Sulfonated Diphenylphosphanes for Homogeneous Biphasic Catalysis via a Combined Protection/Deprotection Protocol

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Keywords: P ligands / Water chemistry / Sulfur / Biphasic catalysis

Oxidation of the sulfonated oxygen-labile alkyl- and benzyldiphenylphosphanes **3a**–**f** during hydrolytic workup of the oleum-containing sulfonation mixture is prevented by "soft" hydrolysis with disodium oxalate or basic aluminum oxide. Furthermore, the use of a protection protocol allows for the synthesis of the air-stable sulfonated phosphanylborane adducts **6a**–**f** for storage and purification purposes. Deprotection yields the corresponding sulfonated alkyl- and benzyldiphenylphosphanes **7a**–**f**.

Introduction

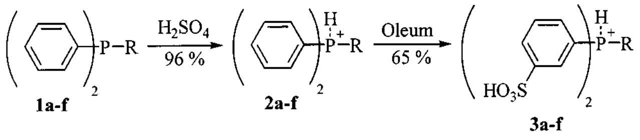
Water-soluble phosphane ligands form transition metal complexes which serve as catalysts in biphasic industrial processes.[1] Several routes towards the synthesis of sulfonated phosphanes have been described in the literature. However, these procedures are often unreliable or tedious.

In the course of our investigations of Pd-catalyzed biphasic aromatic aminations[2] we attempted to prepare new water-soluble phosphane ligands by sulfonation. Following literature procedures we were challenged by considerable oxidation of the oxygen-labile phosphanes. Neither direct sulfonation with concentrated sulfuric acid and oleum in varying ratios and at different temperatures,[3] nor Herrmann's boric acid protocol[4] turned out to be satisfactory. Alkylphosphanes, with the exception of ethyldiphenylphosphane (**1b**), were oxidized at phosphorus in different amounts, while benzyldiphenylphosphane (**1f**) could not be sulfonated without complete oxidation when using the direct route. Attempts to prepare a sulfonated DPEphos-analogue[5] with boric acid/sulfuric acid/oleum resulted in phosphane oxidation of at least 30%. Following Larpent's strategy of silver-mediated esterification of sulfonated phosphane oxides followed by trichlorosilane reduction and deesterification,[6] we found that the esterification step gives results that are difficult to reproduce, while the reduction of sterically congested sulfonated phosphane oxides (e.g. sulfonated diphenyl-*tert*-butylphosphane oxide) did not proceed to completion.

We describe here a new method for the synthesis of sulfonated alkyl- and benzyldiphenylphosphane ligands via P-protected sulfonated tertiary phosphanes.

Results and Discussion

Monitoring the direct sulfonation reaction by ^{31}P NMR spectroscopy we found that after dissolution of the alkyl- or benzyldiphenylphosphanes **1a−f** in degassed concentrated sulfuric acid (96%) protonation to **2a−f** protected the phosphorus atom from oxidation (see Scheme 1). This is evidenced by a large upfield shift of the phosphorus singlet by approximately 20−30 ppm (see Table 1). As a consequence, the addition of oleum (65%) to the reaction mixture at 0 °C did not lead to oxidation of the phosphorus atom. In order to assure complete sulfonation to **3a−f**, the reaction mixture was kept at 30−50 °C for 2 days.



a: R = Me; **b**: R = Et; **c**: R = *n*Bu; **d**: R = *t*Bu; **e**: R = cyclohexyl;
1f, 2f: R = benzyl; **3f**: R = sulfonatobenzyl

Scheme 1

Table 1. ^{31}P NMR chemical shifts of **1** and **2**

Substance	**1** (δ [ppm], $CDCl_3$)	**2** (δ [ppm], D_2O)
a	−26.3	5.5
b	−	13.2
c	−15.1	12.7
d	18.3	32.0
e	−3.2	19.9
f	−9.3	16.8

Substantial oxidation at phosphorus of the more labile **3a−f** occurred, however, during dropwise hydrolysis on crushed ice. In order to minimize this undesired reaction we added the reaction solution containing **3a−f** at low temperature (−78 °C) to the salts of various acids, some of which possess reducing properties. After the addition of water and warming to room temperature, magnesium oxide (MgO), sodium carbonate (Na_2CO_3) or sodium formate (HCO_2Na) yielded a mixture of sulfonated phosphanes and the corresponding phosphane oxides, as judged by ^{31}P NMR spectro-

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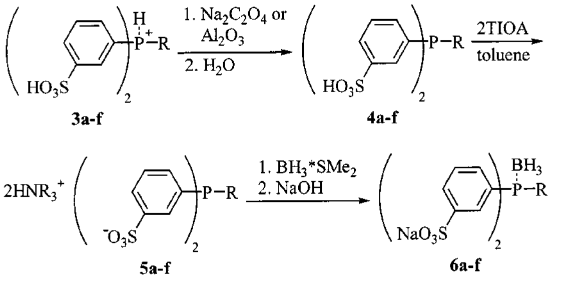
scopy. With disodium oxalate ($Na_2C_2O_4$) or basic aluminum oxide (Al_2O_3), however, no or only little oxidation of phosphorus was observed. Since the use of HCO_2Na, being a reducing agent, leads also to oxidation at phosphorus, which is not the case with Al_2O_3, we do not attribute the observed minimized oxidation in the presence of $Na_2C_2O_4$ to its reducing power. While the reaction of the earlier mentioned salts (Na_2CO_3, MgO, HCO_2Na) with the reaction mixture to give mixed sulfuric acid anhydrides is exothermic (vide infra), the reaction with $Na_2C_2O_4$ or basic Al_2O_3 is less so. Thus we assume the heat formation in this case to be lower than for direct hydrolysis on ice, resulting in less oxidation of phosphorus by SO_3.

Following the procedure described by Herrmann et al. the sulfonic acids **4a−f** were then extracted into toluene with triisooctylamine (TIOA; Scheme 2).[4] The deprotonated sulfonated alkyl- and benzylphosphanes **5a−f** can easily be protected with BH_3 for storage by the reaction with $BH_3 \cdot SMe_2$, yielding the corresponding borane adducts **6a−f** after reextraction of the organic layer with sodium hydroxide solution (Scheme 2).[7] Subsequent drying affords the protected phosphanes **6a−f** as air-stable solids in acceptable yields (see Table 2). During the reextraction step the phosphane oxides can be separated by repeated addition of small amounts of sodium hydroxide solution, as phosphane oxides are more water-soluble than the corresponding borane adducts. Nonprotected sulfonated phosphanes can readily be obtained for immediate use by identical workup, except for protection.

In the case of the trisulfonated benzyldiphenylphosphane **6f**, the *o,m,m* isomer was detected as well as the *p,m,m* isomer.[8] Recrystallisation from water by stepwise addition of methanol/ethanol afforded the *p,m,m* isomer, even though traces of a second compound with identical splitting of signals, but slightly different shifts was detected, too.



a: R = Me; **b**: R = Et; **c**: R = *n*Bu; **d**: R = *t*Bu; **e**: R = cyclohexyl; **f**: R = sulfonatobenzyl

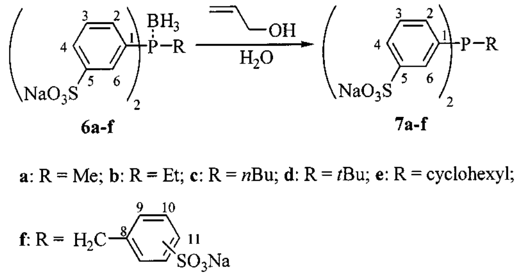
Scheme 2

Table 2. Yields of **6a−f**

Substance	**6** (%)	P-oxide of **6** (%)
a	65	1.0
b	65	0.4
c	67	–
d	69	0.4
e	64	3.9
f	5[a]	–

[a] 56 mg after crystallization from water/methanol. A further 432 mg were isolated as a mixture of *o,m,m* and *p,m,m* isomers from the mother liquor

The deprotection of the borane/phosphane adducts **6a−f** was achieved by heating with allyl alcohol in water (Scheme 3).[9] After extraction with 1-butanol and separation of the phases the sulfonated phosphanes **7a−f** remained in the aqueous layer. Deprotection was complete, and only traces of oxidation at phosphorus were observed (see Table 3).



Scheme 3

Table 3. Yields of **7a−f** from **6a−f**

Substance	**7** (%)	P-oxide of **7** (%)
a	80	5.0
b	93	6.4
c	86	7.0
d	80	5.5
e	82	2.7
f	89	7

Conclusions

We have presented a new and convenient route to water-soluble phosphane ligands. Oxidation of phosphorus by SO_3 that is possibly attributable to the heat of hydrolysis of pyrosulfuric acid in the reaction medium is circumvented by “soft” hydrolysis using disodium oxalate or basic aluminum oxide. Sulfonated alkyl- and benzyldiphenylphosphanes are accessible as their air-stable borane adducts **6a−f**. Further purification, storage and handling in the solid state, as well as in solution, is easily achieved. Deprotection occurs under mild conditions to give the desired, unprotected sulfonated phosphanes **7a−f**.

The ligands **7a−f** mentioned above form complexes with palladium acetate that are catalytically active in Heck reactions. Evaluation of their reactivity in view of their electronic and structural properties in biphasic catalytic arylaminations and Heck reactions is under way and will be communicated soon. Further work is aimed at the preparation of bidentate sulfonated phosphane ligands.

Experimental Section

General: The reagents mentioned in the experimental procedures are commercially available and were used without further purification. Solvents were degassed and dried by standard techniques. Preparations were carried out employing standard Schlenk techniques. The progress of the reactions was determined by ^{31}P NMR spectroscopy. NMR spectra were recorded on Bruker spectrometers ARX-200 MHz, AC-300 MHz, DRX-400 MHz and AMX-500 MHz, respectively. H_3PO_4 was used as an external standard for the ^{1}H-decoupled ^{31}P NMR measurements. $CDCl_3$ in a separate reservoir served as an external standard for the ^{13}C spectra of water-soluble compounds. Coupling constants are quoted in Hz. Mass spectra were determined on a Varian MAT CH7a (EI), a Hewlett Packard Series 1100MSD (ESI) or a Micromass Ltd. Autospec (HRMS) mass spectrometer. For atom labeling see Scheme 3.

The alkyldiphenylphosphanes (**1a−f**) were prepared by published methods or slight modifications thereof:[10] diphenylmethylphosphane (**1a**; see ref.[11]); diphenylethylphosphane (**1b**; purchased from Aldrich and employed without further purification); ***n*-Butyldiphenylphosphane** (**1c**; see ref.[12]); diphenyl-*tert*-butylphosphane (**1d**; see ref.[13]); cyclohexyldiphenylphosphane (**1e**; see ref.[13]); benzyldiphenylphosphane (**1f**; see refs.[13,14]).

Typical Procedure for the Preparation of Sulfonated Alkyl- or Benzyldiphenylphosphaneborane Adducts (6a−f): Diphenylphosphane **1a−f** (10 mmol) was dissolved in 5 mL of degassed, concentrated sulfuric acid (96%) at 0 °C under an inert gas atmosphere. After complete dissolution of the phosphane, 5 mL of oleum (65%) was added to the cooled mixture. The reaction mixture was then warmed to 50 °C for 48 h. In the case of benzyldiphenylphosphane (**1f**) the reaction mixture was warmed to 30 °C for 48 h]. After cooling to room temperature 2 mL of the reaction mixture was slowly added to 2 g (15 mmol) of $Na_2C_2O_4$) or 2 g of Al_2O_3 (aluminum oxide for chromatography, basic) at −78 °C under an inert atmosphere. After warming to room temperature the suspension was stirred in vacuo for 10 min. before cooling to −78 °C. Then 10 mL of degassed water was added and after 20 min. the reaction vessel was warmed to room temperature. The solids were filtered off and the liquid phase was overlaid with 10 mL of toluene. 2 mL (4.06 mmol) of TIOA was then added and the mixture was stirred for 30 min. The organic layer was separated and washed twice with 5 mL of degassed water before 1 mL (2.00 mmol) $BH_3{\cdot}SMe_2$ (2 M in THF) was added. After evolution of SMe_2 had ceased the reaction mixture was washed three times with 20 mL of water. Then, 10 mL of water and 0.4 mL (4.00 mmol) of 10 M sodium hydroxide were added and the biphasic solution was mixed thoroughly. The separated aqueous phase was evaporated under reduced pressure and the remaining residue dried in vacuo. In the case of benzyldiphenylphosphane **1f** 3 mL (6.09 mmol) TIOA, 1.5 mL (3.00 mmol) $BH_3{\cdot}SMe_2$ (2 M in THF) and 0.6 mL (6.00 mmol) of 10 M sodium hydroxide were added].

Typical Procedure for the Deprotection of Sulfonated Alkyl- or Benzyldiphenylphosphanylboranes (6a−f): 100 mg of sulfonated phosphane/borane adduct **6a−f** was dissolved in 5 mL of degassed water. After the addition of 1 mL (14.6 mmol) of degassed allyl alcohol the reaction mixture was stirred at 95 °C for 16 h. The resulting turbid mixture was cooled to room temperature, 5 mL of degassed 1-butanol was added, and the biphasic solution was stirred for 30 min. Separation of the clear aqueous layer, evaporation of the water, and drying in vacuo, yielded the deprotected sulfonated alkyl- or benzyldiphenylphosphanes **7a−f**.

Disodium Salt of the Bis(*m*-sulfonatophenyl)methylphosphaneborane adduct (6a): ^{1}H NMR (200 MHz, D_2O): δ = 0.00−1.65 (br. m, 3 H, BH_3), 1.79 (d, $^{2}J_{H,P}$ = 10.8, 3 H, H_{Me}), 7.39 (ddd, $^{3}J_{H3,H4}$ = 7.5, $^{3}J_{H3,H2}$ = 7.8, $^{4}J_{H,P}$ = 2.0, 2 H, H3), 7.55 (dd, $^{3}J_{H,P}$ = 10.5, $^{3}J_{H2,H3}$ = 9.0, 2 H, H2), 7.77 (dd, $^{3}J_{H4,H3}$ = 8.0, $J_{H,?}$ = 1.3, 2 H, H4), 7.93 (d, $^{3}J_{H,P}$ = 11.0, 2 H, H6). − ^{13}C NMR (100 MHz): δ = 9.6 (d, $^{1}J_{C,P}$ = 41.0, C_{Me}), 130.5 (d, $^{1}J_{C,P}$ = 56.8, C1), 128.4 (d, $^{2}J_{C,P}$ = 11.1, C6), 128.6 (s, C4), 129.9 (d, $^{3}J_{C,P}$ = 9.8, C3), 134.5 (d, $^{2}J_{C,P}$ = 9.0, C2), 143.3 (d, $^{3}J_{C,P}$ = 10.2, C5). − ^{31}P NMR (81 MHz, D_2O): δ = 13.6 (br. s, P). − MS (ESI, neg. mode): *m*/*z* (%) = 395 (18) [M − Na^+], 179 (100) [M − $2Na^+ - BH_3$]. − HRMS (ESI, neg. mode): calculated for $C_{13}H_{11}NaO_6PS_2$: 380.9647; found 380.9632.

Disodium Salt of the Bis(*m*-sulfonatophenyl)ethylphosphaneborane Adduct (6b): ^{1}H NMR (200 MHz, D_2O): δ = 0.00−0.18 (br. m, 3 H, BH_3), 0.84 (dt, $^{3}J_{H,P}$ = 18.5, $^{3}J_{H,H}$ = 7.5, 3 H, H_{Me}), 2.19 (dq, $^{2}J_{H,P}$ = 11.3, $^{3}J_{H,H}$ = 7.3, 2 H, H_{alkyl}), 7.39 (ddd, $^{3}J_{H3,H4}$ = 7.5, $^{3}J_{H3,H2}$ = 7.8, $^{4}J_{H,P}$ = 2.0, 2 H, H3), 7.55 (dd, $^{3}J_{H,P}$ = 9.0, $^{3}J_{H2,H3}$ = 8.8, 2 H, H2), 7.74 (d, $^{3}J_{H4,H3}$ = 7.8, 2 H, H4), 7.88 (d, $^{3}J_{H,P}$ = 10.3, 2 H, H6). − ^{13}C NMR (125 MHz): δ = 6.5 (s, C_{Me}), 17.4 (d, $^{1}J_{C,P}$ = 40.0, C_{alkyl}), 128.9 (s, C4), 129.1 (d, $^{2}J_{C,P}$ = 14.4, C6), 129.6 (d, $^{1}J_{C,P}$ = 54.8, C1), 130.2 (d, $^{3}J_{C,P}$ = 9.5, C3), 135.2 (d, $^{2}J_{C,P}$ = 8.4, C2), 143.6 (d, $^{3}J_{C,P}$ = 10.1, C5). − ^{31}P NMR (81 MHz, D_2O): δ = 21.9 (br. s, P). − MS (ESI, neg. mode): *m*/*z* (%) = 409 (26) [M − Na^+], 193 (51) [M − $2Na^+$], 186 (100) [M − $2Na^+$ − BH_3].

Disodium Salt of the Bis(*m*-sulfonatophenyl)-*n*-butylphosphaneborane Adduct (6c): ^{1}H NMR (200 MHz, D_2O): δ = 0.20−1.80 (br. m, 3 H, BH_3), 0.60 (m, 3 H, H_{Me}), 1.16 (m, 4 H, H_{alkyl}), 2.18 (m, 2 H, H_{alkyl}), 7.41 (ddd, $^{3}J_{H3,H4}$ = 7.5, $^{3}J_{H3,H2}$ = 7.8, $^{4}J_{H,P}$ = 1.8, 2 H, H3), 7.59 (dd, $^{3}J_{H,P}$ = 9.8, $^{3}J_{H2,H3}$ = 8.3, 2 H, H2), 7.78 (d, $^{3}J_{H4,H3}$ = 7.5, 2 H, H4), 7.94 (d, $^{3}J_{H,P}$ = 10.5, 2 H, H6). − ^{13}C NMR (100 MHz): δ = 12.7 (s, C_{Me}), 23.2 (d, $^{1}J_{C,P}$ = 37.8, C_{alkyl}), 23.3 (d, $J_{C,P}$ = 14.2, C_{alkyl}), 24.5 (s, C_{alkyl}), 128.6 (s, C4), 128.9 (d, $^{2}J_{C,P}$ = 10.7, C6), 129.7 (d, $^{1}J_{C,P}$ = 50.2, C1), 129.9 (d, $^{3}J_{C,P}$ = 9.6, C3), 134.8 (d, $^{2}J_{C,P}$ = 8.3, C2), 143.4 (d, $^{3}J_{C,P}$ = 10.2, C5). − ^{31}P NMR (81 MHz, D_2O): δ = 19.6 (br. s, P). − MS (ESI, neg. mode): *m*/*z* (%) = 437 (21) [M − Na^+], 200 (100) [M − $2Na^+$ − BH_3].

Disodium Salt of the Bis(*m*-sulfonatophenyl)-*tert*-butylphosphaneborane Adduct (6d): ^{1}H NMR (200 MHz, D_2O): δ = 0.20−1.60 (br. m, 3 H, BH_3), 1.02 (d, $^{3}J_{H,P}$ = 15.0, 9 H, H_{tBu}), 7.44 (dd, $^{3}J_{H3,H4}$ = 7.8, $^{3}J_{H3,H2}$ = 7.8, 2 H, H3), 7.71 (dd, $^{3}J_{H,P}$ = 8.8, $^{3}J_{H2,H3}$ = 8.8, 2 H, H2), 7.80 (d, $^{3}J_{H4,H3}$ = 7.8, 2 H, H4), 8.05 (d, $^{3}J_{H,P}$ = 10.0, 2 H, H6). − ^{13}C NMR (125 MHz): δ = 26.0 (s, C_{tBu}), 30.7 (d, $^{1}J_{C,P}$ = 31.3, C_{quart}), 127.9 (d, $^{1}J_{C,P}$ = 51.3, C1), 128.6 (s, C4), 129.6 (d, $^{3}J_{C,P}$ = 8.9, C3), 130.5 (d, $^{2}J_{C,P}$ = 9.8, C6), 136.5 (d, $^{2}J_{C,P}$ = 6.9, C2), 143.1 (d, $^{3}J_{C,P}$ = 10.0, C5). − ^{31}P NMR (81 MHz, D_2O): δ = 35.6 (br. s, P). − MS (ESI, neg. mode): *m*/*z* (%) = 437 (30) [M − Na^+], 207 (95) [M − $2Na^+$], 200 (100) [M − $2Na^+$ − BH_3].

Disodium Salt of the Bis(*m*-sulfonatophenyl)cyclohexylphosphaneborane Adduct (6e): ^{1}H NMR (200 MHz, D_2O): δ = 0.30−1.50 (m, 13 H, H_{Cy},BH_3), 2.47 (br. m, 1 H, H_{Cy}), 7.36 (dd, $^{3}J_{H3,H2}$ = 7.3, $^{3}J_{H3,H4}$ = 7.5, 2 H, H3), 7.63 (dd, $^{3}J_{H,P}$ = 9.0, $^{3}J_{H2,H3}$ = 8.3, 2 H, H2), 7.75 (d, $^{3}J_{H4,H3}$ = 7.8, 2 H, H4), 7.96 (d, $^{3}J_{H,P}$ = 10.3, 2 H, H6). − ^{13}C NMR (100 MHz): δ = 26.2 (s, C_{Cy}), 26.7 (d, $J_{C,P}$ = 12.7, C_{Cy}), 27.0 (s, C_{Cy}), 33.0 (d, $^{1}J_{C,P}$ = 35.8, C_{Cy}), 129.3 (d, $^{1}J_{C,P}$ = 53.2, C1), 129.5 (s, C4), 130.2 (d, $^{2}J_{c,P}$ = 10.3, C6), 130.6 (d, $^{3}J_{C,P}$ = 9.1, C3), 135.9 (d, $^{2}J_{C,P}$ = 7.5, C2), 144.3 (d, $^{3}J_{C,P}$ = 9.8; C5). − ^{31}P NMR (81 MHz, D_2O): δ = 24.4 (br. s, P). − MS (ESI, neg. mode): *m*/*z* (%) = 463 (39) [M − Na^+], 220 (100) [M − $2Na^+$], 213 (97) [M − $2Na^+$ − BH_3].

Trisodium Salt of the Bis(*m*-sulfonatophenyl)-*p*-sulfonatobenzylphosphaneborane Adduct (6f): ^{1}H NMR (400 MHz, D_2O): δ = 0.30−1.20 (br. s, 3 H, BH_3), 3.81 (d, $^{2}J_{H,P}$ = 13.0, 2 H, H7), 7.00 (d, $^{3}J_{H9,H10}$ = 7.6, 2 H, H9), 7.49 (dd, $^{3}J_{H3,H2}$ = 8.1, $^{3}J_{H3,H4}$ = 8.1, 2 H, H3), 7.52 (d, $^{3}J_{H10,H9}$ = 7.8, 2 H, H10), 7.66 (dd, $^{3}J_{H,P}$ = 9.5, $^{3}J_{H2,H3}$ = 8.6, 2 H, H2), 7.92 (d, $^{3}J_{H4,H3}$ = 7.9, 2 H, H4), 8.03 (d, $^{3}J_{H,P}$ = 10.9, 2 H, H6). − ^{13}C NMR (100 MHz): δ = 31.8 (d, $^{1}J_{C,P}$ = 32.3, C7), 125.2 (s, C9), 125.7 (s, C8), 128.4 (d, $^{1}J_{C,P}$ = 52.8, C1), 129.0 (s, C4), 129.2 (d, $^{2}J_{C,P}$ = 10.2, C6), 129.9 (d, $^{3}J_{C,P}$ = 9.9, C3), 130.8 (s, C10), 135.3 (d, $^{2}J_{C,P}$ = 8.8, C2), 141.2 (s, C11), 143.4 (d, $^{3}J_{C,P}$ = 9.5, C5). − ^{31}P NMR (81 MHz, D_2O): δ = 211.9 (br. s, P). − MS (ESI, neg. mode): *m*/*z* (%) = 559 (100) [M − Na^+ − BH_3], 366 (86) [M − benzyl − Na^+]; also 575 [M − Na^+ − BH_3 + O] in varying amount depending on the fragmentor current.

Disodium Salt of the Bis(*m*-sulfonatophenyl)methylphosphane (7a):[6] ^{1}H NMR (400 MHz, D_2O): δ = 1.60 (d, $^{2}J_{H,P}$ = 2.4, 3 H, H_{Me}), 7.40 (dd, $^{3}J_{H3,H4}$ = 7.3, $^{3}J_{H3,H2}$ = 8.0, 2 H, H3), 7.44 (dd, $^{3}J_{H,P}$ = 7.1, $^{3}J_{H2,H3}$ = 7.5, 2 H, H2), 7.72 (d, $^{3}J_{H4,H3}$ = 7.3, 2 H, H4), 7.82 (d, $^{3}J_{H,P}$ = 7.1, 2 H, H6). − ^{13}C NMR (100 MHz): δ = 10.6 (d, $^{1}J_{C,P}$ = 10.0, C_{Me}), 125.9 (s, C4), 128.5 (d, $^{2}J_{C,P}$ = 20.1, C6), 129.3 (d, $^{3}J_{C,P}$ = 6.2, C3), 134.9 (d, $^{2}J_{C,P}$ = 17.3, C2), 140.2 (d, $^{1}J_{C,P}$ = 11.4, C1), 142.7 (d, $^{3}J_{C,P}$ = 6.2, C5). − ^{31}P NMR (81 MHz, D_2O): δ = −22.5 (s, P).

Disodium Salt of the Bis(*m*-sulfonatophenyl)ethylphosphane (7b): ^{1}H NMR (400 MHz, D_2O): δ = 0.87 (dt, $^{3}J_{H,P}$ = 17.9, $^{3}J_{H,H}$ = 7.5, 3 H, H_{Me}), 1.94 (q, $^{3}J_{H,H}$ = 7.5, 2 H, H_{alkyl}), 7.32−7.38 (m, 4 H, H2,H3), 7.72 (d, $^{3}J_{H4,H3}$ = 7.0, 2 H, H4), 7.80 (d, $^{3}J_{H,P}$ = 7.0, 2 H, H6). − ^{13}C NMR (100 MHz): δ = 9.0 (d, $^{2}J_{C,P}$ = 15.1, C_{Me}), 18.9 (d, $^{1}J_{C,P}$ = 7.0, C_{alkyl}), 126.0 (s, C4), 129.2 (d, $^{2}J_{C,P}$ = 19.8, C6), 129.3 (d, $^{3}J_{C,P}$ = 6.2, C3), 135.4 (d, $^{2}J_{C,P}$ = 16.6, C2), 138.5 (d, $^{1}J_{C,P}$ = 12.1, C1), 142.8 (d, $^{3}J_{C,P}$ = 6.4, C5). − ^{31}P NMR (81 MHz, D_2O): δ = −10.2 (s, P).

Disodium Salt of the Bis(*m*-sulfonatophenyl)-*n*-butylphosphane (7c): ^{1}H NMR (400 MHz, D_2O): δ = 0.97 (m, 3 H, H_{Me}), 1.51 (m, 4 H, H_{alkyl}), 2.29 (m, 2 H, H_{alkyl}), 7.50 (dd, $^{3}J_{H3,H2}$ = 7.7, $^{3}J_{H3,H4}$ = 7.7, 2 H, H3), 7.56 (dd, $^{3}J_{H,P}$ = 7.0, $^{3}J_{H2,H3}$ = 7.7, 2 H, H2), 7.80 (d, $^{3}J_{H4,H3}$ = 7.7, 2 H, H4), 7.90 (d, $^{3}J_{H,P}$ = 6.0, 2 H, H6). − ^{13}C NMR (100 MHz): δ = 12.9 (s, C_{Me}), 23.4 (d, $J_{C,P}$ = 13.2, C_{alkyl}), 25.9 (d, $^{1}J_{C,P}$ = 7.4, C_{alkyl}), 27.2 (d, $J_{C,P}$ = 14.0, C_{alkyl}), 126.1 (s, C4), 129.3 (d, $^{2}J_{C,P}$ = 26.5, C6), 129.3 (s, C3), 135.5 (d, $^{2}J_{C,P}$ = 16.8, C2), 138.8 (d, $^{1}J_{C,P}$ = 11.7, C1), 142.9 (d, $^{3}J_{C,P}$ = 6.4, C5). − ^{31}P NMR (81 MHz, D_2O): δ = −14.6 (s, P).

Disodium Salt of the Bis(*m*-sulfonatophenyl)-*tert*-butylphosphane (7d): ^{1}H NMR (200 MHz, D_2O): δ = 0.94 (d, $^{2}J_{H,P}$ = 13.5, 9 H, H_{tBu}), 7.31 (dd, $^{3}J_{H3,H2}$ = 7.8, $^{3}J_{H3,H2}$ = 7.8, 2 H, H3), 7.46 (dd, $^{3}J_{H,P}$ = 7.0, $^{3}J_{H2,H3}$ = 7.5, 2 H, H2), 7.64 (d, $^{3}J_{H4,H3}$ = 7.8, 2 H, H4), 7.82 (d, $^{3}J_{H,P}$ = 7.3, 2 H, H6). − ^{13}C NMR (50 MHz): δ = 27.6 (d, $^{2}J_{C,P}$ = 13.4, C_{tBu}), 30.4 (d, $^{1}J_{C,P}$ = 9.7, C_{quart}), 126.2 (s, C4), 129.1 (d, $^{3}J_{C,P}$ = 6.9, C3), 130.9 (d, $^{2}J_{C,P}$ = 20.8, C6), 136.3 (d, $^{1}J_{C,P}$ = 14.8, C1), 137.3 (d, $^{2}J_{C,P}$ = 17.5, C2), 142.5 (d, $^{3}J_{C,P}$ = 6.9, C5). − ^{31}P NMR (81 MHz, D_2O): δ = 19.5 (s, P).

Disodium Salt of the Bis(*m*-sulfonatophenyl)cyclohexylphosphane (7e): ^{1}H NMR (500 MHz, D_2O): δ = 0.95−1.04 (m, 3 H, H_{Cy}), 1.10−1.17 (m, 2 H, H_{Cy}), 1.46−1.53 (m, 5 H, H_{Cy}), 2.22−2.28 (m, 1 H, H_{Cy}), 7.36 (dd, $^{3}J_{H3,H2}$ = 7.6, $^{3}J_{H3,H4}$ = 7.8, 2 H, H3), 7.48 (dd, $^{3}J_{H2,H3}$ = 7.3, $^{3}J_{H,P}$ = 2 H, H2), 7.69 (d, $^{3}J_{H4,H3}$ = 7.8, 2 H, H4), 7.83 (d, $^{3}J_{H,P}$ = 7.5, 2 H, H6). − ^{13}C NMR (125 MHz): δ = 25.8 (s, C_{Cy}), 26.0 (d, $J_{C,P}$ = 12.2, C_{Cy}), 29.0 (d, $J_{C,P}$ = 14.2, C_{Cy}), 34.3 (s, C_{Cy}), 126.3 (s, C4), 129.3 (d, $^{3}J_{C,P}$ = 6.1, C3), 130.2 (d, $^{2}J_{C,P}$ = 21.4, C6), 136.2 (d, $^{2}J_{C,P}$ = 16.3, C2), 136.8 (d, $^{1}J_{C,P}$ = 12.2, C1), 142.8 (d, $^{3}J_{C,P}$ = 7.1, C5). − ^{31}P NMR (81 MHz, D_2O): δ = −3.0 (s, P).

Trisodium Salt of the Bis(*m*-sulfonatophenyl)-*p*-sulfonatobenzylphosphane (7f): ^{1}H NMR (400 MHz, D_2O): δ = 3.42 (s, 2 H), 7.02 (d, *J* = 8.6, 2 H), 7.30−7.40 (m, 4 H), 7.52−7.54 (d, *J* = 8.0, 2 H), 7.72−7.78 (m, 4 H). − ^{13}C NMR (100 MHz, D_2O): δ = 34.1 (d, *J* = 13.2), 125.5 (s), 126.4 (s), 129.3 (d, *J* = 10.9), 129.4 (s), 129.7 (d, *J* = 6.3), 130.0 (s), 1135.7 (d, *J* = 18.4), 137.5 (d, *J* = 14.4), 140.4 (d, *J* = 6.7), 142.8 (br. s). − ^{31}P NMR (81 MHz, D_2O): δ = −5.0 (s, P).

Acknowledgments

We are grateful to the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft, SFB 260, for financial support of this work. We also would like to thank Dr. Th. Wendrich and Dipl. Chem. V. Bergendahl of the Fachbereich Chemie, Philipps-Universität Marburg, for the determination of the ESI mass spectra. Dr. G. Laufenberg of the Fachbereich Pharmazie, Philipps-Universität Marburg, kindly determined the HRMS.

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Received February 23, 2001
[O01093]