Diastereoselective Homochiral Self-Assembly Between Anions and Cation in Solution

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Diastereoselective homochiral self-assembly occurs in solution by mixing the propeller-like racemic tris(DEAS-bpy) ruthenium(II) cation **B** [DEAS-bpy = 4,4′-bis(diethylaminostyryl)-[2,2′]-bipyridine)] and the racemic TRISPHAT anion **A** [TRISPHAT = tris(tetrachlorobenzenediolato)phosphate(V)]. This phenomenon is clearly shown by ^{1}H NMR spectroscopic studies which reveal: (i) the existence of a rapid equilibrium between their homochiral and heterochiral associations, (ii) at room temperature, the preferential formation of the homochiral ion pairs with a ratio homochiral/heterochiral = 72:28, and (iii) at 243 K, the almost pure homochiral associations $(\mathbf{B}^{\Lambda},\mathbf{A}^{\Lambda}_2)$ and $(\mathbf{B}^{\Delta},\mathbf{A}^{\Delta}_2)$.

Introduction

Propeller-like molecules are potential candidates for diastereoselective self-assembly, where chiral supramolecules are spontaneously formed from a mixture of racemic components. Such types of chiral recognition have generally been observed in the solid state.[1] The recognition driving force is mainly due to the formation of intermolecular hydrogen bonds, the helicity of both compounds ensuring the spatial compatibility of the H-donor and acceptor groups.[2] Moreover, a few examples of self-assembly have also been observed for propeller-like H-bond-free molecules: spontaneous homochiral segregation occurred during the formation of columnar liquid crystals[3] or during gel crystallization,[4] the homochiral association of the propellers ensuring the optimal packing. Chiral recognition phenomena have also been observed among guest tris(diimine) metal complexes when intercalated into host mineral clays.[5]

D_3-symmetric propeller-like molecules are particularly interesting as a new class of octupolar chromophores for nonlinear optics (NLO).[6] Coordination chemistry is a powerful tool to design such compounds,[7] and recently we[8] and others[9] have reported the large molecular hyperpolarisability of octahedral ruthenium(II) complexes [Ru(bpy′)$_3$][PF$_6$]$_2$, where bpy′ is a functionalized 2,2′-bipyridine. With the aim of increasing the NLO activity of such systems, we became interested in the association of Ru^{II} cationic octupoles with counter anions also having a D_3 propeller-like topology. We sought to use the propeller-like tris(tetrachlorobenzenediolato)phosphate(V) anion [TRISPHAT] **A** (Figure 1) which was recently described as a chiral shift agent,[10] a chiral inducer onto Fe^{II} complexes[11] and for its ion-pair chromatographic-resolution properties.[12]

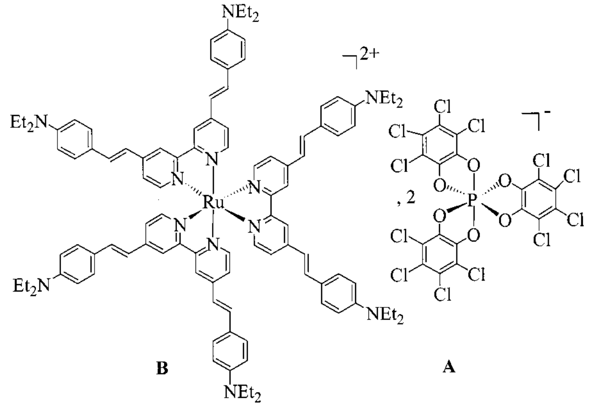

Figure 1. TRISPHAT anion **A** (Δ) and [Ru(DEAS-bpy)$_3$]$^{2+}$ cation **B** (Δ) (DEAS-bpy = 4,4′-bis(diethylaminostyryl)-[2,2′]-bipyridine)

In this article, we wish to describe the synthesis and ^{1}H NMR spectroscopic studies of the association between a racemic D_3-symmetric ruthenium tris(DEAS-bpy) dication {where DEAS-bpy represents 4,4′-bis(diethylaminostyryl)-[2,2′]-bipyridine} and the racemic TRISPHAT anion which reveals a remarkable diastereoselective, homochiral self-assembly phenomenon in solution.

Results and Discussion

The tris(bipyridyl) ruthenium complex (**B**,[PF$_6$]$_2$) is classically prepared by reacting [RuCl$_2$(DMSO)$_4$] with DEAS-bpy (three equivalents) in refluxing DMF, followed by an anionic exchange with NaPF$_6$. The TRISPHAT salt (**B**,**A**$_2$) is obtained either from the chloride or the hexafluorophosphate salts by anion metathesis with [HNBu$_3$][TRISPHAT] (Scheme 1). This new complex is much more soluble than the corresponding PF$_6$ salt in chlorinated solvents allowing its purification by using silica-gel column chromatography with dichloromethane as eluent. The spectroscopic and

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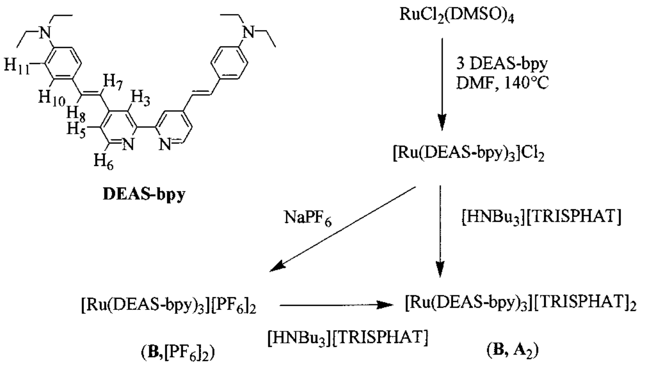
analytical data are given in the Experimental Section. The aromatic parts of the ^{1}H NMR spectra of (**B**,$[PF_6]_2$) and (**B**,A_2) are displayed in Figure 2. For the TRISPHAT salt, a strong deshielding of the H_6 proton is observed ($\Delta\delta = +0.5$ ppm) while the bipyridyl protons H_3 and H_5, as well as the protons of the styryl substituents (H_7-H_{11}), are displaced to higher field when compared to those of the corresponding hexafluorophosphate salt. A similar, but weaker, effect can be observed in the corresponding ^{13}C NMR spectra (see Experimental Section), with the C_6 carbons being shifted downfield ($\Delta\delta = +1.0$ ppm).



Scheme 1. Synthesis of (**B**,A_2) and indexation of DEAS-bpy

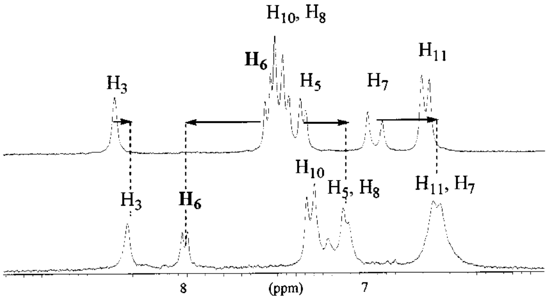


Figure 2. Effect of the counter-anion on the aromatic region of the ^{1}H NMR spectra of (**B**,$[PF_6]_2$) (up) and (**B**,A_2)

It is worth noting that the TRISPHAT anion **A** and the Ru^{II} complex **B** exist as two configurationally stable Λ and Δ enantiomers.[13] Their association should afford a mixture of diastereoisomeric complexes consisting of two couples of enantiomeric homochiral (**B**$^\Lambda$,**A**$^\Lambda_2$), (**B**$^\Delta$,**A**$^\Delta_2$) and heterochiral (**B**$^\Lambda$,**A**$^\Delta_2$), (**B**$^\Delta$,**A**$^\Lambda_2$) derivatives. Surprisingly, the ^{1}H NMR spectrum of the racemic mixture (CD_2Cl_2, 293 K) shows only one set of signals for the bipyridyl ligands (Figure 2) suggesting either a dynamic phenomenon or the selective formation of one diastereoisomer. Lowering the temperature to 243 K results in a slight shift and broadening of the signals, but no splitting of the ^{1}H NMR signals is observed (Figure 3). On the other hand, a direct observation of diastereoisomers by NMR spectroscopy should be possible through exchange between *rac* (**B**,$[PF_6]_2$) and the partially resolved chiral cinchonidinium−Δ TRISPHAT salt **A**$^\Delta$ ($[\alpha]_D = -320$, *de* = 86%).[14] The ^{1}H NMR spectrum of this mixture (298 K), shows two sets of signals for the bipyridyl ligands, corresponding to the expected mixture of homochiral and heterochiral diastereoisomers (Figure 4a).[15] The H_6 and $H_{6'}$ protons give signals of equal intensity at $\delta = 8.17$ and 7.54, values which are notably different from that observed for the racemic mixture (unique signal, $\delta = 7.98$, Figure 4f or Figure 2). At this stage no direct explanation could be given; since the TRISPHAT enantiomeric excess seems to have a large influence on the NMR spectra, two other experiments were carried out.

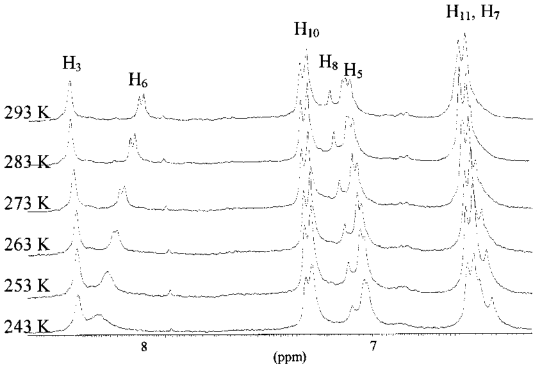


Figure 3. Variable temperature ^{1}H NMR spectra of *rac* (**B**,A_2) complexes (CD_2Cl_2, 300 MHz)

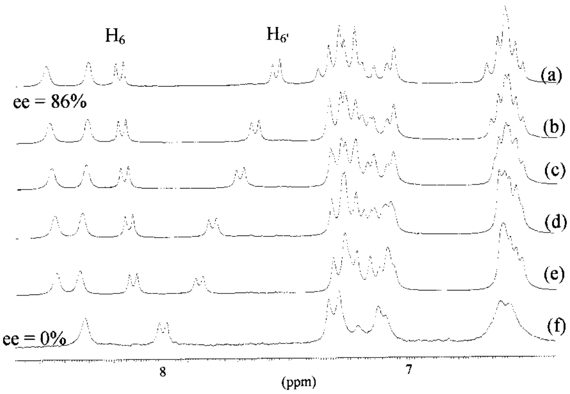


Figure 4. Aromatic part of the ^{1}H NMR spectra (CD_2Cl_2, 200 MHz, 293 K)of (**B**,A_2) (**A**$^\Delta$, *ee* = 86%) (a); *rac* (**B**,A_2) (f); during the addition of *rac* ($[HNBu_3]$,**A**) to the solution of (**B**,A_2) (**A**$^\Delta$, *ee* = 86%) (b-e)

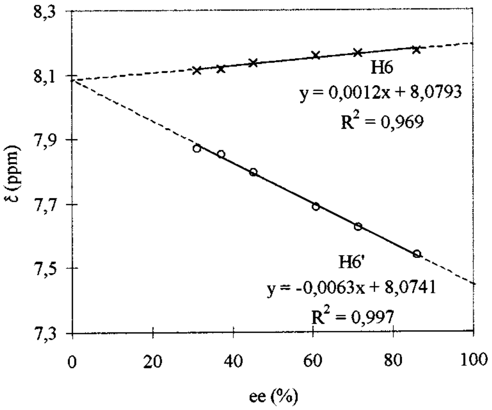
In order to decrease the TRISPHAT enantiomeric excess, *rac* (**B**,A_2) was incrementally added to the solution obtained with partially resolved TRISPHAT, containing mainly the (**B**$^\Delta$,**A**$^\Delta_2$) and (**B**$^\Lambda$,**A**$^\Delta_2$) diastereoisomers (Figure 4a). The convergence of the H_6 and $H_{6'}$ proton NMR probes is observed whereas their relative intensities remain equal, clearly indicating that these two signals are due to $\Delta-[Ru(DEAS\text{-}bpy)_3]^{2+}$ and $\Lambda-[Ru(DEAS\text{-}bpy)_3]^{2+}$ propellers in a TRISPHAT-oriented medium. The dependence of the H_6 and $H_{6'}$ chemical shifts on TRISPHAT′s *ee* is due to rapid equilibria involving the homochiral and heterochiral associations. For the two rapid equilibria, the position of the H_6 and $H_{6'}$ coalescence signals δ_{obs} is given by the equation: $\delta_{obs} = x\delta_{HOMO} + (1 - x)\delta_{HETERO}$ [Equation (a)] where x represents the relative amount of the homochiral species and δ_{HOMO} and δ_{HETERO} the chemical shift of the pure diastereoisomers. This equation allows the determination of the relative amount of both homochiral and heterochiral diastereoisomers.

Finally, in order to quantify the role of the TRISPHAT enantiomeric excess, small amounts of *rac* ([$HNBu_3$],**A**) were successively added to a solution of (**B**,$\mathbf{A_2}$) ($\mathbf{A}^{\Delta}$, *ee* = 86%, Figure 4a). The evolution of the ^1H NMR spectra (Figure 4b–e) also shows that, for both family of protons, the intensity is retained, whereas their chemical shifts converge. For each **B** enantiomer, the positions of H_6 and $H_{6'}$ traduce the homochiral/heterochiral composition of the equilibria in Equations (1) and (2), respectively (vide supra).

$$(\mathbf{B}^{\Delta},\mathbf{A}^{\Delta}{}_2) + 2\,[HNBu_3][\mathbf{A}^{\Lambda}] \rightleftharpoons (\mathbf{B}^{\Delta},\mathbf{A}^{\Lambda}{}_2) + 2\,[HNBu_3][\mathbf{A}^{\Delta}] \quad (1)$$

$$(\mathbf{B}^{\Lambda},\mathbf{A}^{\Delta}{}_2) + 2\,[HNBu_3][\mathbf{A}^{\Lambda}] \rightleftharpoons (\mathbf{B}^{\Lambda},\mathbf{A}^{\Lambda}{}_2) + 2\,[HNBu_3][\mathbf{A}^{\Delta}] \quad (2)$$

As shown in Scheme 2, the chemical shifts of H_6 and $H_{6'}$ vary linearly with the TRISPHAT enantiomeric excess. The validity of Equation (a) is enforced by the fact that the straight lines intercept the Y-axis at the same point ($\delta = 8.07$) corresponding to the racemic mixture *rac* (**B**,$\mathbf{A_2}$), experimentally recorded at $\delta = 7.98$ (Figure 4f). Of particular interest, the slopes of the straight lines are very different, showing a different evolution of the two equilibria in Equations (1) and (2) during the addition of *rac* **A** (and especially the isomer $\mathbf{A}^{\Lambda}$). Both equilibria are displaced to the right but the shift of the equilibrium in Equation (2) is about five times[16] more pronounced than that of the equilibrium in Equation (1), clearly showing that, under these experimental conditions,[17] the homochiral association is spontaneously preferred to the heterochiral one.



Scheme 2. H_6 and $H_{6'}$ chemical shift vs. TRISPHAT's *ee*

Extrapolation of the straight lines to *ee* = 100% allows the determination of the theoretical chemical shift for the pure homochiral (H_6, $\delta_{HOMO} = 8.19$) and heterochiral ($H_{6'}$, $\delta_{HETERO} = 7.44$) isomers. Thus, according to equation (a), the unique $H_6/H_{6'}$ signal of the racemic mixture (**B**,$\mathbf{A_2}$) at $\delta = 7.98$ allows the determination of $x = 0.72$. This traduces for each $[Ru(DEAS\text{-}bpy)_3]^{2+}$ enantiomer, the rapid equilibrium between the 72% homochiral [($\mathbf{B}^{\Lambda}$,$\mathbf{A}^{\Lambda}{}_2$) or ($\mathbf{B}^{\Delta}$,$\mathbf{A}^{\Delta}{}_2$)] and 28% heterochiral [($\mathbf{B}^{\Lambda}$,$\mathbf{A}^{\Delta}{}_2$) and ($\mathbf{B}^{\Delta}$,$\mathbf{A}^{\Lambda}{}_2$)] diastereoisomers. In other words, the homochiral isomer is 0.56 kcal·mol^{-1} more stable than the heterochiral one at 298 K in CH_2Cl_2.

This result can also be used to explain the variable-temperature ^1H NMR experiment of *rac* (**B**,$\mathbf{A_2}$) in CD_2Cl_2 (Figure 3), where the ratio of homochiral/heterochiral diastereoisomers linearly increases with the lowering of the temperature leading toward the formation of the thermodynamically favored homochiral form.

Conclusion

As previously noticed, tris(bipyridyl) metal complexes (M = Fe, Ru) have already been associated with the TRISPHAT anion but only in its enantiopure form,[10–12] the same association with racemic TRISPHAT giving rise to insoluble salts.[11] In contrast, the use of functionalized DEAS-bpy, which leads to an enhanced solubility of the corresponding ruthenium salt, allows the study of the association with racemic TRISPHAT. The enantiopure TRISPHAT anion is known to form a diastereoselective, homochiral ion-pair with the labile tris(4,4′-dimethyl-[2,2′]-bipyridine) iron(II) dication.[11] In the present work, we show that the same homochiral association occurs between racemic TRISPHAT and the nonlabile propeller-like ruthenium complex. Moreover, this recognition is temperature dependant, leading to the almost pure homochiral associations ($\mathbf{B}^{\Lambda}$,$\mathbf{A}^{\Lambda}{}_2$) or ($\mathbf{B}^{\Delta}$,$\mathbf{A}^{\Delta}{}_2$) at 243 K. Such diastereoselective self-assembly has already been observed by Swager et al. for neutral, propeller-like metal complexes during the formation of columnar liquid crystals, the homochiral segregation being driven by the optimization of the packing.[3] In this paper, the self-assembly occurs in solution between charged propeller-like compounds. The driving force is thought to be the minimization of the electrostatic interactions, the anion/cation distance being shorter in the homochiral association (Figure 5).

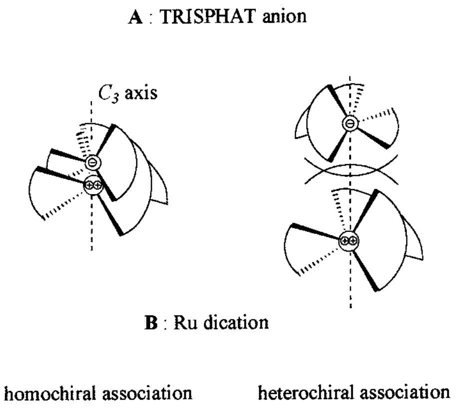


Figure 5. Schematic representation of both homochiral and heterochiral interactions

Finally, the assembly of octupolar anions and cations opens the way towards the design of supramolecular materials for nonlinear optics. Studies are now in progress to examine the NLO activity of such multi-octupolar compounds.

Experimental Section

General: All reactions were routinely performed under argon using Schlenk techniques. − NMR spectra (^{1}H, ^{13}C, ^{31}P) were recorded on a BRUKER DPX 200 (operating at 200.12 MHz for ^{1}H, 50.32 MHz for ^{13}C and 81.91 MHz for ^{31}P) or on a BRUKER AC 300 (operating at 300.13 MHz for ^{1}H) spectrometers. NMR spectroscopic data are listed in parts per million (ppm) and are reported relative to 85% H_3PO_4 (^{31}P) or to tetramethylsilane (^{1}H, ^{13}C), residual solvent peaks being used as internal standard (CD_2Cl_2: ^{1}H: $\delta = 5.25$; ^{13}C: $\delta = 53.45$). Complete attribution of the ^{1}H and ^{13}C spectra required 2D experiments [COSY, H−C correlation (hmqc and hmbc sequences)]. − UV/Vis spectra were recorded on a BIO-TEK/KONTRON UVIKON 941 spectrophotometer in dichloromethane solution. − High resolution mass spectrometry measurements (FAB) were performed by the Centre Regional de Mesures Physiques de l'Ouest (Rennes, France) and elemental analysis by the Service Central d'Analyse du CNRS (Solaize, France). Solvents are simply distilled prior to use. $[RuCl_2(DMSO)_4]$[18] and the ligand 4,4′-bis(diethylaminostyryl)-[2,2′]-bipyridine[19] were prepared using published methods. The complex (**B**,$[PF_6]_2$) has already been published[9] but its NMR spectroscopic data are completed for comparison.

Characterization of (B,$[PF_6]_2$): ^{1}H NMR (CD_2Cl_2, 298 K): $\delta = 8.32$ (br. s, 6 H, H_3), 7.5 (d, $^1J = 6$ Hz, 6 H, H_6), 7.44 (d, $^1J = 8$ Hz, 12 H, H_{10}), 7.35 (d, $^1J = 16$ Hz, 6 H, H_8), 7.31 (d, $^1J = 6$ Hz, 6 H, H_5), 6.89 (d, $^1J = 16$ Hz, 6 H, H_7), 6.6 (d, $J = 8$ Hz, 12H, H_{11}), 3.3 (br. m, 24 H, H_{12}), 1.1 (t, $^1J = 6.5$ Hz, 36H, H_{13}). − ^{13}C NMR (CD_2Cl_2, 298 K): $\delta = 157.0$ (C_2), 150.0 (C_6), 149.1 (C_{12}), 147.6 (C_4), 137.2 (C_8), 129.5 (C_{10}), 122.8 (C_5), 122.3 (C_9), 120.1 (C_3), 117.6 (C_7), 111.6 (C_{11}), 44.6 (C_{13}), 12.4 (C_{14}). − ^{31}P NMR (CD_2Cl_2, 298 K): $\delta = -144$ (hept, $J = 712$ Hz). − UV/Vis (CH_2Cl_2): $\lambda_{max} = 520$ (150000), 446 nm (142000). − HRMS-FAB ($C_{102}H_{114}$ $F_6N_{12}PRu$, $\{[B][PF_6]\}^+$): calcd. 1753.8004; found1753.7971.

Preparation of (B,$[TRISPHAT]_2$): $[RuCl_2(DMSO)_4]$ (250 mg, 51.6 mmol, 1 equiv.) and 4,4′-bis(diethyl-aminostyryl)-2,2′-bipyridine (777 mg, 1.55 mmol, 3 equiv.) were dissolved in dimethylformamide (10 mL). The dark red solution was stirred overnight in refluxing DMF. After cooling to room temperature, $[HNBu_3][TRISPHAT]$ (986 mg, 1.03 10^{-3} mol, 2 equiv.) was added. After stirring for 30 min. at room temperature, a dark red solid was precipitated out by addition of water (100 mL). The complex was filtered off and purified by column chromatography (silica gel, CH_2Cl_2). The solvent was removed under vacuum to afford a dark red microcrystalline powder (1.22 g, 67% yield). − ^{1}H NMR (CD_2Cl_2, 298 K): $\delta = 8.29$ (br. s, 6 H, H_3), 7.98 (d, $^1J = 6$ Hz, 6 H, H_6), 7.3 (d, $^1J = 8$ Hz, 12 H, H_{10}), 7.1 (d, $^1J = 16$ Hz, 6 H, H_8), 7.09 (d, $^1J = 6$ Hz, 6 H, H_5), 6.62 (d, $^1J = 16$ Hz, 6 H, H_7), 6.6 (d, $^1J = 8$ Hz, 12 H, H_{11}), 3.3 (br. m, 24 H, H_{12}), 1.1 (t, $^1J = 6.5$ Hz, 36 H, H_{13}). − ^{13}C NMR (CD_2Cl_2, 298 K): $\delta = 156.9$ (C_2), 151.0 (C_6), 149.0 (C_{12}), 147.0 (C_4), 136.3 (C_8), 129.4 (C_{10}), 122.5 (C_5), 122.2 (C_9), 119.9 (C_3), 117.3 (C_7), 111.4 (C_{11}), 44.5 (C_{13}), 12.4 (C_{14}), 141.6 (d, $J = 6$ Hz, TRISPHAT), 122.66 (TRISPHAT), 114.0 (d, $J = 20$ Hz, TRISPHAT). − ^{31}P NMR (CD_2Cl_2, 298 K): $\delta = -80.5$ (s). − UV/Vis (CH_2Cl_2): $\lambda_{max} = 520$ (146000), 447 nm (143000). − HRMS-FA) ($C_{120}H_{114}$ $Cl_{12}N_{12}O_6PRu$, $\{$**B**$,[TRISPHAT]\}^+$): calcd. 2377.3995; found 2377.3927. − $C_{138}H_{114}$ $Cl_{24}N_{12}O_{12}P_2Ru$: calcd. C 52.68, H 3.65, N 5.34; found C 51.97, H 3.64, N 5.15.

Reaction Between (B,A_2) (A^Δ, *ee* = 86%) and *rac* ($[HNBu_3]$,[A]): In an NMR tube, (**B**,A_2) (A^Δ, *ee* = 86%) (40 mg, 1.3×10^{-5} mol) was dissolved in CD_2Cl_2 (1 mL). *Rac* ($[HNBu_3]$,[**A**]) was added in small fractions directly weighed in the NMR tube. After each addition an NMR spectrum was recorded. The experiment was conducted until a precipitate appeared. The resulting NMR spectra are shown in Figure 4.

Acknowledgments

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[15] The chiral shift-reagent ability of the TRISPHAT anion is confirmed by the downfield shift of the H_6 proton which is more pronounced for the homochiral association (H_6) than for the heterochiral ($H_{6'}$) one. Since H_6 and $H_{6'}$ are the most sensitive protons in term of chemical shift, they are used as NMR probes for this study.

[16] In Scheme 2, the ratio of the slope is equal to 5.25.

[17] All the experiments were carried out in dichloromethane. The influence of the solvent polarity was not studied.

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