Water-Soluble Phosphines. 6.[1] Tailor-Made Syntheses of Chiral Secondary and Tertiary Phosphines with Sulfonated Aromatic Substituents: Structural and Quantum Chemical Studies

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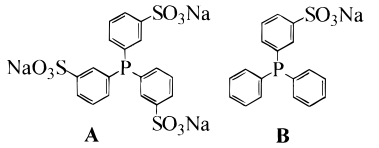
Chiral water-soluble secondary phosphines (**2**−**6**) were obtained by nucleophilic phosphination of FC_6H_4-4-SO_3K (**1a**), FC_6H_3-2,4-$(SO_3K)_2$ (**1b**), and FC_6H_4-2-SO_3K (**1c**) with RPH_2 (R = Ph, 2,4,6-$Me_3C_6H_2$, 2,4,6-$iPr_3C_6H_2$) in the superbasic medium DMSO/KOH by employing steric control of substitution at phosphorus by bulky substituents R and sulfonic groups in the ortho position of the aromatic ring systems in **1b** or **1c**. The secondary phosphines may be deprotonated in DMSO/KOH to give phosphido anions which on reaction with alkyl halides ($PhCH_2Cl$, $Br(CH_2)_3Br$, and $C_{12}H_{25}Br$) yield mono- or bidentate tertiary phosphines (**7**−**10**). Ligands of this type are alternatively accessible by nucleophilic arylation of secondary phosphines, e.g. Ph(Me)PH or Ph(H)$P(CH_2)_3$P(H)Ph with **1a** or **1b**, respectively. The crystal structure of the starting material **1b**·H_2O (space group $P2_1/m$) has been determined. In the solid state of **1b**·H_2O the individual molecules are interconnected by ionic interactions between the potassium cations and the SO_3^- anions. The C−F bond (C(1)−F 1.347(4) Å) is shorter than that in C_6H_5F (1.356(4) Å). The unit cell of **7a**·0.5H_2O (space group $P\bar{1}$), the first structurally characterized chiral phosphine with a sulfonated phenyl substituent, contains the two enantiomers. Due to the asymmetrical substitution at phosphorus the PC_3 skeletons are significantly distorted (P(1)−C(1,11,31) 1.864(10), 1.825(8), 1.841(7) Å). The electronic structure of sulfonated fluorobenzenes $FC_6H_{5-n}(SO_3M)_n$ (M = K, NH_4, $n = 1-3$) is discussed on the basis of quantum chemical calculations. In particular, the reactivity difference toward nucleophilic phosphination within the series is rationalized in terms of steric factors and of the −I effect of the sulfonic groups.

Introduction

Complexes of water-soluble phosphines with sulfonated aromatic substituents like $P(C_6H_4$-*m*-$SO_3Na)_3$ (TPPTS)[3] (**A**) (Chart 1) have been increasingly employed in the last few years as catalysts for the syntheses of organic compounds in two-phase systems[3−5] on industrial and laboratory scale. Two synthetic routes have mainly been used for the preparation of these ligands. On the basis of the early work of Chatt[5a] and Kuntz,[5b] phosphines with *meta*-sulfonated phenyl groups have been obtained by direct sulfonation of neutral phosphines bearing aromatic substituents with oleum. Derivatives of

Chart 1



$Ar^*_{2-m}Ph_mP$-$(CH_2)_x$-$PPh_nAr^*_{2-n}$

C (m, n = 0 - 2; x = 2, 3; Ar* = )

variable degrees of sulfonation are formed (**B**, **C**).[5c,d] Under these rather harsh reaction conditions the electrophilic sulfonation of the aromatic ring systems is, however, accompanied by oxidation of phosphorus. This can be suppressed in some cases by addition of boric acid.[6] An alternative multistep synthetic route leading to TPPTS and sulfonated methyldiphenylphosphine, $MeP(C_6H_4$-*m*-$SO_3Na)_2$, in a small overall yield has been published by Larpent, Patin, Thilmont and Valdor.[7]

Phosphines with *p*-sulfonated and 2,4-disulfonated phenyl substituents are accessible in a more systematic synthetic approach by nucleophilic aromatic phosphination of FC_6H_4-4-SO_3K or FC_6H_3-2,4-$(SO_3K)_2$ with PH_3 and primary and secondary phosphines using superbasic media (e.g. DMSO/KOH).[8ab]

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If primary phosphines RPH_2 with bulky substituents R and fluorobenzene derivatives with SO_3M (M = alkali metal ions) groups in the *ortho* position are employed in these reactions, the substitution of the hydrogen atoms of the PH_2 groups may be controlled by steric effects. Using the reactants in appropriate stoichiometric ratios, secondary phosphines R(Ar*)PH (Ar* = mono- or disulfonated phenyl group) should therefore be accessible by this synthetic route selectively. Due to the reactivity of their P−H bonds the secondary phosphines R(Ar*)-PH are versatile synthons for the preparation of chiral mono- and bidentate water-soluble ligands. In addition to their role as building blocks in ligand syntheses, secondary phosphines R(Ar*)PH are of considerable interest as starting materials for the introduction of strongly hydrophilic phosphido bridges μ_2-P(Ar*)R into oligonuclear complexes and cluster compounds. They may thus contribute significantly to a further development of organometallic chemistry in water, which is an area of emerging interest.[9]

Experimental Section

All operations were carried out under an atmosphere of purified nitrogen in oxygen-free solvents. The fluorobenzene sulfonates **1a**,**b**[8b,c] and the phosphines RPH_2 (R = Ph,[10] 2,4,6-$Me_3C_6H_2$,[11] 2,4,6-$iPr_3C_6H_2$[12]), Me(Ph)PH,[13] and Ph(H)P$(CH_2)_3$P(H)Ph[14,15] were prepared according to literature methods. 2-Fluorobenzenesulfonyl chloride was purchased from Lancaster Synthesis GmbH. The ESI or APCI mass spectra were recorded using a Finigan MAT 95 (MPI, Mühlheim, Germany) or Fisons VG Platform (Bayer AG, Monheim, Germany) mass spectrometer using methanol/water or CH_3CN/water solutions of **4** or **8a**, respectively. The ^{1}H-, ^{19}F-, ^{31}P{^{1}H}-, and ^{13}C{^{1}H}-NMR spectra were obtained on a Bruker AC 400 or AC 250 operating at 400.1, 376.5, 162.0, and 100.6 MHz or 250.1, 235.3, 101.8, and 62.9 MHz, respectively.

Preparation of Potassium Fluorobenzene-2-sulfonate (1c). A mixture of 50 mL of acetic acid and 15.0 g (77.1 mmol) of 2-fluorobenzenesulfonyl chloride was heated under reflux for 1 h. After addition of 100 mL of water refluxing was continued for 2 h. The volatiles were then removed from the reaction mixture by distillation under normal pressure and the remaining colorless residue was dried in vacuo (60 °C, 0.1 mbar). The solid (12.2 g) obtained was dissolved in 50 mL of water and neutralized with 3 M aqueous KOH. After the solvent was removed in vacuo (60 °C, 0.1 mbar) a crystalline colorless solid was obtained; yield 16.5 g (92%). Anal. Calcd for $C_6H_4FKO_3S\cdot H_2O$ (M_r = 232.3): C, 31.03; H, 2.60. Found: C, 31.97; H, 3.01.

Preparation of the Barium and Potassium Salts of Fluorobenzene-2,4,6-trisulfonic Acid (1d,e). A 1 L Teflon-coated autoclave was charged with 80.0 g (1.00 mol) of sulfur trioxide and 16.0 g (0.166 mol) of fluorobenzene. After the autoclave was sealed, the reaction mixture was heated up to 210 °C and kept at this temperature for 76 h. The internal pressure reached about 10 bar. After this time excess SO_3 was stripped off in vacuo leaving 60 g of a brown colored residue. It was dissolved in 200 mL of water, and the solution was neutralized with barium carbonate (ca. 50 g; 0.25 mol). The dark brown solution was filtrated, and the filtrate was decolorized by addition of active charcoal. After evaporation of the filtrate in vacuo, the barium salt of the fluorobenzene-2,4,6-trisulfonic acid was obtained as a colorless powder; yield 33.0 g (34.5%). Anal. Calcd for $C_6H_2FBa_{1.5}O_9S_3\cdot 2H_2O$ (M_r = 575.3): C, 12.53; H, 1.12. Found: C, 13.06; H, 1.14.

The barium salt (6.0 g, 10.4 mmol) obtained above was dissolved in 50 mL of water. The solution was passed through an ion-exchange column (50 cm length, 3.0 cm diameter) filled with the acidic form of Dowex 50. After neutralization of the eluents with 1.0 m KOH the solvent was evaporated in vacuo (25 °C, 0.1 mbar). **1e** was obtained as a colorless crystalline solid; yield 4.1 g (84%). Anal. Calcd for $C_6H_2K_3FO_9S_3\cdot 3H_2O$ (M_r = 468.57): C, 15.38; H, 0.85. Found: C, 15.66; H, 0.91.

Preparation of the Secondary Phosphines 2, 5, and 6. To the solutions of the primary phosphines 2,4,6-$Me_3C_6H_2PH_2$ (3.05 g, 20.0 mmol, or 1.52 g, 10.0 mmol) or $PhPH_2$ (1.71 g, 15.5 mmol) in 25−30 mL of DMSO was added a slight excess of KOH powder (88%) (1.40 g, 22.0 mmol, 0.70 g, 11.0 mmol; 1.09 g, 17.1 mmol). The intensely yellow colored solutions were stirred for 1 h. On addition of the corresponding fluorobenzene sulfonates, FC_6H_4-4-$SO_3K\cdot H_2O$ (4.5 g, 14.0 mmol), FC_6H_3-2,4-$(SO_3K)_2\cdot 2H_2O$ (3.6 g, 9.8 mmol), and FC_6H_4-2-$SO_3K\cdot H_2O$ (3.3 g; 15.5 mmol) the color of the reaction mixtures turned red violet. After 48−72 h stirring at ambient temperature the solvents were removed in vacuo (60−75 °C, 0.05 mbar) giving white or cream colored solids, which were recrystallized from water/methanol (**2**, **6**) or water/ethanol (**5**); yields 3.6 g (71%) for **2**, 3.2 g (64%) for **5**, and 3.6 g (72%) for **6**. Anal. Calcd for $C_{15}H_{16}KO_3PS\cdot H_2O$ (M_r = 364.4) (**2**): C, 49.44; H, 4.98. Found: C, 48.91; H, 4.83. Calcd for $C_{15}H_{15}K_2O_6PS_2\cdot 2H_2O$ (M_r = 500.6) (**5**): C, 35.99; H, 3.83. Found: C, 36.25; H, 3.61. Calcd for $C_{12}H_{10}KO_3PS\cdot H_2O$ (M_r = 322.4) (**6**): C, 44.71; H, 3.75. Found: C, 44.52; H, 3.28.

Preparation of 3. A 1.65 g (7.0 mmol) amount of (2,4,6-triisopropylphenyl)phosphine was added to 0.5 g (7.1 mmol) of KOH (88%) in 20 mL of DMSO. After addition of 1.6 g (6.9 mmol) of FC_6H_4-4-$SO_3K\cdot H_2O$ the suspension was stirred for 60 h at ambient temperature, during which time a colorless precipitate (**3**) was formed. It was collected by filtration, washed with cold water, and dried in vacuo; yield 1.9 g (61%). Anal. Calcd for $C_{21}H_{28}KO_3PS\cdot H_2O$ (M_r = 448.6): C, 56.23; H, 6.74. Found: C, 55.46; H, 7.83.

Preparation of 4. To a solution of 6.4 g (0.1 mol) of KOH powder (88%) in 200 mL of dimethyl sulfoxide was added 20.0 g (0.182 mol) of $PhPH_2$. On addition of 33.2 g (0.09 mol) of solid FC_6H_3-2,4-$(SO_3K)_2\cdot 2H_2O$ (**1b**) an intensely red colored reaction mixture was obtained. It was stirred at ambient temperature for about 5 d. After neutralization with dilute aqueous HF the reaction mixture was poured into 600 mL of 2-propanol. The precipitate formed (**4**, 30.5 g; 74%) contained small amounts of **4a** (ca. 5%). In order to remove **4a** completely, the product obtained was dried in vacuo and dissolved in 50 mL of water. The aqueous solution was poured in small portions into 2 L of ethanol. The white precipitate formed was dried at 20 °C, 0.01 mbar; yield 17.8 g (43%). Anal. Calcd for $C_{12}H_9K_2O_6PS_2\cdot 2H_2O$ (M_r = 458.4): C, 31.42; H, 2.90. Found: C, 31.60; H, 3.12.

Syntheses of the Tertiary Phosphines 7a,b, 8a,b, 9, and 10 by Alkylation of the Secondary Phosphines 2, 4, and 6. (a) Syntheses of 7a,b. KOH powder (88%) was added in about equimolar amounts to the solutions of 1.6 g (4.4 mmol) of **2** or 3.5 g (7.6 mmol)of **4** in 25 mL of DMSO. On addition of 0.56 g (4.4 mmol) or 0.97 g (7.6 mmol) of benzyl chloride (dissolved in 5 mL of DMSO each) the intense red color of the reaction mixture disappeared. After 1 h of stirring the solvent was removed under reduced pressure (70−80 °C, 0.05 mbar). In the case of **7a** the residue was recrystallized from a water/2-propanol mixture; **7b** was precipitated from an aqueous solution by addition of 2-propanol. The product obtained by this procedure was contaminated by appreciable quantities of KCl, which could not completely be separated even by repeated recrystallization from water/2-propanol mixtures. It was identified by its NMR spectroscopic data. Yield: 1.4 g (70%) of **7a.** Anal. Calcd for $C_{22}H_{22}KO_3PS\cdot H_2O$ (M_r = 454.6) (**7a**): C, 58.13; H, 5.32. Found: C, 57.78; H, 5.15.

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(b) Synthesis of 8a,b. The solution of 1.2 g (17.6 mmol) of KOH (88%) in 50 mL of DMSO and 7.3 g (16.0 mmol) of **4** was stirred for 1 h at ambient temperature. A 4.0 g (16.0 mmol) amount of 1-bromododecane was added to this mixture within 15 min. Half of the DMSO was then removed in vacuo (0.01 mbar, 50 °C). The precipitate formed on addition of 200 mL of 2-propanol was filtered off and recrystallized from 10 mL of water. The product thus obtained contained appreciable amounts of KBr which could not be separated. **8a** was identified by its ^{31}P- and ^{13}C-NMR spectra and ESI mass spectrometry.

In order to yield an analytically pure derivative of **8a**, the Ba salt **8b** was precipitated from an aqueous solution of **8a** (3.5 g of the mixture as obtained above in 50 mL of water) by addition of 1.3 g (6.1 mmol) of barium chloride. The precipitate formed was filtered off, washed five times with 20 mL of water, and dried in vacuo. Yield: 0.5 g. Anal. Calcd for $C_{24}H_{33}BaO_6PS_2 \cdot 2H_2O$ (M_r = 685.9) (**8b**): C, 42.02; H, 5.44. Found: C, 40.93; H, 5.20.

(c) Syntheses of 9 and 10. The secondary phosphines **6** (1.88 g, 5.8 mmol) or **4** (2.52 g, 5.5 mmol), respectively, were treated with a suspension of 0.41 g (6.4 mmol) or 0.40 g (6.3 mmol) of KOH (88%) in 25 mL of DMSO. After 30 min of stirring, 0.59 g (2.9 mmol) or 0.57 g (2.8 mmol), 1,3-dibromopropane in 5−10 mL of DMSO was added within a period of 30 min, during which time the red color of the reaction mixture disappeared. The ^{31}P{^{1}H}-NMR spectra of the reaction mixtures indicated that the reactions were complete in both cases. The solvent was removed in vacuo (80 °C, 0.025 mbar). The remaining residues were dissolved in 10 mL of water. After a while **9** precipitated from this solution as a colorless powder. Yield: 1.65 g (83%). By repeated recrystallization from water one diastereoisomer could be obtained in pure form. Anal. Calcd for $C_{27}H_{24}K_2O_6P_2S_2 \cdot 2H_2O$ (M_r = 684.8) (**9**): C, 47.36; H, 4.12. Found: C, 47.62; H, 3.97.

For the isolation of **10**, the residue obtained after removing the solvent in vacuo (70−80 °C, 0.025 mbar) was dissolved in 10 mL of water and neutralized with aqueous HF. When this solution was poured into 200 mL of 2-propanol, **10** was precipitated as a white powder, which was filtered off and dried in vacuo (yield 1.5 g). According to the results of the elemental analysis, it contained some KBr which could not completely be separated by repeated recrystallization from water. **10** was identified by NMR spectroscopy.

Preparation of 2a, 11, and 12. The solutions of the phosphines 2,4,6-$Me_3C_6H_2PH_2$ (2.03 g, 13.3 mmol) or Me(Ph)PH (5.75 g, 46.3 mmol; 1.38 g, 11.1 mmol) in 50−100 mL of DMSO were treated with about the 2-fold (1.92 g, 27.4 mmol) (**2a**) or roughly equimolar amount of powdered KOH (88%) (3.24 g, 50.9 mmol; 0.74 g, 11.6 mmol) (**11**, **12**). After addition of 5.58 g (24.0 mmol) or 9.0 g (38.7 mmol) of FC_6H_4-4-SO_3K or 3.90 g (10.6 mmol) of FC_6H_3-2,4-$(SO_3K)_2$, respectively, the reaction mixtures were stirred at ambient temperature for 72 h (**2a**), 60 h (**11**), or 20 h (**12**), respectively. The sulfonated phosphine ligands thus formed were precipitated from the reaction mixture on addition of ca. 200 mL of 2-propanol. The precipitates formed in case of **2a** and **11** were collected by filtration, washed with 2-propanol, and dried in vacuo. **12** was obtained as a colorless oil. Further purification was achieved by recrystallization from ethanol/methanol (**2a**) or water/2-propanol (**11**); yield 4.3 g (62%) for **2a**, 7.9 g (61%) for **11**, and 3.6 g (72%) for **12**. Anal. Calcd for $C_{21}H_{19}K_2O_6PS_2 \cdot 2H_2O$ (M_r = 576.7) (**2a**): C, 43.74; H, 4.02. Found: C, 42.93; H, 4.20. Calcd for $C_{13}H_{12}KO_3PS \cdot H_2O$ (M_r = 336.4) (**11**): C, 46.42; H, 4.19. Found: C, 45.55; H, 4.01. Calcd for $C_{13}H_{11}K_2O_6PS_2 \cdot 2H_2O$ (M_r = 472.6) (**12**): C, 33.04; H, 3.20. Found: C, 33.81; H, 3.88.

X-ray Crystal Structure Determination of 1b·H$_2$O and 7a·0.5H$_2$O. Experimental data for the X-ray structure determinations are collected in Table 1. The structures were solved by direct methods and refined by full-matrix least squares. Non-hydrogen atoms were refined anisotropically. The weighting scheme was $w^{-1} = \sigma^2(F_o) + p|F_o|^2$ (p = 0.00001). H atoms were included at geometrically calculated positions using the riding model (C−H = 0.95 Å). The SHELXTL program package was used for all calculations.

Table 1. Experimental Data for the X-ray Structural Analyses of **1b**·H_2O and **7a**·0.5H_2O

	1b·H_2O	**7a**·0.5H_2O
empirical formula	$C_6H_5FK_2O_7S_2$	$C_{44}H_{44}K_2O_7P_2S_2$
M_r	318.2	889.1
cryst size (mm)	0.44 × 0.46 × 0.58	0.24 × 0.33 × 0.42
cryst system	monoclinic	triclinic
space group	$P2_1/m$	$P\bar{1}$
a (Å)	9.726(3)	9.403(2)
b (Å)	6.207(2)	9.895(2)
c (Å)	9.815(3)	25.715(5)
α (deg)	90	96.01(3)
β (deg)	106.95(4)	94.77(3)
γ (deg)	90	110.77(3)
V (Å^3)	566.8(5)	2206.0(8)
Z	2	4
D (Mg m^{-3})	1.864	1.338
T (K)	293	293
F(000)	317.60	928
μ (cm^{-1})	12.19	
abs corr	semi-empirical	semi-empirical
radiation	Mo Kα (λ = 0.710 73 Å)	Cu Kα (λ = 1.541 78 Å)
monochromator	graphite	graphite
diffractometer	Siemens P4	Siemens P4
scan	ω	ω
2θ range (deg)	4.0−60.0	4.0−115.0
ω-scan range (deg)	1.20	1.30
scan speed (deg min^{-1})	2.09−14.65	3.20−19.50
reflcns measd	1870	6437
indepdt reflcns	1787	6001
obsd reflcns [$F_o > 4.0\sigma(F_o)$]	1583	3721
params refined	112	413
R (%)	3.16	7.65
R_w (%)	3.12	6.93
$\Delta\delta_{max}$ (e Å^{-3})	0.52/−0.42	0.92/−0.76

Computational Details

The semiempirical quantum chemical calculations were carried out with the help of the program VAMP,[16] employing the PM3 parametrization.[17] As no parameters were available for potassium, an ammonium cation was chosen as counterion for the sulfonic groups because the effective radius of ammonium is very similar to the radius of a potassium cation. Atomic charges were determined by a natural atomic orbital analysis.[18]

Results and Discussions

Syntheses of Chiral Water-Soluble Secondary Phosphines. On reaction of the bulky primary phosphines RPH_2 (R = 2,4,6-$R'_3C_6H_2$, R′ = Me, iPr) with the potassium salt of *p*-fluorobenzenesulfonic acid (**1a**)[8b] in the superbasic medium DMSO/KOH the secondary phosphines **2** and **3** are obtained in good yields (eqs 1 and 3) (Scheme 1). In order to avoid the formation of the tertiary phosphine **2a** the 2,4,6-$Me_3C_6H_2PH_2$ has to be employed in about a 1:1.5 stoichiometric ratio (**1a**:phosphine). If 2,4,6-$Me_3C_6H_2PH_2$ is reacted with 2 equiv of **1a** the tertiary phosphine **2a** is formed exclusively (eq 2).

For the synthesis of **3**, however, no excess of the primary phosphine 2,4,6-$iPr_3C_6H_2PH_2$ was necessary. Steric restrictions due to the bulky iPr substituents in the *o*-position in addition to the low solubility of this ligand in the reaction mixture completely prevent further substitution at phosphorus with formation of the tertiary phosphine.

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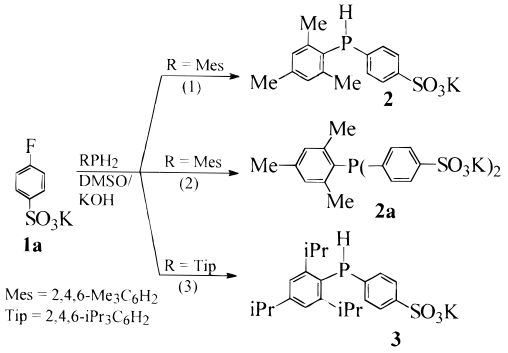
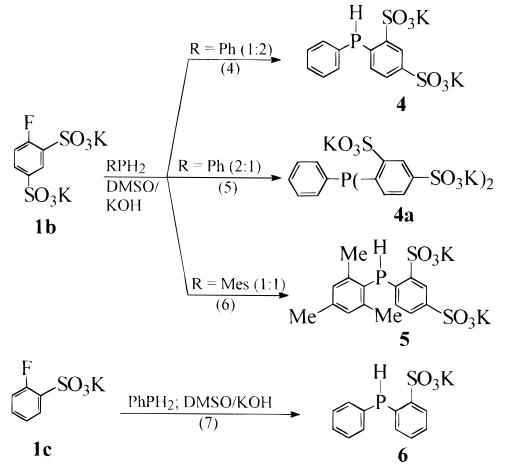
Scheme 1



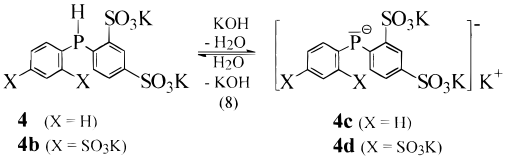
Scheme 2



Steric control of substitution at the phosphorus atoms of the primary phosphines RPH_2 can also be effected by a sulfonic group in the *o*-position to the C−F bond in the sulfonated fluorobenzenes employed in these reactions. Thus reaction of **1b** with the sterically low demanding $PhPH_2$ gives the secondary phosphine **4** in good yields, only traces of **4a** being formed if a 1:2 stoichiometric ratio of **1b**:$PhPH_2$ is used. The tertiary phosphine **4a** is obtained, however, quantitatively, if $PhPH_2$ is reacted with 2 equiv of **1b**. The disulfonated fluorobenzene **1b**[8b] was obtained by sulfonation of FC_6H_4-4-SO_2Cl or FC_6H_4-4-SO_3K with oleum at elevated temperature. The SO_3K substituents in **1b** are in the 2,4-positions of the aromatic ring system. This has been inferred from the analysis of the $^{13}C\{^1H\}$- and ^{13}C-NMR spectra[8b] and was proven by an X-ray structural analysis (see below). ESI and APCI mass spectra have been employed for the first time for the identification of water-soluble phosphines containing sulfonated aromatic substituents. Thus the ESI mass spectrum[19] (positive scan mode) of **4** shows peaks at m/z = 461, 883, and 1305, which may be assigned to the ions $[M + K^+]$, $[2M + K^+]$, $[3M + K^+]$. A value of 422 may be calculated for M from these m/z values for **4**. In the APCI mass spectra[20] (negative scan mode) of **4** intense peaks were observed at m/z = 172 $[M - 2K^+]^{2-}$ and 383 $[M - K^+]^-$.

Nucleophilic phosphination of **1b** with the bulkier mesityl phosphine in the superbasic medium (eq 6) (Scheme 2) yields only the secondary phosphine **5**, irrespective of the molar ratio of the reactands. A molar ratio of **1b**:mesitylphosphine ranging from 1:1 to 1:2 has been employed in the synthesis of **5**. The same applies for the reaction between PH_3 and **1b** which under analogous conditions gives the secondary phosphine $HP[C_6H_3$-2,4-$(SO_3K)_2]_2$ (**4b**) exclusively.[8b] The formation of the tertiary phosphines is obviously hampered in both cases by the steric bulk of the 2,4-disulfonated phenyl substituent. If **1a** is used instead of **1b** for the reaction with PH_3, however, the tertiary phosphine $P(C_6H_4$-4-$SO_3K)_3$ is the final product.[8b]

Scheme 3



The monosulfonated fluorobenzene **1c** reacts with $PhPH_2$ in the superbasic medium in an analogous manner to **1b**,[8b] which like **1c** has an SO_3K group in the *o*-position to the C−F bond. A secondary phosphine is formed as the main product (eq 7). Since the aromatic C−F bond in **1c** is less activated, however, than in **1b** with two SO_3K groups, the reaction proceeds much slower. Only small amounts of a tertiary phosphine $PhP(C_6H_4$-2-$SO_3K)_2$ (**6a**) are formed as indicated by a signal of low intensity at −10.2 ppm in the $^{31}P\{^1H\}$-NMR spectrum of the reaction mixture (cf. **2a**, δ(P) −14.9; **4a**, δ(P) −13.2; $Ph_2PC_6H_4$-4-SO_3K, δ(P) −7.9; $Ph_2PC_6H_3$-2,4-$(SO_3K)_2$, δ(P) −10.8 ppm). The trisulfonated fluorobenzene derivative FC_6H_2-2,4,6-$(SO_3M)_3$, **1d** (M = 0.5 Ba^{2+}) or **1e** (K^+), reacted neither with $PhPH_2$ nor with PH_3 in the superbasic medium at ambient temperature. The two sulfonic groups in the *ortho* position obviously shield the reaction center (*C*−F) quite effectively thus preventing the attack of the phosphido nucleophiles at the activated aromatic ring system.

As shown before,[8b] the solubility of the sulfonated phosphines in water is roughly dependent on the number of SO_3K groups/phenyl group and increases within the series **7a** (75), **3** (90), **9** (130), **6** (140), **2** (150), **11** (280), **2a** (340), **12** (510), **4** (600), **4b**, **5** (800), and **4a** (1300) (approximate values in g of phosphine/kg of water at 20 °C).

Chiral Tertiary Phosphines with Sulfonated Phenyl Substituents. Due to the reactivity of their P−H bonds the secondary phosphines R(Ar*)PH (**2**−**6**) are useful starting materials for the syntheses of chiral tertiary phosphine ligands by P-alkylation reactions. In DMSO the secondary phosphines may be deprotonated by solid KOH, strongly solvated potassium phosphides, e.g. **4c**, **4d**, being formed in an equilibrium reaction (eq 8) (Scheme 3).

The phosphides **4c**,**d** have been identified by $^{31}P\{^1H\}$-NMR spectroscopy, separate signals being observed for the phosphines **4** (−46.2 ppm), **4b** (−46.5 ppm) and the corresponding anions **4c** (8.5 ppm), **4d** (14.8 ppm). Using the stronger base KH instead of KOH, the deprotonation equilibrium (eq 8) is shifted completely to the right as shown for **4** (**4c**: 9.5 ppm). The $^{31}P\{^1H\}$-NMR resonances of the intensely red colored anion **4c**,**d** are shifted downfield by 20−30 ppm compared with the δ(P) value of Ph_2PK (−20 ppm) prepared under the same conditions. A similar ^{31}P-NMR shift (−22.5 ppm) has been reported for Ph_2PNa.[21]

On reaction of **2** or **4** with $C_6H_5CH_2Cl$ in the superbasic medium the chiral tertiary phosphines **7a** or **7b**, respectively, are obtained in good yields (eq 9) (Scheme 4). By a similar reaction of **4b** the achiral ligands $RP[C_6H_3$-2,4-$(SO_3K)_2]_2$ (R = Ph (**4a**), $PhCH_2$, nBu) were formed.[8b] Alkylation of **4** with $C_{12}H_{25}Br$ in the superbasic medium yields the long-chain tertiary

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(21) Bachelor, R.; Birchall, T. *J. Am. Chem. Soc.* **1984**, *104*, 674.

Scheme 4

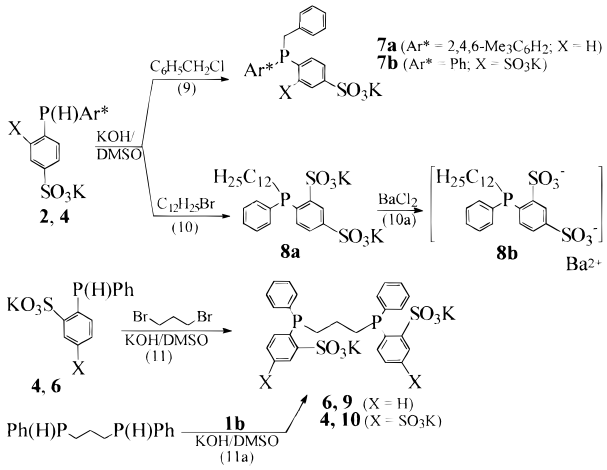
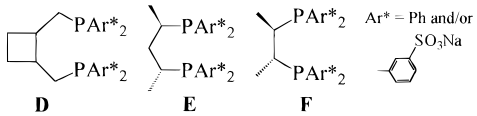


Chart 2



phosphine **8a** with a polar headgroup (eq 10). In order to remove potassium bromide it was transformed into its less soluble Ba derivative **8b** by precipitation with $BaCl_2$ in aqueous solution (eq 10a). **8a** was identified by ESI mass spectrometry (positive scan mode). The intense line observed at $m/z = 629$ may be assigned to the ion $[M + K^+]$.

P-chiral ditertiary phosphines are also accessible by this synthetic route using α,ω-dihalogenoalkanes as coupling reagents. Thus if 1,3-dibromopropane is reacted with **4** or **6**, the bidentate ligands **9** or **10** with sulfonated phenyl groups are formed (eq 11).

Ditertiary phosphines with *m*-sulfonated phenyl substituents and chiral backbones, e.g. **D**−**F** (Chart 2), have been reported in the literature.[22ab] They were synthesized by direct sulfonation of the corresponding phenyl derivatives (cyclobutanediop, chiraphos, BDPP) with concentrated sulfuric acid or oleum. This synthetic procedure is, however, rather unselective a mixture of ligands with a variable degree of sulfonation including phosphine oxides being formed.

Nucleophilic phosphination of **1a** or **1b** with unsymmetrically substituted secondary phosphines RR′PH, some of which may conveniently be obtained by stepwise alkylation of $LiPH_2$ (prepared from red phosphorus, lithium, and tBuOH in liquid ammonia)[23] or PH_3 and primary phosphines RPH_2 in superbasic media,[24,25] provides an alternative synthetic approach to water-soluble chiral tertiary phosphines. The chiral tertiary alkylarylphosphines **11** or **12** were thus obtained in fair yields by reaction of PhP(Me)H with **1a** or **1b**, respectively (eqs 12 and 13) (Scheme 5). Using this alternative synthetic route, the bidentate ligand **10** was synthesized by reaction of **1b** with Ph(H)P(CH$_2$)$_3$P(H)Ph in the superbasic medium (eq 11a). This reaction proceeds, however, very slowly, the bidentate ligand **10** being formed only in low yield.

Scheme 5

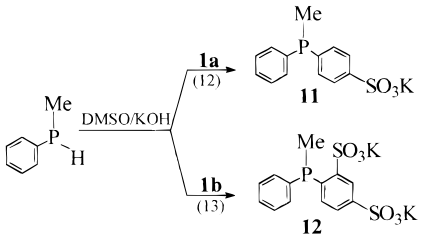


Table 2. $^{31}P\{^1H\}$-NMR Data for **2**−**12**[a]

2	−73.3 (227)	**6**[b]	−43.2 (241)
2a	−14.9	**7a**[b]	−17.6
3[b]	−78.1 (223)	**7b**	−15.4
4	−43.0 (220)	**8a**	−20.4
4a[8b]	−13.2	**9**	−21.3
4b	−46.5 (245)	**10**	−22.4[c] −21.4
4c[b]	+8.5	**11**	−24.3
4d[b]	+14.8	**12**	−29.1
5	−73.2 (249)		

[a] Chemical shift δ(P) relative to H_3PO_4 (85%); solvent D_2O; coupling constants ^1J(PH) in Hz in parentheses. [b] Solvent d_6-DMSO. [c] Diastereoisomers.

NMR Spectra of the Phosphine Ligands 2−12. The solution structure of the phosphines synthesized according to eqs 1−13 is based mainly on $^{31}P\{^1H\}$- and $^{13}C\{^1H\}$-NMR spectroscopy. ^{1}H-NMR spectra will be discussed only in some cases where appropriate.

The degree of sulfonation of the aromatic ring systems is of little influence on the ^{31}P-NMR shift values as shown by comparison of the δ(P) values of **2**/**5**, **4**/**6**, **7a**/**7b**, **9**/**10**, and **11**/**12**, respectively. The δ(P) values of the nonsulfonated analogues of the secondary phosphines **2**−**6** and $HP[C_6H_3$-2,4-$(SO_3K)_2]_2$ (**4b**) differ but little from those of their neutral analogues, e.g. 2,4,6-$iPr_3C_6H_2P(Ph)H$ (−84.7 ppm)[26] and Ph_2-PH (−41.1 ppm).[27] The $^{31}P\{^1H\}$-NMR signals of the secondary phosphines **2**, **3**, and **5** bearing bulky 2,4,6-substituted phenyl groups are shifted upfield by ca. 30 ppm compared with those of the phenyl derivatives **4** and $PhP(H)C_6H_4$-4-SO_3K (−41.3 ppm)[28] (Table 2).

Assignment of all $^{13}C\{^1H\}$-NMR signals of **2**−**5**, **7a**,**b**, **8a**, and **10**−**12** was achieved by comparison with the corresponding data of Ph_3P,[29a] $HPPh_2$,[29b] $HP[C_6H_3$-2,4-$(SO_3K)_2]_2$,[8b] $P(C_6H_4$-4-$SO_3K)_3$,[8b] and $[Me_3NCH_2CH_2P(C_8H_{17})_2]^+Br^-$ [8d] (Table 3). Additional information was obtained from the $^{13}C-^1H$ coupling fine structure (^nJ(CH), $n = 1-4$) in the ^{13}C-NMR spectra. Using the relation $^2J(CH) < {}^3J(CH)$[29a,c] and $^4J(CH) \approx 0$, the

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(28) Herd, O.; Hessler, A.; Hingst, M.; Tepper, M.; Stelzer, O. *J. Organomet. Chem*., submitted for publication. ^{31}P-NMR spectrum: δ(P) = −41.3 ppm, ^1J(PH) = 226 Hz. $^{13}C\{^1H\}$-NMR spectrum (D_2O): 138.2 (C1), 134.3 (16.7, C2,6), 125.8 (6.0, C3,5), 143.0 (C4), 127.3 (C7), 133.6 (15.2, C8), 129.0 (6.3, C9), 129.2 (C10) ppm.

(29) (a) Kalinowski, H. O.; Berger, S.; Braun, S. In *^{13}C-NMR Spectroscopy*; Georg Thieme Verlag: Stuttgart, New York, 1984; p 424. (b) $^{13}C\{^1H\}$-NMR spectrum (d_6-DMSO): 134.2 (10.5. C1), 133.5 (16.6, C2), 128.4 (5.2, C3), 128.2 (C4) ppm. (c) Levy, G. C.; Lichter, R. L.; Nelson, G. L. In *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; Wiley Interscience: New York, Chichester, Brisbane, Toronto, 1980; p 125. (d) Burum, D. P.; Ernst, R. R. *J. Magn. Resn*. **1980**, *39*, 163. Bendall, M. R.; Doddrell, D. M.; Pegg, D. T. *J. Am. Chem. Soc*. **1981**, *103*, 4603.

Table 3. $^{13}C\{^1H\}$-NMR Data for **1c**, **1d**, and **2**−**12**[a]

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14
1c	159.1 (249.5)[b]	130.2 (14.6)	128.8	125.0 (3.9)	134.5 (8.4)	117.2 (21.4)								
1d	157.6 (261.0)[b]	133.1 (17.3)	130.3 (2.8)	139.8 (4.5)										
2	138.9 (14.2)	132.5 (15.6)	126.3 (5.4)	144.3	126.3 (5.4)	132.5 (15.6)	127.8 (9.6)	143.6 (13.0)	129.9 (3.7)	140.4	23.3[c] (12.0)	21.3[d]		
2a	139.8 (12.9)	132.0 (18.3)	125.9 (5.8)	142.6	125.9 (5.8)	132.0 (18.3)	126.6 (8.5)	146.0 (16.2)	130.5 (4.9)	142.2	23.5[c] (17.3)	22.0[d]		
3	136.9 (14.0)	131.2 (16.2)	126.6 (5.1)	148.5	126.6 (5.1)	131.2 (16.2)	125.6 (11.3)	154.3 (12.2)	122.3 (3.3)	151.2	33.3[e] (14.3)	34.5[f]	24.8[g], 24.6	25.4[h] (1.8)[g]
4[i]	138.8 (22.4)	146.3 (15.6)	124.8	143.4	130.1	136.7 (4.7)	133.2 (7.1)	136.1 (17.7)	129.5 (6.8)	128.1				
5	139.7 (2.6)	145.2 (14.3)	124.3	142.3	127.7 (1.6)	132.7 (8.7)	127.6 (8.8)	145.0 (13.7)	129.6 (3.4)	141.3	22.6[c] (12.1)	20.8[d]		
6	133.9 (18.6)	145.5 (15.5)	127.5 (1.7)	129.1	131.5	136.3 (4.2)	134.2 (7.5)	135.4 (17.3)	129.3 (6.2)	129.6				
7a	142.7 (18.4)	129.1 (15.3)	126.5 (3.2)	147.4 (1.7)	126.5 (3.2)	129.1 (15.3)	129.5 (20.4)	145.5 (15.4)	130.4 (4.0)	140.1	138.8[j] (9.5)	129.8 (7.1)	129.0 (1.7)	126.6[k] (2.8)
7b	139.9 (28.5)	148.2 (25.4)	124.2 (5.1)	143.6	126.5 (2.0)	135.5	133.1 (18.3)	133.1 (18.3)	128.9 (7.1)	127.8	137.1[j] (14.2)	129.8 (7.1)	128.8	126.5[k]
8a	140.3 (27.5)	148.2 (25.4)	122.7	143.8	124.8	133.9	138.3 (13.2)	132.7 (19.3)	128.7 (6.1)	127.6	31.6 (14.3)	26.1 (18.3)	28.0 (11.2)	29.4[l]
9[m]	135.9 (23.8)	148.1 (25.9)	127.5 (4.8)	129.7	131.5	134.4	139.5 (13.2)	132.4 (17.5)	129.0 (5.5)	128.7	29.2[n] (12.2)	22.5[o] (16.3)		
9[m]	135.4 (25.3)	147.2 (24.9)	128.2 (3.8)	129.7	131.4	134.3	139.2 (13.6)	132.5 (17.9)	129.0 (5.5)	128.7	29.2[n] (12.2)	22.8[o] (16.3)		
10	139.4 (4.1)	148.5 (26.5)	122.8	143.6	125.0	134.4	139.5	131.4 (10.2)	129.1 (5.1)	127.7	28.3[p]	22.4[m] (17.3)	22.3[m] (9.5)	
11	146.5 (13.2)	134.2 (17.6)	127.8 (5.8)	145.0	127.8 (5.8)	134.2 (17.6)	140.9 (9.5)	134.7 (18.9)	131.1 (4.4)	131.4	13.5[q] (12.5)			
12	142.9 (27.2)	148.1 (26.5)	124.4 (4.5)	143.6	128.3	135.5 (2.7)	139.9 (10.5)	132.2 (17.7)	129.2 (5.5)	129.1	12.1[q] (13.0)			

[a] Chemical shift δ(C) relative to TMS; coupling constants ^nJ(PC) in Hz in parentheses, solvent D_2O. Numbering scheme of the carbon atoms: C_6H_4-4-SO_3K or C_6H_4-2-SO_3K, C1 (ipso), C2 (*o* or C−SO_3K), C3/5 (*m*), C4 (C−SO_3K or *p*), C6 (*o*); C_6H_3-2,4-$(SO_3K)_2$, C1 (ipso), C2/4 (C−SO_3K), C3/5 (*m*), C6 (*o*); C_6H_5 and 2,4,6-$R_3C_6H_3$ (R = Me, iPr), C7 (ipso), C8 (*o*), C9 (*m*), C10 (*p*). [b] ^nJ(CF) (*n* = 1−4). [c] *o*-Me. [d] *p*-Me. [e] CH, *o*-iPr. [f] CH, *p*-iPr. [g] Me, *o*-iPr. [h] Me, *p*-iPr. [i] δ(C) values and ^nJ(PC) coupling constants for **4** in DMSO solution: C(1) 135.9 (11.9), C(2) 149.0 (12.1), C(3) 124.2 (1.0), C(4) 146.6, C(5) 125.3 (3.1), C(6) 133.1 (10.4), C(7) 134.6 (20.5), C(8) 135.3 (17.3), C(9) 128.5 (6.0), C(10) 129.8 ppm. [j] $CH_2C_6H_5$: **7a**, **7b** (C(11)−C(14)). [k] $CH_2C_6H_5$: **7a**, 32.4 (18.1); **7b**, 34.4 (14.2) ppm; o-CH_3, p-CH_3 (**7a**), 22.6 (12.1), 20.8. [l] $C_{12}H_{25}$ substituent, C(14)−C(19): 29.4−30.0 ppm, C(20) 32.1, C(21) 22.8, C(22) 14.1 ppm. [m] Diastereoisomers. [n] −$CH_2CH_2CH_2$, X part of an ABX spin system. [o] −$CH_2CH_2CH_2$, first-order triplet. [p] Multiplet. [q] P−*Me*.

Figure 1. (a) $^{13}C\{^1H\}$-NMR spectrum of **4**. (b) DEPT-$^{13}C\{^1H\}$-NMR spectrum of **4**.

Figure 2. (a) $^{13}C\{^1H\}$-NMR spectrum of **6**. (b) ^{13}C-NMR spectrum of **6**.

^{13}C-NMR spectrum of **4** could be analyzed using a first-order approximation. The assignment of the signals at 138.8, 146.3, 143.4, and 133.2 ppm in the $^{13}C\{^1H\}$-NMR spectrum of **4** (Figure 1a) to quaternary carbon atoms was proved to be correct by DEPT experiments[29d] (Figure 1b). Further support was gained from the relative magnitude of the coupling constants ^nJ(PC), which in most cases decrease within the order ^2J(PC) > ^3J(PC) > ^4J(PC). The absolute values of ^1J(PC) and ^2J(PC) are in the range between 2.5 and 28 Hz, with ^1J(PC) being in most cases smaller than ^2J(PC) (e.g. Ph_3P[30a,c]).

The assignment of the $^{13}C\{^1H\}$-NMR signals of the carbon atoms in the C_6H_4-2-SO_3K-substituted phosphines **6** (Figure 2a) and **9** is based upon intensity arguments and the analysis of the $^{13}C-^1H$ coupling fine structure in the ^{13}C-NMR spectra. Thus for all signals in the range A (Figure 2b) assigned to the carbon atoms C(3), C(4), C(5), C(8), and C(9) a large $^{13}C-^1H$ doublet splitting ^1J(CH) is observed. The resonances of C(1) and C(7) (range B) show only fine structure due to long-range $^{13}C-^1H$ coupling (^nJ(CH), $n = 2, 3$). The $^{13}C\{^1H\}$-NMR signals of the SO_3K-substituted carbon atoms (δ(C) = 145.5 (**6**) or 147.2, 148.1 ppm (**9**), respectively) display a doublet splitting (15.5 (**6**) or 25.9, 24.9 Hz (**9**)) in the range typical for ^2J(PC).[30a,b] As

(30) (a) Reference 29a, p 530. (b) Sorensen, S.; Hansen, R. S.; Jacobsen, H. J. *J. Am. Chem. Soc*. **1972**, *94*, 5900. Llinas, J. R.; Vincent, E. J.; Pfeiffer, G. *Bull. Soc. Chim. Fr*. **1973**, *11*, 3209. (c) Quin, L. D. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; p 391.

for other *ortho*-substituted aromatic phosphines, e.g. (2-Me-$C_6H_4)_3P$ or (2-Me-4-Cl-$C_6H_3)_3P$, the coupling constant ^2J(PC) involving the *ortho*-substituted carbon atom C(2) (26.44 or 27.90 Hz) is larger than this coupling for the unsubstituted *ortho* carbon (C(6), 0.41 or 0.63 Hz, respectively). For Ph_3P the value of ^2J(PC) is 19.65 Hz. In general ^2J(PC) is large, when the lone pair is close to the C atom, and it is small when remote.[30b,c] According to quantum chemical calculations on the hypothetical primary phosphines containing *o*-sulfonated phenyl substituents, the phosphorus lone pair is approximately coplanar with the aromatic ring and occupies the trans position to C(2) (see below) in the most favorable conformation. If, however, larger substituents R are introduced at P instead of hydrogen, it is forced into close proximity (cis or gauche position) to C(2)−SO_3K due to R/SO_3^- repulsion.

For some of the carbon atoms (C(1)−C(3), C(5)−C(8)) of **9** (which in the $^{31}P\{^1H\}$-NMR spectrum shows only a singlet) two narrow lying signals (singlets or doublets) with an intensity ratio of about 1:2 are observed in the $^{13}C\{^1H\}$-NMR spectra indicating the presence of two diastereoisomers (meso form and racemate). Correspondingly two triplets (X parts of two A_2X spin systems; A = ^{31}P, X = ^{13}C) are obtained for the central carbon atom of the propylene chain in **9**. The fine structure of the $^{13}C\{^1H\}$-NMR signals assigned to the α-carbon atoms of the two diastereoisomers are not well resolved (two overlapping X parts of ABX spin systems,[31ab] A, B = ^{31}P, X = ^{13}C). By repeated recrystallization of **9** from water, one diastereoisomer was obtained almost pure. It shows a symmetrical seven-line pattern in the ^1H-NMR spectrum for the central CH_2 group indicating the chemical equivalence of the two hydrogen atoms. This would be expected for the racemate, while the meso form should give a more complicated pattern due to the chemical inequivalence of the hydrogens of the CH_2 group in this case. In case of **10** the presence of two diastereoisomers is indicated by the observation of two narrow lying $^{31}P\{^1H\}$-NMR resonances (Table 1) and two $^{13}C\{^1H\}$-NMR signals for C(12) (Table 3).

As a result of the unsymmetrical substitution at phosphorus in the secondary phosphine **3**, the Me groups of the *ortho*-iPr substituents in the four possible rotamers (I−IV) (Figure 3b) are diastereotopic, two $^{13}C\{^1H\}$-NMR signals being observed, one of which shows a small doublet splitting due to P−C coupling (^4J(PC) = 1.8 Hz) (Figure 3a). Correspondingly, two signals (δ(H(1)) = 1.11 ppm, ^3J(HH) = 6.6 Hz; δ(H(2)) = 1.12 ppm, ^3J(HH) = 6.6 Hz) are obtained in the ^1H-NMR spectrum of **3** for the *o*-Me_2CH substituents. Their CH groups, however, give only one $^{13}C\{^1H\}$-NMR signal which is split into a doublet by $^{13}C-^{31}P$ coupling ^3J(PC) (Figure 3a). Rapid rotation about the P−C_{ipso} (i$Pr_3C_6H_2$) bond equilibrates the C−H groups (lying in the plane of the aromatic ring system) on the NMR time scale.[32ab]

The chirality of the phosphorus atom renders the benzylic hydrogen atoms in **7a**,**b** inequivalent. Their ^1H-NMR spectra therefore represent the AB part of an ABX spin system[31a,b] (A, B = ^1H, X = ^{31}P). For **7a** a well-resolved eight-line pattern (Figure 3c) is observed from which the shift values $\delta(H_A)$ = 3.6, $\delta(H_B)$ = 3.7 ppm and coupling constants $^2J(H_AH_B)$ = −13.0, $^2J(PH_A)$ = 4.0, and $^2J(PH_B)$ = 4.9 Hz could be extracted.

X-ray Structures of 1b and 7a. In order to gain detailed information about the influence of the sulfonic groups in the *ortho*- and *para*-positions on the geometry of the aromatic ring system and the C−F bond in **1b**, a structure determination has been performed. The results are collected in Tables 4 and 5.

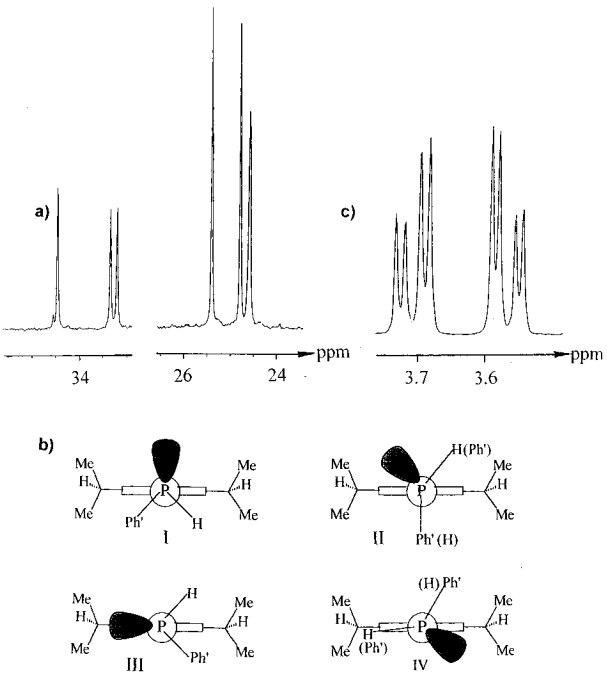

Figure 3. (a) $^{13}C\{^1H\}$-NMR spectrum of **3** (iPr substituents). (b) Rotamers I−IV for the P−aryl rotation in **3** (rectangle = C_6H_2 part of the 2,4,6-i$Pr_3C_6H_2$ substituent, Ph′ = C_6H_4-4-SO_3K). c) ^1H-NMR spectrum of **7** (CH_2(Ph) part of the spectrum).

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Temperature Factors (Å^2 × 10^3) for **1b**·H_2O

	x	*y*	*z*	U_{eq}[a]
K(1)	2975(1)	2500	−5019(1)	36(1)
K(2)	5518(1)	2500	2058(1)	30(1)
C(1)	−1712(3)	2500	−628(3)	27(1)
C(2)	−1735(3)	2500	−2046(3)	22(1)
C(3)	−448(3)	2500	−2370(3)	22(1)
C(4)	834(3)	2500	−1286(3)	23(3)
C(5)	835(3)	2500	126(3)	27(1)
C(6)	−452(3)	2500	459(3)	29(1)
S(1)	−3379(1)	2500	−3444(1)	26(1)
O(1)	−2968(2)	2500	−4750(2)	35(1)
O(2)	−4124(2)	551(3)	−3267(2)	46(1)
F	−2967(2)	2500	−307(2)	50(1)
S(2)	2448(1)	2500	−1778(1)	26(1)
O(4)	2387(2)	573(3)	−2640(2)	35(1)
O(6)	3616(3)	2500	−483(3)	54(1)
O(7)	−74(3)	2500	4072(3)	44(1)
F(5)	2061(13)	2500	1170(15)	51(6)

[a] U_{eq} is defined as $^1/_3$ of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

On recrystallization of **1b** from concentrated aqueous solution crystals of composition **1b**·H_2O were obtained. The anions [FC_6H_3-2,4-(SO_3^-)$_2$] display crystallographic C_s symmetry and are interconnected by a network of ionic interactions between the potassium cations and the sulfonic groups (Figure 4a). A degree of disorder is observed for the anions with partial occupation of the fluorine sites at C(1) (site occupation factor 0.95) and F(5) at C(5) (site occupation factor 0.05). The C−F bond (C(1)−F = 1.347(4) Å) in **1b** (Figure 4b, Tables 4 and 5) is shorter than that in C_6H_5F (1.356(4) Å).[33a] This may be attributed to the delocalization of the negative charge in the *o*- and *p*-positions of the reference compound by the SO_3 substituents in **1b** favoring the back-donation of fluorine p-electrons to the π-system.[33b]

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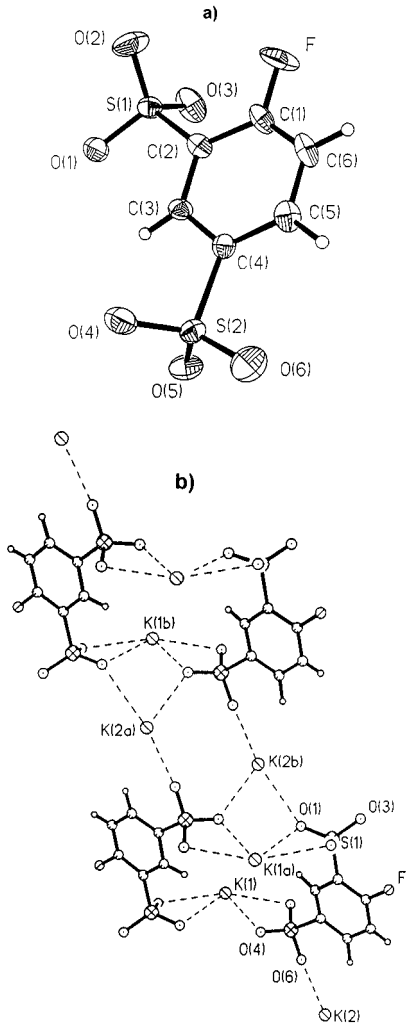

Figure 4. X-ray structure of **1b**·H_2O: (a) Anion of **1**b; (b) unit cell of **1b**·H_2O.

Table 5. Bond Lengths (Å) and Bond Angles (deg) for **1b**·H_2O

Bond Lengths			
C(1)−F	1.347(4)	C(5)−C(6)	1.383(5)
C(2)−S(1)	1.778(3)	C(1)−C(6)	1.370(4)
C(4)−S(2)	1.772(3)	S(1)−O(1)	1.450(3)
C(1)−C(2)	1.385(5)	S(1)−O(2)	1.446(2)
C(2)−C(3)	1.379(4)	S(2)−O(4)	1.456(2)
C(3)−C(4)	1.383(3)	S(2)−O(6)	1.437(2)
C(4)−C(5)	1.386(4)		
Bond Angles			
C(2)−C(1)−F	119.0(2)	C(1)−C(6)−C(5)	118.8(3)
C(6)−C(1)−F	118.9(3)	C(2)−C(1)−C(6)	122.1(3)
C(1)−C(2)−C(3)	118.8(2)	C(3)−C(2)−S(1)	119.7(2)
C(2)−C(3)−C(4)	119.9(3)	C(1)−C(2)−S(1)	121.5(2)
C(3)−C(4)−C(5)	120.4(3)	C(3)−C(4)−S(2)	117.5(2)
C(4)−C(5)−C(6)	120.0(2)	C(5)−C(4)−S(2)	122.1(2)

With exception of C(1)−C(2) (1.385(5) Å) the C−C bond distances within the aromatic ring system of **1b** are about 0.02 Å shorter than the corresponding values in C_6H_5F[33a,b] (e.g. **1b**/C_6H_5F, bond lengths C(*n*)-C(*n* + 1) (*n* = 1−5) and C(1)−C(6): 1.385(5)/1.387(3), 1.379(4)/1.399(3), 1.383(3)/1.401(3), 1.386(4)/1.401(3), 1.383(5)/1.399(3), 1.370(4)/1.387(3) Å). Stabilization of the negative charge in the *o*- and *p*-positions of C_6H_5F by the electron-withdrawing effect of the SO_3^- substituents obviously causes a shrinkage of the C−C bond distances. The angle at the ipso carbon atom C(1) (C(2)−C(1)−C(6) 122.1(3)°) is opened up compared with the ideal 120° value. This was also observed for the parent molecule C_6H_5F (123.4(1)°).[33a,b]

The C−S bond lengths in **1b** (C(2)−S(1) 1.778(3), C(4)−S(2) 1.772 (3) Å) do not differ significantly and may be compared with that in ammonium *o*-carboxybenzenesulfonate (1.775(4) Å).[34] They are, however, slightly longer than the C−S distance in *p*-toluenesulfonic acid monohydrate (1.752(2),[35] 1.738(5) Å[36]). This may be due to the mutual repulsion of the negatively charged (COO^-, SO_3^-) or high electron density substituents (F) in **1b** or $[OOCC_6H_4\text{-}2\text{-}SO_3]^{2-}$.

Crystals of composition **7a**·0.5H_2O suitable for X-ray structural analysis (Tables 6 and 7) have been obtained by recrystallization of **7a** from water/2-propanol mixtures. The unit cell contains the two enantiomers (*R*- and *S*-forms) as crystallographically independent molecules (Figure 5a). The sulfonic groups of the $C_6H_4SO_3^-$ substituents are in close proximity and held together by ionic interactions with the potassium cations repesenting the hydrophilic layer in the crystal while the benzyl and mesityl substituents represent the lipophilic part of the molecules.

With exception of C(11)−P(1)−C(31) (101.4(4)°) and C(41)−P(2)−C(61) (105.1(4)°), respectively, the corresponding P−C bond lengths and C−P−C bond angles of the two independent molecules are within experimental error similar to each other (Figure 5b). Due to the unsymmetrical substitution at phosphorus the geometry of the PC_3 skeletons are rather distorted (e.g. P(1)−C(1) = 1.864(10), P(1)−C(11) = 1.825(8), P(1)−C(31) = 1.841(7) Å; C(1)−P(1)−C(11) = 103.6(4), C(11)−P(1)−C(31) = 101.4(4)°, C(31)−P(1)−C(1) = 105.5(4)°).

The P−C bond lengths between P(1) and the ipso atoms of the aromatic ring systems in **7a** are shorter than the corresponding values in $P(C_6H_4\text{-}4\text{-}SO_3K)_3$·KCl·0.5$H_2O$[8a,b] (1.843(4) Å). The planes of the two aromatic ring systems bound directly to the phosphorus atoms P(1) or P(2) are rotated by 83.3 or 73.2° (mesityl) and −26.1 or −26.7° ($C_6H_4\text{-}4\text{-}SO_3K$), respectively, against the plane spanned by C(1), C(11), C(31) or C(2), C(41), C(61), thus minimizing the steric interaction between the C_6H_4-4-SO_3K and the mesityl substituent.

The mean C−S bond length in **7a**·0.5H_2O (1.776(8) Å) does not differ significantly from that in **1b** (1.775(3) Å) or $P(C_6H_4\text{-}4\text{-}SO_3K)_3$·KCl·0.5$H_2O$ (1.776(4) Å).[8]

Quantum Chemical Calculations. The object of the quantum chemical calculations on **1b** was to explore how and to what extent the sulfonic groups influence the electronic and spatial structure of the aromatic ring system and the C−F bond. They were also intended to help in rationalizing the reactivity of the ipso carbon atom in **1b** ($FC_6H_3\text{-}2,4\text{-}(SO_3K)_2$) toward nucleophiles like phosphido anions PH_2^- compared to C_6H_5F or **1a** ($FC_6H_4\text{-}4\text{-}SO_3K$) and **1c** ($FC_6H_4\text{-}2\text{-}SO_3K$) and the missing reactivity of $FC_6H_2\text{-}2,4,6\text{-}(SO_3K)_3$, (**1e**).

The feasibility of a nucleophilic aromatic substitution is generally discussed in terms of a mesomeric +M and an inductive −I effect of the substituents. In addition, steric factors may play a role. As a model, we analyzed the reaction of these sulfonated fluoroaromatic systems with PH_2^- to separate the electronic and the steric effects. For technical reasons we used ammonium NH_4^+ as counter ion instead of potassium (see the section Computational Details); the corresponding compounds

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Table 6. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Temperature Factors ($Å^2 \times 10^3$) for **7**·0.5H_2O

	x	*y*	*z*	U_{eq}[a]
K(1)	1796(2)	2550(2)	174(1)	85(1)
C(1)	2776(9)	1167(9)	2219(3)	72(4)
P(1)	3991(3)	81(2)	2360(1)	62(1)
S(1)	8098(3)	695(3)	481(1)	59(1)
O(11)	9280(6)	116(6)	584(2)	78(3)
O(12)	6926(6)	−200(6)	54(2)	76(3)
O(13)	8679(7)	2205(6)	391(2)	83(3)
C(11)	5166(9)	298(9)	1822(3)	55(4)
C(12)	5875(9)	−691(9)	1700(3)	60(4)
C(13)	6804(9)	−558(9)	1314(3)	57(4)
C(14)	7091(9)	613(8)	1034(3)	50(4)
C(15)	6473(9)	1655(9)	1160(3)	62(4)
C(16)	5530(10)	1499(9)	1551(3)	66(4)
C(22)	2218(5)	1910(6)	3114(3)	86(1)
C(23)	1195	1849	3482	86(1)
C(24)	−353	976	3348	86(1)
C(25)	−878	164	2847	86(1)
C(26)	146	226	2479	86(1)
C(21)	1694	1098	2613	86(1)
C(31)	2705(9)	−1845(0)	2189(3)	54(4)
C(32)	2653(9)	−2693(10)	2608(3)	57(4)
C(321)	3470(11)	−2049(10)	3152(3)	83(5)
C(33)	1837(10)	−4176(10)	2509(4)	65(5)
C(34)	1061(10)	−4876(10)	2017(4)	69(5)
C(341)	241(11)	−6493(10)	1915(5)	105(6)
C(35)	1123(9)	−4038(10)	1620(4)	66(4)
C(36)	1896(9)	−2537(10)	1697(3)	60(4)
C(361)	1786(11)	−1760(10)	1226(3)	83(5)
K(2)	4158(2)	7713(2)	204(1)	76(1)
P(2)	7450(3)	6614(3)	3319(1)	65(1)
C(2)	9531(9)	6982(9)	3410(3)	71(4)
S(2)	5289(3)	5203(2)	828(1)	57(1)
O(41)	3833(7)	5411(7)	771(2)	93(4)
O(42)	5079(8)	3737(6)	643(2)	92(3)
O(43)	6400(7)	6264(7)	594(2)	100(3)
C(41)	6936(9)	6086(8)	2605(3)	52(4)
C(42)	5385(10)	5485(8)	2409(3)	54(4)
C(43)	4881(9)	5214(8)	1874(3)	55(4)
C(44)	5939(10)	5534(8)	1519(3)	48(4)
C(45)	7483(10)	6121(9)	1711(3)	60(4)
C(46)	7958(10)	6398(9)	2239(3)	60(4)
C(52)	10169(8)	8311(7)	4341(3)	126(1)
C(53)	10740	8448	4870	126(1)
C(54)	11278	7406	5043	126(1)
C(55)	11245	6227	4687	126(1)
C(56)	10674	6090	4158	126(1)
C(51)	10136	7132	3985	126(1)
C(62)	5769(11)	5015(10)	4025(4)	79(1)
C(63)	5137(10)	3768(9)	4263(4)	79(1)
C(64)	5315(10)	2492(10)	4116(4)	79(1)
C(65)	6126(10)	2389(10)	3699(3)	79(1)
C(66)	6759(10)	3584(10)	3436(4)	79(1)
C(61)	6611(10)	4914(10)	3600(3)	79(1)
C(621)	5575(15)	6417(13)	4235(4)	127(8)
C(641)	4598(15)	1133(12)	4396(5)	143(8)
C(661)	7589(10)	3335(10)	2977(3)	80(5)
O′	8773(11)	−4978(10)	233(4)	205(7)

[a] U_{eq} is defined as $^1/_3$ of the trace of the orthogonalized U_{ij} tensor.

will be differentiated by primes, e.g. FC_6H_3-2,4-$(SO_3NH_4)_2$ as **1b′** and $(PH_2)C_6H_3$-2,4-$(SO_3NH_4)_2$ as **1b″**.

A mesomeric stabilization of a distinct orientation of the SO_3^- groups due to favourable overlap of S and O p-orbitals with the benzene π-system may be estimated from the rotational barrier. In FC_6H_4-4-SO_3NH_4 (**1a′**) a barrier of only 0.3 kcal/mol was calculated. The calculated barriers for the two sulfonic groups in FC_6H_3-2,4-$(SO_3NH_4)_2$, **1b′**, differ significantly. While the same value as in **1a′** is found for the *p*-sulfonic group of **1b′**, a larger barrier, 1.9 kcal/mol, results for the SO_3 group in the *o*-position due to the repulsive interaction of the oxygen

Table 7. Bond Lengths (Å) and Bond Angles (deg) for **7a**·0.5 H_2O

Bond Lengths

P(1)−C(1)	1.864(10)	C(11)−C(16)	1.392(12)
P(1)−C(11)	1.825(8)	C(15)−C(16)	1.382(12)
P(1)−C(31)	1.841(7)	C(14)−C(15)	1.375(13)
S(1)−C(14)	1.766(8)	C(13)−C(14)	1.387(12)
S(1)−O(11)	1.438(7)	C(12)−C(13)	1.361(12)
S(1)−O(12)	1.452(5)	C(11)−C(12)	1.390(14)
S(1)−O(13)	1.448(6)	C(1)−C(21)	1.484(11)

Bond Angles

C(1)−P(1)−C(11)	103.6(4)	C(14)−C(15)−C(16)	119.8(8)
C(11)−P(1)−C(31)	101.4(4)	C(13)−C(14)−C(15)	119.5(8)
C(1)−P(1)−C(31)	105.5(4)	S(1)−C(14)−C(15)	119.6(6)
P(1)−C(1)−C(21)	111.0(6)	S(1)−C(14)−C(13)	120.6(7)
C(12)−C(11)−C(16)	116.6(8)	C(12)−C(13)−C(14)	119.8(9)
C(11)−C(16)−C(15)	121.7(9)	C(11)−C(12)−C(13)	122.5(8)

and the fluorine lone pairs. Accordingly, the *o*-sulfonic group is oriented such that the two O atoms close to the fluorine substituent are located symmetrically above and below the plane of the aryl ring (see Figure 6). Thus, not unexpectedly, any significant mesomeric effects on a nucleophilic substitution of the aryl ring may be ruled out.

As a measure for the importance of the inductive effect of the SO_3^- group, one may take the charge calculated for the ipso carbon atom (Table 8). The sulfonic groups hardly influence the charge of the fluorine atom, $q(F) = \sim 0.1$ au, or the C−F bond length which is calculated to about 1.34 Å, in good agreement with experiment (1.347(4) Å; see above). The expected electron-withdrawing effect of the sulfonic group is clearly visible. The positive charge of the ipso carbon atom increases with the number of SO_3^- substituents; it is smaller for a sulfonic group in the *p*- rather than in the *o*-position (**1a′**, **1c′**), but the compound effect of several groups is not additive. However, the inductive effect cannot be the decisive factor of influence on the phosphination of the fluoroaryls as this reaction is not observed for FC_6H_2-2,4,6-$(SO_3K)_3$ (**1e**). Thus, it is important to take steric interactions into account.

The reaction enthalpies calculated for the phosphination of various sulfonated fluoroaryls are compared in Table 9. These data clearly show that a sulfonic group in the *p*-position has little influence on the reactivity of the fluorobenzene derivatives. With comparison of the heats of formation calculated for **1a′** and **1c′** and the corresponding phosphino analogues **1a″** and **1c″** (Table 9), it becomes evident that some steric hindrance is encountered during phosphination due to a sulfonic group in the *o*-position. This is also reflected in the resulting reaction enthalpy, −8.4 kcal/mol for the formation of **1c″** compared to −13.6 kcal/mol for **1a″.** On the other hand, the reaction enthalpy for the formation of **1b″**, −11.6 kcal/mol, is indicative for the −I effect which drives the phosphination reaction to some extent. On the other hand, the value of the reaction enthalpy calculated for the formation of **1e″**, +2.5 kcal/mol, is in line with the failure of **1e′** to react.

The steric interaction between adjacent PH_2^- and SO_3^- groups, apparent from this finding, warrants further discussion. In the series of primary arylphosphines ($PhPH_2$, 4-$SO_3KC_6H_4PH_2$, 2-$SO_3KC_6H_4PH_2$, 2,4-$(SO_3K)_2C_6H_3PH_2$, and 2,4,6-$(SO_3K)_3C_6H_2PH_2$) investigated here, the PH_2 group retains its structure, only acquiring different rotational orientations (see the dihedral angles α_1 and α_2, Figure 7 and Table 10). Significant structural changes as a consequence of steric crowding due to sulfonic groups in the *o*-position are the elongation of the C−P and C−S bonds. In particular, the planarity of the aryl ring (dihedral angle δ, Table 10) is significantly reduced when sulfonic groups are substituted in both *o*-positions (**1e″**); in all other compounds it is calculated

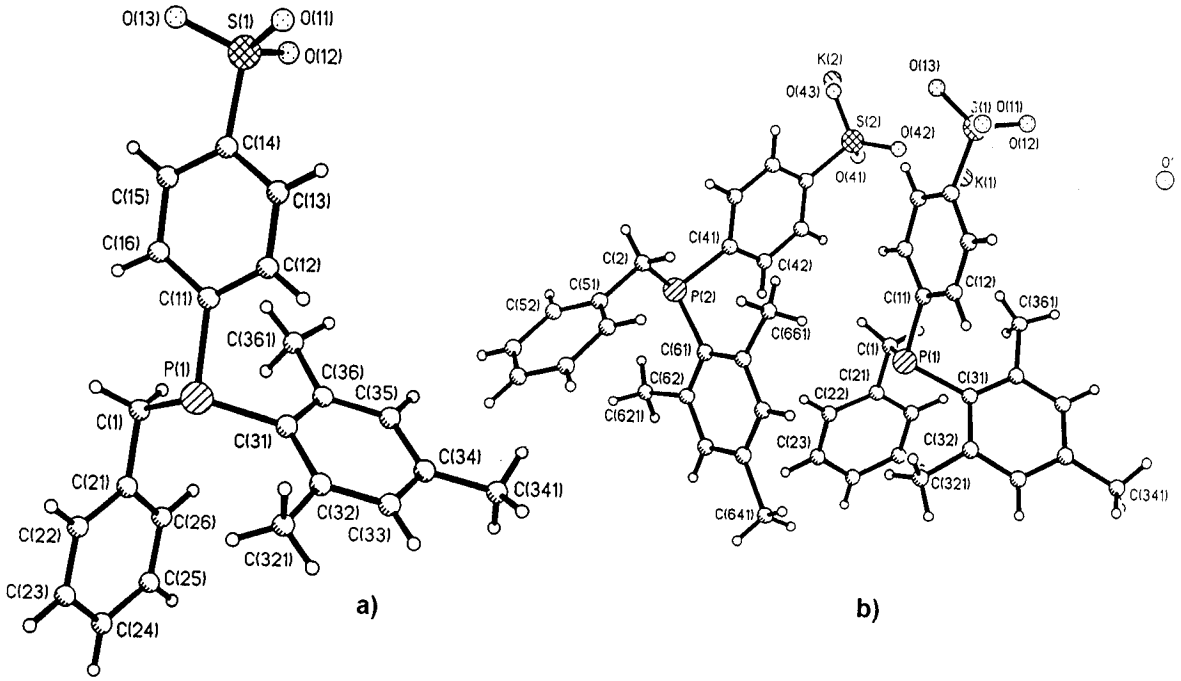

Figure 5. X-ray structure of **7a**·0.5H_2O: (a) Anion of **7a** (molecule 1); (b) unit cell of **7a**·0.5H_2O.

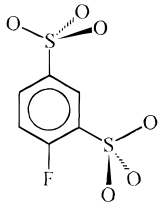

Figure 6. Orientation of sulfonic groups in FC_6H_3-2,4-$(SO_3NH_4)_2$ (**1b′**) relative to the aromatic ring plane.

Table 8. Charge q (in au) of the ipso-Carbon Atom C(1) from a PM3 Natural Atomic Orbital Analysis for Differently Substituted Fluorobenzene Systems

compd	q	compd	q
C_6H_6	−0.20	FC_6H_4-2-(SO_3NH_4) (**1c′**)	0.14
FC_6H_5	0.06	FC_6H_3-2,4-$(SO_3NH_4)_2$ (**1b′**)	0.21
FC_6H_4-4-(SO_3NH_4) (**1a′**)	0.10	FC_6H_2-2,4,6-$(SO_3NH_4)_3$ (**1d′**)	0.24

Table 9. Calculated (PM3) Values of the Heat of Formation ΔH_f of Fluorobenzene (FAr) and Phenylphosphine Derivatives ($ArPH_2$) and Reaction Enthalpies ΔH_r for the Phosphination[a] of ArF with PH_3 (All Energies in kcal/mol)

	ΔH_f		
system	X = F	X = PH_2	ΔH_r
XC_6H_5	−20.2	29.1	−13.7
XC_6H_4-4-(SO_3NH_4)	−140.0	−90.6	−13.6
XC_6H_4-2-(SO_3NH_4)	−138.0	−83.4	− 8.4
XC_6H_3-2,4-$(SO_3NH_4)_2$	−251.2	−199.8	−11.6
XC_6H_2-2,4,6-$(SO_3NH_4)_3$	−373.6	−308.1	2.5

[a] Calculated values: $\Delta H_f(PH_3) = 0.2$ kcal/mol, $\Delta H_f(HF) = -62.8$ kcal/mol.

to remain planar. The C−P bond length calculated for $PhPH_2$ compares quite well with the value (1.839(5) Å) obtained from electron diffraction studies.[37a]

(37) (a) Naumov, V. A.; Kataeva, O. A. *J. Struct. Chem. USSR* **1983**, *24*, 160. (b) Ratovskii, G. V.; Panov, A. M.; Yakutina, O. A. *Zh. Obshch. Khim.* **1978**, *48*, 1520. Jones, I. W.; Tebby, J. C. *Perkin Trans. 2* **1979**, 501. (c) Cabelli, D. E.; Cowley, A. H.; Dewar, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 3286. (d) Nyulaszi, L.; Szieberth, D.; Csonka, G.; Reffy, J.; Heinicke, J.; Veszpremi, T. *Struct. Chem.* **1995**, *6*, 1.

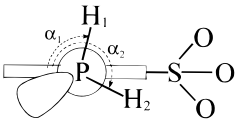

Figure 7. Conformation of the PH_2 group relative to the aromatic ring plane for the phosphino aryls $H_2PC_6H_5$ and **1a″**, **1b″**, **1c″** and **1d″** ($\alpha_i = \angle C(6)C(1)PH_i$).

Table 10. Selected Calculated Structural Parameters of Phenylphosphine Derivatives: C−P and C−S Bond Lengths (in Å) and Dihedral Angles $\alpha_i = \angle C(6)C(1)PH_i$ and $\delta = \angle C(4)C(3)C(2)C(1)$ (in deg)[a,b]

	r(C−P)	r(C−S)	α_1	α_2	δ
$H_2PC_6H_5$	1.841		42.6	142.6	−0.1
$H_2PC_6H_4$-4-(SO_3NH_4)	1.841	1.800	42.7	142.9	0.0
$H_2PC_6H_4$-2-(SO_3NH_4)	1.870	1.871	97.1	197.9	0.0
$H_2PC_6H_3$-2,4-$(SO_3NH_4)_2$	1.873	1.884 (*o*) 1.777 (*p*)	97.0	198.6	0.1
$H_2PC_6H_2$-2,4,6-$(SO_3NH_4)_3$	1.892	1.855 (*o*) 1.824 (*o*) 1.783 (*p*)	82.4	182.7	14.1

[a] Only Parameters that differ significantly between the various compounds are listed. [b] Bond angles $\beta_i = < CPH_i = 101 \pm 1.5°$, PH_2 wagging angle $\gamma = 106 \pm 1.5°$.

The rotational barrier for PH_2^- around the C−P bond is determined by the interaction of the phosphorus lone pair with the aryl substituents. In case of an otherwise unsubstituted aryl ring and for a sulfonic group in the *p*-position, **1a″**, the orientation of the phosphido group minimizes the repulsion of the lone pair with the aromatic ring system. In the case of a sulfonic group in the *o*-position, **1b″** and **1c″**, the orientation represents a compromise between this interaction and the repulsion of the phosphorus and oxygen lone pairs. However, the distance between the hydrogens and the oxygen is more than 3 Å, even in **1c″**, depicted in Figure 7, so that hydrogen bonds may be ruled out as a factor influencing the orientation of the phosphido group. For **1b″**, the energy difference between the two orientations where the phosphorus lone pair is coplanar with the ring is calculated to 4.9 kcal/mol, with the more favorable orientation having dihedral angles α_1 and α_2 about

97.0 and 198.6°, respectively (Table 10). The rotational barrier for this motion amounts to 8.4 kcal/mol. A bisector conformation I with the hydrogen atoms lying symmetrically at different sides of the benzene ring was assumed in an electron diffraction study of $PhPH_2$. Its predominance was also derived from the analysis of the UV absorption spectra, although a certain amount of a second conformer II in which the hydrogen atoms of the PH_2 group lie at one side of the ring could not be excluded.[37b] The existence of this conformer was confirmed by photoelectron spectroscopic studies.[37c] According to very recent work, however, the photoelectron spectrum of $PhPH_2$ cannot be explained by considering the most stable rotamer only, but all possible conformers should be taken into account. The energy difference between rotamer I and II was calculated to be only 0.3 kcal/mol at the MP2 level of theory, indicating that the rotation in $PhPH_2$ is nearly free.[37d] Thus, one expects larger phosphine substituents to be forced "away" from a sulfonic group in the *o*-position (see above) and the formation of tertiary phosphines to become less exothermic.

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Supporting Information Available: Listings of crystallographic data, hydrogen positional and thermal parameters, anisotropic thermal parameters, and bond distances and angles and ORTEP diagrams (14 pages). Ordering information is given on any current masthead page.

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