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Internal vs. external ionic functionality—a comparative study in the asymmetric hydrogenation in water as solvent

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Abstract

Coupling of the benzoylsulfonate moiety to chiral hydroxy phosphines by acylation with *o*-sulfobenzoic anhydride (SBA) affords unique ligands bearing one or two sulfonate groups in distinguished positions in the molecular framework. Rhodium complexes based on the new ligands have been proven in the asymmetric hydrogenation of functionalized chelating olefins in methanol and in water. Results observed are compared to those featured by the corresponding non-sulfonated catalysts. In methanol as solvent only one of the complexes bearing a sulfonate group in a flexible ligand differed significantly from its parent complex, while in water all sulfonated complexes were superior. In the most cases, addition of the amphiphile sodium dodecylsulfate (SDS) improved the catalytic performance of the parent catalysts as well as that of the sulfonated complexes in water. Other ionic additives (e.g., Na_2SO_4, camphersulfonate, benzenesulfonate) which do not bear the long alkyl chain gave poor results illustrating the importance of the particular structure of SDS.

Keywords: Water soluble catalysts; Phosphine; Asymmetric hydrogenation; Rhodium complexes; Amphiphile

1. Introduction

Homogeneously catalyzed asymmetric reactions in water or aqueous biphasic systems represent a rapidly growing field due to its industrial potential and academic challenge [1–3]. Applying water soluble metal complexes the separation of the catalyst from the products can be simply carried out by phase separation. Less water-soluble catalysts act in the organic phase and can be subsequently recovered by extraction with water. In general, the vast majority of known chiral catalysts feature low solubility in water. Several concepts have been developed to enhance mutual solubility of catalysts and substrates in water or across the phase boundary of an aqueous biphasic system [4–6]. Herein, we will consider and compare two of them, e.g., the reaction in the presence of anionic amphiphiles and

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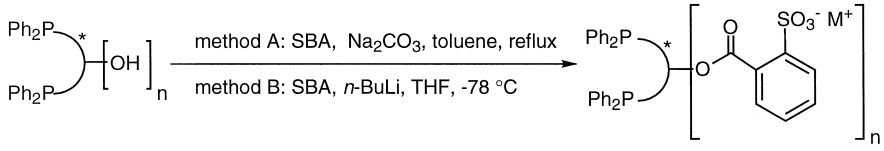
the catalysis with chiral sulfonated complexes. The special aim of this contribution is to show differences and similarities between these both approaches.

In a series of papers Oehme and co-workers [7–10] investigated the influence of organized anionic surfactant media built up, e.g., by sodium dodecyl sulfate (SDS) upon the rhodium catalyzed asymmetric hydrogenation of chelating enamides. In comparison to the reaction in blank water striking improvement of reactivity and selectivity was observed. The authors explained these effects by the assumption of the formation of micelles, since the salient catalytic effects were dependent upon the chain length. In the case of the amphiphilic zwitterionic sulfobetains they were only observable beyond their critical micelle concentration (cmc) [11]. It was argued that micellar associates act as 'microreactors' [12] and adjust thus the catalyst-substrate orientation or distinguished conformations of the chirality inducing catalyst similar as featured in organic solvents.

Buriak and Osborn [13] also observed an enhancement of the enantioselectivity in the rhodium catalyzed hydrogenation of monodentate imines in benzene in the presence of reversed micelles. However, they found that even non-surfactant sulfonates induced comparable effects provided the corresponding cation was encapsulated by water, crown-ethers or other ether units. Spectroscopic studies of the catalytically active Rh-species in benzene revealed that the sulfonate anion was bound to the metal. In comparison to blank experiments improved chemical yield, but constant enantioselectivity was reported by Takaya and co-workers in the ruthenium-catalyzed transfer hydrogenation in polar (aprotic) as well as in non-polar solvents containing equimolar amounts of catalyst and SDS [14]. Based on these results both research groups concluded the dominance of a salt effect based on a more or less strong coordination of the ionic moiety to the metal and denied that—at least in the solvents considered—micellar structures are operative. However, this rationalization got no support by results derived from the asymmetric hydrogenation with hydroxy phosphinite-Rh complexes in water in the presence of ionic amphiphiles [15]. Remarkable enhanced reactivity and selectivity were observed only under the influence of amphiphilic additives carrying longer alkyl chains.

In response to these observations, we wish to contribute our results with a series of chiral sulfonated phosphine rhodium complexes which may have relevance to this discussion. The new ligands were derived from the acylation of chiral hydroxy phosphines **1** with *o*-sulfobenzoic anhydride (SBA) (Eq. (1)) [16]. This soft methodology proliferates a variety of uniform enantiopure sulfonated phosphines **3** and allows—provided a suitably placed hydoxy group is available—the placement of the sulfonate unit in any part of the chiral ligand.



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Due to the remote position of the ionic functionality in the corresponding metal complexes, electronic or steric influences upon the catalytically active metal mediated by the phosphine can be excluded. In addition, intramolecular interactions between sulfonate and metal can be allowed or prevented by an appropriate placement of the sulfonate group. For comparison, ligands of the same basic structure but without sulfonate group were prepared. The new complexes were tested in the asymmetric hydrogenation of functionalized olefins in methanol as well as in water. The addition of SDS to the reaction allowed the assessment of the effect caused by the internal or external ionic functionality.

2. Experimental

All reactions and measurements were conducted under argon by using standard Schlenk techniques. All solvents were dried and distilled under argon. The hydroxy phosphines serving as precursors for the synthesis of benzoylated and sulfobenzoylated ligands were prepared according to previously described procedures [17–19].

2.1. Reagents and instrumentations

Thin-layer chromatography: precoated TLC plates (silica gel 60 F_{254}, Merck). Flash chromatography: Silica gel 60 (0.040–0.063 mm, Merck). Melting points are corrected. Optical rotations: 'Gyromat-HP' (Firma Dr. Kernchen). IR: Nicolet Magna—IR 550 instrument. NMR: Bruker ARX 400, at 303 K [400.13 MHz (^{1}H), 100.63 MHz (^{13}C) and 161.98 MHz (^{31}P) with TMS as internal or with H_3PO_4 as external standard]. The key to the NMR data is: s, singlet; d, doublet; t, triplet. MS: AMD 402 (Firma Intectra), at an ionization voltage 70 eV. CH analysis: LECO CHNS-932.

2.2. Ligands

*2.2.1. Benzoylated ligands **2a–d** (parent ligands)*

General procedure for the reaction of benzoyl chloride with hydroxy phosphines **1a–d**: To the appropriate hydroxy phosphine (0.29 mmol) dissolved in 5 ml of THF, NEt_3 (0.31 mmol) was added. The solution was cooled to 0°C and then benzoyl chloride (35 μl, 0.3 mmol) was dropped via a syringe. After stirring over-night the mixture was slowly warmed up at ambient temperature. After the removal of solvent under reduced pressure, the residue was purified by flash-chromatography (eluent: *n*-hexane/ethyl acetate = 2:1).

*2.2.1.1. (2S)-O-Benzoyl-1,4-bis(diphenylphosphino)butane-2-ol (**2a**).* Yield: 81%. Anal. Calc. for $C_{35}H_{32}O_2P_2$ (546.59): calc. C 76.91, H 5.90, P 11.33; found: C 76.24, H 5.81, P 11.51; ^{1}H NMR ($CDCl_3$) δ 7.78–7.12 (25H, arom.), 5.31 (m, 1H, OCH), 2.59–2.27 (m, 2H, CH_2), 1.96 (m, 4H, CH_2); ^{13}C NMR ($CDCl_3$) δ 166.4 (C=O), 138.7–128.7 (arom.), 74.2 (dd, J = 17.6, 14.4 Hz, HCO), 34.2 (d, J = 16.2 Hz, CH_2), 32.0 (dd, J = 17.2, 8.6 Hz, CH_2), 23.9 (d, J = 12.4 Hz, CH_2); ^{31}P NMR ($CDCl_3$) δ: −15.4, −22.8; IR (Nujol) 1746 cm^{-1} (C=O); MS m/z 547 (M^+ + H).

*2.2.1.2. (2R,3R)-Di-O-benzoyl-1,4-bis(diphenylphosphino)butane-2,3-diol (**2b**).* Analogously as described in the general procedure, but using the double amount of NEt_3 and benzoyl chloride. Yield: 82%. Anal. Calc. for $C_{42}H_{36}O_4P_2$ (666.69): calc. C 75.67, H 5.44, P 9.29; found: C 75.52, H 5.47, P 9.17; ^{1}H NMR ($CDCl_3$) δ 7.77–7.19 (30H, arom.), 4.95 (m, 2H, HCO), 2.42 (m, 4H, CH_2P); ^{13}C NMR ($CDCl_3$) δ 165.7 (C=O), 135.9–126.7 (arom.), 74.2 (dd, J = 15.3, 13.2 Hz, HCO), 34.4 (d, J = 15.2 Hz, CH_2P); ^{31}P NMR ($CDCl_3$) δ: −23.1; IR (Nujol) 1746, 1729 cm^{-1} (C=O); MS m/z 667 (M^+ + H).

*2.2.1.3. (4R,5R)-2-(2′-Benzoyloxyphenyl)-4,5-bis(diphenylphosphinomethylen)-1,3-dioxolane (**2c**).* Yield: 92%. Anal. Calc. for $C_{42}H_{36}O_4P_2$ (666.69): calc. C 75.67, H 5.44, P 9.29; found: C 75.52, H 5.36, P 9.50; ^{1}H NMR ($CDCl_3$) δ 7.61–7.15 (29H, arom.), 6.10 (s, 1H, HCO_2), 4.03 (m, 2H, HCO), 2.33 (m, 4H, CH_2P); ^{13}C NMR ($CDCl_3$) δ 164.8 (C=O), 138.2–122.8 (arom.), 99.2 (HCO_2), 81.3 (dd, J = 17.1, 7.6 Hz, HCO), 79.8 (dd, J = 16.2, 7.6 Hz, HCO), 32.4 (J = 19.1, 1.9 Hz, CH_2P), 31.2 (J = 15.3, 1.9 Hz, CH_2P); ^{31}P NMR ($CDCl_3$) δ: −22.4, −24.2; IR (Nujol) 1728 cm^{-1} (C=O); MS m/z 667 (M^+ + H).

*2.2.1.4. (4R,5R)-2-(4′-Benzoyloxyphenyl)-4,5-bis(diphenylphosphinomethylen)-1,3-dioxolane (**2d**).* Yield: 77%. Anal. Calc. for $C_{42}H_{36}O_4P_2$ (666.69): calc. C 75.67, H 5.44, P 9.29; found: C 75.31, H 5.49, P 9.09; ^{1}H NMR ($CDCl_3$) δ 8.11–7.03 (29H, arom.), 5.93 (s, 1H, HCO_2), 4.18 (m, 2H, HCO), 2.65–2.51 (m, 4H, CH_2P); ^{13}C NMR ($CDCl_3$) δ 166.7 (C=O), 135.4–122.1 (arom.), 98.7 (HCO_2), 80.5 (dd, $J = 17.3$, 7.4 Hz, HCO), 79.1 (dd, $J = 17.3$, 7.6 Hz, HCO), 32.7 (dd, $J = 16.5$, 2.5 Hz, CH_2P), 32.4 (dd, $J = 16.2$, 2.6 Hz, CH_2P); ^{31}P NMR (D_8-THF) δ: −20.7, −21.5; IR (Nujol) 1739 cm^{-1} (C=O); MS m/z 667 ($M^+ + H$).

2.2.2. Sulfobenzoylated ligands **3a–d**

*2.2.2.1. Conformationally flexible ligands **3a**,**b**.* General procedure for the reaction of *o*-sulfonylbenzoic anhydride (SBA) with hydroxy phosphines **1a**,**b** in the presence of Na_2CO_3: The appropriate hydroxy phosphine (0.5 mmol) dissolved in 15 ml of toluene was stirred together with Na_2CO_3 (87.5 mg, 0.825 mmol) for ca. 30 min at room temperature. In another flask *o*-sulfonylbenzoic anhydride (100 mg, 0.55 mmol) in 10 ml of toluene was dispersed by means of ultrasonic treatment. The dispersion formed in turn was added via a syringe to the solution of the hydroxy phosphine. The mixture was heated under reflux until all starting hydroxy phosphine had disappeared. The reaction could be advantageously followed by tlc (eluent: *n*-hexane/ethyl acetate = 2:1) where the newly formed sulfonate remained on the start (R_f value of hydroxy phosphines: ca. 0.35). After completion of the reaction toluene was distilled off under reduced pressure. The residue was washed several times with CH_2Cl_2.

*Sodium (2′S)-2-[1′,4′-bis(diphenylphosphino)butane-2′-yloxycarbonyl]benzenesulfonate (**3a**).* Yield: 87%. Anal. Calc. for $C_{35}H_{31}O_5P_2SNa$ (648.63): calc. C 64.81, H 4.82, P 9.55; found: C 65.02, H 4.78, P 9.71; ^{1}H NMR ($CDCl_3$) δ 7.88–6.85 (24H, arom.), 5.09 (m, 1H, HCO), 2.48–2.13 (m, 4H, CH_2), 1.81 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 169.2 (C=O), 142.9 (C-SO_3), 131.8–127.8 (arom.), 74.4 (t, $J = 14.6$ Hz, HCO), 33.7 (d, $J = 18.4$ Hz, CH_2), 31.7 (dd, $J = 16.8$, 8.6 Hz, CH_2), 22.3 (d, $J = 12.6$ Hz, CH_2); ^{31}P NMR (D_8-THF) δ: −15.6, −23.2; IR (Nujol) 1747 cm^{-1} (C=O); MS m/z 625 (M^+–Na).

*Sodium (2′R,3′R)-2-[1′,4′-bis(diphenylphosphino)-3′-(2-sodiumsulfonylbenzoyloxy)-butane-2′-yloxycarbonyl]benzenesulfonate (**3b**).* Analogously as described in the general procedure, but using the double amounts of SBA and Na_2CO_3. Yield: 92%. Anal. Calc. for $C_{42}H_{34}O_{10}P_2S_2Na_2$ (870.77): calc. C 57.93, H 3.94, P 7.11; found: C 58.11, H 4.07, P 7.03; ^{1}H NMR (CD_3OD) δ 8.03–7.16 (28H, arom.), 5.72 (m, 2H, HCO), 2.98 (ddd, $J = 14.0$, 7.8, 1.2 Hz, 2H, $CH_{2a}P$), 2.64 (dd, $J = 14.0$, 5.9 Hz, 2H, $CH_{2b}P$); ^{13}C NMR (CD_3OD) δ 163.4 (C=O), 144.2 (C-SO_3), 139.9–128.9 (arom.), 74.7 (dd, $J = 18.1$, 8.6 Hz, HCO), 29.8 (d, $J = 14.3$ Hz, CH_2P); ^{31}P NMR (CD_3OD) δ: −22.0; IR (Nujol) 1773 cm^{-1} (C=O).

*2.2.2.2. Conformationally rigid ligands **3c**,**d**.* General procedure for the reaction of *o*-sulfonylbenzoic anhydride (SBA) with hydroxy phosphines **1c**,**d** in the presence of *n*-BuLi: To the appropriate hydroxy phosphine (200 mg, 0.36 mmol) dissolved in 4 ml of tetrahydrofurane was added at −78°C a 2.5 M solution of *n*-BuLi (144 ml, 0.36 mmol) in *n*-hexane. In another flask *o*-sulfonylbenzoic anhydride (66 mg, 0.36 mmol) was dissolved in 3 ml of tetrahydrofurane. Then the SBA-solution was added at −78°C to the hydroxy phosphine and the mixture allowed slowly to warm up at room

temperature. Then the volatiles were removed under reduced pressure until approximately 2–3 ml of toluene remained. By addition of the five-fold amount of diethyl ether the sulfonated phosphine precipitated. Filtration afforded the new ligand in a quantitative yield.

*Lithium 2-{(4″R,5″R)-2′-[4″,5″-bis(diphenylphosphinomethylen)-1″,3″-dioxolane-2″-yl]-2′-(phenoxy-carbonyl)]}-benzenesulfonate (**3c**)*. Anal. Calc. for $C_{42}H_{35}O_7P_2SLi$ (752.68): calc. C 67.02, H 4.69, P 8.23; found: C 66.64, H 4.62, P 8.31; ^{1}H NMR ($CDCl_3$) δ 7.76–6.86 (28H, arom.), 5.84 (s, 1H, HCO_2), 3.91 (m, 2H, HCO), 2.45–2.29 (m, 4H, CH_2P); ^{13}C NMR ($CDCl_3$) δ 166.3 (C=O), 148.5 (C-SO_3), 135.6–122.1 (arom.), 98.8 (HCO_2), 80.7 (dd, $J = 16.2$, 7.6 Hz, HCO), 79.3 (dd, $J = 17.3$, 7.6 Hz, HCO), 33.1 (dd, $J = 15.6$, 1.9 Hz, CH_2P), 32.7 (dd, $J = 16.2$, 2.0 Hz, CH_2P); ^{31}P NMR (D_6-DMSO) δ: −23.0, −23.9; IR (Nujol) 1747 cm^{-1} (C=O); MS m/z 745 (M^+–Li).

*Lithium 2-{(4″R,5″R)-4′-[4″,5″-bis(diphenylphosphinomethylen)-1″,3″-dioxolane-2″-yl]-4′-(phenoxy-carbonyl)]}-benzenesulfonate (**3d**)*. Anal. Calc. for $C_{42}H_{35}O_7P_2SLi$ (752.68): calc. C 67.02, H 4.69, P 8.23; found: C 67.15, H 4.58, P 8.31; ^{1}H NMR (D_8-THF) δ 7.98–6.94 (m, 28H, arom.), 5.79 (s, 1H, HCO_2), 4.02 (m, 2H, HCO), 2.51–2.32 (m, 4H, CH_2P); ^{13}C NMR (D_8-THF) δ 168.0 (C=O), 144.6 (C-SO_3), 135.0–123.8 (arom.), 98.1 (HCO_2), 80.2 (dd, $J = 17.1$, 7.6 Hz, HCO), 78.6 (dd, $J = 17.3$, 7.6 Hz, HCO), 33.4 (dd, $J = 16.4$, 1.8 Hz, CH_2P), 33.1 (dd, $J = 16.7$, 1.8 Hz, CH_2P); ^{31}P NMR (D_8-THF) δ: −20.3, −21.2; IR (Nujol) 1742 cm^{-1} (C=O); MS m/z 745 (M^+–Li).

2.3. Rhodium complexes

2.3.1. General procedure for the preparation of the complexes

The diphosphine (0.262 mmol) and $[Rh(COD)_2]BF_4$ (106 mg, 0.262 mmol) were stirred in THF (2 ml) at ambient temperature for 1.5 h. After the addition of diethyl ether (8 ml) a precipitate yielded which was filtered off and washed with a small quantity of diethyl ether to give the complexes as yellow-orange powders.

*2.3.1.1. [Rh(**2a**)COD]BF_4*. Anal. Calc. for $C_{43}H_{44}O_2P_2RhBF_4$ (844.48): calc. C 61.16, H 5.25, P 7.34, Rh 12.19; found: C 60.12, H 5.20, P 7.75, Rh 11.79; ^{1}H NMR (CD_3OD) δ 8.01–7.22 (m, 25H, arom.), 5.26 (s, 1H, CH), 4.90 (m, 2H, CH), 4.26 (m, 2H, CH), 2.62 (m, 2H, CH_2), 2.31–1.80 (m, 12H, CH_2); ^{13}C NMR (CD_3OD) δ 166.8 (C=O), 132.3–121.9 (arom.), 104.1, 97.7, 73.4 (d, $J = 22.1$ Hz) (CH), 33.1 (d, $J = 28.0$ Hz), 32.8, 31.4, 27.6 (d, $J = 26.7$ Hz) (CH_2); ^{31}P NMR (D_8-THF) δ: 15.2. (dd, $J_{Rh-P} = 145.8$ Hz, $J_{P-P} = 38.9$ Hz), 29.3 (dd, $J_{Rh-P} = 144.2$ Hz); IR (Nujol) 1715 cm^{-1} (C=O); MS m/z 757 (M^+–BF_4).

*2.3.1.2. [Rh(**2b**)COD]BF_4*. Anal. Calc. for $C_{50}H_{48}O_4P_2RhBF_4$, (964.59): calc. C 62.26, H 5.02, P 6.42, Rh 10.67; found: C 61.83, H 5.09, P 6.16, Rh 10.23; ^{1}H NMR ($CDCl_3$) δ 8.17–7.23 (m, 30H, arom.), 5.75 (m, 2H, HCO), 5.10 (m, 2H, HC), 4.49 (m, 2H, HC), 2.76–2.59 (m, 7H, CH_2), 2.38 (m, 5H, CH_2); ^{13}C NMR ($CDCl_3$) δ 165.9 (C=O), 134.9–128.4 (arom.), 103.2 (HCO_2), 101.9 (CH), 72.8 (CH), 31.9, 28.5 (CH_2); ^{31}P NMR (CD_3OD) δ: 19.9 (d, $J_{Rh-P} = 147.4$ Hz); IR (Nujol) 1718 cm^{-1} (C=O); MS m/z 877 (M^+–BF_4).

*2.3.1.3. [Rh(**2c**)COD]BF_4*. Anal. Calc. for $C_{50}H_{48}O_4P_2RhBF_4$ (964.59): calc. C 62.26, H 5.02, P 6.42, Rh 10.67; found: C 61.75, H 4.97, P 6.30, Rh 9.99; ^{1}H NMR ($CDCl_3$) δ 8.02–6.81 (m, 29H, arom.),

5.72 (s, 1H, CH), 4.53–4.19 (m, 4H, CH), 3.91 (m, 1H, CH), 3.85 (m, 1H, CH), 3.12 (m, 2H, CH_2), 2.63 (m, 2H, CH_2), 2.43–2.03 (m, 8H, CH_2); ^{13}C NMR ($CDCl_3$) δ 165.7 (C=O), 138.4–127.2 (arom.), 105.2, 103.5, 101.7, 99.9, 78.5 (d, $J = 8.1$ Hz), 76.2 (d, $J = 8.0$ Hz) (CH), 33.2, 31.8, 28.5 (CH_2); ^{31}P NMR (D_8-THF) δ: 14.5 (dd, $J_{Rh-P} = 134.5$ Hz, $J_{P-P} = 35.6$ Hz), 15.4 (dd, $J_{Rh-P} = 139.3$ Hz); IR (Nujol) 1734 cm^{-1} (C=O); MS m/z 877 (M^+–BF_4).

*2.3.1.4. [Rh(**2d**)COD]BF_4*. Anal. Calc. for $C_{50}H_{48}O_4P_2RhBF_4$ (964.59): calc. C 62.26, H 5.02, P 6.42, Rh 10.7; found: C 62.31, H 4.93, P 6.31, Rh 10.34; ^1H NMR (D_8-THF) δ 8.02–6.89 (29H, arom.), 5.52 (s, 1H, CH), 4.46–4.19 (m, 4H, (CH)), 3.46 (m, 2H, (CH)), 3.28 (m, 1H, CH_2), 2.81 (m, 2H, CH_2), 2.46 (m, 1H, CH_2), 2.33–2.05 (m, 8H, CH_2); ^{13}C NMR (D_8-THF) δ 166.4 (C=O), 138.3–123.5 (arom.), 105.2, 104.1, 101.9, 101.6, 81.2, 79.8 (CH), 32.9, 32.7, 31.8, 30.1 (CH_2); ^{31}P NMR (D_8-THF) δ: 14.9 (dd, $J_{Rh-P} = 144.8$ Hz, $J_{P-P} = 35.6$ Hz), 15.8 (dd, $J_{Rh-P} = 144.2$ Hz); IR (Nujol) 1733 cm^{-1} (C=O); MS m/z 877 (M^+–BF_4).

*2.3.1.5. [Rh(**3a**)COD]BF_4*. Anal. Calc. for $C_{43}H_{43}NaO_5BF_4RhP_2S$ (946.52): calc. C 54.57, H 4.58, P 6.54, Rh 10.87; found: C 53.62, H 4.47, P 6.16, Rh 10.46; ^1H NMR ($CDCl_3$) δ 7.92–6.93 (m, 24H, arom.), 5.51 (m, 1H, CH), 4.79 (m, 2H, (CH), 4.30 (m, 2H, CH), 2.75 (m, 2H, CH_2), 2.51–1.88 (m, 12H, CH_2); ^{13}C NMR ($CDCl_3$) δ 169.0 (C=O), 143.1 (C-SO_3), 136.1–127.7 (arom.), 101.4, 99.7, 67.8 (d, $J = 19.2$ Hz) (CH), 33.2 (d, $J = 25.9$ Hz), 31.4, 30.1, 29.3, 25.4 (d, $J = 25.9$ Hz) (CH_2); ^{31}P NMR (D_8-THF) δ: 18.4 (dd, $J_{Rh-P} = 145.8$ Hz, $J_{P-P} = 37.3$ Hz), 21.5 (dd, J_{Rh-P} 144.2 Hz); IR (Nujol) 1727 cm^{-1} (C=O); MS m/z 859 (M^+–BF_4).

*2.3.1.6. [Rh(**3b**)COD]BF_4*. Anal. Calc. for $C_{50}H_{46}O_{10}P_2S_2Na_2BF_4Rh$ (1168.67): calc. C 51.39, H 3.97, P 5.30, Rh 8.81; found: C 50.99, H 3.86, P 4.92, Rh 9.23; ^1H NMR (CD_3OD) δ 7.99–6.85 (m, 28H, arom.), 5.48 (m, 2H, CH), 4.81 (m, 1H, CH), 4.19 (m, 1H, CH), 3.98 (m, 1H, CH), 3.92 (m, 1H, CH), 3.43–2.85 (m, 4H, CH_2), 2.50–1.83 (m, 8H, CH_2); ^{13}C NMR (CD_3OD) δ 168.8 (C=O), 143.9 (C-SO_3), 135.2–127.8 (arom.), 102.6, 78.0 (d, $J = 15.2$ Hz), 74.3 (CH), 32.9, 31.1 (d, $J = 9.5$ Hz), 29.3 (CH_2); ^{31}P (CD_3OD) δ: 16.8 (d, $J_{Rh-P} = 144.3$ Hz); IR (Nujol) 1734 cm^{-1} (C=O).

*2.3.1.7. [Rh(**3c**)COD]BF_4*. Anal. Calc. for $C_{50}H_{47}O_7SP_2RhLiBF_4$ (1050.58): calc. C 57.16, H 4.51, P 5.90, Rh 9.80; found: C 56.79, H 4.48, P 6.06, Rh 9.32; ^1H NMR (CD_3OD) δ 7.91–7.11 (m, 28H, arom.), 5.52 (s, 1H, CH), 4.53–4.27 (m, 4H, CH), 4.02 (m, 1H, CH), 3.84 (m, 2H, CH and CH_2), 2.90 (m, 2H, CH_2), 2.49 (m, 2H, CH_2), 2.31–1.96 (m, 7H, CH_2); ^{13}C NMR (CD_3OD) δ 167.2 (C=O), 149.1 (C-SO_3), 133.8–126.4 (arom.), 102.1, 100.8, 98.5, 79.4 (d, $J = 8.0$ Hz), 77.9 (d, $J = 8.0$ Hz) (CH), 34.1, 33.5, 28.6, 25.5 (CH_2); ^{31}P NMR (D_8-THF) δ: 12.4 (dd, $J_{Rh-P} = 144.2$ Hz, $J_{P-P} = 35.6$ Hz), 13.9 (dd, $J_{Rh-P} = 142.6$ Hz); IR (Nujol) 1732 cm^{-1} (C=O); MS m/z 963 (M^+–BF_4).

*2.3.1.8. [Rh(**3d**)COD]BF_4*. Anal. Calc. for $C_{50}H_{47}O_7SP_2RhLiBF_4$ (1050.58): calc. C 57.16, H 4.51, P 5.90, Rh 9.80; found: C 55.39, H 4.39, P 6.23, Rh 9.59; ^1H NMR (CD_3OD) δ 8.09–7.21 (28H, arom.), 5.41 (s, 1H, CH), 4.52–4.22 (m, 4H, CH), 3.43 (m, 2H, CH), 3.22 (m, 1H, CH_2), 2.70 (m, 2H, CH_2), 2.60 (m, 1H, CH_2), 2.41–2.09 (m, 8H, CH_2); ^{13}C NMR (CD_3OD) δ 167.2 (C=O), 152.4 (C-SO_3), 134.8–127.8, 121.9 (arom.), 104.6, 103.9, 98.7, 97.2, 77.9, 76.3 (CH), 32.4, 31.3, 25.5 (CH_2); ^{31}P NMR (D_6-acetone) δ: 12.7 (dd, $J_{Rh-P} = 144.2$ Hz, $J_{P-P} = 35.6$ Hz), 13.6 (dd, $J_{Rh-P} =$ 142.6 Hz); IR (Nujol) 1734 cm^{-1} (C=O); MS m/z 963 (M^+–BF_4).

2.4. General procedure for hydrogenation reactions

The experiments have been carried out under normal pressure and isobaric conditions (1.0 atm overall pressure over the solution). The experiments were carried out under standard conditions with 0.01 mmol of precatalyst, 1.0 mmol of prochiral olefin in 15 ml of solvent at 25°C.

3. Results and discussion

3.1. Ligand synthesis

As mentioned in Section 1, acylation of chiral hydroxy phosphines (available in a large variety [20] with *o*-sulfobenzoic anhydride (SBA)), is a smooth and selective method for the preparation of sulfonated phosphines. For our investigations presented here as chiral hydroxy phosphines the conformationally flexible 1,4-bis(diphenylphosphino)butanols **1a** [17] and **1b** [18] have been chosen (Fig. 1). The acylation proceeded with SBA in the presence of sodium carbonate as a base in toluene to afford sulfonated phosphines **3a** and **3b** with good or excellent yield. Unfortunately, this methods failed in case of the HO-derivatives of DIOP **1c**,**d** [19]. For the latter, we succeeded in the acylation at low temperatures with *n*-BuLi as the base which gave rise to the ligands **3c** and **3d**. The corresponding benzoylated ligands **2a**–**d** required for comparison were easily obtained by esterifaction of the hydroxy phosphines with benzoyl choride in THF and triethylamine.

3.2. Preparation of the precatalysts and asymmetric hydrogenations

Precatalysts of the type $[Rh(COD)(P–P)]BF_4$ were produced by the reaction of the isolated ligands with $[Rh(COD)_2]BF_4$ in THF. The chiral complexes were precipitated with ether. With the exception of the precatalyst bearing two sulfonate groups ($[Rh(COD)(\mathbf{3b})]BF_4$) all other complexes were only sparingly soluble in water. In general, the ^{31}P NMR data of the new complexes were in close

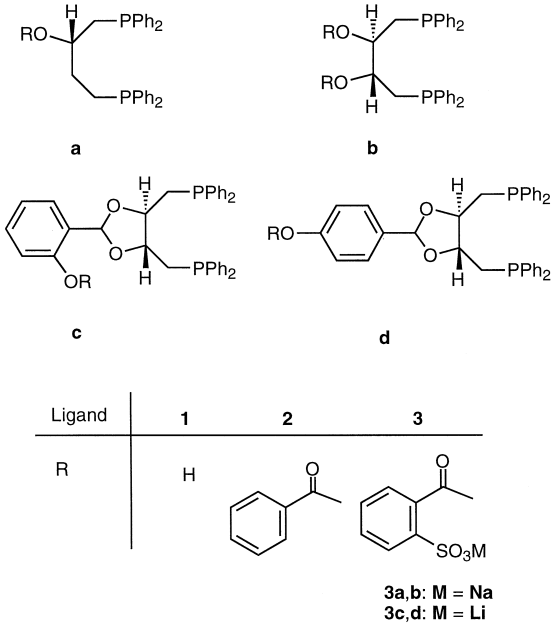

Fig. 1. Benzoylated (**2a**–**d**) and sulfonatobenzoylated (**3a**–**d**) ligands obtained by acylation of hydroxy phosphines **1a**–**d**.

agreement to those reported with other diphosphine Rh(I)-complexes bearing COD as ancillary ligand. Differences between sulfonated complexes and parent complexes could not be found, even not at low temperatures.

In order to assess the efficiency of the new catalysts in the asymmetric catalysis the chelating enamides methyl (*Z*)-α-acetamidocinnamate (AMe), (*Z*)-α-acetamidocinnamic acid (AH), methyl α-acetamidoacrylate (aMe) and α-acetamidoacrylic acid (aH) were hydrogenated at normal pressure at room temperature. The results obtained in methanol are displayed in Table 1.

For all catalysts a very fast reaction was observed. It is especially remarkable for catalysts bearing a conformationally flexible ligand, since the complexes based on the corresponding hydroxy phosphine precursors performed rather sluggish [17,18]. In several instances, half-times were shorter than 2 min. That means, they are in a range where the generation of the catalyst from the precatalyst and the diffusion of the hydrogen to the catalyst, respectively, become decisive [21]. Therefore, the specification of exact times to characterize the activity of the catalyst is without relevance.

The comparison of the enantioselectivities observed with sulfonated and parent catalysts shows some interesting features. Thus, with the remarkable exception of the complex based on the flexible ligand **3a,** all other sulfonatobenzoylated catalysts did not substantially differ from their benzoylated counterparts. It is noteworthy, that the addition of sodium benzenesulfonate to the reaction of the benzoyl complex [Rh(COD)(**2a**)]BF_4 did not increase the enantioselectivity to that level obtained with [Rh(COD)(**3a**)]BF_4. These observations indicate an intramolecular effect caused by the sulfonatobenzoyl group. We assume that with **3a** as ligand a directed interaction of the sulfonate unit and rhodium takes place. Interactions of this type may reversibly operate within the intra- or intermolecular conversion of the diastereomeric substrate complexes or may favorize the formation of selectivity determining intermediates. Such 'arm-off arm-on mechanism' effecting the outcome of the asymmetric hydrogenation has been suggested for alkylether groups [22] and is also assumed for sulfonate groups [23]. Obviously, in the complex based on **3b** the second sulfonate group suspends the effect of the first. In the rigid complexes derived from **3c** and **3d** where intramolecular interactions between the remote sulfonyl group and the metal are not favourized the influence of the anionic group is small. The superiority of mono-sulfonated catalysts in comparison to di- or higher sulfonated species in a

Table 1
Asymmetric hydrogenation in MeOH[a]

Ligand	AMe		AH		aMe		aH	
	$t_{1/2}$ [min]	*ee* [%][b]	$t_{1/2}$ [min]	*ee* [%][b]	$t_{1/2}$ [min]	*ee* [%][b]	$t_{1/2}$ [min]	*ee* [%][b]
2a	2.4	29.3[c]	< 2	38.8[c]	< 2	32.3[c]	< 2	39.4[c]
2a[d]	2.2	30.0[c]	< 2	37.0[c]	< 2	32.4[c]	< 2	39.6[c]
3a	2.4	43.9[c]	< 2	54.5[c]	< 2	52.8[c]	< 2	57.2[c]
2b	3.6	30.2	3.9	21.4	< 2	31.3	< 2	23.2
3b	4.6	31.3	3.5	16.6	< 2	35.2	< 2	20.9
2c	< 2	72.8	< 2	79.0	< 2	66.0	< 2	71.5
3c	< 2	71.6	< 2	78.2	< 2	63.5	< 2	70.3
2d	< 2	68.3	< 2	78.9	< 2	62.1	< 2	74.1
3d	< 2	70.5	< 2	79.4	< 2	61.5	< 2	71.9

[a]Reaction conditions: 0.1 MPa H_2; 15 ml MeOH, 1 mmol substrate; 0.01 mmol precatalyst.
[b]If not otherwise stated (*R*)-configurated product was formed. The enantiomeric excess was determined by GC on chiral phases. The hydrogenation products of AH and aH were esterified with trimethylsilyl diazomethane or diazomethane before the GC-measurements. GC 5890 Series II; FID, Carrier gas: Ar: 1 ml/min. fused silica; 10 m, XE-60-L-valin-*tert*-butylamide; ID 0.2 mm; oven temperature: 150°C (methyl *N*-acetylphenylalaninate), 100°C (methyl *N*-acetylalaninate).
[c](*S*)-Configurated product yielded in accordance with the (*S*)-configuration of the ligand.
[d]Addition of 1 mmol $PhSO_3Na$.

range of different reactions in aqueous systems has been already noted by Amrani et al. [24], Lensink and co-workers [25,26] and Bakos et al. [27]. However, our results indicate that the position of the only sulfonate group may be also important.

The replacement of methanol by water as solvent changed dramatically the course of the asymmetric hydrogenation. Browsing the values listed in Table 2 several tendencies become discernible. Generally, in neat water with benzoyl catalysts all substrates were converted with disappointingly low rates. Unfortunately, AH was so slowly reduced that half-times could not be reached. Therefore these data are omitted from the table. In accordance to other investigations with complexes based on large Rh-chelates also we stated a serious loss of the enantioselectivity in comparison to the reaction in methanol [7,15,28–32]. In several cases products with the opposite configuration as observed in methanol were preferentially formed.

In all trials the introduction of the sulfonate group into the backbone of the complexes caused an remarkable acceleration of the reaction. With complexes based on rigid ligands **3c** and **3d** in comparison to the parent catalysts an enhancement of the enantioselectivity resulted. When precatalysts with flexible ligands **3a** and **3b** were applied a loss of selectivity or even a reversal of the configuration in the product took place. Obviously, these observations correspond to the fact, that the stereodifferentiating mechanism, which is operative in methanol became again more dominant.

It is remarkable, that the addition of SDS to the reaction with the parent complexes caused a similar effect. In a few examples with sulfonated complexes equal or even superior results were achieved compared to benzoyl catalysts in the presence of SDS.

Detailed investigations of the hydrogenation of AMe with [Rh(COD)(**2c**)]BF_4 showed that already equimolar amounts of precatalyst and SDS (0.01 mmol) in the aqueous reaction mixture decreased the half-time by orders of magnitudes ($t/2 = 22$ min) in comparison to the reaction in blank water ($t/2 = 520$ min). The gain in reactivity was accompanied by an enhancement of the enantioselectivity from 14.2 to 25.3%*ee*. With increasing concentration of the amphiphile (0.02–0.1 mmol) a continual increase up to 38.9%*ee* resulted. That means a single characteristic jump in the selectivity could not be found. The addition of more than 0.1 mmol SDS had no further effect. It is interesting to note, that the effects were observed long before the cmc of SDS in blank water was reached (8.1×10^{-3} mol/l [33]; this corresponds to 0.1215 mmol/15 ml). In contrast to the action of SDS, the presence of

Table 2
Asymmetric hydrogenation in H_2O[a]

Ligand	Benzoyl-ligands type **2**					MSO_3–benzoyl-ligands type **3**			
	Substrate	Without SDS		With 0.1 mmol SDS		Without SDS		With 0.1 mmol SDS	
		$t_{1/2}$ [min]	*ee* [%]	$t_{1/2}$ [min]	*ee* [%]	$t_{1/2}$ [min]	*ee* [%]	$t_{1/2}$ [min]	*ee* [%]
a	AMe	460	4.0 (*R*)	26	3.3 (*S*)	45	20.6 (*S*)	4	31.7 (*S*)
b	AMe	520	13.7 (*S*)	81	3.4 (*S*)	22	7.2 (*S*)	10	2.4 (*S*)
c	AMe	520	14.2 (*R*)	12	38.9 (*R*)	23	37.7 (*R*)	5	66.3 (*R*)
d	AMe	430	8.0 (*R*)	22	18.7 (*R*)	35	31.5 (*R*)	6	61.0 (*R*)
a	aMe	26	8.5 (*R*)	6	7.3 (*S*)	9	0	2	28.7 (*S*)
b	aMe	75	15.6 (*S*)	15	11.7 (*R*)	6	0	3	5.3 (*R*)
c	aMe	37	1.3 (*S*)	5	35.9 (*R*)	9	14.2 (*R*)	3	39.1 (*R*)
d	aMe	80	1.2 (*S*)	8	16.0 (*R*)	11	16.6 (*R*)	3	38.0 (*R*)
a	aH	69	0.7 (*S*)	6	5.2 (*S*)	15	9.8 (*S*)	4	31.1 (*S*)
b	aH	420	16.4 (*S*)	12	11.1 (*R*)	11	7.5 (*R*)	6	3.0 (*S*)
c	aH	117	9.7 (*R*)	9	41.3 (*R*)	16	16.3 (*R*)	2	54.4 (*R*)
d	aH	90	10.1 (*R*)	14	14.5 (*R*)	23	27.1 (*R*)	4	57.3 (*R*)

[a] Conditions and analytic features as described in Table 1.

different amounts of sodium benzenesulfonate (0.01–0.1 mmol) did not accelerate the reaction at all. In all runs pronounced agglutination took place and more than 8 h were required to reach the half-time. The selectivities were similarly low as found in blank water.

Surprisingly, the addition of SDS to the hydrogenation with mono-sulfonated catalysts still enforced the efficiency of the latter: That means the catalytically benign effects of the internal ionic moiety and that of the amphiphile are additive. In general, highest rates and enantioselectivities were obtained with complexes based on **3c** and **3d** in the presence of the amphiphile illustrating besides the effect of the internal sulfonate group the additional and well-known effect of a rigid backbone in the ligand. But, no example can be quoted where corresponding results in methanol as solvent were achieved. In contrast to the hydrogenation with mono-sulfonated complexes, the selectivity of the complex based on the di-sulfonated ligand **3b** decreased for the substrate AMe in the presence of SDS. This result is in accordance to findings of Hanson who observed a significant lowering of the %*ee* when a higher (tetra-) sulfonated phosphine Rh-complex in the presence of SDS was applied for the hydrogenation of AMe [34].

Fundamentally, the addition of salts increases the ionic strength of an aqueous solution. As a consequence the solubility of water-unsoluble catalysts and substrates in water is diminished resulting in a lowering of the reaction rate [35]. In order to proof if our sulfonated catalysts shows the characteristic property of surface active compounds [36] and if other ionic additives are capable to mimic the effect of the SDS an excess of Na_2SO_4 was added to the hydrogenation of AMe with catalysts based on sulfonated phosphine ligands **3a**–**c** (Table 3). In comparison to the reaction without additive in all trials (runs 2, 5 and 8) a serious loss of reactivity was observed. The enantioselectivity was only slightly affected. These results indicate that our sulfonated Rh-complexes are not able to form micelles. This conclusion gets support from the result observed with [Rh(COD)(**3c**)]BF_4 and sodium benzenesulfonate (run 9). It is interesting to note that no effect upon the stereoselectivity by the presence of a chiral anion could be observed, as to be seen in the reaction of [Rh(COD)(**3d**)]BF_4 with (−)- or (+)-camphersulfonate (run 13 and 14). Although the longest half-times in this series resulted, the %*ee* as well as the configuration of the hydrogenation product were the same.

Table 3
Effects of the addition of ionic additives to the hydrogenation of AMe in water[a,b]

Run	Precatalyst	Additive [mmol]	$t_{1/2}$ [min]	*ee* [%]
1	[Rh(COD)(**3a**)]BF_4	none	45	20.6 (*S*)
2	[Rh(COD)(**3a**)]BF_4	0.1 Na_2SO_4	109	19.4 (*S*)
3	[Rh(COD)(**3a**)]BF_4	0.1 SDS	4	31.7 (*S*)
4	[Rh(COD)(**3b**)]BF_4	none	22	7.2 (*S*)
5	[Rh(COD)(**3b**)]BF_4	0.1 Na_2SO_4	94	5.7 (*S*)
6	[Rh(COD)(**3b**)]BF_4	0.1 SDS	10	2.4 (*S*)
7	[Rh(COD)(**3c**)]BF_4	none	23	37.3 (*R*)
8	[Rh(COD)(**3c**)]BF_4	0.1 Na_2SO_4	43	32.3 (*R*)
9	[Rh(COD)(**3c**)]BF_4	0.1 $PhSO_3Na$	63	34.1 (*R*)
10	[Rh(COD)(**3c**)]BF_4	0.1 SDS	5	66.3 (*R*)
11	[Rh(COD)(**3c**)]BF_4	0.1 SDS + 0.1 $PhSO_3Na$	4	61.5 (*R*)
12	[Rh(COD)(**3d**)]BF_4	none	35	31.5 (*R*)
13	[Rh(COD)(**3d**)]BF_4	0.1 Na-(−)-Camphersulfonate	265	10.6 (*R*)
14	[Rh(COD)(**3d**)]BF_4	0.1 Li-(+)-Camphersulfonate	242	11.4 (*R*)
15	[Rh(COD)(**3d**)]BF_4	0.1 SDS	6	61.0 (*R*)

[a] For comparison some values from Table 2 are added also to the list.
[b] Conditions and analytic features as described in Table 1.

Table 4
Asymmetric hydrogenation of AMe with [Rh(COD)(**3b**)]BF_4 in an aqueous two phase-system[a]

Solvents	$t_{1/2}$ [min]	*ee* [%]
Water	22	7.2 (*S*)
Ethyl acetate	270	24.2 (*R*)
Water/Ethyl acetate (1/1)	26	22.1 (*R*)

[a]Conditions and analytic features as described in Table 1.

In sum, our results clearly illustrate that in water the aforementioned ionic additives are not able to mimic the effect of the SDS (runs 3, 6, 10 and 15). In all cases inferior reaction rates and with the exclusion of the disulfonated complex [Rh(COD)(**3c**)]BF_4 diminished selectivities were observed with non-surfactants. These results are in strong contrast to those found in non-aqueous solvents with monodentate substrates by Buriak and Osborn [13] although the importance of the long alkyl chain of SDS was already noted by Nozaki et al. [14]. Of particular interest is the observation that SDS can counterbalance the negative effect on the reactivity excerted by the other ionic additives (e.g., sodium benzenesulfonate, run 11).

Finally, the only water-soluble complex in our series the precatalyst [Rh(COD)(**3b)**]BF_4 was investigated in the hydrogenation of AMe in ethyl acetate as well as in the two-phase system H_2O/ethyl acetate (Table 4). Similar as discussed for the reaction in methanol by the switch from water to the pure organic solvent a change of the configuration of the hydrogenation was observed. Obviously, the long half-time in ethyl acetate is caused by the poor solubility of [Rh(COD)(**3b)**]BF_4. Addition of water speeded up the reaction comparable to the half-time observed in water. It is interesting to note, that the enantioselectivity observed reached the value as found in pure ethyl acetate. This experiment illustrates nicely that the catalytically active metal is held close to the interface where the asymmetric hydrogenation proceeds, while the hydrophilic unit constituted by the sulfonate groups is localized in the aqueous phase.

4. Conclusions

A smooth and convenient method for the incorporation of sulfonate groups in chiral phosphine ligands by acylation of chiral hydroxy phosphines with *o*-sulfobenzoic anhydride is described in detail. In the subsequent asymmetric hydrogenation with Rh-complexes in methanol only the complex based on the flexible mono-sulfonatobenzoyl ligand gave higher selectivities in comparison to the corresponding benzoyl complex, whereas the other sulfonatobenzoylated complexes did not differ from their benzoylated counterparts. In contrast, in the hydrogenation in water as solvent without exception the sulfonate complexes are much more active than their parent complexes. With catalysts bearing only one sulfonate group hydrogenation products with the same sense of chirality as preferentially observed in methanol were obtained. By addition of SDS to the reaction of the parent complexes similar effects could be achieved. Surprisingly, the catalytic performance of the mono-sulfonated complexes could also be significantly improved by the presence of SDS. This illustrates that the effects of a single internal sulfonate group and those of the amphiphile are additive. It is important to note, that these effects could not be mimicked by other non-amphiphilic ionic additives, evidencing the importance of the particular structure of SDS. Based on these phenomenologic investigations and in accordance with our recent results under the same reaction conditions but

applying chiral hydroxy phosphine complexes [37] we conclude that the assumption of an individual salt effect do not satisfyingly explain the role of SDS in the hydrogenation reaction performed in water. Mechanistic investigations in order to elaborate the unique effect of SDS are in due course.

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