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Synthesis and Characterization of New Water Soluble Tertiary Phosphines Having Terminally Substituted Alkylene Sulfonate or Alkylene Phosphonate Chains

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The synthesis of water soluble tertiary phosphines is a subject of long-term continuing interest. This interest primarily lies in their use as ligands for reactions where it is desirable to have the tertiary phosphine complex dissolved in aqueous solution. The water solubility of these modified phosphines results from the incorporation of a charged sulfonate[1] or alkylammonium[2] functionality into the molecule. The importance of these water soluble phosphines and their complexes is highlighted by the use of a sulfonated triphenylphosphine as a ligand for rhodium in the design of a water soluble homogeneous catalyst for the hydroformylation reaction.[3] The metal complexes that are formed from this sulfonated triphenylphosphine can be purified by means of an adaptation and optimization of the gel permeation chromatography technique.[4] Because of recent renewed interest in the use of tertiary phosphine complexes of palladium(II) and platinum(II) as catalysts for the hydration of alkenes, there is an increased need for the availability of a range of different water soluble tertiary phosphines. We now report that we have synthesized two new tertiary phosphines that have a high solubility in water. These diphenylphosphino compounds have either a sulfonate or a phosphonate group at the end of an alkylene chain. To our knowledge, this sulfonated phosphine is the first example of its kind with the sulfonate ion attached to an aliphatic rather than to an aromatic carbon, and this new phosphonate substituted tertiary phosphine is the first example of such a compound that has both diphenylphosphine and phosphonic acid moieties at the opposite ends of an ethylene chain.

The new alkylene sulfonate compound sodium 2-(diphenylphosphino)ethanesulfonate, $Ph_2PCH_2CH_2SO_3Na$, has been prepared in 80% yield by reacting equimolar amounts of sodium diphenylphosphide and sodium 2-bromoethanesulfonate in ammonia as solvent (eq 1). The compound was isolated by addition

$$Ph_2PNa + BrCH_2CH_2SO_3Na \rightarrow Ph_2PCH_2CH_2SO_3Na + NaBr \quad (1)$$

of THF to the solution, followed by evaporation of the ammonia to give a cream colored solid. The colorless crystalline complex that was obtained by slow cooling of a solution of this cream solid compound in hot methanol is soluble in aqueous solution. The mass spectrum (FAB with *m*-nitrobenzyl alcohol as matrix) of the compound shows peaks at *m/z* 293 ($Ph_2PCH_2CH_2SO_3$), 213 ($Ph_2PCH_2CH_2$), 199 (Ph_2PCH_2), and 185 (Ph_2P). The compound in $CDCl_3$ solution shows a single resonance in the $^{31}P\{^1H\}$ NMR spectrum for the tertiary phosphine at δ −16.5.[5] The compound is oxidized in air to the phosphine oxide, $Ph_2P(O)CH_2CH_2SO_3Na$, which shows a single resonance in the $^{31}P\{^1H\}$ NMR spectrum at δ 36.3.

The new alkylene phosphonate compound, disodium 2-(diphenylphosphino)ethanephosphonate, $Ph_2PCH_2CH_2P(O)(ONa)_2$, has been prepared by the hydrolysis of the intermediate diethyl ester, diethyl 2-(diphenylphosphino)ethanephosphonate, $Ph_2PCH_2CH_2P(O)(OEt)_2$. This intermediate diethyl ester has been obtained in 95% yield by treating lithium diphenylphosphide with diethyl 2-bromoethanephosphonate (eq 2). The product was

$$Ph_2PLi + BrCH_2CH_2P(O)(OEt)_2 \rightarrow Ph_2PCH_2CH_2P(O)(OEt)_2 + LiBr \quad (2)$$

obtained as a colorless liquid after removal of the THF solvent, extraction of the residue into dichloromethane, followed by filtration of the resulting solution, and evaporation under vacuum. The mass spectrum (FAB with *m*-nitrobenzyl alcohol as matrix) of this diethyl ester shows peaks at *m/z* 350.1192 (calcd *m/z* 350.1120) ($Ph_2PCH_2CH_2P(O)(OEt)_2$), 322 ($Ph_2PCH_2CH_2P(O)(OH)(OEt)$), 293 ($Ph_2PCH_2CH_2P(O)H(OH)$), 213 ($Ph_2PCH_2CH_2$), and 185 ($Ph_2P$). The compound in $CDCl_3$ solution shows an AB pair in the $^{31}P\{^1H\}$ NMR spectrum at δ −11.8 and 33.0 with $^3J(PP)$ = 62.2 Hz. These respective chemical shifts are characteristic of a tertiary phosphine and a phosphonate group. The compound is oxidized in air to $Ph_2P(O)CH_2CH_2P(O)(OEt)_2$, which shows an AB pair of resonances at δ 31.3 and 33.3, with $^3J(PP)$ = 68 Hz. Since no compounds or metal complexes are known having both a tertiary phosphine and a phosphonato group within the same molecule, we have now prepared and crystallized a dibromopalladium(II) complex using $Ph_2PCH_2CH_2P(O)(OEt)_2$ as ligand. The crystal structure of this palladium complex has been solved in order to obtain more detailed structured information about the coordinated compound. This yellow complex *trans*-$PdBr_2(Ph_2PCH_2CH_2P(O)(OEt)_2)_2$ has been prepared by reacting $Ph_2PCH_2CH_2P(O)(OEt)_2$ with Na_2PdCl_4 in aqueous ethanol in the presence of excess bromide ion (eq 3). The crystal structure

$$PdCl_4^{2-} + 2Ph_2PCH_2CH_2P(O)(OEt)_2 + 2Br^- \rightarrow \textit{trans}\text{-}PdBr_2(Ph_2PCH_2CH_2P(O)(OEt)_2)_2 + 4Cl^- \quad (3)$$

shows that the complex has a trans stereochemistry with the ligands coordinated via the tertiary phosphines.[6] An ORTEP representation of the structure is shown in Figure 1. The mixed phosphine–phosphonato ligand is coordinated to palladium via the phosphorus atom of the phosphine group with a bond distance of 2.325 (3) Å for Pd–P(1). The phosphonato groups are not coordinated. The Pd–Br distance in the complex is 2.412 (1) Å. The structure

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(5) Spectral data for $Ph_2PCH_2CH_2SO_3Na$ are as follows. ^1H NMR (D_2O): δ 2.41–2.46 m (2 H, PCH_2), 2.76–2.85 m (2 H, SCH_2), 7.33–7.48 m (10 H, C_6H_5). $^{31}P\{^1H\}$ NMR (D_2O): δ −16.5. $^{13}C\{^1H\}$ NMR (D_2O): δ 22.3 d (SCH_2, $^2J(PC)$ = 11 Hz), 48.2 d (PCH_2, $^1J(PC)$ = 18 Hz), 129.4 d (phenyl, $J(PC)$ = 6 Hz), 131.3 s (phenyl), 133.1 d (phenyl, $J(PC)$ = 19 Hz), 137.0 d (phenyl, $J(PC)$ = 9 Hz). IR (KBr): $\nu(CH_2)$ 2922 cm^{-1}, $\nu(CH_2)$ 2850 cm^{-1}, $\nu(SO)$ 1435, 1172, 1068, $\nu(CS)$ 1251 cm^{-1}, ν(P-phenyl) 725, 705 cm^{-1}.

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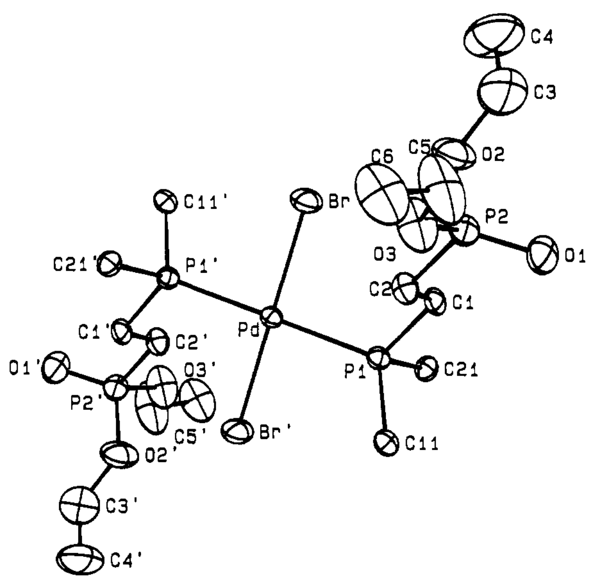

Figure 1. Perspective view of $PdBr_2(Ph_2PCH_2CH_2P(O)(OEt)_2)_2$ with thermal ellipsoids drawn at the 30% probability level. Only the ipso carbon atoms of the phenyl groups are shown. Primed atoms are related to the unprimed atoms by the crystallographic center of symmetry.

shows that the ligand has a short phosphorus oxygen distance for the phosphoryl (P=O) group (P(2)–O(1) = 1.434 (8) Å) and longer distances for the phosphorus–oxygen distances of the phosphonate ester groups (P(2)–O(2) = 1.54 (1) Å, P(2)–O(3) = 1.567 (9) Å.

The hydrolysis of the ester groups of diethyl 2-(diphenylphosphino)ethanephosphonate into the phosphonic acid derivative has been carried out using a stepwise reaction sequence. In the first step of this sequence, the diethyl ester is converted into the bis(trimethylsilyl) ester by treatment with bromotrimethylsilane (eq 4).[7] This trimethylsilyl substituted compound, $Ph_2PCH_2CH_2P(O)(OSiMe_3)_2$, is characterized in the $^{31}P\{^1H\}$ NMR

$$Ph_2PCH_2CH_2P(O)(OEt)_2 + 2BrSiMe_3 \rightarrow Ph_2PCH_2CH_2P(O)(OSiMe_3)_2 + 2EtBr \quad (4)$$

spectrum ($CDCl_3$) by the presence of an AB pair of resonances centered at δ −5.8 and 12.3, with $^3J(PP)$ = 62 Hz. In the second step of the stepwise procedure, this bis(trimethylsilyl) ester is hydrolyzed to the free acid, $Ph_2PCH_2CH_2P(O)(OH)_2$. This product again shows a characteristic AB pair in the $^{31}P\{^1H\}$ NMR spectrum, with the resonances being now centered at δ −12.2 and 25.0, with $^3J(PP)$ = 63 Hz (eq 5). No evidence is seen for pro-

$$Ph_2PCH_2CH_2P(O)(OSiMe_3)_2 + H_2O \rightarrow Ph_2PCH_2CH_2P(O)(OH)_2 + (Me_3Si)_2O \quad (5)$$

tonation of the phosphine phosphorus atom of this compound in aqueous solution by the phosphonic acid group. Neutralization of this free phosphonic acid with sodium hydroxide (eq 6) results

$$Ph_2PCH_2CH_2P(O)(OH)_2 + 2NaOH \rightarrow Ph_2PCH_2CH_2P(O)(ONa)_2 + 2H_2O \quad (6)$$

in the formation of the disodium salt, $Ph_2PCH_2CH_2P(O)(ONa)_2$, which is characterized by the presence of a small shift of the phosphine resonance from δ −12.2 to −11.3 and a larger shift in the phosphonate resonance from δ 25.0 to 22.3, between the free acid and the disodium salt.[8]

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Supplementary Material Available: Tables of crystal data and data collection and refinement details, positional parameters, anisotropic thermal parameters, bond distances, and bond angles, and general displacement parameter expressions (7 pages). Ordering information is given on any current masthead page.

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(6) Crystal data: monoclinic, space group $P2_1/n$, a = 14.513 (2) Å, b = 7.906 (1) Å, c = 18.690 (3) Å, β = 105.21 (1)°, V = 2069 (1) Å^3, Z = 2, d_{calc} = 1.55 g cm^{-3}, data collected at 298 K with Mo Kα radiation, $\lambda(K\alpha)$ = 0.710 69 Å, 2θ limits 3–50°; data corrected for absorption by ψ-scan method, μ = 25.5 cm^{-1}, transmission factors 0.756–0.996. The structure was solved by a combination of Patterson and direct methods. After anisotropic refinement, all the hydrogen atoms except for those attached to C(4), which could not be reliably located, were included as fixed contributions in calculated positions (C–H = 0.95 Å) with isotropic thermal parameters 1.2 times those of the attached carbons atoms and updated periodically. One ethyl group which includes C(3) and C(4) showed considerably greater thermal parameters than any other part of the molecule suggesting possible disorder, but a careful inspection of a difference map did not indicate any resolved alternate locations for these atoms, and calculated intermolecular contacts suggest this group occupies a relatively unconstricted space in the crystal. The final refinement cycle resulted in $R(F)$ = 0.055 and $R_w(F)$ = 0.062 for the 2131 reflections with $F_o^2 > 3\sigma(F_o^2)$ and the 223 variables. The final difference map showed peaks ranging from 1.1 to −0.2 e/Å^3 with the largest peaks closely associated with the heavy atoms.

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(8) Spectral data for $Ph_2PCH_2CH_2P'(O)(OEt)_2$ are as follows. ^1H NMR ($CDCl_3$): δ 1.26 m (6 H, CH_3, $^3J(HH)$ = 8 Hz), 1.7–2.0 m (2 H, PCH_2), 2.25–2.55 m (2 H, CH_2P'), 4.0–4.1 m (4 H, OCH_2), 7.3–7.55 m (10 H, phenyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −12.3 d (P), 31.9 d (P′) ($^3J(PP)$ = 63 Hz). $^{13}C\{^1H\}$ NMR $(CD_3)_2CO$): δ 16.6 d (CH_3, $^3J(P'C)$ = 6 Hz), 22.5 dd (CH_2P', $^1J(P'C)$ = 140 Hz, $^2J(PC)$ = 22 Hz), 23.1 dd (PCH_2, $^1J(PC)$ = 62 Hz, $^2J(P'C)$ = 3 Hz), 62.0 dd (OCH_2, $^2J(P'C)$ = 25 Hz, $^5J(PC)$ = 6 Hz), 129.3 s, 129.4 d ($J(PC)$ = 2 Hz), 129.5 d ($J(PC)$ = 2 Hz), 129.6 s, 131.4 d ($J(PC)$ = 10 Hz), 133.3 d ($J(PC)$ = 19 Hz). IR (KBr): ν(P=O) 1296 cm^{-1}, ν(P–O) 1058, 1031, 960 cm^{-1}. Spectral data for $Ph_2PCH_2CH_2P'(O)(OSiMe_3)_2$ are as follows. ^1H NMR ($CDCl_3$): δ 0.3 s (18 H, CH_3), 2.1 m (2 H, CH_2P), 3.1 m (2 H, CH_2P'), 7.5–8.0 m (phenyl). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −5.8 m, 11.5 d ($^3J(PP)$ = 62 Hz). Spectral data for $Ph_2PCH_2CH_2P'(O)(ONa)_2$ are as follows. ^1H NMR (D_2O): δ 1.26–1.52 m (2 H, CH_2P), 2.22–2.28 m (2 H, CH_2P'), 7.35–7.68 m (10 H, phenyl). $^{31}P\{^1H\}$ NMR (D_2O): δ −11.3 d (P), 22.3 d (P′) ($^3J(PP)$ = 63 Hz).