Water-Soluble Electron-Donating Phosphines: Sulfonation of Tris(ω-phenylalkyl)phosphines

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The series of phosphines $P[(CH_2)_x(C_6H_5)]_3$, x = 1, 2, 3, and 6, are sulfonated under relatively mild conditions to yield the corresponding sulfonated phosphines $P[(CH_2)_x(C_6H_4\text{-}p\text{-}SO_3Na)]_3$. Sulfonation occurs at both the para and ortho positions; the exclusively para-substituted products are isolated. The sulfonated phosphines are freely water soluble. Nickel carbonyl and palladium chloride derivatives of the phosphines are prepared, $(PR_3)Ni(CO)_3$ and $(PR_3)_2Ni(CO)_2$ in THF/H_2O solution and *trans*-$(PR_3)_2PdCl_2$, under two-phase reaction conditions. Examination of the spectroscopically determined electronic and steric parameters shows that when x is large, the donor character of the water-soluble phosphines is virtually identical to that of the alkyl phosphine $P(nBu)_3$.

The chemistry of the water-soluble phosphine trisulfonated triphenylphosphine, TPPTS,[1-5] and the catalysis possible in water with complexes of this ligand have recently received considerable attention.[6-12] The steric and electronic character of TPPTS are thought to be very similar to triphenylphosphine although some differences have been noted by high-pressure NMR studies in the dissociation equilibria of $HRh(CO)(PPh_3)_3$ and $HRh(CO)(TPPTS)_3$.[6] Also TPPTS is more oxidation sensitive than triphenylphosphine. It has been noted for example that aqueous solutions of TPPTS are catalytically oxidized to TPPTS oxide in the presence of rhodium(III).[5]

Comparatively little has been done to prepare new water-soluble phosphines with steric and electronic properties different from TPPTS. Such phosphines would be of interest for the development of water-soluble catalysts for which TPPTS is too electron withdrawing. For example phosphine-modified cobalt carbonyl hydroformylation catalysts require electron-donating trialkylphosphines such as $P(nBu)_3$ to give catalysts with good selectivity for linear products.[12] Triphenylphosphine apparently dissociates too readily from the cobalt center and is thus ineffective in providing good selectivity for this reaction.[12]

Here we show that the preparation of electron-donating water-soluble phosphines can be accomplished by the sulfonation of the tris(ω-phenylalkyl)phosphines $P[(CH_2)_x(C_6H_5)]_3$, x = 1, 2, 3, and 6. The sulfonation occurs at both the ortho and para positions; however, para sulfonation dominates and the completely para-substituted phosphines can be isolated in pure form. For x = 2, 3, and 6 formation of the corresponding oxide during the sulfonation is not observed. Potentiometric titrations indicate that stable phosphonium salts may be formed depending on the pH for the phosphines $x \geq 2$. Electronic and steric parameters for the newly synthesized phosphorus ligands are estimated from the spectroscopic characterization of their respective nickel tricarbonyl and *trans*-dichloropalladium complexes. For comparison the experimental electronic and steric parameters of TPPTS have also been determined.

Experimental Section

General Methods. All syntheses were performed under prepurified nitrogen using standard Schlenk techniques. Reagent grade solvents were dried and deoxygenated by distillation under nitrogen before use. In house, distilled deionized water was used in all instances where water is specified; the water was further distilled under nitrogen immediately prior to use. The reagents benzyl chloride, 1-chloro-3-phenylpropane, (2-chloroethyl)benzene, 1,6-dichlorohexane, phenyllithium, PCl_3, fuming sulfuric acid (20%), H_2O_2 (30%), and NaOH were obtained from Aldrich and used without further purification. Nickel tetracarbonyl was received from Alfa Chemicals, and $(PhCN)_2PdCl_2$ was purchased from Strem Chemical Co. The deuterated solvents $CDCl_3$, D_2O, CD_3OD, and TMS were obtained from Cambridge Isotope Laboratories. The water-soluble chemical shift standard sodium 3-(trimethylsilyl)tetradeuteriopropionate (TSP) was obtained from Wilmad Glass Co. Routine NMR measurements were done on a Bruker WP 200 at 200.133 MHz for ^1H, 50.323 MHz for ^{13}C, and 81.015 MHz for ^{31}P. Infrared spectra were recorded on a Nicolet 5DXB FTIR in either matched 0.1-mm CaF_2 cells (nonaqueous solvents) or matched 0.1-mm Irtran cells (aqueous samples). The standard deviations of the repeated measurements are ±0.05 cm^{-1}. The potentiometric titrations were carried out on a Microcomputer pH-Vision, Cole/Parmer Model 05669-20,

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with pH combination electrodes. Melting points were determined in sealed capillaries on a Büchi 510 apparatus. Elemental analyses were performed by Atlantic Microlab, Inc., and Schwarzkopf Microanalytical Laboratory.

The phosphines $P[(CH_2)_x(C_6H_5)]_3$, x = 1, 2, 3, and 6, were prepared by standard literature methods from PCl_3 and the corresponding Grignard reagent.[13] While tribenzylphosphine is known,[13] the other phosphines, to the best of our knowledge, have not been synthesized previously although there is nothing remarkable about their preparation.

Key to NMR data: s, singlet, d, doublet; t, triplet; quin, quintet; sex, sextet; m, multiplet; br, broad; asterisk, pseudo. Carbon atoms in the phosphines are numbered from the phosphorus atom with the α carbon labeled (1)C. Key to IR data: vs, very strong; s, strong; m, medium; w, weak.

Synthesis of *p,p,p*-Trisulfonated Tribenzylphosphine (1a). Tribenzylphosphine, 9.13 g (30.0 mmol), was added in portions to 20 mL of concentrated H_2SO_4 at room temperature. Fuming sulfuric acid (20% SO_3), 20 mL, was slowly added to the reaction solution. The reaction was followed by ^1H and ^{31}P NMR as described for the sulfonation of triphenylphosphine.[14] The reaction was terminated after 2 h by slowly neutralizing with 20% aqueous NaOH at 0 °C. The volume was then increased by a factor 10 with the addition of methanol and the mixture heated to reflux. Filtration removed most of the Na_2SO_4. The solid was further extracted with 10:1 hot methanol/water. The extracts were concentrated to ~100 mL, and 500 mL of ethanol was added. A white solid separates, which was filtered out and dried. By ^1H NMR it was estimated that the crude product contained 36% para, para, para (*p,p,p*), 41% ortho, para, para (*o,p,p*), 7% ortho, ortho, para (*o,o,p*), and 1% ortho, ortho, ortho (*o,o,o*) trisulfonated tribenzylphosphine. Additionally, by ^{31}P NMR spectroscopy it was found that 12% of the product was disulfonated and 3% was oxidized. It was observed that, of all the components of the reaction mixture, the *p,p,p* isomer is the least soluble in ethanol. Thus a special extraction apparatus (Figure 1) was designed for the exhaustive extraction with agitation of the air-sensitive phosphine. The solid remaining on the frit is the *p,p,p* isomer in up to 20% isolated yield and 90% purity (^1H NMR). The observable impurities are the *o,p,p* isomer and the corresponding phosphine oxides.

1a: White crystals, mp > 360 °C. ^1H NMR δ (D_2O): 2.94 (s, 6H, (1)CH_2), 7.25 (d, J_{HH} = 7.96 Hz, 6H, (3)CH + (7)CH), 7.72 (d, J_{HH} = 8.16 Hz, 6H, (4)CH + (6)CH). ^{13}C NMR δ (D_2O): 35.41 (d, J_{PC} = 15.09 Hz, 3C, (1)CH_2), 142.90 (s br, 3C, (2)C), 128.28 (s, 6C, (3)CH + (7)CH), 132.17 (s, 6C, (4)CH + (6)CH), 144.07 (s, 3C, (5)C-SO_3Na). ^{31}P NMR δ (D_2O): −5.48. Anal. Calcd for $C_{21}H_{18}Na_3O_9PS_3$ (M_r = 610.49): C, 41.31; H, 2.97. Calcd for $C_{21}H_{18}Na_3O_9PS_3 \cdot 3H_2O$ (M_r = 664.49): C, 37.96; H, 3.64; Found: C, 39.59; H, 3.80.[15]

Synthesis of *p,p,p*-Trisulfonated Tribenzylphosphine Oxide (1b). A 1-mmol amount of the corresponding phosphine was dissolved in 2 mL of H_2O; H_2O_2 (30%), 0.5 mL, was added and the reaction stirred at room temperature for 2–5 h. The solvent was then removed under vacuum. The resulting white solid compound was identified as the oxide.

1b: White crystals, mp > 360 °C. ^1H NMR δ (D_2O): 3.33 (d, J_{HH} = 12.99 Hz, 6H, (1)CH_2), 7.33 (d, J_{HH} = 7.82 Hz, 6H, (3)CH + (7)CH), 7.84 (d, J_{HH} = 7.82 Hz, 6H, (4)CH + (6)CH). ^{13}C NMR δ (D_2O): 37.07 (d, J_{PC} = 60.00 Hz, 3C, (1)CH_2), 136.94 (d, J_{PC} = 9.01 Hz, 3C, (2)C), 128.53 (s, 6C, (3)CH + (7)CH), 133.06 (s, 6C, (4)CH + (6)CH), 144.09 (s, 3C, (5)C-SO_3Na). ^{31}P NMR δ (D_2O): 47.26. Anal. Calcd for $C_{21}H_{18}Na_3O_{10}PS_3$ (M_r = 626.49): C, 40.26; H, 2.89. Calcd for $C_{21}H_{18}Na_3O_{10}PS_3 \cdot 3H_2O$ (M_r = 680.49): C, 37.14; H, 3.54. Found: C, 38.32; H, 3.74.[15]

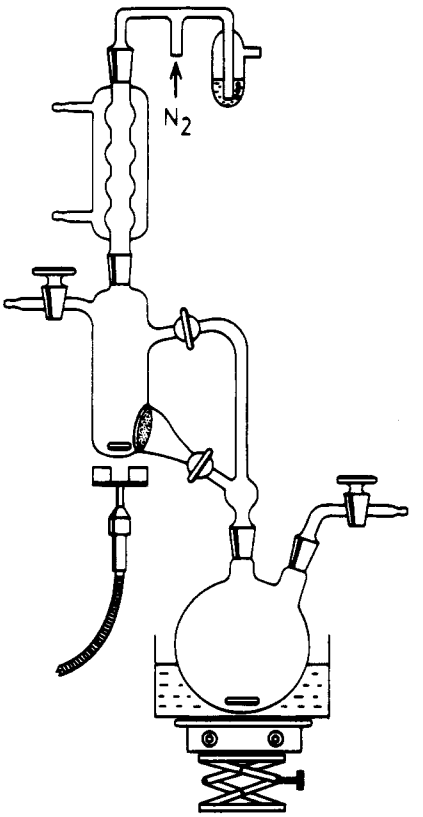

Figure 1. Apparatus for the continuous extraction under nitrogen with simultaneous magnetic stirring of the air-sensitive phosphines. The porosity of the frit is coarse to allow rapid filtration. All joints are ¥ ground glass. The stirrer consists of a horseshoe magnet fixed to a flexible overhead stirring motor shaft.

Synthesis of Tris(2-phenylethyl)phosphine (2a). Tris(2-phenylethyl)phosphine was obtained in 84% yield as white needles from the reaction of PCl_3 with $C_6H_5(CH_2)_2MgBr$ in diethyl ether by published procedures for phosphine synthesis.[13]

2a: White needles, mp = 43 °C. ^1H NMR δ ($CDCl_3$): 1.65 (m, 6H, (1)CH_2), 2.66 (m, 6H, (2)CH_2), 7.05–7.25 (m, 15H, (4–8)-C_6H_5). ^{13}C NMR δ ($CDCl_3$): 29.46 (d, J_{PC} = 13.6 Hz, 3C, (1)CH_2), 32.77 (d, J_{PC} = 14.04 Hz, 3C, (2)CH_2), 143.31 (d, J_{PC} = 9.21 Hz, 3C, (3)C), 129.93 (s, 6C, (4)CH + (8)CH), 128.66 (s, 6C, (5)CH + (7)CH), 125.48 (s, 3C, (6)CH). ^{31}P NMR δ ($CDCl_3$): −26.84. Anal. Calcd for $C_{24}H_{27}P$ (M_r = 346.45): C, 83.20; H, 7.86. Found: C, 83.03; H, 7.94.

Synthesis of Tris(2-phenylethyl)phosphine Oxide (2b). A 1-mmol amount of the corresponding phosphine was dissolved in 10 mL of $CHCl_3$. Oxygen was bubbled through the stirred solution for 4–20 h. The solvent was removed under vacuum and the residue recrystallized from acetone.

2b: White plates, mp = 141 °C. ^1H NMR δ ($CDCl_3$): 2.83 (s, 12H, (1)CH_2 + (2)CH_2), 7.22 (s, 15H, (3–8)C_6H_5). ^{13}C NMR δ ($CDCl_3$): 21.33 (d, J_{PC} = 43.18 Hz, 3C, (1)CH_2), 27.60 (s, 3C, (2)CH_2), 138.37 (d, J_{PC} = 12.13 Hz, 3C, (3)C), 128.88 (s, 6C, (4)-CH + (8)CH), 128.24 (s, 6C, (5)CH + (7)CH), 127.15 (s, 3C, (6)-CH). ^{31}P NMR δ ($CDCl_3$): 34.15. Anal. Calcd for $C_{24}H_{27}OP$ (M_r = 362.45): C, 79.53; H, 7.51. Found: C, 79.76; H, 7.83.

Synthesis of *p,p,p*-Trisulfonated Tris(2-phenylethyl)-phosphine (3a). Tris(2-phenylethyl)phosphine, 8.69 g (25.1 mmol), was dissolved in 20 mL of concentrated H_2SO_4 at room temperature. Partial sulfonation occurs without addition of oleum. Addition of 8 mL of 20% fuming sulfuric acid over 10 min and stirring for 2 h at room temperature completed the sulfonation. The reaction was quenched at 0 °C with 20%

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(15) The sulfonated phosphines were precipitated from solutions containing a minimum of water and further extracted or precipitated with nonaqueous solvents as described in the text. C, H analyses were done on separately purified samples until consistent results were obtained. Calculated compositions are given for both the anhydrous and trihydrated trisulfonated compounds. The experimental C, H values are most consistent with the isolation of nonstoichiometric hydrates with between 0 and 3 waters of hydration/phosphorus.

aqueous NaOH. The reaction solution was reduced in volume to ca. 75 mL followed by the addition of 750 mL of methanol. After filtration the solids were further extracted with 500 mL of 10:1 hot methanol/water. The extracts were combined and reduced in volume to ca. 120 mL. Addition of 500 mL of acetone gives the trisulfonated product as a white solid with *p,p,p* purity of >95%. A second crop of trisulfonated tris(2-phenylethyl)-phosphine can be recovered from the filtrate by the further addition of 500 mL of acetone. The second crop contained 85% of the *p,p,p* isomer. The combined yield of *p,p,p*-trisulfonated product was 52% based on $P[(CH_2)_2C_6H_5]_3$.

3a: White crystals, mp > 360 °C. ^{1}H NMR δ (D_2O): 1.52 (t, J_{HH} = 7.36 Hz, 6H, (1)CH_2), 2.58 (d of t, J_{HH} = 9.05 Hz/J_{PH} = 6.88 Hz, 6H, (2)CH_2), 7.25 (d, J_{HH} = 7.41 Hz, 6H, (4)CH + (8)-CH), 7.75 (d, J_{HH} = 7.41 Hz, 6H, (5)CH + (7)CH). ^{13}C NMR δ (D_2O): 29.30 (d, J_{PC} = 9.20 Hz, 3C, (1)CH_2), 33.67 (d, J_{PC} = 21.58 Hz, 3C, (2)CH_2), 148.77 (d, J_{PC} = 8.98 Hz, 3C, (3)C), 128.07 (s, 6C, (4)CH + (8)CH), 131.18 (s, 6C, (5)CH + (7)CH), 142.71 (s, 3C, (6)C-SO_3Na). ^{31}P NMR δ (D_2O): -28.79. Anal. Calcd for $C_{24}H_{24}Na_3O_9PS_3$ (M_r = 652.57): C, 44.17; H, 3.71. Calcd for $C_{24}H_{24}Na_3O_9PS_3{\cdot}3H_2O$ (M_r = 706.57): C, 40.80; H, 4.28. Found: C, 42.51; H, 3.91.[15]

Synthesis of *p,p,p*-Trisulfonated Tris(2-phenylethyl)-phosphine Oxide (3b). The oxidation of **3a** was done in the same manner as described above in **1b**.

3b: White crystals, mp > 360 °C. ^{1}H NMR δ (D_2O): 2.95 (m, 6H, (1)CH_2), 2.65 (m, 6H, (2)CH_2), 7.34 (d, J_{HH} = 8.20 Hz, 6H, (4)CH + (8)CH), 7.76 (d, J_{HH} = 8.20 Hz, 6H, (5)CH + (7)CH). ^{13}C NMR δ (D_2O): 22.24 (d, J_{PC} = 44.08 Hz, 3C, (1)CH_2), 29.05 (s, 3C, (2)CH_2), 144.92 (d, J_{PC} = 12.33 Hz, 3C, (3)C), 128.72 (s, 6C, (4)CH + (8)CH), 131.33 (s, 6C, (5)CH + (7)CH), 144.07 (s, 3C, (6)C-SO_3Na). ^{31}P NMR δ (D_2O): 35.54. Anal. Calcd for $C_{24}H_{24}Na_3O_{10}PS_3$ (M_r = 668.57): C, 43.11; H, 3.62. Calcd for $C_{24}H_{24}Na_3O_{10}PS_3{\cdot}3H_2O$ (M_r = 722.57): C, 39.86; H, 4.15. Found: C, 41.23; H, 3.89.[15]

Synthesis of Tris(3-phenylpropyl)phosphine (4a). Tris-(3-phenylpropyl)phosphine was obtained in 80% yield as a white solid from the reaction of $C_6H_5(CH_2)_3MgCl$ and PCl_3 in ether by standard methods.[13]

4a: White crystals, mp = 39 °C. ^{1}H NMR δ ($CDCl_3$): 1.28 (t*, J_{HH} = 9.00 Hz, 6H, (1)CH_2), 1.61 (sex*, J_{HH} = 7.65 Hz, 6H, (2)-CH_2), 2.56 (t, J_{HH} = 7.48 Hz, 6H, (3)CH_2), 7.03-7.24 (m, 15H, (5-9)C_6H_5). ^{13}C NMR δ ($CDCl_3$): 26.47 (d, J_{PC} = 12.23 Hz, 3C, (1)CH_2), 27.64 (d, J_{PC} = 14.44 Hz, 3C, (2)CH_2), 37.48 (d, J_{PC} = 9.30 Hz, 3C, (3)CH_2), 142.05 (s, 3C, (4)C), 128.46 (s, 6C, (5)CH + (9)CH), 128.35 (s, 6C, (6)CH + (8)CH), 125.80 (s, 3C, (7)CH). ^{31}P NMR δ ($CDCl_3$): -30.65. Anal. Calcd for $C_{27}H_{33}P$ (M_r = 388.53): C, 83.47; H, 8.56. Found: C, 84.01; H, 8.31.

Synthesis of Tris(3-phenylpropyl)phosphine Oxide (4b). The oxidation of **4a** was made in the same manner as described above in **2b**.

4b: White crystals, mp = 123 °C. ^{1}H NMR δ ($CDCl_3$): 2.34 (m, 6H, (1)CH_2), 1.64 (m, 6H, (2)CH_2), 2.71 (t, J_{HH} = 7.12 Hz, 6H, (3)CH_2), 7.22 (s, 15H, (5-9)C_6H_5). ^{13}C NMR δ ($CDCl_3$): 18.26 (d, J_{PC} = 46.70 Hz, 3C, (1)CH_2), 23.35 (s, 3C, (2)CH_2), 36.06 (d, J_{PC} = 22.34 Hz, 3C, (3)CH_2), 139.47 (s, 3C, (4)C), 128.69 (s, 6C, (5)CH + (9)CH), 128.49 (s, 6C, (6)CH + (8)CH), 126.66 (s, 3C, (7)CH). ^{31}P NMR δ ($CDCl_3$): 34.38. Anal. Calcd for $C_{27}H_{33}OP$ (M_r = 404.53): C, 80.17; H, 8.22. Found: C, 80.57; H, 8.11.

Synthesis of *p,p,p*-Trisulfonated Tris(3-phenylpropyl)-phosphine (5a). The sulfonation of tris(3-phenylpropyl)-phosphine is carried out in concentrated H_2SO_4. Typically 9.74 g (25.1 mmol) of $P[(CH_2)_3C_6H_5]_3$ was dissolved in portions in 40 mL of concentrated H_2SO_4 at room temperature. The sulfonation is complete after 1 h as determined by ^{1}H and ^{31}P NMR and is quenched by the slow addition of 20% aqueous NaOH at 0 °C. The reaction solution was reduced in volume to ca. 75 mL, and then 750 mL of methanol was added and the mixture brought to reflux. After filtration the solids were further extracted with 500 mL of 10:1 hot methanol/water. The extracts were combined and reduced in volume to 100 mL. Addition of 500 mL of acetone yields *p,p,p*-trisulfonated tris(3-phenylpropyl)phosphine in 98% purity. A second crop of crystals (89% *p,p,p*) can be recovered from the filtrate upon addition of 500 mL of acetone. The combined yield of *p,p,p*-trisulfonated product was 65% based on $P[(CH_2)_3C_6H_5]_3$.

5a: White crystals, mp > 360 °C. ^{1}H NMR δ (D_2O): 1.20 (q, br, 6H, (1)CH_2), 1.52 (sex*, J_{HH} = 7.29 Hz/J_{PH} = 6.34 Hz, 6H, (2)CH_2), 2.55 (t, J_{HH} = 6.86 Hz, 6H, (2)CH_2), 7.19 (d, J_{HH} = 7.98 Hz, 6H, (5)CH + (9)CH), 7.75 (d, J_{HH} = 7.98 Hz, 6H, (6)CH + (8)CH). ^{13}C NMR δ (D_2O): 27.51 (d, J_{PC} = 7.50 Hz, 3C, (1)CH_2), 29.31 (d, J_{PC} = 11.49 Hz, 3C, (2)CH_2), 38.97 (d, J_{PC} = 11.58 Hz, 3C, (3)CH_2), 142.97 (s, 3C, (4)C), 128.28 (s, 6C, (5)CH + (9)CH), 131.51 (s, 6C, (6)CH + (8)CH), 148.32 (s, 3C, (7)C-SO_3Na). ^{31}P NMR δ (D_2O): -31.97. Anal. Calcd for $C_{27}H_{30}Na_3O_9PS_3$ (M_r = 694.65): C, 46.68; H, 4.35. Calcd for $C_{27}H_{30}Na_3O_9PS_3{\cdot}3H_2O$ (M_r = 748.65): C, 43.28 H, 4.85. Found: C, 44.39; H, 4.42.[15]

Synthesis of *p,p,p*-Trisulfonated Tris(3-phenylpropyl)-phosphine Oxide (5b). The oxidation of **3a** was done in the same manner as described above in **1b**.

5b: White crystals, mp > 360 °C. ^{1}H NMR δ (D_2O): 1.92 (s br, 6H, (1)CH_2), 1.58 (s br, 6H, (2)CH_2), 2.67 (t br, 6H, (3)CH_2), 7.28 (d, J_{HH} = 8.26 Hz, 6H, (5)CH + (9)CH), 7.77 (d, J_{HH} = 8.26 Hz, 6H, (6)CH + (8)CH). ^{13}C NMR δ (D_2O): 19.02 (d, J_{PC} = 48.86 Hz, 3C, (1)CH_2), 24.48 (s, 3C, (2)CH_2), 37.49 (d, J_{PC} = 15.25 Hz, 3C, (3)CH_2), 143.46 (s, 3C, (4)C), 128.42 (s, 6C, (5)CH + (9)CH), 131.75 (s, 6C, (6)CH + (8)CH), 146.55 (s, 3C, (7)C-SO_3-Na). ^{31}P NMR δ (D_2O): 35.08. Anal. Calcd for $C_{27}H_{30}Na_3O_{10}P_1S_3$ (M_r = 710.65): C, 45.63; H, 4.25. Calcd for $C_{27}H_{30}Na_3O_{10}PS_3{\cdot}3H_2O$ (M_r = 764.65): C, 42.37; H, 4.71. Found: C, 44.73; H, 4.39.[15]

Preparation of 1-Chloro-6-phenylhexane (6). 1,6-Dichlorohexane, 83.7 g (0.54 mol), and 200 mL of diethyl ether were placed into a three-neck flask equipped with reflux condenser and equal-pressure dropping funnel. After the addition of 100 mL of 0.18 M PhLi in cyclohexane/diethyl ether the reaction was heated at reflux for 4 days. Lithium chloride was removed by filtration and the solvent removed by distillation. The resulting oil was vacuum distilled, and the fractions were checked by GC. The fraction collected at 125-130 °C and 2-3 Torr contained $Ph(CH_2)_6Cl$. Yield: 24.8 g, 70% based on PhLi.

6: Slightly yellow oil, bp (2-3 Torr) = 125-130 °C, n_D^{20} = 1.5105. ^{1}H NMR δ ($CDCl_3$): 3.47 (t, J_{HH} = 6.68 Hz, 2H, (1)CH_2), 1.70 (quin, J_{HH} = 6.77 Hz, 2H, (2)CH_2), 1.21-1.49 (m, 4H, (3)CH_2 + (4)CH_2), 1.59 (quin, J_{HH} = 7.68 Hz, 2H, (5)CH_2), 2.57 (t, J_{HH} = 7.84 Hz, 2H, (6)CH_2), 7.05-7.30 (m, 5H, (8-12)C_6H_5). ^{13}C NMR δ ($CDCl_3$): 44.96 (s, 1C, (1)CH_2), 35.80 (s, 1C, (2)CH_2), 31.26 (s, 1C, (3)CH_2), 26.71 (s, 1C, (4)CH_2), 28.47 (s, 1C, (5)CH_2), 32.58 (s, 1C, (6)CH_2), 142.50 (s, 1C, (7)C), 128.34 (s, 2C, (8)CH + (12)-CH), 128.23 (s, 2C, (9)CH + (11)CH), 125.66 (s, 1C, (10)CH). The formula is $C_{12}H_{17}Cl$ (M_r = 196.72).

Synthesis of Tris(6-phenylhexyl)phosphine (7a). Tris-(6-phenylhexyl)phosphine was prepared from the reaction of $C_6H_5(CH_2)_6MgCl$ and PCl_3 in ether.[13] The product is obtained as a yellow oil in 72% yield.

7a: Yellow oil, mp = -51 °C. ^{1}H NMR δ ($CDCl_3$): 1.15-1.37 (m, 24H, (1-4)CH_2), 1.52 (quin, J_{HH} = 6.50 Hz, 6H, (5)CH_2), 2.51 (t, J_{HH} = 7.40 Hz, 6H, (6)CH_2), 7.02-7.19 (m, 15H, (8-12)C_6H_5). ^{13}C NMR δ ($CDCl_3$): 26.98 (d, J_{PC} = 13.26 Hz, 3C, (1)CH_2), 27.33 (d, J_{PC} = 12.04 Hz, 3C, (2)CH_2), 31.40 (d, J_{PC} = 11.02 Hz, 3C, (3)CH_2), 29.15 (s, 3C, (4)CH_2), 31.46 (s, 3C, (5)CH_2), 36.06 (s, 3C, (6)CH_2), 142.90 (s, 3C, (7)C), 128.48 (s, 6C, (8)CH + (12)CH), 128.30 (s, 6C, (9)CH + (11)CH), 125.68 (s, 3C, (10)CH). ^{31}P NMR δ ($CDCl_3$): -30.14. The formula is $C_{36}H_{51}P$ (M_r = 514.77).

Synthesis of Tris(6-phenylhexyl)phosphine Oxide (7b). The oxidation of **7a** was done in the same manner as described above in **2b**.

7b: Yellow oil. ^{1}H NMR δ ($CDCl_3$): 2.34 (s br, 6H, (1)CH_2), 1.10-1.81 (m, 24H, (2-5)CH_2), 2.58 (t, J_{HH} = 7.38 Hz, 6H, (6)-CH_2), 7.07-7.32 (m, 15H, (8-12)C_6H_5). ^{13}C NMR δ ($CDCl_3$): 19.15 (d, J_{PC} = 46.75 Hz, 3C, (1)CH_2), 21.60 (d, J_{PC} = 6.45 Hz, 3C, (2)CH_2), 30.37 (d, J_{PC} = 14.94 Hz, 3C, (3)CH_2), 28.28 (s, 3C, (4)-CH_2), 30.83 (s, 3C, (5)CH_2), 35.50 (s, 3C, (6)CH_2), 142.11 (s, 3C, (7)C), 128.14 (s, 12C, (8)CH + (9)CH + (11)CH + (12)CH), 125.49

(s, 3C, (10)CH). ^{31}P NMR δ ($CDCl_3$): 33.35. The formula is $C_{36}H_{51}OP$ (M_r = 530.77).

Synthesis of *p,p,p*-Trisulfonated Tris(6-phenylhexyl)-phosphine (8a). The sulfonation of tris(6-phenylhexyl)phosphine was accomplished as following: 2.58 g (5.01 mmol) of $P[(CH_2)_6C_6H_5]_3$ was dissolved in 10 mL of concentrated sulfuric acid at room temperature. After 30 min the reaction was quenched at 0 °C by the addition of 20% aqueous NaOH. The reaction solution was reduced in volume to 15 mL followed by the addition of 150 mL of methanol. The mixture was filtered to remove Na_2SO_4, and the solid was further extracted with 200 mL of methanol. The combined extracts were reduced in volume to 30 mL and filtered. A 150-mL volume of acetone was added to the clear solution to yield solid $P[(CH_2)_6C_6H_4$-*p*-$SO_3Na]_3$. NMR analysis showed that the initial crop of crystals contained 95% of the *p,p,p* isomer. The second crop, obtained after the addition of another 150 mL of acetone, contained 78% *p,p,p* and 22% *o,p,p*. The yield of *p,p,p*-trisulfonated product was 79% based on $P[(CH_2)_6C_6H_5]_3$.

8a: White crystals, mp > 360 °C. ^{1}H NMR δ (D_2O): 1.05–1.55 (m, 30H, (1–5)CH_2), 2.44 (t, J_{HH} = 7.80 Hz, 6H, (6)CH_2), 7.13 (d, J_{HH} = 8.12 Hz, 6H, (8)CH + (12)CH), 7.67 (d, J_{HH} = 8.12 Hz, 6H, (9)CH + (10)CH). ^{13}C NMR δ (D_2O): 28.30 (d, J_{PC} = 12.08 Hz, 3C, (1)CH_2), 29.35 (d, J_{PC} = 8.05 Hz, 3C, (2)CH_2), 33.84 (d, J_{PC} = 12.06 Hz, 3C, (3)CH_2), 31.52 (s, 3C, (4)CH_2), 33.45 (s, 3C, (5)-CH_2), 37.88 (s, 3C, (6)CH_2), 143.08 (s, 3C, (7)C), 128.24 (s, 6C, (8)CH + (12)CH), 131.14 (s, 6C, (9)CH + (11)CH), 148.50 (s, 3C, (10)C–SO_3Na). ^{31}P NMR δ (D_2O): -31.24. Anal. Calcd for $C_{36}H_{48}Na_3O_9PS_3$ (M_r = 820.89): C, 52.67; H, 5.89. Calcd for $C_{36}H_{48}Na_3O_9PS_3{\cdot}3H_2O$ (M_r = 874.89): C, 49.38; H, 6.17. Found: C, 49.64; H, 5.60.[15]

Characterization of the Phosphonium Salt Intermediates. The phosphonium salts were prepared in situ from the corresponding trisulfonated phosphines by dissolving the phosphine in D_2O and adjusting the pH to 3 with concentrated sulfuric acid. The NMR spectra were measured directly on the samples prepared in this manner.

$[HP(CH_2C_6H_4$-*p*-$SO_3H)_3]HSO_4$ (9). ^{1}H NMR δ (D_2O): 3.83 (d, J_{HH} = 15.2 Hz, 6H, (1)CH_2), 7.28 (d, J_{HH} = 8.2 Hz, 6H, (3)CH + (7)CH), 7.77 (d, J_{HH} = 8.2 Hz, 6H, (4)CH + (7)CH). ^{31}P NMR δ (D_2O): 16.24 (s).

$\{HP[(CH_2)_2C_6H_4$-*p*-$SO_3H]_3\}HSO_4$ (10). ^{1}H NMR δ (D_2O): 2.32 (quin*, J_{HH} = 7.3 Hz, 6H, (1)CH_2), 2.71 (quin*, J_{HH} = 7.3 Hz, 6H, (2)CH_2), 7.07 (d, J_{HH} = 8.0 Hz, 6H, (4)CH + (8)CH), 7.57 (d, J_{HH} = 8.0 Hz, 6H, (5)CH + (7)CH). ^{31}P NMR δ (D_2O): 11.32 (s br).

$\{HP[(CH_2)_3C_6H_4$-*p*-$SO_3H]_3\}HSO_4$ (11). ^{1}H NMR δ (D_2O): 1.59 (m, 6H, (1)CH_2), 1.91 (m, 6H, (2)CH_2), 2.54 (t, J_{HH} = 6.9 Hz, 6H, (3)CH_2), 7.12 (d, J_{HH} = 8.2 Hz, 6H, (5)CH + (9)CH), 7.58 (d, J_{HH} = 8.2 Hz, 6H, (6)CH + (8)CH). ^{31}P NMR δ (D_2O): 12.78 (t* br).

$\{HP[(CH_2)_6C_6H_4$-*p*-$SO_3H]_3\}HSO_4$ (12). ^{1}H NMR δ (D_2O): 1.05–1.65 (m, 24H, (1–4)CH_2), 2.03 (m, 6H, (5) CH_2), 2.55 (t, J_{HH} = 7.4 Hz, 6H, (6)CH_2), 7.25 (d, J_{HH} = 7.9 Hz, 6H, (8)CH + (12)-CH), 7.72 (d, J_{HH} = 7.9 Hz, 6H, (9)CH + (11)CH). ^{31}P NMR δ (D_2O): 11.66 (t* br).

Synthesis of $L_yNi(CO)_{4-y}$ Complexes (y = 1, 2; L = 1a, 2a, 3a, 4a, 5a, 7a, 8a, TPPTS). The complexes $LNi(CO)_3$ and L_2-$Ni(CO)_2$ were prepared from the nonsulfonated ligands in CH_2-Cl_2 following literature procedures.[16,17] The complexes were characterized by their infrared spectra in the carbonyl region and by ^{31}P NMR spectroscopy. All of the nickel complexes **13a,b**, **14a,b**, and **15a,b** were oils.

$P[(CH_2)_2C_6H_5]_3Ni(CO)_3$ (13a). IR (CH_2Cl_2) ν(CO): 2064.9 (w), 1986.6 (vs) cm^{-1}. ^{31}P NMR δ ($CDCl_3$): 15.27.

$\{P[(CH_2)_2C_6H_5]_3\}_2Ni(CO)_2$ (13b). IR (CH_2Cl_2) ν(CO): 1990.2 (s), 1926.9 (s) cm^{-1}. ^{31}P NMR δ ($CDCl_3$): 15.23.

$P[(CH_2)_3C_6H_5]_3Ni(CO)_3$ (14a). IR (CH_2Cl_2) ν(CO): 2062.8 (w), 1986.0 (vs) cm^{-1}. ^{31}P NMR δ ($CDCl_3$): 13.86.

$\{P[(CH_2)_3C_6H_5]_3\}_2Ni(CO)_2$ (14b). IR (CH_2Cl_2) ν(CO): 1984.8 (s), 1918.7 (s) cm^{-1}. ^{31}P NMR δ ($CDCl_3$): 13.31.

$P[(CH_2)_6C_6H_5]_3Ni(CO)_3$ (15a). IR (CH_2Cl_2) ν(CO): 2061.4 (w), 1981.9 (vs) cm^{-1}. ^{31}P NMR δ ($CDCl_3$): 13.80.

$\{P[(CH_2)_6C_6H_5]_3\}_2Ni(CO)_2$ (15b). IR (CH_2Cl_2) ν(CO): 1982.6 (s), 1915.2 (s) cm^{-1}. ^{31}P NMR δ ($CDCl_3$): 13.37.

The nickel complexes of the water-soluble phosphines were prepared in situ in 5:1 THF/H_2O for infrared spectroscopic measurements. Infrared spectra of the water-soluble complexes were measured in matched 0.1-mm Irtran-2 cells. Samples for NMR characterization were also prepared in THF/H_2O. After removal of solvent the solids were extracted with D_2O for ^{31}P NMR analysis.

$P(C_6H_4$-*m*-$SO_3Na)_3Ni(CO)_3$ (16a). IR (THF/H_2O) ν(CO): 2070.3 (w), 1996.0 (vs) cm^{-1}. ^{31}P NMR δ (D_2O): 34.89.

$[P(C_6H_4$-*m*-$SO_3Na)_3]_2Ni(CO)_2$ (16b). IR(D_2O) ν(CO): 2012.5 (m), 1953.9 (vs) cm^{-1}. ^{31}P NMR δ (D_2O): 33.44.

$P(CH_2C_6H_4$-*p*-$SO_3Na)_3Ni(CO)_3$ (17a). IR (THF/H_2O) ν-(CO): 2066.6 (w), 1990.1 (vs) cm^{-1}. ^{31}P NMR δ (D_2O): 39.10.

$[P(CH_2C_6H_4$-*p*-$SO_3Na)_3]_2Ni(CO)_2$ (17b). IR (D_2O) ν(CO): 1999.2 (m), 1935.9 (vs) cm^{-1}. ^{31}P NMR δ (D_2O): 23.21.

$P[(CH_2)_2C_6H_4$-*p*-$SO_3Na]_3Ni(CO)_3$ (18a). IR (THF/H_2O) ν(CO): 2062.8 (w), 1984.8 (vs) cm^{-1}. ^{31}P NMR δ (D_2O): 17.25.

$\{P[(CH_2)_2C_6H_4$-*p*-$SO_3Na]_3\}_2Ni(CO)_2$ (18b). IR (D_2O) ν-(CO): 1987.5 (m), 1918.7 (vs) cm^{-1}. ^{31}P NMR δ (D_2O): 17.46.

$P[(CH_2)_3C_6H_4$-*p*-$SO_3Na]_3Ni(CO)_3$ (19a). IR (THF/H_2O) ν(CO): 2060.8 (w), 1983.3 (vs) cm^{-1}. ^{31}P NMR δ (D_2O): 13.67.

$\{P[(CH_2)_3C_6H_4$-*p*-$SO_3Na]_3\}_2Ni(CO)_2$ (19b). IR (D_2O) ν-(CO): 1978.7 (m), 1910.7 (vs) cm^{-1}. ^{31}P NMR δ (D_2O): 12.76.

$P[(CH_2)_6C_6H_4$-*p*-$SO_3Na]_3Ni(CO)_3$ (20a). IR (THF/H_2O) ν(CO): 2060.2 (w), 1982.6 (vs) cm^{-1}. ^{31}P NMR δ (D_2O): 14.22.

$\{P[(CH_2)_6C_6H_4$-*p*-$SO_3Na]_3\}_2Ni(CO)_2$ (20b). IR (D_2O) ν-(CO): 1978.1 (m), 1914.1 (vs) cm^{-1}. ^{31}P NMR δ (D_2O): 13.88.

Preparation of L_2PdCl_2 Complexes (L = 1a, 2a, 3a, 4a, 5a, 7a, 8a, TPPTS). The bis(phosphine)palladium complexes of the nonsulfonated ligands were prepared in chloroform at room temperature from $(PhCN)_2PdCl_2$ by following literature procedures.[18]

$\{P[(CH_2)_2C_6H_5]_3\}_2PdCl_2$, Trans Isomer (21): Yellow crystals, mp = 176 °C. ^{1}H NMR δ ($CDCl_3$): 2.30 (m, 12H, (1)CH_2), 3.02 (m, 12H, (2)CH_2), 7.17–7.32 (m, 30H, (4–8)C_6H_5). ^{13}C NMR δ ($CDCl_3$): 24.66 (t, J_{PCP} = 12.1 Hz, 6C, (1)CH_2), 30.85 (s, 6C, (2)CH_2), 141.52 (t, J_{PCP} = 6.0 Hz, 6C, (3)C), 128.78 (s, 12C, (4)CH + (8)CH), 128.36 (s, 12C, (5)CH + (7)CH), 126.18 (s, 6C, (6)CH). ^{31}P NMR δ ($CDCl_3$): 13.31. Anal. Calcd for $C_{48}H_{54}Cl_2P_2Pd$ (M_r = 870.23): C, 66.25; H, 6.25. Found: C, 66.26; H, 6.18.

$\{P[(CH_2)_3C_6H_5]_3\}_2PdCl_2$, Trans Isomer (22): Yellow oil. ^{1}H NMR δ ($CDCl_3$): 1.77 (s br, 24H, (1)CH_2 + (2)CH_2), 2.65 (t* br, 12 H, (3)CH_2), 7.03–7.30 (m, 30H, (5–9)C_6H_5). ^{13}C NMR δ ($CDCl_3$): 21.49 (t, J_{PCP} = 14.3 Hz, 6C, (1)CH_2), 25.87 (s, 6C, (2)CH_2), 37.16 (t, J_{PCP} = 5.89 Hz, 6C, (3)CH_2), 126.12 (s, 6C, (4)C), 128.53 (s, 24C, (5)CH + (6)CH + (8)CH + (9)CH), 141.37 (s, 6C, (7)CH). ^{31}P NMR δ ($CDCl_3$): 11.79. The formula is $C_{54}H_{66}$-Cl_2P_2Pd (M_r = 954.39).

$\{P[(CH_2)_6C_6H_5]_3\}_2PdCl_2$, Trans Isomer (23): Yellow oil. ^{1}H NMR δ ($CDCl_3$): 1.15–1.62 (m, 48 H, (1–4)CH_2), 1.70 (s br, 12H, (5)CH_2), 2.50 (t, J_{HH} = 7.3 Hz, 12H, (6)CH_2), 7.02–7.20 (m, 30H, (8–12)C_6H_5). ^{13}C NMR δ ($CDCl_3$): 21.62 (t, J_{PCP} = 12.1 Hz, 6C, (1)CH_2), 24.06 (s, 6C, (2)CH_2), 31.15 (t, J_{PCP} = 6.0 Hz, 6C, (3)-CH_2), 28.97 (s, 6C, (4)CH_2), 31.40 (s, 6C, (5)CH_2), 36.01 (s, 6C, (6)CH_2), 142.73 (s, 6C, (7)C), 128.30 (s, 12C, (8)CH + (12)CH), 128.48 (s, 12C, (9)CH + (11)CH), 125.69 (s, 6C, (10)CH). ^{31}P NMR δ ($CDCl_3$): 10.91. The formula is $C_{72}H_{102}Cl_2P_2Pd$ (M_r = 1208.87).

The L_2PdCl_2 complexes of the sulfonated phosphines were prepared in situ in a two-phase reaction. Typically, 0.14 g (0.50 mmol) of $(PhCN)_2PdCl_2$ was dissolved in 2 mL of CH_2Cl_2 to give a yellow solution. A 2-mL aqueous solution (30% D_2O) containing 0.5 mmol of the desired sulfonated phosphine was then added.

(16) Strohmeier, W.; Müller, F. J. *Chem. Ber.* **1967**, *100*, 2812.
(17) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
(18) Hayashi, T.; Konishi, M.; Kumada, M. *Tetrahedron Lett.* **1979**, 1871.

After the mixture is stirred for 10–30 min, the color is completely transferred to the aqueous layer. The yellow water phase was separated and washed twice with 2 mL of CH_2Cl_2. The residual CH_2Cl_2 was removed under vacuum, and finally the pH was adjusted to 6 with the addition of HCl. The ^{31}P NMR spectra were recorded directly on these solutions.

$[P(C_6H_4$-*m*-$SO_3Na)_3]_2PdCl_2$, Trans Isomer (24). ^{31}P NMR δ (H_2O/D_2O): 34.81.

$[P(CH_2C_6H_4$-*p*-$SO_3Na)_3]_2PdCl_2$, Trans Isomer (25). ^{31}P NMR δ (H_2O/D_2O): 15.71.

$\{P[(CH_2)_2C_6H_4$-*p*-$SO_3Na]_3\}_2PdCl_2$, Trans Isomer (26). ^{31}P NMR δ (H_2O/D_2O): 14.98.

Cis Isomer. ^{31}P NMR δ (H_2O/D_2O): 28.97.

$\{P[(CH_2)_3C_6H_4$-*p*-$SO_3Na]_3\}_2PdCl_2$, Trans Isomer (27). ^{31}P NMR δ (H_2O/D_2O): 12.67.

Cis Isomer. ^{31}P NMR δ (H_2O/D_2O): 28.72.

$\{P[(CH_2)_6C_6H_4$-*p*-$SO_3Na]_3\}_2PdCl_2$, Trans Isomer (28). ^{31}P NMR δ (H_2O/D_2O): 11.16.

Cis Isomer. ^{31}P NMR δ (H_2O/D_2O): 27.21.

Results and Discussion

Water-Soluble Phosphine Synthesis by Sulfonation of Tris(ω-phenylalkyl)phosphines. All the sulfonations described here were monitored by NMR spectroscopy in a manner similar to that described previously.[14] The sulfonation of tris(ω-phenylalkyl)phosphines becomes progressively more facile as the length of the alkyl chain between the phosphorus atom and the phenyl ring increases. Also when $x \geq 2$, very little of the corresponding oxide is formed during the sulfonation procedure. Upon workup by neutralization with aqueous sodium hydroxide when an end point of pH = 7 is reached only TPPTS and trisulfonated tribenzylphosphine are isolated as the pure sodium salt. For those phosphines where $x \geq 2$ ^{31}P NMR spectroscopy is consistent with the formation of the phosphonium salt, $\{HP[(CH_2)_xC_6H_4$-*p*-$SO_3Na]_3\}^+$, when the reactions are worked up at pH 7. The reason for this is seen from the potentiometric titrations of the sulfonated phosphines.

Figure 2a shows the overlaid titration curves for the complete series of phosphines including TPPTS for comparison. For the phosphines with $x \geq 2$ buffering plateaus are observed in the curves. Figure 2b gives a comparison of the titration curves for $P[(CH_2)_3C_6H_4$-*p*-$SO_3Na]_3$ and its corresponding oxide, $O{=}P[(CH_2)_3C_6H_4$-*p*-$SO_3Na]_3$. The buffering capacity of the phosphine near pH 9 is lost upon oxidation. Thus, the last titration waves which give equivalence points of 8.6, 9.9, and 10.5 for the phosphines $P[(CH_2)_2C_6H_4$-*p*-$SO_3Na]_3$, $P[(CH_2)_3C_6H_4$-*p*-$SO_3Na]_3$, and $P[(CH_2)_6C_6H_4$-*p*-$SO_3Na]_3$, respectively, are all assigned to the neutralization of the phosphonium salt. All of these phosphines are sufficiently basic to form stable phosphonium ions.

Isolation of pure phosphonium salts is complicated by the presence of different possible counterions. The source of the proton may be either H_2SO_4 or the sulfonic acid groups bound to the phosphine itself, $-SO_3H$; thus, the possible anions are $[HSO_4]^-$, $[SO_4]^{2-}$, and $[-SO_3]^-$.

As the number of methylene groups increases, the corresponding phosphonium salt becomes a weaker acid (compare the equivalence points above, and see Figure 2a). This is consistent with the assumption that the tris(ω-phenylalkyl)phosphines should be more basic than triphenylphosphine. Interestingly the phosphines with higher basicity are not oxidized during the sulfonation procedure. This is most likely due to the protection of the

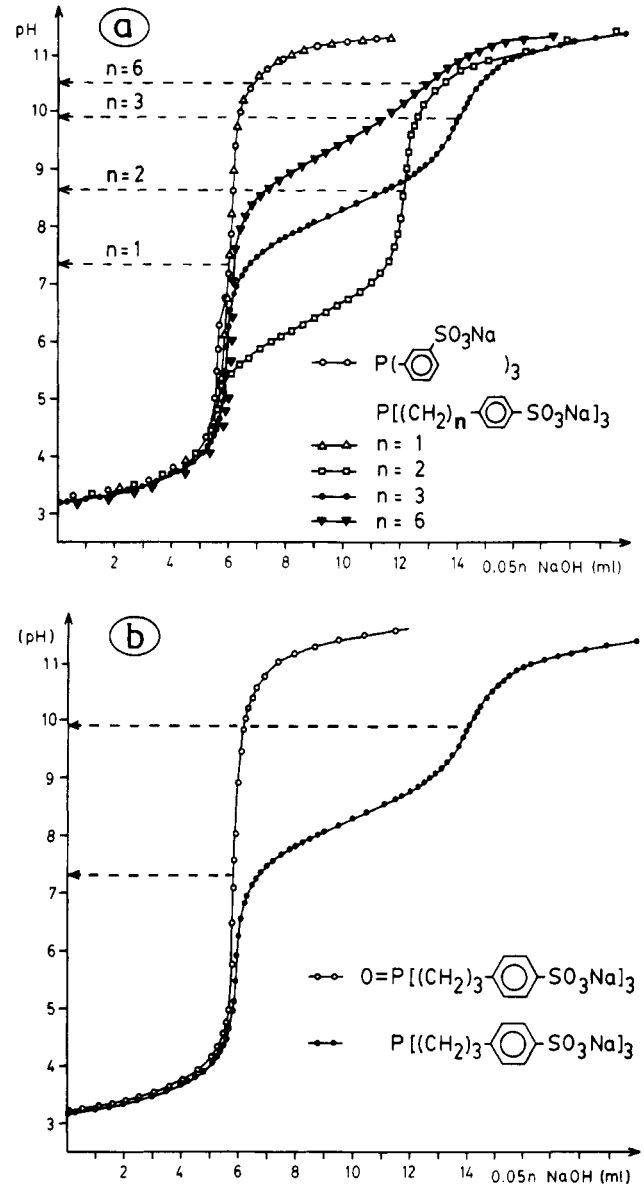

Figure 2. Potentiometric titration curves for the sulfonated phosphines. The phosphines were dissolved in aqueous H_2SO_4 to generate the acid form of the pendant sulfonate groups. (a) compares all sulfonated phosphines including TPPTS. (b) shows the curves for **5a** and its oxide **5b**.

phosphorus atom by formation of the phosphonium salt in the acidic sulfonation medium. In examining the sulfonation of PPh_3 and $AsPh_3$, Chatt et al. suggest that the former is protected against oxidation by formation of a phosphonium salt while the latter is oxidized and then sulfonated.[19] Complete sulfonation of PPh_3 is generally accompanied by ca. 20% oxidation,[8,14] which is consistent with the results obtained here which show that TPPTS does not form a stable phosphonium ion.

There is a slight step in the titration curve of TPPTS at pH 6.5 (see Figure 2a) that is not observed in the curve for *p,p,p*-trisulfonated tribenzylphosphine. This suggests that the $-SO_3H$ groups on *p,p,p*-trisulfonated tribenzylphosphine are isolated and act independently as acids and thus give a single step in the titration curve. The step in the titration curve for TPPTS is more typical of a

(19) Ahrland, S.; Chatt, J.; Davies, N. R.; Williams, A. A. *J. Chem. Soc.* **1950**, *264*, 276.

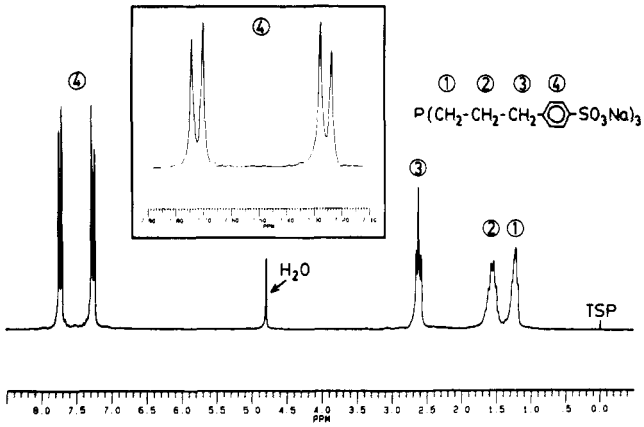

Figure 3. Proton NMR spectrum for **5a** in D_2O. The phenyl region clearly shows the expected para substitution pattern.

polyprotic acid in that ionization of one proton affects the pK_a of the remaining protons.

The phenyl region of the ^1H NMR spectra of the purified sulfonated tris(ω-phenylalkyl)phosphines is very distinctive and characteristic of para aromatic substitution. For clarity the pattern is shown in Figure 3 for *p,p,p*-trisulfonated tris(3-phenylpropyl)phosphine; observation of this pattern is proof that the *p,p,p* isomer is isolated. NMR data (see Experimental Section) are provided for the complete series of compounds $P[(CH_2)_xC_6H_5]_3$, $P[(CH_2)_xC_6H_4$-*p*-$SO_3Na]_3$, and appropriate oxides, x = 1, 2, 3, and 6. Additionally the ^1H and ^{31}P NMR spectra of the phosphonium salts, $[HP[(CH_2)_xC_6H_4$-*p*-$SO_3H_3]^+$-$[HSO_4]^-$ were recorded. The sulfonated phosphine oxides were obtained by oxidation of the corresponding sulfonated phosphine.

Determination of the Electronic Parameter of the New Nonsulfonated and Sulfonated Phosphines. The ν(CO) A_1 stretching frequency in $PR_3Ni(CO)_3$ complexes correlates with the electronic character of the phosphorus ligand.[16] Tolman defined for PR_3 the electronic parameter χ as

$$\chi_{PR_3} = \nu(CO)A_{1\ PR_3Ni(CO)_3} - \nu(CO)A_{1\ P(tBu)_3Ni(CO)_3}$$

where the stretching frequencies are measured in CH_2Cl_2.[16,17] With increasing basicity of the phosphine the χ value decreases.

The nickel complexes of the nonsulfonated ligands were prepared in situ in CH_2Cl_2 from $Ni(CO)_4$ and a slight excess of the phosphine. The complexes $PR_3Ni(CO)_3$ were recognized from their characteristic carbonyl stretching pattern in the infrared spectrum.

Determination of the electronic parameter of the sulfonated phosphines is complicated by the following problems: (i) Complexes of the type $\{P[(CH_2)_xC_6H_4$-*p*-$SO_3Na]_3\}Ni(CO)_3$, x = 1, 2, 3, and 6, are not soluble in CH_2Cl_2. (ii) the ν(CO) A_1 stretching frequency is solvent dependent. (iii) χ is defined from ν(CO) A_1 as measured in CH_2Cl_2.

It was found that aqueous THF (5:1 THF/H_2O) dissolves the nickel complexes of both nonsulfonated and sulfonated phosphines. With this solvent mixture the infrared spectra of the complete series of compounds, $TPPTSNi(CO)_3$ and $P[(CH_2)_xC_6H_4$-*p*-$SO_3Na]_3Ni(CO)_3$, x = 1, 2, 3, and 6, and $TPPNi(CO)_3$ and $P[(CH_2)_xC_6H_5]_3Ni(CO)_3$, x = 1, 2, 3, and 6, were measured. The difference in the basicity of nonsulfonated and sulfonated ligand pairs can be compared directly in this manner. Furthermore a χ value for

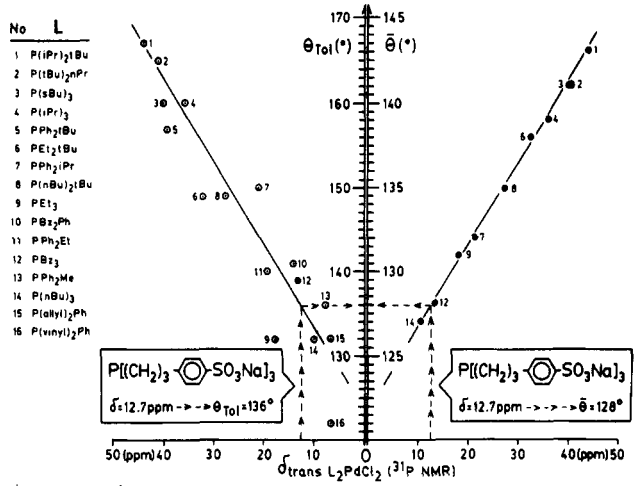

Figure 4. Plots of θ_{Tol} vs δ *trans*-L_2PdCl_2 (left side) and $\bar{\theta}$ vs δ *trans*-L_2PdCl_2 (right side). The $\bar{\theta}$ values shown are those calculated in ref 21. The θ values were obtained as illustrated by the dashed arrows for $P[(CH_2)_3C_6H_4$-*p*-$SO_3Na]_3$. A chemical shift of 12.7 ppm corresponds to a θ_{Tol} value of 136° and $\bar{\theta}$ value of 128°.

the sulfonated phosphines can be calculated for comparison with known nonsulfonated phosphines. For example, the electronic parameter of TPPTS can be calculated in the following manner:

$$\chi_{TPPTS} = \chi_{TPPTS(THF/H_2O)} + [\chi_{TPP} - \chi_{TPP(THF/H_2O)}]$$

The electronic parameters for all new phosphines are presented in Table I. For comparison the electronic parameters for TPP, $P(CH_2C_6H_5)_3$, and $PnBu_3$ are also given.[20] From the data in Table I it is evident that for the series $P[(CH_2)_xC_6H_5]_3$ the electronic parameters begin to approach tri-*n*-butylphosphine when $x \geq 3$. The effect of sulfonation on the electronic parameter is strongest for TPPTS and diminishes as x increases.

Determination of the Steric Parameter of the New Nonsulfonated and Sulfonated Phosphines. It has been shown that the ^{31}P NMR chemical shift of *trans*-$(PR_3)_2PdCl_2$ complexes correlates well with the bulkiness of phosphine ligands, L.[21] The *trans*-L_2PdCl_2 complexes were prepared to determine the steric parameters of the new nonsulfonated and sulfonated phosphines. The palladium dichloride complexes are commonly prepared by the reaction of bis(benzonitrile)palladium dichloride with the appropriate phosphine.[17] The reactions of the nonsulfonated phosphines were done in CH_2Cl_2, and the complexes could be isolated. On the other hand, the reactions with the sulfonated phosphines were prepared in situ under two-phase reaction conditions with the phosphines in the aqueous phase.

The steric parameter defined by Tolman, θ_{Tol}, is measured mechanically from space-filling models, while the value defined by Musco, $\bar{\theta}$, is derived from X-ray diffraction data and calculated by integration to determine the volume excluded by the substituents on the phosphorus atoms.[22] Both steric parameters correlate with the chemical shift of the *trans*-bis(phosphine)palladium dichloride complexes described above.[21] Figure 4 shows the plot obtained for the chemical shift of the palladium complexes

(20) Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29.
(21) Bartik, T.; Himmler, T. *J. Organomet. Chem.* **1985**, *293*, 343.
(22) Immirzi, A.; Musco, A. *Inorg. Chim. Acta* **1977**, *25*, L41.

Table I. Electronic and Steric Parameters for the Nonsulfonated and Sulfonated Phosphines[a]

no.	ligand	FT_χ (cm^{-1})	θ_{Tol} (deg)	$\bar{\theta}$ (deg)	no.	ligand	FT_χ (cm^{-1})	θ_{Tol} (deg)	$\bar{\theta}$ (deg)
	TPP	13.25[18]	145[16]	128[19]		TPPTS	15.55	166	139
	$P(CH_2C_6H_5)_3$	10.35[18]	139[16]	128[19]	**1a**	$P(CH_2C_6H_4$-*p*-$SO_3Na)_3$	12.75	141	130
2a	$P[(CH_2)_2C_6H_5]_3$	8.90	137	128	**3a**	$P[(CH_2)_2C_6H_4$-*p*-$SO_3Na]_3$	8.80	139	129.5
4a	$P[(CH_2)_3C_6H_5]_3$	6.70	135	127.5	**5a**	$P[(CH_2)_3C_6H_4$-*p*-$SO_3Na]_3$	6.20	136	128
7a	$P[(CH_2)_6C_6H_5]_3$	5.30	134	127	**8a**	$P[(CH_2)_6C_6H_4$-*p*-$SO_3Na]_3$	4.95	134	127
	$P(nBu)_3$	5.25[18]	132[16]	127[19]					

[a] FT: As determined by FTIR to ±0.05 cm^{-1}.

of several known phosphines versus θ_{Tol} (left side). The calculated plot and interpolated values for and $\bar{\theta}$ vs chemical shift are shown on the right side of Figure 4. The steric parameters for the new phosphines were taken from the plots as indicated for $P[(CH_2)_3C_6H_4$-*p*-$SO_3Na]_3$ in the figure.

The derived steric parameters both θ_{Tol} and $\bar{\theta}$ for the new phosphines are collected in Table I. NMR measurements on the palladium complexes of the sulfonated phosphines were made in water and are not corrected for solvent. The solvent dependence on chemical shift is small compared to the uncertainty in assigning $\bar{\theta}$. For example, a 1 ppm difference in ^{31}P NMR chemical shift for *trans*-L_2PdCl_2 corresponds to a difference of ~1.5° in θ_{Tol}.

The steric parameters of the sulfonated and nonsulfonated phosphines, as determined by the ^{31}P NMR method described above, show that the sulfonated phosphines are only slightly larger than their neutral analogs. This is expected for the tris(ω-phenylalkyl)phosphines since sulfonation occurs at the para position. The difference in cone angle for the phosphines is greatest when the length of the methylene chain separating the phosphorus atom and the phenyl ring is short. For $x = 6$ there is no measurable difference in bulkiness between the nonsulfonated and sulfonated phosphines as determined by the method described. Interestingly the effective steric bulk of TPPTS is significantly larger than triphenylphosphine, θ_{Tol}, 166° [23] vs 145°, and $\bar{\theta}$, 139° vs 128°, respectively. Sulfonation occurs at the meta position in TPPTS so it is reasonable that it should be larger than that for triphenylphosphine. The difference in size may, in part, account for the excellent linear to branched ratios obtained in the water-soluble catalysts of Rhone Poulenc for the hydroformylation of propylene.[8] The θ_{Tol} value obtained here by spectroscopic methods for TPPTS is in good agreement with the value calculated by Darensbourg et al. (170°) from the crystal structure of [Na-crypt]$_3$-[$W(CO)_5$(TPPTS)].[24]

The availability of water-soluble phosphines with electronic and steric character similar to that of linear alkyl phosphines will allow catalytic processes that require alkylphosphines for good activity and selectivity to be investigated in water. One such process is the phosphine-modified cobalt hydroformylation of alkenes.

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(23) In the assignment of a θ_{Tol} value for TPPTS based on the results obtained here the following logic was used. From the difference in chemical shift between *trans*-$(TPP)_2PdCl_2$ and *trans*-$(TPPTS)_2PdCl_2$ and the slope of the plot of θ_{Tol} vs δ *trans*-L_2PdCl_2 we estimate that the cone angle of TPPTS is 21° larger than TPP.

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