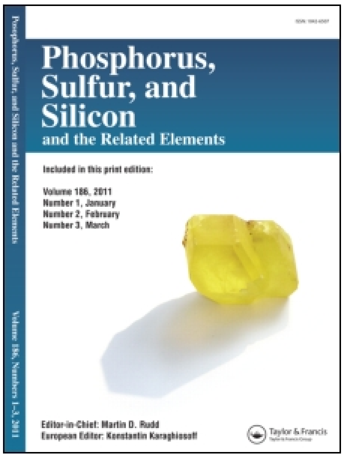

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Synthesis and Characterization of Sulfonated and Poly(Ethylene Glycol)-Calix[4]Arene Tertiary Phosphines

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SYNTHESIS AND CHARACTERIZATION OF SULFONATED AND POLY(ETHYLENE GLYCOL)-CALIX[4]ARENE TERTIARY PHOSPHINES

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Sulfonation of triphenylphosphine with a 30% oleum solution gave phenyl-di-(3-sulfonatophenyl) phosphine. The structure was confirmed by a combination of ^{1}H and ^{13}C NMR spectroscopy. A pair of calix[4]arenes with a tertiary phosphine group on one rim and a methoxy ethylene glycol group on the other were prepared and characterized. One had the phosphine moiety on the narrow rim, and the other had the phosphine on the wide rim. Structural characterization was again by a combination of ^{1}H and ^{13}C NMR spectroscopy.

Keywords: : oleum; water soluble phosphines; sulfonated phosphines; calixarene phosphines; methoxy ethylene glycol

INTRODUCTION

Tertiary phosphines have found widespread use as ligands for late transition metal ions. An important use of these complexes is in their application as homogeneous catalysts. The majority of these tertiary phosphine metal complexes are hydrophobic and soluble in hydrocarbon solvents. Such complexes are suitable for use as homogeneous catalysts in reactions such as alkene hydroformylation. A challenge in the application of homogeneous catalysis is that of catalyst recovery. One solution to this problem is to

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use a biphasic system where the catalyst is soluble in water, and the organic products are soluble in the organic phase. Such catalysts require the use of water soluble tertiary phosphines as the ligand.[1–5]

As we move from a fossil-based economy to one based on renewable resources, it can be anticipated that it may be advantageous to have available homogeneous catalysts that are water soluble and effective in a biphasic system. This will likely require tertiary phosphines that are compatible with such reaction conditions. This paper addresses two aspects of this problem. The first reports the water soluble tertiary phosphine that can be obtained from the commercially available oleum, and the second reports a new class of water soluble tertiary phosphines that can be prepared using a calix[4]arene framework as template.

Water soluble tertiary phosphines can be obtained by the sulfonation of triphenylphosphine with oleum.[6–13] A by-product of this sulfonation is oxidation, and sulfonated triarylphosphine oxides are formed in addition to the desired sulfonated triphenylphosphines. A method of circumventing this problem is to use boric acid in the sulfonation step in addition to a 65% oleum solution. A problem with this method, however, is that sulfuric acid solutions containing such high concentrations of sulfur trioxide are not presently available in the United States. Since solutions of 30% oleum are readily available, we have investigated whether these solutions can be used to prepare water soluble triarylphosphines. The use of water soluble triarylphosphine complexes as homogeneous catalysis, although advantageous in some ways, has some limitations. [14–26] One limitation is that organometallic reactions may occur differently in an aqueous medium. [27–30] Another aspect is that since the catalyzed reactions occur in the aqueous phase, hydrophobic compounds may be incompatible with the system. Phase transfer catalysts containing tertiary phosphines having both hydrophilic and hydrophobic ends can be used to address this problem.[31] Calixarenes are cyclic oligomers formed by a condensation reaction between a phenol and formaldehyde. Since calixarenes have been widely used as phase transfer agents between an aqueous and an organic phase they are particularly attractive for the assembly of tertiary phosphines that have this property,[32] In this paper we report such a tertiary phosphine that also has a hydrophilic oxy(ethylene)tail group.

EXPERIMENTAL

All materials and solvents were standard reagent grade, and were used without further purification unless otherwise noted. Reagents were purchased from Aldrich Chemical Co. and used as supplied. Dry toluene and THF were distilled from the ketyl prepared from sodium and benzophenone. Dry chloroform was distilled from CaH_2. MeO-PEG-OH was dried under vacuum or by azeotropic distillation from toluene prior to use. The ^1H, ^{31}P and ^{13}C NMR spectra were measured using Bruker AC-200 and Varian Unity INOVA 500 spectrometers. The starting calix[4]arene compounds were prepared by literature methods. Microanalytical data were not obtained for the new poly(ethylene glycol)-calix[4]arene tertiary phosphines because the poly(ethylene glycol) side-chain is a statistical distribution of oligomers rather than a single species.

Synthesis of phenyl-di-(3-sulfonatophenyl) phosphine

Oleum (15 mL) was added dropwise to Ph_3P (3.5 g, 13 mmol) at 0°C. After stirring for 24 h at room temperature, the mixture was hydrolyzed with cold water and extracted with triisooctylamine (5 mL) in toluene (50 mL). The organic phase was washed with H_2O (4 x 25mL). After reextraction with NaOH (25%) to pH = 13, the white precipitate collected from the aqueous phase was washed with H_2O and MeOH, and dried under vacuum. Yield 3.1 g (50%). ^{31}P NMR (D_2O): –5.42. ^1H NMR (D_2O): δ 7.21–7.33 (m, 7H), 7.37 (ddd, $^3J_{HH} = 8.0$ Hz, $^3J_{HH} = 8.0$ Hz, $^4J_{PH} = 1.5$ Hz, 2H), 7.59 (ddd, $^3J_{PH} = 7.5$ Hz, $^4J_{HH} = 1.5$ Hz, $^4J_{HH} = 1.5$ Hz, 2H), 7.67 (ddd, $^3J_{HH} = 8.0$ Hz, $^4J_{HH} = 1.5$ Hz, $^4J_{HH} = 1.5$ Hz, 2H). ^{13}C NMR (D_2O): δ 126.6 (s), 129.5 (d, $^3J_{PC} = 7.3$ Hz), 129.8 (d, $^3J_{PC} = 6.5$ Hz), 130.2 (s), 130.4 (s), 130.5 (s), 134.2 (d, $^2J_{PC} = 19.9$ Hz), 136.7 (d, $^2J_{PC} = 17.5$ Hz), 137.5 (d, $^1J_{PC} = 10.2$ Hz), 143.2 (d, $^3J_{PC} = 7.3$ Hz).

Synthesis of 5,11,17,23-tetrachloromethyl-25,26,27,28-tetra [(((4-methylphenyl)sulfonyl)oxy)ethoxy]calix[4]arene (1)

To a solution of 1.7 g (1.4 mmol) of 25,26,27,28-tetra[(((4-methylphenyl)sulfonyl)oxy)ethoxy]calix[4]arene and 8.0 g (45 mmol) of chloromethyl-n-octyl ether in 80 mL of $CHCl_3$, cooled at –10°C, 2.6 mL (22 mmol) of $SnCl_4$ were added dropwise. After the resulting red solution was stirred at room temperature for 1 h, water was added and the organic phase was separated and washed twice with water, dried with Na_2SO_4, and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and treated with hexane. The white precipitate was collected, washed with hexane, and dried in vacuum. Yield, 1.4 g (71%). ^1H NMR ($CDCl_3$): δ 2.41 (s, 12 H $ArCH_3$), 3.03 (d, J = 13.6 Hz, 4H, $ArCH_2Ar$), 4.12–4.37 (m, 28 H, $ArCH_2Ar$, OCH_2CH_2OTs, CH_2Cl), 6.58 (s, 8H, ArH), 7.31 (d, J = 8.2 Hz, 8H, ArH), 7.73 (d, J = 8.2 Hz, 8H, ArH). ^{13}C NMR ($CDCl_3$): δ 21.6 ($ArCH_3$), 30.6 ($ArCH_2Ar$), 46.1 ($ArCH_2Cl$), 69.5 ($ArOCH_2CH_2OTs$), 71.9 ($ArOCH_2CH_2OTs$), 127.8, 128.8, 129.9, 131.8, 132.6, 134.6, 144.9 and 155.2 (Ar).

Synthesis of 5,11,17,23-tetra-[MeO-PEG-OCH_2]-25,26,27,28-tetra [(((4-methylphenyl)sulfonyl)oxy)ethoxy]calix[4] arene (2a) and 5,11,17,23-tetrachloromethyl-25,26,27,28-tetra [MeO-PEG-OCH_2CH_2O]-calix[4]arene (2b)

To a cold solution of MeO-PEG-OH (M = 2000, 2.84 g, 1.4 mmol) in dry toluene (20 mL), was added sodium hydride (150 mg, 6.3 mmol). The mixture was stirred at room temperature for 3 h, then at 50°C for 1 h. The mixture was filtered, cooled to 0°C and **1** (500 mg, 0.4 mmol) was added. The solution was stirred at room temperature for 60 h and at 60°C for 36 h. Upon cooling to room temperature, the solution was filtered and treated with diethyl ether. The crude product was collected on a glass frit and reprecipitated twice from CH_2Cl_2 with diethyl ether, and dried in vacuum. Yield 2.4 g (73%). ^1H NMR ($CDCl_3$): δ 2.41 (s, $ArCH_3$), 3.08 (m, $ArCH_2Ar$), 3.39 (s, OCH_3), 3.60–4.45 (m, $(OCH_2CH_2)_n$, $ArCH_2Ar$, $ArOCH_2CH_2OTs$, $ArCH_2$), 7.25, 7.70 (m, ArH).

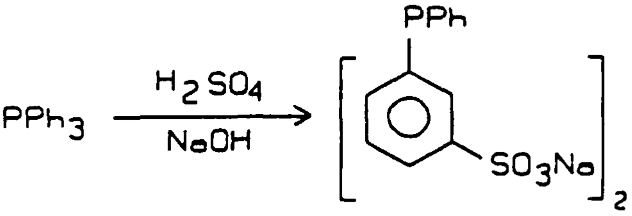
Synthesis of 5,11,17,23-tetra-[MeO-PEG-OCH_2]-25,26,27,28-tetra-[$OCH_2CH_2PPh_2$]calix[4]arene (3a) and 5,11,17,23-tetra-[CH_2PPh_2]-tetra-25,26,27,28-[MeO-PEG-OCH_2CH_2O]calix[4]arene (3b)

To a solution of Ph_2PH (135 mg, 0.7 mmol) in THF (6 mL, –78°C) was added n-BuLi (1.6 M, 0.46 mL, 0.7 mmol). The resulting red solution was transferred via a cannular to a stirred solution of **2** (1.2 g, 0.1 mmol) in THF (20 mL, –78°C). The mixture was stirred at room temperature for 12 h and at 60°C for 4 h. Upon cooling to room temperature, diethyl ether was added. The resulting precipitate was collected and recrystallized from CH_2Cl_2 and diethyl ether. Yield 0.8 g (66%). ^{31}P NMR ($CDCl_3$): δ −10.6(m), −23.6(m). ^{1}H NMR ($CDCl_3$): δ 3.40 (s, OCH_3), 3.50–4.10 (m, $(OCH_2CH_2)_n$, $ArCH_2Ar$, $ArOCH_2CH_2PPh_2$, $ArCH_2$), 7.45 (m, ArH).

RESULTS AND DISCUSSION

Sulfonation of Triphenylphosphine

Treating triphenylphosphine with 30% oleum at ambient temperature results in sulfonation at the *meta* positions of two of the phenyl rings (equation 1). The water soluble product is phenyl-di-(3-sulfonatophenyl) phosphine. The compound has been characterized by nuclear magnetic resonance spectroscopy. The $^{31}P\{^{1}H\}$ NMR spectrum shows a resonance at δ − 5.42 for the tertiary phosphine phosphorus. The only other resonances, which account for less than 10% of the total phosphorus-containing compounds, are observed at δ −5.18 and δ 35.42. The latter resonance corresponds to the tertiary phosphine oxide.



(1)

The ^{1}H NMR spectrum shows a series of multiplets for the hydrogens of the P-phenyl groups in the δ 7.21–7.33 range which correspond in intensity to seven hydrogens. These resonances can be assigned to the five hydrogens of the PPh group, along with H_d in the phenylsulfonic acid group (Figure 1). A resonance corresponding to two hydrogens is found at δ 7.37. This resonance shows coupling to two hydrogens $^{3}J_{HH}$ = 8.0 Hz, and a long range coupling with phosphorus, $^{4}J_{PH}$= 1.5 Hz. We assign this resonance to H_C. The two downfield shifted hydrogens with short range coupling to hydrogen and phosphorus are assigned to H_b and H_a. The resonance at δ 7.59 shows $^3J_{PH} = 7.5$ Hz, along with two long range $^4J_{HH} = 1.5$ Hz couplings. Decoupling at the ^{31}P resonance frequency collapses the short range coupling, thereby confirming its assignment as H_a. The resonance at δ 7.67 is assigned to H_b. This resonance shows a short range $^3J_{HH} = 8.0$ Hz and two long range $^4J_{HH} = 1.5$ Hz couplings. Decoupling at δ 7.37, the resonant frequency, causes this short range coupling to collapse, thereby confirming its assignment as H_c (Figure 2). In integration confirms that two of the phenyl rings have been sulfonated.

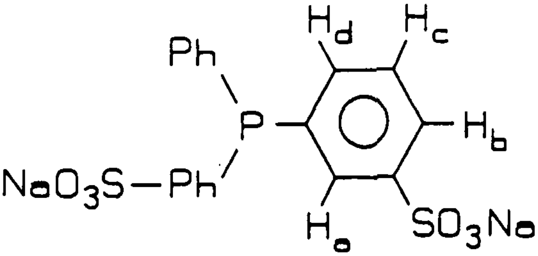


FIGURE 1 Peak Identification of the Proton Resonances in phenyl-di-(3-sulfonatophenyl) phosphine

The $^{13}C\{^1H\}$NMR spectrum shows the expected ten resonances for Carbon-1 through Carbon-10 (Figure 3). Of these ten resonances, four are singlets, and six are doublets due to coupling with ^{31}P. The following assignments have been made to these resonances. C_1 is assigned to the doublet at δ 137.5 ($^1J_{PC} = 10.2$ Hz)[7], and C_2 to the doublet at δ 134.2 ($^2J_{PC} = 19.9$ Hz).[33–35] C_3 is assigned to the doublet at δ 143.2 ($^3J_{PC} = 7.3$ Hz)[8,9,11], and C_4 to the singlet at δ 126.6. C_5 is assigned to the doublet at δ 129.8 ($^3J_{PC} = 6.5$ Hz)[7], and C_6 to the doublet at δ 136.7 ($^2J_{PC} = 17.5$ Hz)[7]. These assignments are based on literature precedent for carbon chemical shifts of C(phenyl)-P and C(phenyl)-SO_3Na groups, and large values of $^2J_{PC}$in similar systems.[7-9,11,31–33]

The assignments of the four resonances in the unsubstituted phenyl ring are more tentative, especially since three of these are closely spaced singlets. Based on chemical shift sequences we assign the singlets at δ 130.5, 130.4 and 130.2 to C_7, C_8 and C_{10} respectively, and the doublet at δ 129.5 ($^3J_{PC} = 7.3$ Hz) to C_9. If, however, coupling constant comparisons are given precedence, the assignments for C_8 and C_7will be reversed.

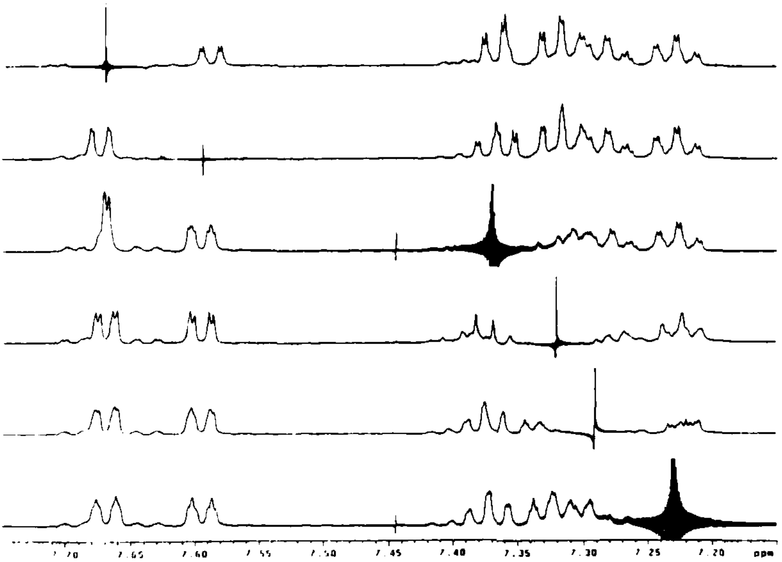


FIGURE 2 Stacked ^{1}H NMR Spectra from the Selective Proton-Proton Decoupling Experiments with phenyl-di-(3-sulfonatophenyl) phosphine

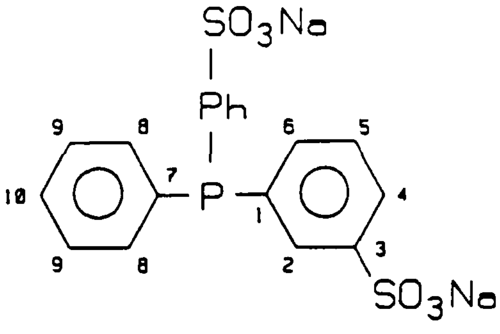
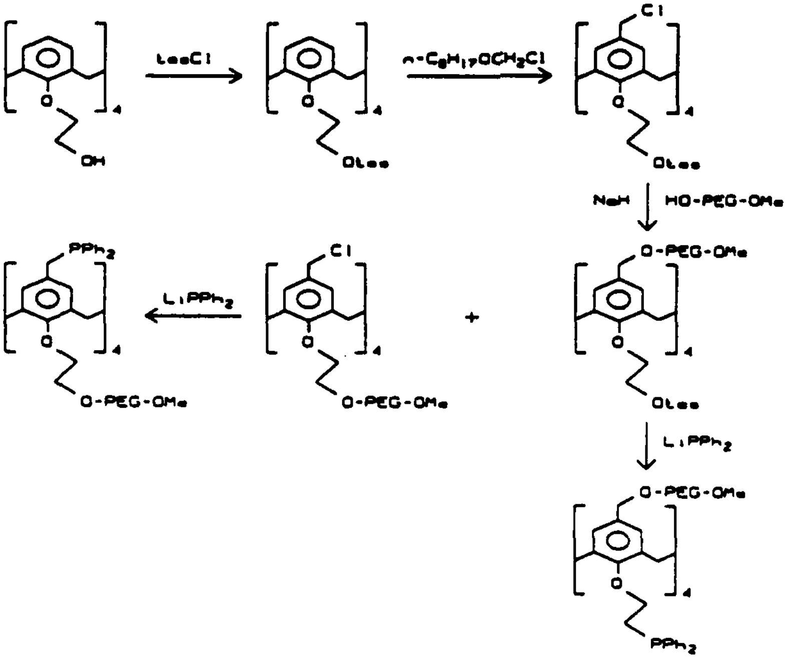


FIGURE 3 Peak Identification of the Carbon Resonances in phenyl-di-(3-sulfonatophenyl) phosphine

Synthesis of Water Soluble Calixphosphines

Although there are examples of calixarenes having phosphorus containing functionalities appended to both their wide and narrow rims, the problem of synthesizing water soluble calixphosphines has not been addressed. Sulfonation is one possible approach, but an alternate strategy uses the hydrophilic oxy(ethylene) functionality to confer solubility in aqueous solution. Since the oxy(ethylene) moiety can be readily appended to a calixarene, we have opted for this approach. Our goal therefore is to synthesize compounds having tertiary phosphine functionalities on either the wide or narrow rim of a calix[4]arene, with the oxy(ethylene) tail being bound to the other rim. We have avoided compounds with P-O bonds because of their hydrolytic instability.[36]



The synthetic strategy we have used is shown in the scheme. By this strategy we can place the tertiary phosphine on either the wide or narrow rim of the calix[4]arene, with the oxyethylene groups being appended onto the other. In following this strategy we have used MeO-PEG-OH to introduce the oxyethylene groups. This compound contains a distribution of oxyethylene chain lengths, thereby resulting in a tertiary phosphine product that mirrors this distribution. In designing this strategy we had anticipated that the chloromethyl functionality on the wide rim would have a higher electrophilicity than the alkyl tosylate group on the lower rim. Any such selectivity is not apparent in their reactivities to the diphenylphosphide nucleophile, however, since both tertiary phosphines are found in approximately equal amounts, as confirmed by thin layer chromatography and ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum has two peaks of close to equal intensity at δ −10.6(m), −23.6(m). These shifts correspond to those expected for compounds having a tertiary phosphine group on the upper and lower rims. The upper rim derivatives are expected to show a shift at δ −10.1,[37] and the lower rim derivatives at δ −23.93 [38]. Each peak is a closely-spaced multiplet of resonances due to the different number of oxy(ethylene) groups in the oligomeric chains.

This pair of tertiary phosphines is, as anticipated, soluble in water. Experiments are underway to separate this mixture of upper and lower rim substituted tertiary phosphines, although this separation is complicated by each compound having multiple oligomeric chain lengths in their oxyethylene moieties.

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