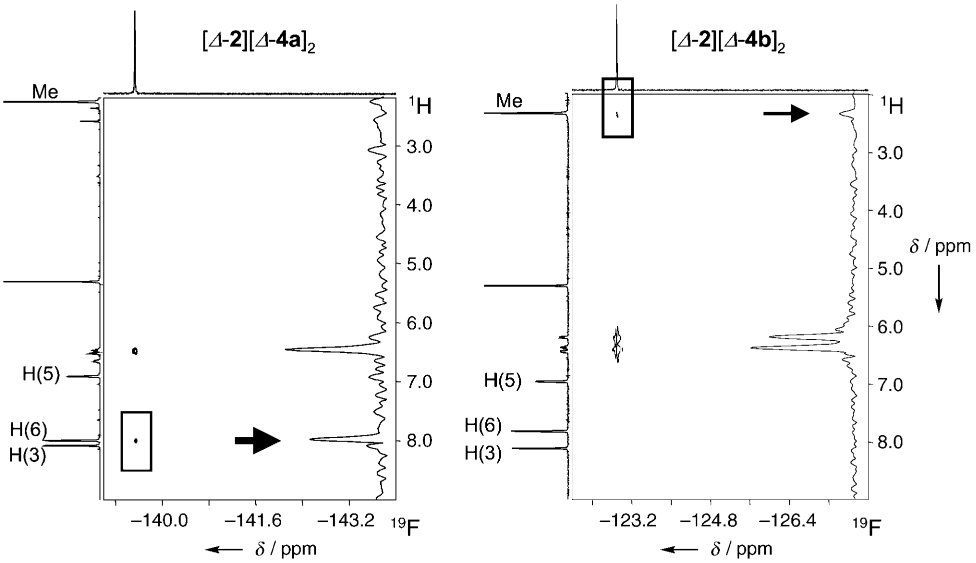


Figure 4. The $^1H,^{19}F$-HOESY NMR spectra (470.59 MHz, CD_2Cl_2, $\tau_m = 0.7$ s) of [Δ-**2**][Δ-**4a**]$_2$ and [Δ-**2**][Δ-**4b**]$_2$ showing the "heteronuclear interionic contacts". The F1 trace (indirect dimension) relative to one component of the fluorine is shown on the right.

catecholate ligands apparently has a negative effect (anion **4b**). The presence of Cl or F atoms at the C4 positions cannot compensate the disappearance at C3 and C6.

The positioning of electronegative elements (Cl, F) along the C_3 axis of the anion is thus crucial for both NMR enantiodifferentiation and chiral recognition among the propellers. Only an approach of the cation along this axis can explain the results. As electronegative halogen atoms can participate in charge-assisted C−H···X hydrogen bonds,[19] one can propose that such intermolecular interactions occur upon the alignment of the C_3 axes of the homochiral complexes. The downfield shifts of the H(6,6′) protons is a good indication of the hydrogen-bonding situation with chlorine or fluorine at the C3 positions.

Final and conclusive evidence for this preferred geometry was gathered through ^{1}H,^{19}F-HOESY NMR experiments (CD_2Cl_2) of salts [Δ-**2**][Δ-**4a**]$_2$ and [Δ-**2**][Δ-**4b**]$_2$. In both cases, strong intramolecular interactions between the protons of the anions and the neighboring fluorine atoms were observed. More importantly, selective cross-peaks showing interionic contacts could be determined, from the fluorines at the C3 and C4 positions of Δ-**4a** and Δ-**4b** towards the H(6,6′) and the methyl protons of cation Δ-**2**, respectively (Figure 4).[20,21] These interactions can only be rationalized through an alignment of the propeller ions along their C_3 axes.[22,23]

In conclusion, enantiopure anions **4a** and **4b** can be readily synthesized in two steps from commercially available materials. They display effective NMR discriminating abilities useful for structural determinations of asymmetric ion pairing geometries. Their application in the context of enantioselective homogeneous catalysis is currently in progress.

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[13] Crystal data: The cell dimensions and intensities were measured at 200 K on a Stoe IPDS diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). (−)-[**5**][Δ-**4a**] $(C_{18}H_3O_6FPCl_8)^-(C_{26}H_{29}N_2O)^+(C_3H_6O)$: $M_r = 1092.4$; orthorhombic space group, $P2_12_12_1$, $a = 11.5311(5)$, $b = 19.2565(10)$, $c = 22.6497(13)$ Å; $V = 5029.3(4)$ Å^3, $Z = 4$, $\mu = 0.537$ mm^{-1}, $\rho_{calcd} = 1.443$ g cm^{-3}. Of 70173 measured reflections, 10859 were unique and 4837 were observed ($|F_o| > 4\sigma\ (F_o)$); $R = 0.039$, $\omega R = 0.035$, Flack parameter x = −0.03(8). (−)-[**5**][Δ-**4b**] $(C_{18}H_3O_6FPCl_8)^-(C_{26}H_{29}N_2O)^+(C_3H_6O)$: $M_r = 1092.4$; orthorhombic space group, $P2_12_12_1$, $a = 11.3676(5)$, $b = 19.0586(11)$,

$c = 22.9182(12)$ Å; $V = 4965.2(4)$ Å^3, $Z = 4$, $\mu = 0.544\ \text{mm}^{-1}$, $\rho_{\text{calcd}} = 1.461\ \text{g cm}^{-3}$. Of 69474 measured reflections, 10668 were unique and 5449 were observed ($|F_o| > 4\sigma(F_o)$); $R = 0.036$, $\omega R = 0.035$, Flack parameter $x = -0.03(8)$, the fluorine atom is disordered on the C4 and C5 positions with refined population parameters of 0.70(1) and 0.30(1) respectively. CCDC-265389 and CCDC-265390 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] Circular dichroism analysis of salts (−)-[**5**][Δ-**4a**] and (−)-[**5**][Δ-**4b**] (MeOH, ≈10^{-6} M) revealed strong exciton coupling in the π–π* region with positive and negative Cotton effects at lowest and highest wavelengths, confirming the Δ configuration: D. Bas, T. Bürgi, J. Lacour, J. Vachon, J. Weber, *Chirality* **2005**, 15, S143–S145.

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[20] The ^{1}H,^{19}F-HOESY measurements were carried out on a 500-MHz Bruker DRX spectrometer equipped with a QNP probe; mixing time 700 ms, sample concentration 5 mM, number of scans 96, number of increments in the F1 dimension 256.

[21] The ^{1}H,^{19}F-HOESY NMR experiment on salt [*rac*-**2**](PF_6)$_2$ shows cross-peaks of the achiral anions with all the protons of the coordination complex (see the Supporting Information).

[22] The DFT calculations on the preferred geometry of interaction between ions Δ-**1** and Δ-**2** clearly showed this preferred topography. I. Dance, unpublished results.

[23] Anions **4a** and **4b** also possess H nuclei on the fluorine-containing ligands, which can be equally used for detecting interionic contacts. The results of the ^{1}H,^{1}H-NOESY experiments on salts [Δ-**2**][Δ-**4a**]$_2$ and [Δ-**2**][Δ-**4b**]$_2$ are reported in the Supporting Information and confirm the data from the HOESY experiments. These experiments further show that the preferred interaction of the anion with the cation comes indeed from the face containing the fluorine substituent.