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Convenient Synthesis of the Water-Soluble Ligand Hexasodium Tris(4-phosphonatophenyl)phosphine

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Over the last 25 years, there has been considerable interest in aqueous and biphasic homogeneous transition metal catalysis. The most frequently used ligands in the metal complexes employed for these reactions are functionalized triarylphosphines.[1] Triarylphosphines are sufficiently good σ-donors and π-acceptors to stabilize synthetically useful transition metal species, yet, compared to alkylphosphines, are relatively resistant to oxidation by adventitious oxygen. This is an important factor for aqueous catalytic reactions, given the difficulty in removing oxygen from aqueous media.

A wide variety of cationic, anionic, and nonionic hydrophilic functional groups have been utilized to impart water solubility to triarylphosphines. Sulfonated phosphine ligands such as $P(3\text{-}C_6H_4SO_3Na)_3$ (triphenylphosphine trisulfonate, TPPTS) were demonstrated to be effective in the biphasic hydroformylation reaction commercialized by Rhone-Poulenc in the mid-1970s and remain the most common.[2] However, we have instead focused on the synthesis and reactivity of phosphonate-functionalized phosphine ligands. Phosphonate groups and their corresponding salts also impart a high degree of water solubility to these ligands and offer a further advantage in being an excellent functionality for the synthesis of hybrid inorganic−organometallic materials. These materials have found broad application in the molecular fabrication of materials, including supported catalysts,[3] chemical sensors,[4] electroluminescent materials,[5] and nonlinear optical materials.[6]

Knight, et al., previously reported the synthesis of $4\text{-}Ph_2PC_6H_4PO_3Na_2$ (triphenylphosphine monophosphonate, TPPMP) from $4\text{-}Ph_2PC_6H_4Br$.[7] Metal−halogen exchange with *n*-butyllithium followed by subsequent reaction of the aryllithium species with diethyl chlorophosphate gave the intermediate phosphonate ester $4\text{-}Ph_2PC_6H_4PO_3Et_2$. Transesterification with $BrSiMe_3$,[8] followed by hydrolysis and neutralization with NaOH gave the desired compound. The phosphonate ester has also been prepared by the Pd-catalyzed reaction of $4\text{-}PPh_2C_6H_4Br$ and diethyl phosphite.[9] In our hands, neither of these strategies was satisfactory for the preparation of the corresponding tris-phosphonate compound, as they gave mixtures of products which were difficult to purify.

Nucleophilic aromatic substitution of fluoroarylsulfonates by phosphine or primary or secondary phosphines in the superbasic medium KOH/DMSO has been shown to be a flexible and efficient route to secondary and tertiary phosphines with sulfonated aromatic substituents.[10] Similarly, it has been reported that the triphenylphosphine diphosphonates $PhP(4\text{-}C_6H_4PO_3Na_2)_2$ and $PhP(3\text{-}C_6H_4PO_3Na_2)_2$ can be prepared by nucleophilic aromatic substitution of $4\text{-}FC_6H_4P(O)(NEt_2)_2$ or $3\text{-}FC_6H_4P(O)(NEt_2)_2$ by $PhPLi_2$, followed by acid hydrolysis of the resulting arylphosphine−phosphonodiamide and neutralization of the free phosphonic acid with NaOH.[11] From these reports, it was reasonable to assume that $P(4\text{-}C_6H_4PO_3Na_2)_3$ (triphenylphosphine triphosphonate, TPPTP) could be prepared from nucleophilic aromatic substitution of the appropriate aryl fluoride by PH_3. We were dissuaded, however, by the toxic and pyrophoric properties of phosphine gas.

It is known that phosphide anions can be generated directly from red phosphorus by the action of alkali metals in liquid ammonia.[12] The reduction is believed to proceed via a diphosphide anion, $[P{-}P]^{4-}$, which, in the absence of a proton source more acidic than ammonia, is resistant to further reduction.[13] Addition of alkyl halides gives tetraalkyldiphosphines, $R_2P{-}PR_2$, along with small amounts of R_3P.[14] When the reduction is carried out by the slow addition of 1 molar equivalent of a proton source such as *t*-BuOH to a 1:3 molar mixture of red phosphorus and lithium, fission of the P−P bond of the intermediate diphosphide is facilitated. Subsequent addition of 2 equivalents of RX gives dialkylphosphines R_2PH in good yields (eq 1).[15] These results suggested that phosphonate-

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$$\mathrm{P + 3\,Li + \mathit{t}\text{-}BuOH + 2\,RX \xrightarrow[NH_3\ (liq)]{} R_2PH + 2\,LiX + \mathit{t}\text{-}BuOLi} \qquad (1)$$

functionalized arylphosphines might also be prepared from red phosphorus, rather than phosphine gas.

Results and Discussion

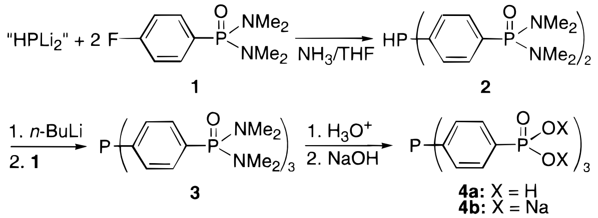
We envisioned a synthesis of TPPTP using a 1:3:1 molar ratio of P/Li/t-BuOH in liquid ammonia/THF to generate "$HPLi_2$" and subsequent reaction of this species with 2 equivalents of $4\text{-}FC_6H_4P(O)(NMe_2)_2$ (**1**) to give the secondary phosphine **2** (Scheme 1). In situ treatment of this intermediate with a base such as *n*-BuLi, followed by an additional equivalent of $4\text{-}FC_6H_4P(O)(NMe_2)_2$ was expected to give the desired tertiary phosphine **3**. Acid hydrolysis would furnish **4a**, and neutralization with base would give the salt **4b**.

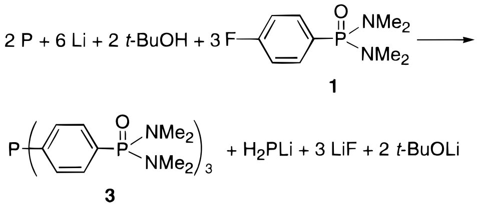
Carrying out the first step of the reaction sequence gave a deep red solution, which was presumed to be the lithium salt of **2**. However, analysis of the reaction mixture by ^{31}P NMR showed little or no formation of secondary phosphine **2**, or the corresponding lithium salt. Instead, the tertiary phosphine **3** was observed. Also present was unreacted **1**, which was identified by ^{31}P and ^{19}F NMR spectroscopies. When the reaction was repeated using a stoichiometry of 2:3 for $HPLi_2$ and aryl fluoride **1**, the aryl fluoride was completely consumed, with phosphine **3** being the major product.

The exact nature of the phosphide species is not known. The species $HPLi_2$ would seem unlikely to exist as such in liquid ammonia, since the pK_a of HP^{2-} is estimated to be about 42, well above the pK_a of ammonia (ca. 35).[16] It has been suggested that $HPLi_2$ is an equilibrium mixture of H_2P^- and MNH_2 (for M = Li or Na).[17] To investigate this, the liquid ammonia was allowed to evaporate from a preparation of P/Li/*t*-BuOH in a 1:3:1 molar ratio in NH_3/THF. A gray suspension in a pale yellow solution was obtained. Analysis of the THF-soluble fraction by $^{31}P\{^1H\}$ NMR showed a 1:2:1 triplet at −281 ppm, $J_{PLi} = 38$ Hz, which is similar to the coupling constant observed for a cyclic H_2PLi dimer in ether and THF solutions.[18] We also observed a small set of doublets at −167 and −266 ppm, $J_{PP} = 225$ Hz, presumed to be either a mixed dimer or diphosphide species. In the presence of an additional molar equivalent of *t*-BuOH, the spectrum consisted of essentially one singlet at −282 ppm; the pair of doublets was barely discernible in the baseline. Further addition of *t*-BuOH (excess) gave a homogeneous solution and the only signal observed was a singlet at −244 ppm, corresponding to PH_3.

The fact that little of the secondary phosphine **2** is observed may be attributable to the relative pK_as of the reaction intermediates. In contrast to alkyl substitution, progressive aryl substitution of PH_3 (pK_a = 29) to give $PhPH_2$ (pK_a = 25) and Ph_2PH (pK_a = 22) results in an increase in the acidity of the phosphine as substitution increases.[16] Thus, as arylated phosphine intermediates are formed, they are metalated by more basic species such as $LiPH_2$ or $LiNH_2$, and quickly undergo further reaction with the aryl fluoride. The net reaction is presented in eq 2.

Scheme 1





(2)

The nature of the arylphosphonate used as a precursor had a significant influence on the course of the reaction. Use of the diethyl ester of 4-fluorophenylphosphonic acid resulted in greatly decreased yields of the tertiary phosphine $P(4\text{-}C_6H_4PO_3Et_2)_3$ (**5**). The principle product was instead the monodealkylated ester, $4\text{-}FC_6H_4P(O)(OH)(OEt)$, identified by ^{31}P, ^{19}F, and ^1H NMR and mass spectral analysis. In contrast, the precursor **1** appeared to be relatively resistant to cleavage by phosphide anions, yet intermediate **3** was easily hydrolyzed to the free phosphonic acid by refluxing in deoxygenated 2.4 M hydrochloric acid. Use of the disodium salt of 4-fluorophenylphosphonic acid gave no reaction, presumably due to lack of solubility in the reaction medium. The bulk of the starting material was recovered unchanged.

The water solubility of TPPTP was determined to be approximately 550 mg/mL. This was unexpectedly low. In comparison, the monophosphonate $Ph_2P(4\text{-}C_6H_4PO_3Na_2)$ has a water solubility of 400 mg/mL[7] and the diphosphonate $PhP(4\text{-}C_6H_4PO_3Na_2)_2$ is reported to have a water solubility of 1000 mg/mL.[11] The reason for the relatively low water solubility of the triphosphonate may be due to the fact that the molecule is already highly solvated in the solid state, with extensive hydrogen bonding in the crystal matrix.[19]

From the crystal structure, an empirical formula of $C_{18}H_{12}Na_6O_9P_4{\cdot}27H_2O$ was determined. The TPPTP molecules stack along a C_3-axis defined by the central phosphorus atoms. Surrounding the molecules is a lattice of sodium atoms and water molecules (Figure 1). The water molecules form an extensive hydrogen-bonding network linking the sodium atoms, phosphonate oxygens, and lattice water. From the 18 water molecules in the unit cell, 33 hydrogen bonds are formed. The sodium atoms are hexacoordinate, with only one sodium atom in the asymmetric unit having a phosphonate oxygen in its coordination sphere, i.e., Na(4)−O−P(2). The rest of the coordination sites are occupied by water, a fact that may contribute the relatively low water solubility, since a favorable enthalpy of mixing from ion solvation would not be realized. Interestingly, the solubility of **4b** in methanol displays an inverse temperature dependence,

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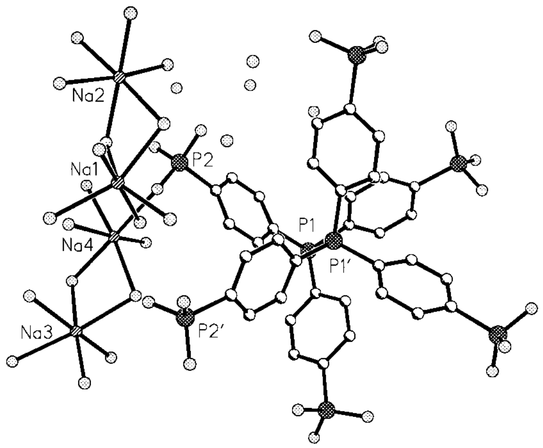

Figure 1. The figure shows the two crystallographically unique triarylphosphine rows, completed by symmetry operations. The hydrogens have been omitted for clarity. The asymmetric unit consists of four sodium ions, 18 water molecules, and two independent [triarylphosphine]/3 moieties in which the central phosphorus atoms lie on a 3-fold axis of symmetry. The coordination spheres of the sodium ions have been completed with symmetry-generated oxygens. The sodium and phosphorus atoms are labeled; the oxygen atoms are light gray spheres. Unbonded oxygens represent hydrogen-bonded lattice water.

forming an insoluble mass at reflux, and redissolving upon cooling. The neutral phosphine **3** has appreciable water solubility as well.[20]

In summary, we have found that the phosphonate-functionalized phosphine TPPTP may be prepared directly from red phosphorus by reduction of the phosphorus with lithium metal in liquid ammonia and reaction of the resulting phosphide anion with *N,N,N′,N′*-tetramethyl-4-fluorophenylphosphonodiamide to give intermediate **3**, which can be converted to TPPTP by subsequent acid hydrolysis and neutralization with NaOH. In this procedure, the need to generate or handle phosphine gas is avoided. The method is comparable in yield with the $S_{RN}1$ reaction of phosphide anions with aryl halides described by Rossi et al.,[21] but does not require photostimulation and does not incur phosphine oxide formation.

Experimental Section

General. All reactions were conducted under dry, prepurified nitrogen using standard Schlenk line techniques when appropriate. NMR spectra were referenced to internal TMS or 2,2,3,3-d_4-3-trimethylsilylpropionic acid (TSP) for ^{1}H spectra, TSP or solvent for ^{13}C spectra, external H_3PO_4 for ^{31}P spectra, and external $PhCF_3$ for ^{19}F spectra. Mass spectra were acquired using electrospray ionization techniques by Dr. John Callahan of the Chemistry Division, Code 6100, Naval Research Laboratory, Washington DC. The following solvents and reagents were obtained from Aldrich Chemical Co. and used as is (purity and grade): red phosphorus (99%), lithium (99.9%), *tert*-butyl alcohol (99.5%, anhydrous), tetrahydrofuran (99.9%, anhydrous), methanol (99.8+%), chloroform (99+%, anhydrous), ether (99+%, anhydrous), hexane (95+%), sodium hydroxide (99.99%), *n*-butyllithium (2.5 M in hexanes), and 1-bromo-4-fluorobenzene (99%). *N,N,N′,N′*-Tetramethylphosphonodiamidic chloride (Fluka, > 95%) and liquid ammonia (Matheson, 99.99%, anhydrous) were used as received. Diethyl 4-fluorophenylphosphonate was prepared by known methods.[22] Flash chromatography was performed using silica gel (70−230 mesh, 60 Å pore size) under nitrogen pressure. Thin-layer chromatography was done on silica gel plates (250 μm thickness, Merck) with fluorescent indicator. Components were visualized with UV light or 5% ethanolic phosphomolybic acid.

***N,N,N′,N′*-Tetramethyl-4-fluorophenylphosphonodiamide (1).** *n*-Butyllithium (69 mL of a 2.5 M solution in hexanes, 0.17 mol) was cooled to −78 °C (dry ice/acetone), and a solution of 1-bromo-4-fluorobenzene (19.7 mL, 0.173 mol) in THF (100 mL) was added dropwise with stirring. The resulting light-yellow suspension was then added slowly via cannula to a stirred solution of $(Me_2N)_2P(O)Cl$ (25 mL, 0.17 mol) in THF (150 mL) at −78 °C. Once the addition was complete, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature. The solvent was removed, and the residue was taken up in dichloromethane and washed with water. The organic phase was dried ($MgSO_4$), filtered, and concentrated by rotary evaporation to give a light yellow oil. The crude product was vacuum distilled, collecting the fraction at bp 104−106 °C/0.2 mmHg to give 21.25 g of product (54% yield). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 29.3 (s). ^{19}F{^{1}H} NMR ($CDCl_3$) δ −108.6 (s). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 162.4 (dd, $J = 251$, 3.3 Hz), 134.1 (t, $J = 8.6$, 8.9 Hz), 125.9 (dd, $J = 3.8$, 155.5 Hz), 115.1 (dd, $J = 15.1$, 15.0 Hz), 35.8 (d, $^{2}J_{CP} = 3.9$ Hz). ^{1}H NMR ($CDCl_3$): δ 7.76 (m, 2H, C_6H_4), 7.14 (m, 2H, C_6H_4), 2.64 (d, $^{4}J_{CP} = 10.1$ Hz, 12H, $PNMe_2$). IR (thin film), cm^{-1}: 1290 (vs), 1205 (vs, broad), 1159 (vs), 1113 (vs).

Tris[4-(*N,N,N′,N′*-tetramethylphosphonodiamido)phenyl]-phosphine (3). To a suspension of red phosphorus (0.469 g, 15.1 mmol) in liquid ammonia (ca. 100 mL) was introduced lithium metal (0.315 g, 45.4 mmol). To the resulting deep blue mixture was added dropwise a solution of *tert*-butyl alcohol (1.122 g, 15.14 mmol) in THF (20 mL) over the course of 1 h. A yellow-orange suspension resulted, to which a solution of **1** (5.222 g, 22.70 mmol) in THF (20 mL) was added dropwise over several minutes. The reaction mixture was stirred overnight at room temperature, allowing the ammonia to evaporate. The suspension was filtered under nitrogen, and the filtrate was concentrated under oil-pump vacuum to give a sticky yellow foam. Trituration with ether−hexane gave a yellow-tinged powder (5.08 g). The product is sufficiently pure to be used directly for hydrolysis to the acid or may be further purified by chromatography on silica gel using $CHCl_3$ as the eluant, followed by 2% MeOH−$CHCl_3$, and collecting the component at R_f 0.40 (10% MeOH−$CHCl_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 27.9 (s, PO), −4.8 (s, P). ^{1}H NMR ($CDCl_3$): δ 7.73 (m, 6H, C_6H_4), 7.36 (m, 6H, C_6H_4), 2.65 (d, $^{4}J_{HP} = 10.0$ Hz, 18H, $PNMe_2$).

Tris[4-(*O,O′*-diethylphosphono)phenyl]phosphine (5). The above procedure was used with $4\text{-}FC_6H_4PO_3Et_2$ as the substrate. Red phosphorus (0.123 g, 3.97 mol) and lithium (0.083 g, 12 mmol) were stirred in liquid NH_3 (50 mL) and treated with a solution of *t*-BuOH (0.19 mL, 2.0 mmol) in THF (5 mL). A solution of $4\text{-}FC_6H_4PO_3Et_2$ (1.392 g, 6.000 mmol) in THF (15 mL) was then added dropwise. After overnight stirring of the reaction mixture, the reddish-brown solution was worked up by addition of 20% aqueous NH_4Cl (30 mL) and ether (50 mL). The phases were separated, and the aqueous phase was extracted with an additional portion of ether. The combined ether phases were dried ($MgSO_4$) and concentrated by rotary evaporation and then placed under oil-pump vacuum to give 0.630 g of crude product. This was chromatographed on a column (20 mm) of silica gel (40 g) using 4% MeOH-Et_2O as the eluant. The first component, R_f 0.51 (8% MeOH−Et_2O), was collected to give 0.200 g of a white solid (∼16% yield). This crystallized from hexane−acetone as white needles. The compound was identified as $4\text{-}FC_6H_4P(O)(OH)(OEt)$ from ^{31}P, ^{19}F, ^{13}C, and ^{1}H NMR and the mass spectrum. The eluant was changed to 8% MeOH−Et_2O, and a second component, R_f 0.17, eluted. It was isolated as a clear, slightly yellow oil, 0.112 g (∼3% yield). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 18.6 (s, PO), −4.1 (s, P). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 140.6 (dd, $J_{CP} = 16.1$, 3.1 Hz), 133.3 (dd, $J_{CP} = 19.9$, 19.5 Hz), 131.5 (dd, $J_{CP} = 10.4$, 9.5 Hz), 129.3 (d, $J_{CP} = 188.8$ Hz), 62.0 (d, $J_{CP} = 5.4$

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[20] Crude **3** was found to dissolve readily in 5−10 volumes of water.

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Hz), 16.1 (d, $J_{CP} = 5.8$ Hz). ^{1}H NMR ($CDCl_3$): δ 7.81 (m, 6H, C_6H_4), 7.40 (m, 6H, C_6H_4), 4.16 (m, 12H, OCH_2), 1.35 (m, 18H, CH_3). IR (neat film), cm^{-1}: 1257 (vs), 1040 (vs, broad). ESMS: 671.1 $[M + H]^+$ (100%).

Tris(4-phosphonatophenyl)phosphine Hexasodium Salt (TPPTP) (4b). Starting from 21.25 g (92.39 mmol) of **1**, using the above procedure, the reaction was worked up by addition of deoxygenated ether and water to the organic phase remaining after overnight evaporation of the ammonia. The aqueous phase was separated and sparged vigorously with nitrogen to remove volatile materials. The mixture was then acidified with deoxygenated hydrochloric acid to a pH of 1, resulting in the formation of a viscous brown oil. The mixture was heated and stirred vigorously under a nitrogen atmosphere until a suspension was obtained. The reaction mixture was filtered to give 4.80 g of phosphonic acid **4a** as a light tan powder. Cooling the filtrate at 5 °C for 48 h gave another 5.49 g of **4a** as an off-white powder, for a total recovery of 10.29 g. Both samples were nearly pure by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopies. To obtain salt **4b**, a portion of crude **4a** was dissolved in methanol and neutralized with the stoichiometric amount of 50% aqueous NaOH. The solvent was removed by rotary evaporation, and the resulting material was crystallized from warm, deoxygenated water layered with small amount of ethanol. Colorless needles were obtained, which turned white upon drying. ^{31}P{^{1}H} NMR (D_2O): δ 11.4 (s, PO), −7.2 (s, P); ^{1}H NMR (D_2O): δ 7.74 (m, 6H, C_6H_4), 7.44 (m, 6H, C_6H_4). ^{13}C{1H} NMR (D_2O): δ 144.5 (d, $J_{CP} = 268$ Hz), 138.9 (d, $J_{CP} = 9.2$ Hz), 135.6 (dd, $J_{CP} = 30.5$, 9.5 Hz), 133.2 (apparent triplet; $J_{CP} = 13.1$, 12.5 Hz). IR (KBr disk), cm^{-1}: 1073 (vs, broad), 970 (vs). ESMS: 261.1 $[M - 5Na + 3H]^{2-}$ (100%), 166.4 $[M - 6Na + 3H]^{3-}$ (40%). The efflorescent nature of the material precluded obtaining a satisfactory elemental analysis. The identity of the product was confirmed by single-crystal X-ray diffraction, and the purity was established by ^{31}P, ^{13}C, and ^{1}H NMR analyses (see the Supporting Information).

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Supporting Information Available: NMR data for compounds **1** (^{31}P, ^{13}C, ^{1}H), **3** (^{31}P, ^{1}H), **4b** (^{31}P, ^{13}C, ^{1}H), and **5** (^{31}P, ^{13}C, ^{1}H); X-ray crystallographic data for **4b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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