Preparation of New Sulfonated Triarylphosphanes: Control of the Selectivity by Structural Assistance

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A synthetic approach for the selective preparation of tri-, di-, and monosulfonated triarylphosphanes is presented. PPh_nAr_{3-n} parent phosphanes (**1a**–**8a**) having aryl rings (Ar) activated by simple electron donating groups (CH_3, CH_3O) were prepared by the standard Grignard method. The activated rings could be sulfonated selectively under mild conditions and with short reaction times (0.8–3 h). Using a very simple workup procedure, the corresponding tri-, di-, and monosulfonated phosphanes (**1b**–**8b**) were isolated in outstanding yields (88–99%) and found to contain negligible amount of phosphane oxides (0–4%).

Introduction

There is an increasing worldwide demand for environmentally friendly chemical processes. Aqueous organometallic catalysis can play a key role in the introduction of such sustainable technologies for several reasons: it provides access to a great variety of valuable chemicals, often under mild conditions and with high atom efficiency; the basic properties of the catalysts can be fine-tuned in order to maximize activity and selectivity. Additionally, these favorable features can be integrated with facile catalyst separation to avoid product contamination, resulting in commercially attractive catalyst systems.

An impressive example of a "green" chemical technology based on this concept is the Ruhrchemie − Rhône Poulenc process for manufacturing butyraldehyde. Today, the oxo-plant of Celanese AG (Ruhrchemie, 1984), together with a new plant in South Korea, produce about 600,000 tons of butyraldehyde annually by hydroformylation of propylene.[1]

Rhodium complexes of TPPTS (trisulfonated triphenylphosphane) are utilized as the catalyst in this technology. Generally TPPTS and TPPMS (monosulfonated triphenylphophane; Figure 1) are the most frequently used hydrophilic ligands in aqueous organometallic catalysis. Accordingly, a tremendous amount of work has been devoted to the direct sulfonation of triphenylphosphane, and generally to the sulfonation of arylphosphanes.[2]

Control of the degree of sulfonation is a characteristic difficulty in the preparation of sulfonated arylphosphanes. In the case of triphenylphosphane, the sulfonation of the phenyl rings theoretically could take place in a consecutive manner. However, due to the slight differences between the activation energies of the sulfonation of the non-, mono-, and disulfonated species, TPPTS, TPPMS, and particularly TPPDS (disulfonated triphenylphosphane) are difficult to prepare selectively and/or in good yields.

Beside selectivity, oxidation should be mentioned as a typical side-reaction. Due to the presence of the strongly oxidizing sulfur trioxide and the long reaction times (generally several days), the phosphane is usually partly oxidized during the reaction.

Numerous general and specific methods have been developed to overcome these obstacles. Notably, in 1996 Herrmann and co-workers suggested the use of a superacidic medium for sulfonation of arylphosphanes to suppress the side-reaction leading to the oxides.[2g] More recently Atwood has established that controlling the pH during workup allows synthesis of TPPTS without interference from the oxide (70% yield and only 5% of oxide at pH 3).[2m] Joó and co-workers prepared analytically pure TPPMS by *incomplete monosulfonation* of triphenylphosphane. Although the yield is rather low (29% after recrystallization), the unreacted triphenylphosphane can be recovered and reused.[2i] In 2000 Williams et al. selectively prepared the disulfonated triphenylphosphane in 60% yield by careful control of the reaction conditions.[2o]

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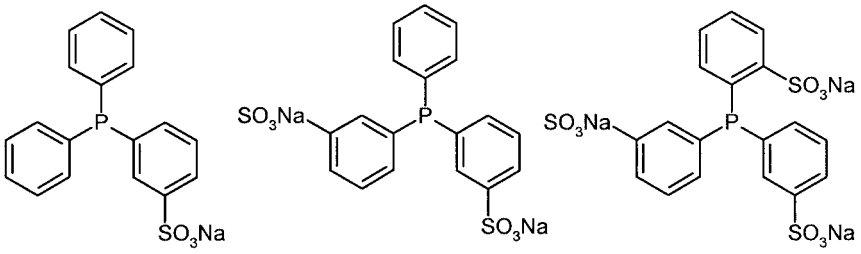
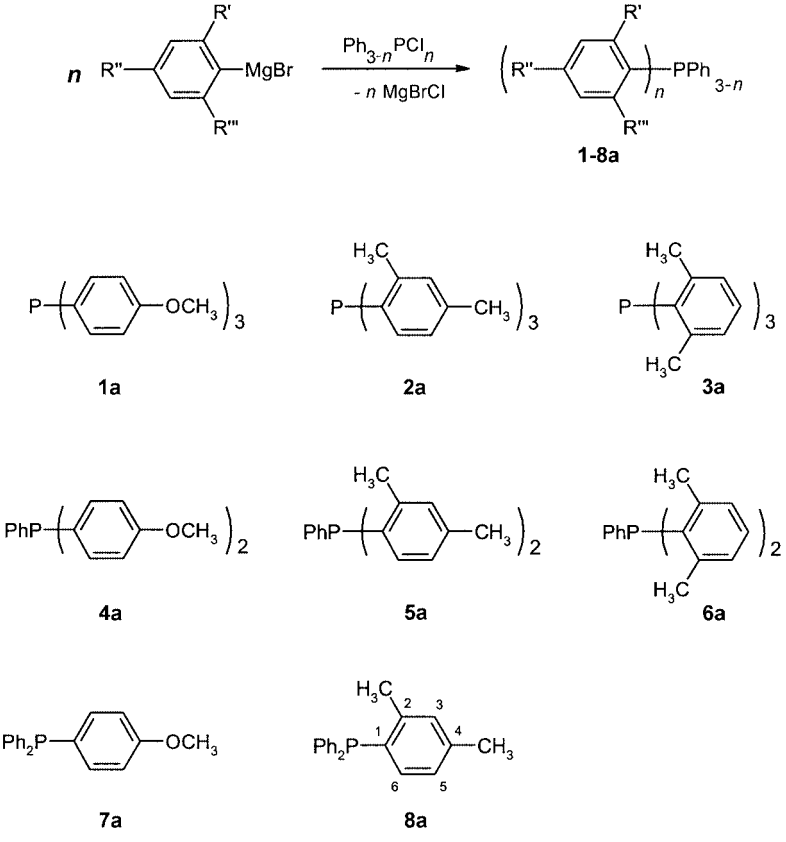


Figure 1. Mono-, di- and trisulfonated triphenylphosphane

Despite the great progress in this area, there remains a strong demand for improved strategies and pure synthetic routes towards hydrophilic ligands. Prompted by this demand, we have recently briefly described an approach to the selective sulfonation of triarylphosphanes.[3] Following this approach, which is based on the activation of certain phenyl rings by simple electron-donating groups, we have compiled a pool of new sulfonated phosphanes. Now, we report the full details of our synthetic study and show that by systematic variation of the number of activated rings and the number and position of the activating groups, mono- di and trisulfonated phosphanes with different steric and electronic properties can easily be prepared.

Results and Discussion

Triarylphosphanes **1a**−**8a** were prepared by classical synthetic methods (Scheme 1). Phosphanes **1a**−**7a** are known compounds.[4] To the best of our knowledge **8a** has not been prepared previously, although there is nothing remarkable about its preparation. All of these molecules contain methyl and methoxy substituents in the *ortho*- and/or *para*-positions to the phosphorus. Thus, in the course of the sulfonation, the directing effect of these activating groups is in accordance with the directing effect of the phosphorous protonated in the sulfonating medium. It should be noted that the substituents in these positions influence the elec-



Scheme 1. Activation of aryl rings by methyl and methoxy substituents

tronic and steric properties of the triarylphosphanes quite significantly.[2n,4e,5]

The reaction conditions and results of the sulfonation procedures are summarized in Table 1. Sulfonation of the phosphanes was carried out in fuming sulfuric acid containing usually 20% of free SO_3 (Scheme 2). In most cases 1 g of a phosphane was sulfonated in 2.5 mL of oleum, regardless of the slight differences between the molecular weights or even the desired degree of sulfonation. Thus, we wished to demonstrate that the outstanding selectivities were exclusively due to the appropriate activation. However, it is important to note that the applied amount and concentration of the fuming sulfuric acid provided an excess of free sulfur trioxide even in the case of trisulfonations. The solid starting materials were slowly added to the chilled oleum, then the reaction mixtures were stirred at room temperature for 0.8−3 hours.

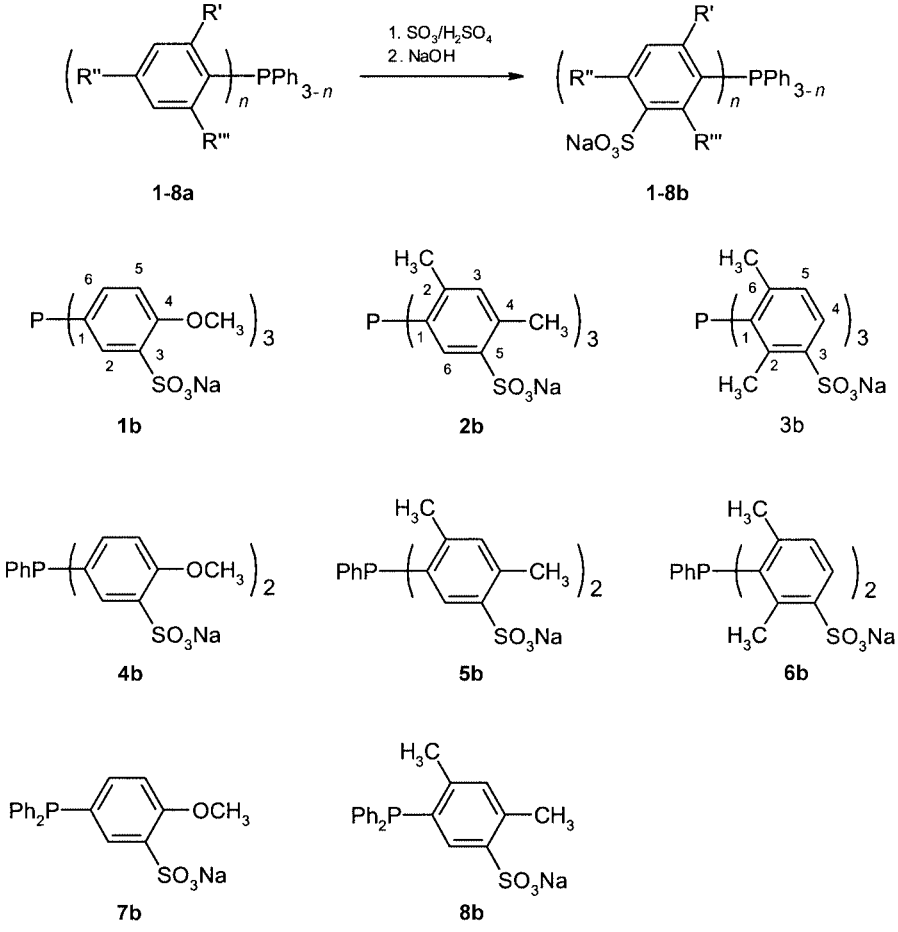
Table 1. Selected details of the preparation of **1b**−**8b**

Phosphane	Reaction time (h)	Isolated yield (%)	Oxide content (%)	^{31}P NMR (δ, ppm)
1b[a]	3	89	1	−8.5
2b[a]	3	91	0	−27.0
3b[b]	3	99	0	−29.5
4b[a]	2.5	95	1.5	−7.5
5b[a]	1.5	92	4.4	−22.1
6b[a]	0.83	89	<1	−18.5
7b[a]	1	95	0	−3.6
8b[a]	0.83	88	1	−10.9

[a] Reaction conditions: 1 g (2.89−3.45 mmol) of the phosphane was dissolved in 2.5 mL of fuming sulfuric acid (20% free SO_3) at between −8 and −3 °C, then the mixture was stirred at room temperature for the given reaction time. [b] Reaction conditions: 1.05 g (3.00 mmol) of **3a** was sulfonated in 3 mL of fuming sulfuric acid (30% free SO_3).

A number of methods can be found in the literature for the isolation of sulfonated phosphanes after direct sulfonation, although many of these methods are quite laborious. Our process is simple, and eliminates sodium sulfate contamination of the product. After careful neutralization of the reaction mixture with NaOH solution, the water was completely removed, and the product was separated from sodium sulfate by extraction with methanol. The methanol was either dry or contained only a controlled amount of water.

We designed phosphanes **1a**−**3a** (Scheme 1) for the preparation of trisulfonated ligands. In the case of **1a** each phenyl ring is activated by only one *para*-substituent. As a consequence, the steric properties of the corresponding sulfonated phosphane **1b** (Scheme 2) should not differ signifi-



Scheme 2. Selective preparation of sulfonated triarylphosphanes

cantly from that of the extensively used TPPTS. However, while the preparation of TPPTS usually requires 7−10 days reaction time, **1b** can be prepared in 3 hours and isolated in 89% yield; the product contained only traces of the oxide.

The phenyl rings of **2a** are activated by the methyl groups at C-2 and C-4. Despite the fact, that the two activated *meta*-positions are not equivalent, under the applied conditions one single product is formed: the substitution took place selectively at C-5, probably due to steric reasons.[6] The reaction was complete in 3 hours and oxidation of the desired product was negligible.

The preparation of **3b** demonstrates that these phosphanes can tolerate higher concentrations of SO_3, too. When 1.05 g of **3a** was sulfonated in 3 mL of 30% oleum, the product could be isolated in quantitative yield, and no side reaction was observed (Figure 2, top). With all its *ortho*-positions occupied by methyl groups, **3b** is probably the bulkiest sulfonated triarylphosphane prepared up to now.

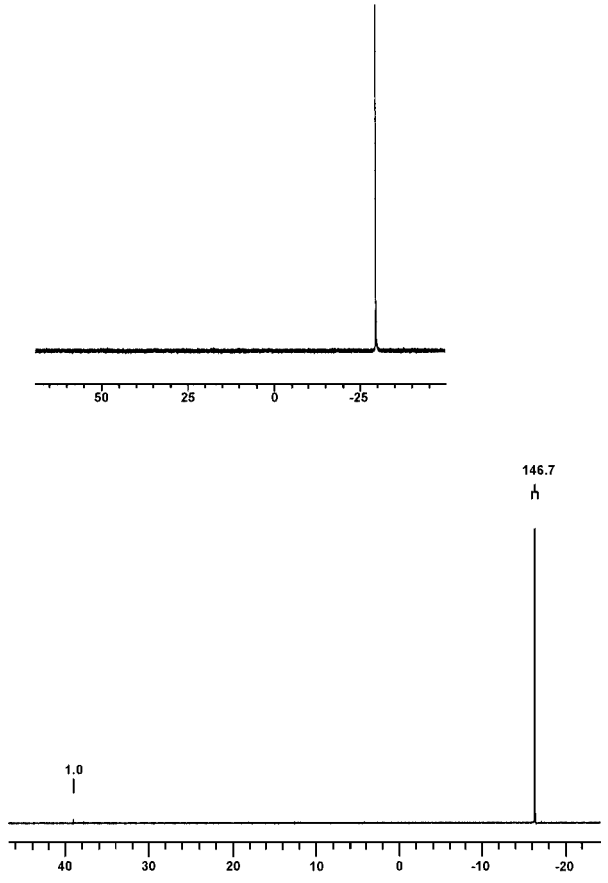


Figure 2. (top) ^{31}P NMR spectrum (D_2O) of **3b**; phosphane **3a** tolerates the use of 30% oleum as sulfonating agent very well; (bottom) ^{31}P NMR spectrum (D_2O) of **6b**; phosphane **6a** can be disulfonated selectively in 50 minutes

In **4a**−**6a** two phenyl rings are activated by electron-donating groups. While the preparation of TPPDS requires careful optimization of the reaction conditions and constant monitoring of the reaction mixture by NMR spectroscopy, these phosphanes were smoothly converted into their disulfonated derivatives **4b**−**6b** within 2.5 hours. The reactions are completely ring-selective and, in the case of **5b**, regioselective. The products were isolated in high yields and only traces of the oxides could be observed.

It is interesting to note that in our first experiments for the preparation of **5b** and **6b** we used a reaction time of 2.5 hours, as for the preparation of **4b**. Both products contained about 4% of oxide. We reasoned, therefore, that a shorter reaction time (shorter residence time in the strongly oxidizing oleum) might be beneficial. Indeed, when we decreased the reaction time to 50 minutes in the case of **6a**, the corresponding sulfonated phosphane could be isolated in 88% yield and contained no oxide (Figure 2, bottom), whereas, despite the most careful control of workup conditions and purity of the parent phosphane **5a**, systematic decrease of the reaction time in the preparation of **5b** (2.5 h, 2 h, 1.5 h) did not allow a further improvement in the quality of the product. However, this magnitude of oxide content should not limit the catalytic applications or complex chemical studies of the new ligand.

The monosulfonation of **7a** and **8a** was carried out similarly to the multiple sulfonations, although, due to the approximately 3.5-fold excess of free SO_3, the reactions are sensitive to the reaction time. For instance, when the reaction mixture of **8a** was stirred for 2.5 hours at room temperature, 6.2% of oxide and 2.6% of disulfonated phosphane was observed in the ^{31}P NMR spectrum of the isolated product. When the reaction time was decreased to 50 minutes, these side reactions were completely suppressed and the pure product was isolated in 88% yield.

Conclusion

In conclusion, we have described a new strategy to control the degree of sulfonation in the direct sulfonation of arylphosphanes. Our approach provides an easy access to a great variety of hydrophilic ligands. The syntheses are characterised by exceptionally short reaction times, complete selectivity, high yields and lack of oxidation. We believe that this method provides an opportunity for the systematic variation of the hydrophilic, steric and electronic characters of the ligands, and that it could therefore be useful for practical and theoretical comparative studies in aqueous organometallic catalysis and related areas. Our current research is focused on the catalytic study of the ligands, primarily in hydrogenation and hydroformylation, and an extension of the synthetic work for bidentate and chiral arylphosphanes.

Experimental Section

General Remarks: Organic solvents were purified, dried and deoxygenated by standard techniques. Water was double-distilled and deoxygenated by bubbling argon for at least 30 min. All preparations were carried out under argon atmosphere using standard Schlenk techniques. Phosphanes **1a**−**7a** are known compounds and were prepared by published methods.[4] ^1H NMR, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ spectra were recorded on either a Varian Unity 300 spectrometer

operating at 300.15 MHz, 75.43 MHz and 121.42 MHz, respectively, or on a Bruker DRX-500 spectrometer operating at 500.13 MHz, 125.76 MHz and 202.45 MHz, respectively. Chemical shifts are reported in parts per million (ppm) downfield (positive values) or upfield (negative values) from tetramethylsilane (external standard for ^1H and $^{13}C\{^1H\}$) or 85% H_3PO_4 (external standard for $^{31}P\{^1H\}$). Assignments of the resonances in ^1H and $^{13}C\{^1H\}$ spectra are based in part on $^1H\{^{31}P\}$, NOESY, APT, HMQC and HMBC experiments. The abbreviations Ph and Ar are used for phenyl and substituted aryl rings. The carbon atoms of the phenyl rings are labelled as follows: *ipso*: a; *ortho*: b; *meta*: c; *para*: d. The carbon atoms of the substituted aryl rings are labelled with numbers according to the IUPAC nomenclature (see Scheme 1 and 2). Mass spectrometric measurements were performed using a PE SCIEX API 2000 triple quadrupole instrument. Electrospray ionization was used and negative ions were detected. ICP elemental analyses were carried out using a GBC Integra XM (Australia) spectrometer.

(2,4-Dimethylphenyl)diphenylphosphane (8a): Chlorodiphenylphosphane (22.1 g, 18 mL, 0.1 mol) was added dropwise to (2,4-dimethylphenyl)magnesium bromide (0.12 mol) dissolved in THF (110 mL) at 0 °C (ice bath). THF (20 mL) was layered onto the surface of the $ClPPh_2$ to rinse the residue into the reaction mixture. After addition of the chlorodiphenylphosphane, the reaction mixture was stirred for 30 min at 0 °C, for 2 hours at room temperature, and then refluxed for an hour. The reaction mixture was cooled again in an ice bath and carefully hydrolyzed by addition of 200 g of 10% NH_4Cl solution. Having removed the THF in vacuo, the reaction mixture was extracted with 2 × 100 mL of CH_2Cl_2. The organic phase was washed with 100 g of 5% $NaHCO_3$ solution and 2 × 100 mL of water then dried over $MgSO_4$ for one day. The $MgSO_4$ was then filtered off. Removal of the CH_2Cl_2 in vacuo yielded the raw product as a yellow oil. The oil solidified upon washing it with cold MeOH. Recrystallization (MeOH/EtOH) of this white microcrystalline solid gave 15.11 g of product as colorless crystals. Over one week a further 2.76 g of pure product crystallized from the mother liquor. Yield: 17.87 g (61.6%). Mp: 61−63 °C. ^1H NMR ($CDCl_3$): δ = 2.30 (s, 3 H, CH_3), 2.37 (s, 3 H, CH_3), 6.67 (dd, $^3J_{P,H}$ = 4.5, $^3J_{H,H}$ = 7.8 Hz, 1 H, C6-H), 6.89 (d, $^3J_{H,H}$ = 7.8 Hz, 1 H, C5-H), 7.04 (d, $^4J_{P,H}$ = 4.6 Hz, 1 H, C3-H) 7.2−7.4 (m, 10 H, Ph) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 21.19 (d, $^3J_{P,C}$ = 20.9 Hz, C2-*CH*$_3$), 21.21 (s, C4-*CH*$_3$), 126.89 (s, C5), 128.55 (d, $^4J_{P,C}$ = 7.7 Hz, Cc), 128.65 (s, Cd), 131.08 (d, $J_{P,C}$ = 5.5 Hz, Ar), 132.41 (d, $^1J_{P,C}$ = 10.6 Hz, C1), 132.98 (s, Ar), 133.94 (d, $^2J_{P,C}$ = 19.8 Hz, Cb), 136.70 (d, $^1J_{P,C}$ = 11.0 Hz, Ca), 138.68 (s, C4), 142.22 (d, $^2J_{P,C}$ = 26.4 Hz, C2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −13.6 (s) ppm. $C_{20}H_{19}P$ (290.34): calcd. C 82.73, H 6.59; found C 82.64, H 6.54.

General Procedure for the Sulfonation of Triarylphosphanes: The finely ground phosphane was added in small portions to the fuming acid at −8 to −3 °C (ice/salt bath). Addition of the total amount of the phosphane took at least 1 hour. Having added the phosphane the ice/salt bath was removed and the reaction mixture was stirred at room temperature for the given reaction time. The mixture was chilled again using an ice/salt bath, then crushed ice (approximately 10 g) was added over 30 minutes in order to stop the reaction. During the procedure the argon atmosphere was changed several times above the solution. A calculated amount of NaOH dissolved in deoxygenated water (30 mL) was added over at least 40 minutes to neutralize the solution. During neutralization a temperature of between −5 and 0 °C was maintained. [Lower temperatures should be avoided. If the stir bar is stuck in the first part of the neutralization process (**5b**−**8b**), blending should be maintained by shaking the flask gently.] Careful adjustment of the pH to 6−8 was carried out using either a digital pH meter or special pH paper. The water was then removed in vacuo. The white solid residue was extracted with dry or wet methanol, then the remaining Na_2SO_4 was washed again. From the combined methanol phases the solvent was evaporated in vacuo and the phosphane was dissolved in water. Removal of the water in vacuo yielded the methanol-free sulfonated phosphane.

Trisodium Salt of Tris(4-methoxy-3-sulfonatophenyl)phosphane (1b): Starting material: 1 g (2.84 mmol) of **1a**. Oleum: 2.5 mL (20% of free SO_3). Reaction time: 3 hours. Neutralization: 3.7 g (92.6 mmol) of NaOH. Extraction: a mixture of MeOH and water (190 mL/10 mL), then MeOH and water (190 mL/10 mL) again. The product was isolated as a white powder (1.80 g, 89%). ^1H NMR (D_2O): δ = 3.83 (s, 9 H, OCH_3), 6.95 (d, $^3J_{H,H}$ = 9.5 Hz, 3 H, C5-H), 7.17 (m, 3 H, C6-H), 7.68 (dd, $^3J_{P,H}$ = 8.0, $^4J_{H,H}$ = 2.0 Hz, 3 H, C2-H) ppm. $^{13}C\{^1H\}$ NMR (D_2O): δ = 56.44 (s, OCH_3), 113.65 (d, $^3J_{P,C}$ = 7.5 Hz, C5), 127.20 (d, $J_{P,C}$ = 6.2 Hz, Ar), 130.90 (d, $J_{P,C}$ = 8.4 Hz, Ar), 133.46 (d, $^2J_{P,C}$ = 23.9 Hz, C2), 138.85 (d, $^2J_{P,C}$ = 18.0 Hz, C6), 157.76 (s, C4) ppm. $^{31}P\{^1H\}$ NMR (D_2O): δ = −8.5 (s) ppm. MS (ESI^-): *m*/*z* = 614.2 $[M - 2Na^+ + H^+]^-$, 591.4 $[M - 3Na^+ + 2H^+]^-$, 295.6 $[M - 3Na^+ + H^+]^{2-}$, 196.3 $[M - 3Na^+]^{3-}$. $C_{21}H_{18}Na_3O_{12}PS_3 \cdot 3H_2O$ (712.55): calcd. P 4.35, S 13.50, Na 9.68; found (ICP): P 4.42, S 13.80, Na 9.64; S/P = 3.01.

Trisodium Salt of Tris(2,4-dimethyl-5-sulfonatophenyl)phosphane (2b): Starting material: 1 g (2.89 mmol) of **2a**. Oleum: 2.5 mL (20% of free SO_3). Reaction time: 3 hours. Neutralization: 3.7 g (92.4 mmol) of NaOH. Extraction: a mixture of MeOH and water (50 mL/2 mL), then MeOH and water (50 mL/1 mL) again. The product was isolated as a white powder (1.92 g, 94%). ^1H NMR (D_2O): δ = 1.96 (s, 9 H, C2-CH_3), δ = 2.32 (s, 9 H, C4-CH_3), 6.75 (broad s, 3 H, C3-H), 7.18 (d, $^3J_{P,H}$ = 4.0 Hz, 3 H, C6-H) ppm. $^{13}C\{^1H\}$ NMR (D_2O): δ = 19.69 (s, C4-*CH*$_3$), 20.61 (d, $^3J_{P,C}$ = 21.4 Hz, C2-*CH*$_3$), 130.86 (d, $^1J_{P,C}$ = 10.1 Hz, C1), 131.60 (s, C6), 134.45 (d, $^3J_{P,C}$ = 4 Hz, C3), 137.80 (s, C4), 139.62 (s, C5), 146.47 (d, $^2J_{P,C}$ = 27.7 Hz, C2) ppm. $^{31}P\{^1H\}$ NMR (D_2O): δ = −27.0 (s) ppm. MS (ESI^-): *m*/*z* = 629.2 $[M - Na^+]^-$, 303.1 $[M - 2Na^+]^{2-}$, 292.0 $[M - 3Na^+ + H^+]^{2-}$, 194.5 $[M - 3Na^+]^{3-}$. $C_{24}H_{24}Na_3O_9PS_3 \cdot 3H_2O$ (706.63): calcd. P 4.38, S 13.61, Na 9.76; found (ICP): P 4.56, S 14.1, Na 9.43; S/P = 2.99.

Trisodium Salt of Tris(2,6-dimethyl-3-sulfonatophenyl)phosphane (3b): Starting material: 1.04 g (3 mmol) of **3a**. Oleum: 3 mL (30% of free SO_3). Reaction time: 3 hours. Neutralization: 4.5 g (112.3 mmol) of NaOH. Extraction: MeOH (2 × 70 mL). The product was isolated as a yellowish-white powder (2.10 g, 99%). ^1H NMR (D_2O): δ = 1.97 (s, 9 H, C6-CH_3), 2.47 (s, 9 H, C2-CH_3), 7.09 (dd, $^3J_{H,H}$ = 7.5, $^4J_{P,H}$ = 2.8 Hz, 3 H, C5-H), 7.85 (d, $^3J_{H,H}$ = 7.5 Hz, 3 H, C4-H) ppm. $^{13}C\{^1H\}$ NMR (D_2O): δ = 19.62 (d, $^3J_{P,C}$ = 20.8 Hz, C2-*CH*$_3$), 23.35 (d, $^3J_{P,C}$ = 12.8 Hz, C6-*CH*$_3$), 128.08 (s, C4), 129.30 (s, C5), 137.49 (d, $^1J_{P,C}$ = 20.6 Hz, C1), 140.68 (d, $^3J_{P,C}$ = 3.6 Hz, C3), 140.85 (d, $^2J_{P,C}$ = 21.8 Hz, C2), 146.8 (d, $^2J_{P,C}$ = 16.9 Hz, C6) ppm. $^{31}P\{^1H\}$ NMR (D_2O): δ = −29.5 (s) ppm. MS (ESI^-): *m*/*z* = 607.3 $[M - 2Na^+ + H^+]^-$, 585.1 $[M - 3Na^+ + 2H^+]^-$, 303.4 $[M - 2Na^+]^{2-}$, 292.3 $[M - 3Na^+ + H^+]^{2-}$, 194.5 $[M - 3Na^+]^{3-}$. $C_{24}H_{24}Na_3O_9PS_3 \cdot 3H_2O$ (706.63): calcd. P 4.38, S 13.61, Na 9.76; found (ICP): P 4.56, S 13.8, Na 9.41; S/P = 2.92.

Disodium Salt of Bis(4-methoxy-3-sulfonatophenyl)phenylphosphane (4b): Starting material 1 g (3.1 mmol) of **4a**. Oleum: 2.5 mL (20% of free SO_3). Reaction time: 2.5 hours. Neutralization: 3.8 g

(94.9 mmol) of NaOH. Extraction: a mixture of MeOH and water (40 mL/2 mL), then MeOH (40 mL). The product was isolated as a shiny white powder (1.65 g, 95%). ^{1}H NMR (D_2O): δ = 3.74 (s, 6 H, OCH_3), 6.74 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, C5-H), 7.05−7.1 (m, 4 H, C6-H and Cb-H), 7.19 (pseudo t, 2 H, Cc-H), 7.23 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, Cd-H), 7.67 (dd, $^3J_{P,H}$ = 7.5, $^4J_{H,H}$ = 2.0 Hz, 2 H, C2-H) ppm. ^{13}C{^{1}H} NMR (D_2O): δ = 56.35 (s, OCH_3), 113.48 (d, $^3J_{P,C}$ = 7.3 Hz, C5), 127.15 (d, $J_{P,C}$ = 7.2 Hz, Ar), 129.38 (d, $^3J_{P,C}$ = 7.6 Hz, Cc), 129.83 (s, Cd), 130.87 (d, $J_{P,C}$ = 7.3 Hz, Ar), 133.53 (d, $^2J_{P,C}$ = 19.5 Hz, Cb), 133.62 (d, $^2J_{P,C}$ = 22.7 Hz, C2), 136.43 (d, $^1J_{P,C}$ = 7.3 Hz, Ca), 138.96 (d, $^2J_{P,C}$ = 20.9 Hz, C6), 157.67 (s, C4) ppm. ^{31}P{^{1}H} NMR (D_2O): δ = −7.5 (s) ppm. MS (ESI^-): *m/z* = 503.2 [M − Na^+]$^-$, 481.0 [M − 2Na^+ + H^+]$^-$, 240.1 [M − 2Na^+]$^{2-}$. $C_{20}H_{17}Na_2O_8PS_2{\cdot}2H_2O$ (562.46): calcd. P 5.51, S 11.40, Na 8.17; found (ICP): P 5.53, S 11.50, Na 8.21; S/P = 2.02.

Disodium Salt of Bis(2,4-dimethyl-5-sulfonatophenyl)phenylphosphane (5b): Starting material: 1 g (3.14 mmol) of **5a**. Oleum: 2.5 mL (20% of free SO_3). Reaction time: 1.5 hours. Neutralization: 3.8 g (94.8 mmol) of NaOH. Extraction: a mixture of MeOH and water (50 mL/2 mL), then MeOH (50 mL). The product was isolated as a white powder (1.62 g, 92%). ^{1}H NMR (D_2O): δ = 2.03 (s, 6 H, C2-CH_3), 2.35 (s, 6 H, C4-CH_3), 6.83 (d, $^4J_{P,H}$ = 4.4 Hz, 2 H, C3-H), 6.92 (pseudo t, 2 H, Ph), 7.01 (pseudo t, 2 H, Ph), 7.12 (t, $^3J_{H,H}$ = 7.4 Hz, 1 H, Cd-H), 7.18 (d, $^3J_{P,H}$ = 3.9 Hz, 2 H, C6-H) ppm. ^{13}C{^{1}H} NMR (D_2O): δ = 19.62 (s, C4-*CH_3*), 20.70 (d, $^3J_{P,C}$ = 21.0 Hz, C2-*CH_3*), 129.30 (d, $^1J_{P,C}$ = 7.2 Hz, Cc), 129.76 (s, Cd), 131.56 (s, C6), 132.52 (d, $^2J_{P,C}$ = 12.1 Hz, C1), 134.19−134.40 (C3, Cb, Ca), 137.43 (s, C4), 139.44 (s, C5), 146.03 (d, $^2J_{P,C}$ = 25.8 Hz, C2) ppm. ^{31}P{^{1}H} NMR (D_2O): δ = −21.5 (s) ppm. MS (ESI^-): *m/z* = 477.4 [M − 2Na^+ + H^+]$^-$, 238.3 [M − 2Na^+]$^{2-}$. $C_{22}H_{21}Na_2O_6PS_2{\cdot}2H_2O$ (558.51): calcd. P 5.54, S 11.48, Na 8.23; found (ICP): P 5.48, S 11.7, Na 7.67; S/P = 2.06.

Disodium Salt of Bis(2,6-dimethyl-3-sulfonatophenyl)phenylphosphane (6b): Starting material: 1 g (3.14 mmol) of **6a**. Oleum: 2.5 mL (20% of free SO_3). Reaction time: 50 min. Neutralization: 3.8 g (94.8 mmol) of NaOH. Extraction: a mixture of MeOH and water (50 mL/2 mL), then MeOH (50 mL). The product was isolated as a white powder (1.55 g, 89%). ^{1}H NMR (CD_3OD): δ = 2.12 (s, 6 H, C6-CH_3), δ = 2.64 (s, 6 H, C2-CH_3), 7.08 (dd, $^3J_{H,H}$ = 8.0, $^4J_{P,H}$ = 2.0 Hz, 2 H, C5-H), 7.25−7.45 (broad m, 5 H, Ph), 7.95 (d, $^3J_{H,H}$ = 8.0 Hz, 2 H, C4-H) ppm. ^{13}C{^{1}H} NMR (125.76, CD_3OD): δ = 19.41 (d, $^3J_{P,C}$ = 21.8 Hz, C2-*CH_3*), δ = 22.99 (d, $^3J_{P,C}$ = 13.34 Hz, C6-*CH_3*), 128.16 (s, C4), 128.51 (s, C5), 128.55 (d, $^3J_{P,C}$ = 5.0 Hz, Cc), 128.64 (s, Cd), ≈134.1 (broad d, $^2J_{P,C}$ ≈ 23 Hz, Cb), 136.52 (d, $^1J_{P,C}$ = 21.8 Hz, C1), 136.75 (d, $^1J_{P,C}$ = 12.2 Hz, Ca), 141.30 (d, $^2J_{P,C}$ = 19.3 Hz, C2), 142.78 (d, $^3J_{P,C}$ = 2.2 Hz, C3), 145.31 (d, $^2J_{P,C}$ = 13.3 Hz, C6) ppm. ^{31}P{^{1}H} NMR (CD_3OD): δ = −18.5 (s) ppm. MS (ESI^-): *m/z* = 499.0 [M − Na^+]$^-$, 477.1 [M − 2Na^+ + H^+]$^-$, 237.7 [M − 2Na^+]$^{2-}$. $C_{22}H_{21}Na_2O_6PS_2{\cdot}2H_2O$ (558.51): calcd. P 5.54, S 11.48, Na 8.23; found (ICP): P 5.24, S 11.0, Na 7.43; S/P = 2.03.

Sodium Salt of (4-Methoxy-3-sulfonatophenyl)diphenylphosphane (7b): Starting material: 1 g (3.42 mmol) of **7a**. Oleum: 2.5 mL (20% of free SO_3). Reaction time: 1 hour. Neutralization: 3.9 g (97.7 mmol) of NaOH. Extraction: MeOH (2 × 50 mL). The product was isolated as a white powder (1.40 g, 95%). ^{1}H NMR (CD_3OD): δ = 3.91 (s, 3 H, OCH_3), 7.08 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, C5-H), 7.2−7.4 (m, 10 H, Ph), 7.89 (dd, $^3J_{P,H}$ = 7.7, $^4J_{H,H}$ = 2.0 Hz, 1 H, C2-H) ppm. ^{13}C{^{1}H} NMR (CD_3OD): δ = 56.67 (s, OCH_3), 113.66 (d, $^3J_{P,C}$ = 6.9 Hz, C5), 128.37 (d, $J_{P,C}$ = 10.2 Hz, Ar), 129.80 (d, $^3J_{P,C}$ = 6.9 Hz, Cc), 130.09 (s, Cd), 133.64 (d, $J_{P,C}$ = 8.1 Hz, Ar), 134.49 (d, $^2J_{P,C}$ = 19.1 Hz, Cb), 135.43 (d, $^2J_{P,C}$ = 25.1 Hz, C2), 138.53 (d, $^1J_{P,C}$ = 9.2 Hz, Ca), 139.27 (d, $^2J_{P,C}$ = 19.6 Hz, C6), 159.16 (s, C4) ppm. ^{31}P{^{1}H} NMR (CD_3OD): δ = −3.6 (s) ppm. MS (ESI^-): *m/z* = 371.2 [M − Na^+]$^-$. $C_{19}H_{16}NaO_4PS{\cdot}2H_2O$: calcd. P 7.20, S 7.45, Na 5.34; found (ICP): P 6.84, S 7.10, Na 4.99; S/P = 1.00.

Sodium Salt of (2,4-Dimethyl-5-sulfonatophenyl)diphenylphosphane (8b): Starting material: 1 g (3.45 mmol) of **8a**. Oleum: 2.5 mL (20% of free SO_3). Reaction time: 1 hour. Neutralization: 3.9 g (97.7 mmol) of NaOH. Extraction: mixture of MeOH and water (50 mL/2 mL) then MeOH (50 mL). The product was isolated as a white powder (1.30 g, 88%). ^{1}H NMR (CD_3OD): δ = 2.35 (s, 3 H, C2-CH_3), 2.65 (s, 3 H, C4-CH_3), 7.14 (d, $^4J_{P,H}$ = 4.5 Hz, 1 H, C3-H), 7.2−7.4 (m, 10 H, Ph), 7.56 (d, $^3J_{P,H}$ = 4.5 Hz, 1 H, C6-H) ppm. ^{13}C{^{1}H} NMR (CD_3OD): δ = 19.42 (s, C4-*CH_3*), 20.04 (d, $^3J_{P,C}$ = 21.8 Hz, C2-*CH_3*), 128.72 (d, $^1J_{P,C}$ = 7.0 Hz, Cc), 128.99 (s, Cd), 131.88 (s, C6), 133.13 (d, $^1J_{P,C}$ = 13.2 Hz, C1), 133.46 (d, $^3J_{P,C}$ = 4.9 Hz, C3), 133.98 (d, $^2J_{P,C}$ = 19.3 Hz, Cb), 136.51 (d, $^1J_{P,C}$ = 9.9 Hz, Ca), 137.43 (s, C4), 141.37 (s, C5), 144.64 (d, $^2J_{P,C}$ = 25.4 Hz, C2) ppm. ^{31}P{^{1}H} NMR (CD_3OD): δ = −10.9 (s) ppm. MS (ESI^-): *m/z* = 369.1 [M − Na^+]$^-$, MS (ESI^+, *m/z*): 393.1 [M + H^+]$^-$, 370.9 [M − Na^+ + 2H^+]$^-$. $C_{20}H_{18}NaO_3PS{\cdot}2H_2O$: calcd. P 7.22, S 7.45, Na 5.37; found (ICP): P 6.77, S 7.09, Na 5.02; S/P = 1.01.

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[6] Beside multinuclear and two-dimensional NMR techniques, X-ray analysis also proves the position of the sulfonate group. However, because of its stereochemical relevance, the structure will be published elsewhere.

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