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New Oligophosphines and (Hydroxymethyl)phosphonium Chlorides

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The new oligophosphines $[H_2P(CH_2)_2]_2PH$, $[H_2P(CH_2)_2P(H)CH_2]_2$, and $\{[(H_2P(CH_2)_2]_2PCH_2\}_2$ have been made by hydrophosphination of diethyl vinylphosphonate (**2**) with $H_2P(CH_2)_2PH_2$ (**1**), using different ratios of **2**/**1**, followed by $LiAlH_4$ reduction of the phosphonate intermediates; the three phosphonate precursors were obtained as oils of varying purity (∼90–95%) in low (∼20%) to almost quantitative yield. The tri-, tetra-, and hexaphosphines were then treated with formaldehyde in the presence of hydrochloric acid to generate the corresponding water-soluble (hydroxymethyl)phosphonium chlorides $\{(HOCH_2)_3P[(CH_2)_2P(CH_2OH)_2]_n(CH_2)_2P(CH_2OH)_3\}Cl_m$ ($n = 1$, $m = 3$; $n = 2$, $m = 4$) and $\{[(HOCH_2)_3P(CH_2)_2]_2P(CH_2OH)CH_2\}_2Cl_6$ that were characterized by NMR spectroscopy and elemental analysis. The known (hydroxymethyl)bisphosphonium chloride $[(HOCH_2)_3P(CH_2)_2]_2Cl_2$ was similarly prepared from $H_2P(CH_2)_2PH_2$, and the determined crystal structure revealed strong hydrogen bonding between the chloride anions and the hydrogen atoms of the hydroxymethyl groups.

Introduction

The chemistry of hydroxyalkyl-containing phosphines and their corresponding phosphonium salts is of fundamental and industrial interest. Recently, a new class of bleaching and brightness-stabilizing agents for mechanical and chemical pulps has been discovered. These agents are water-soluble tertiary phosphines and quaternary (hydroxymethyl)phosphonium salts, such as tris(hydroxymethyl)phosphine [THP; $P(CH_2OH)_3$] and tetrakis(hydroxymethyl)phosphonium chloride {THPC; $[P(CH_2OH)_4]Cl$}; the THP is the effective reagent, and in the aqueous pulp bleaching conditions, this is generated from the more easily handled THPC.[1] Later studies on related systems showed that the water-soluble diphosphine 1,2-bis[bis(hydroxymethyl)phosphino]ethane {BBHPE; $[(HOCH_2)_2PCH_2]_2$} possesses higher bleaching activity.[2] Although the nature of the reactions of these water-soluble phosphines with components in the pulp lignin remains to be established, it seemed possible that (hydroxymethyl)phosphines or phosphonium salts containing three or more phosphorus atoms might possess even stronger bleaching activity than mono- or diphosphine compounds. This paper thus reports on the synthesis and characterization of tri-, tetra-, and hexaphosphonium chlorides containing (like BBHPE) ethane carbon backbones between the phosphorus atoms.

There is considerable literature on the syntheses of (hydroxymethyl)phosphorus compounds. THP and the phosphonium chloride THPC are made via the reaction of phosphine (PH_3) with formaldehyde in the presence of a transition-metal catalyst[3] or hydrochloric acid,[4] respectively; other α-(hydroxyalkyl)monophosphines can be prepared similarly by the reaction of phosphorus hydrides or tertiary phosphines with aldehydes;[5] (β-hydroxyalkyl)monophosphines can be prepared by the hydrolysis of (*tert*-butoxyethyl)phosphines[6] or (2-acetoxyethyl)phosphines[7] or by the reaction of phosphine with ethylene oxide;[8] and (γ-hydroxyalkyl)monophosphines can be prepared by the radical addition of a phosphine to allyl alcohol.[9] The water-soluble diphosphines $[HO(CH_2)_n]_2P(CH_2)_mP[(CH_2)_nOH]_2$ ($n = 1$ and

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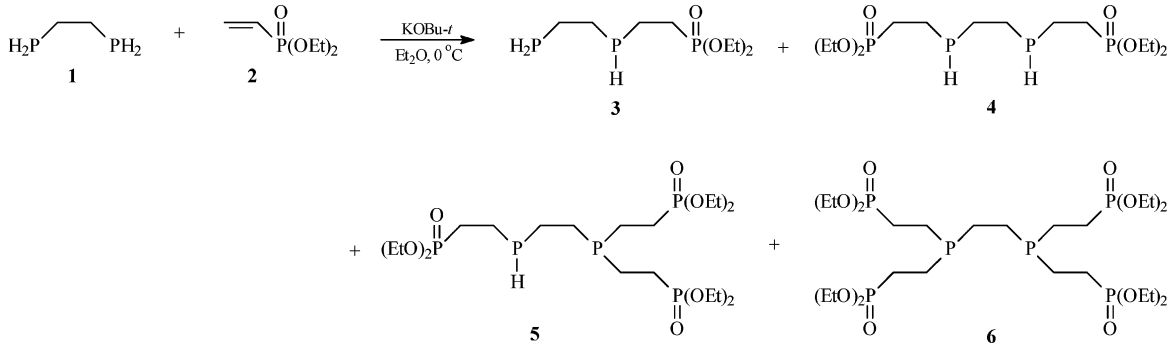
Scheme 1



3−8; $m = 2$ and 3)[10] and $(HOCH_2)_2PC_6H_4P(CH_2OH)_2$[11] have been prepared by the reaction of the corresponding diphosphines H_2P- - - -PH_2 with formaldehyde or unsaturated alcohols. There is one report of a water-soluble triphosphine, namely, $PhP[CH_2CH_2P(CH_2OH)_2]_2$,[12] and the phosphonium salt $[(HOCH_2)_3PCH_2P(CH_2OH)_3]I_2$ has been mentioned in a patent, but no characterization data were presented.[13]

Experimental Section

General Procedures. All synthetic procedures were carried out using standard Schlenk techniques under argon, and at room temperature (∼20 °C), unless stated otherwise. Reagent-grade solvents were distilled under nitrogen from the appropriate drying agents, degassed, and saturated with argon. $CDCl_3$ (Cambridge Isotope Laboratories) was dried over CaH_2 and vacuum transferred into storage vessels containing activated molecular sieves (4 Å) or directly into NMR tubes fitted with J. Young polytetrafluoroethylene valves or rubber septa. Deuterated dimethyl sulfoxide (DMSO-d_6; Cambridge Isotope Laboratories) was used as received. NMR spectra were recorded on a Bruker AV300 spectrometer at 300 K (300 MHz for ^{1}H; 121 MHz for $^{31}P\{^1H\}$), with a residual deuterated solvent proton (relative to external $SiMe_4$) and 85% aqueous H_3PO_4 being used as references; br = broad, s = singlet, d = doublet, t = triplet, qn = quintet, m = multiplet; J values are given in Hertz. Elemental analyses were performed by M. Lakha of this department using a Carlo Erba 1108 analyzer. Mass spectrometry was performed on a Bruker Esquire electrospray ion (ESI) trap instrument with samples dissolved in methanol or water and infused at 10 μL/min, with positive ion polarity, scanning from m/z 100 to 1000.

Diethyl vinylphosphonate $[CH_2{=}CHP(O)(OEt)_2]$ was purchased from Aldrich and used without purification. 1,2-Bis(phosphino)ethane ($H_2PCH_2CH_2PH_2$) was obtained from Strem Chemicals or prepared by a literature procedure[14] using the Arbuzov reaction between triethyl phosphite [$P(OEt)_3$, Aldrich] and 1,2-dibromoethane (Aldrich), followed by the reduction of the resulting tetraethyl(ethylenediphosphonate) $[(EtO)_2(O)PCH_2]_2$ with an ether suspension of $LiAlH_4$ (Aldrich). KO^{t}Bu and other chemicals were Aldrich products.

Syntheses. $H_2P(CH_2)_2P(H)(CH_2)_2P(O)(OEt)_2$ (3). To a stirred solution of $H_2P(CH_2)_2PH_2$ (**1**) (0.94 g, 10 mmol) in Et_2O (10 mL) cooled at 0 °C was added KO^{t}Bu (1.12 g, 10 mmol). After 5 min, an Et_2O solution (5 mL) of 1 mol equiv of $CH_2{=}CHP(O)(OEt)_2$ (**2**; 1.64 g, 10 mmol) was added dropwise over 30 min; after a further 30 min, the mixture was filtered under argon to remove inorganic products. The $^{31}P\{^1H\}$ NMR spectrum of the ether filtrate showed unreacted diphosphine and compounds **3** and **4** (see below and Scheme 1) in the amounts of 25, 45, and 30%, respectively. Removal of ether and the diphosphine in vacuo yielded a mixture of **3** and **4** as an oil; **3** was separated as a colorless oil by distillation at ∼100 °C and 0.1 Torr. Yield: 0.5 g (19%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.8 (d, 1P, $P{=}O$, $^3J_{PP} = 43$), −59.7 (dd, 1P, PH, $^3J_{PP} = 43$, $^3J_{PP} = 10$), −128.9 (d, 1P, PH$_2$, $^3J_{PP} = 10$). ^{1}H NMR ($CDCl_3$): δ 4.15−3.94 (m, 4H, OCH_2), 2.84 (pseudo dt, 1H, PH, $^1J_{PH} = 195$, $^3J_{HH} = 7$), 2.75 (dt, 2H, PH_2, $^1J_{PH} = 195$, $^3J_{HH} = 7$), 1.89−1.50 (m, 8H, CH_2CH_2), 1.27 (t, 6H, OCH$_2$CH_3, $^3J_{HH} = 7$).

$[(EtO)_2(O)P(CH_2)_2P(H)CH_2]_2$ (4). The procedure used follows that given above except that 3.45 g of the vinylphosphonate **2** was used (**2**/**1** = 2); ether removal yielded **4** as a colorless oil. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 31.7 (m, 2P, $P{=}O$), −58.0 (m, 2P, PH); in Et_2O, δ 30.4 (m, 2P, $P{=}O$), −58.6 (m, 2P, PH); see text. ^{1}H NMR ($CDCl_3$): δ 4.18−3.98 (m, 8H, OCH_2), 3.23 (br d, 2H, PH, $^1J_{PH} = 198$), 1.98−1.57 (m, 12H, CH_2CH_2), 1.30 (t, 12H, OCH$_2$CH_3, $^3J_{HH} = 7$). The NMR yield of **4** was 88%, contaminated with **3** (5%) and **5** (7%, see below).

$(EtO)_2(O)P(CH_2)_2P(H)(CH_2)_2P[(CH_2)_2P(O)(OEt)_2]_2$ (5). The procedure used for **3** and **4** was repeated but using 0.2 g (2.1 mmol) of **1**, 0.24 g (2.1 mmol) of KO^{t}Bu, and 1.05 g (6.3 mmol) of **2** (i.e., a **2**/**1** ratio of 3). Ether removal afforded a mixture of **4**−**6** as

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a yellowish, viscous oil in respective yields of 28, 50, and 22% (according to the $^{31}P\{^1H\}$ NMR data). $^{31}P\{^1H\}$ NMR of **5** ($CDCl_3$): δ 31.9 (m, 3P, *P*═O), −17.6 (dt, 1P, *P*(CH_2CH_2)$_3$, $^3J_{PP}$ = 22, $^3J_{PP}$ = 50), −56.6 (dd, 1P, *P*H, $^3J_{PP}$ = 22, $^3J_{PP}$ = 43). Because of the presence of **4** and **6**, signals in the ^1H NMR spectrum could not be assigned.

{[(EtO)$_2$(O)P(CH$_2$)$_2$]$_2$PCH$_2$}$_2$ (6). KO^{t}Bu (112 mg, 1 mmol) was added to a THF (5 mL) solution of **1** (94 mg, 1 mmol) at 0 °C. The procedure was then the same as for synthesizing **3**−**5**, except that excess **2** (0.82 g, 5 mmol) was used. Final removal of THF in vacuo gave a yellowish, viscous oil, containing **6** in close to quantitative yield (750 mg). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 32.0 (m, 4P, *P*═O), −16.5 (m, 2P, *P*(CH_2CH_2)$_3$); see text. ^1H NMR ($CDCl_3$): δ 4.12−3.96 (m, 16H, OC*H*$_2$), 1.82−1.52 (m, 16H, O═PC*H*$_2$C*H*$_2$P), 1.47−1.40 (m, 4H, PC*H*$_2$C*H*$_2$P), 1.26 (t, 24H, OCH$_2$C*H*$_3$, $^3J_{HH}$ = 7).

[H$_2$P(CH$_2$)$_2$]$_2$PH (7). Compound **3** (0.52 g, 2 mmol) was placed in dry Et_2O (5 mL) at 0 °C, and the mixture was stirred as a suspension of $LiAlH_4$ (0.15 g, 4 mmol) in Et_2O (5 mL) was added dropwise; after 30 min, an aqueous solution of oxygen-free, 20% HCl (2 mL) was added dropwise to remove excess $LiAlH_4$. The ether layer was separated by a cannula, and the aqueous layer was washed with Et_2O (2 × 5 mL). The ether layers were dried overnight with CaH_2, and after filtration and removal of Et_2O, a colorless liquid was obtained. Yield: ∼0.15 g (∼50%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −62.6 (t, 1P, *P*H, $^3J_{PP}$ = 10), −128.8 (d, 2P, *P*H$_2$, $^3J_{PP}$ = 10). ^1H NMR ($CDCl_3$): δ 2.79 (dt, 4H, PH$_2$, $^1J_{PH}$ = 195, $^3J_{HH}$ = 7; the expected d qn for the P*H* was hidden in the shoulders of the dt for the PH$_2$), 1.83−1.56 (m, 8H, C*H*$_2$C*H*$_2$).

[H$_2$P(CH$_2$)$_2$P(H)CH$_2$]$_2$ (8). Compound **8** was obtained by $LiAlH_4$ reduction (0.30 g, 8 mmol) of **4** (0.84 g, 2 mmol, containing **3** and **5** as impurities; see above) by the procedure similar to that used for **7**. After removal of Et_2O, the resulting liquid was distilled at ∼120 °C and 0.1 Torr to give **8** as a colorless liquid. Yield: ∼0.19 g (∼45%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −60.7 (br s, 2P, *P*H), −128.7 (br s, 2P, *P*H$_2$). ^1H NMR ($CDCl_3$): δ 2.85 (pseudo dt, 2H, P*H*, $^1J_{PH}$ = 195, $^3J_{HH}$ = 7), 2.77 (dt, 4H, PH$_2$, $^1J_{PH}$ = 195, $^3J_{HH}$ = 7), 1.82−1.57 (m, 12H, C*H*$_2$C*H*$_2$).

{[H$_2$P(CH$_2$)$_2$]$_2$PCH$_2$}$_2$ (9). As for **7** and **8**, **9** was obtained by $LiAlH_4$ reduction (0.30 g, 8 mmol) of **6** (0.75 g, 1 mmol). Removal of ether gave a colorless, syruplike semisolid (0.13 g, 40%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −19.1 (br s, 2P, *P*(CH_2)$_3$), −126.8 (br s, 4P, *P*H$_2$). ^1H NMR ($CDCl_3$): δ 2.82 (dt, 8H, PH$_2$, $^1J_{PH}$ = 195, $^3J_{HH}$ = 7), 1.73−1.53 (m, 16H, H$_2$PC*H*$_2$C*H*$_2$P), 1.53−1.45 (m, 4H, PC*H*$_2$C*H*$_2$P).

{[(HOCH$_2$)$_3$P(CH$_2$)$_2$]$_2$P(CH$_2$OH)$_2$}Cl$_3$ (10). A stirring mixture of CH_2O (0.24 g of 37% aqueous solution, 2.9 mmol) and HCl (0.18 g of a 20% aqueous solution, 1 mmol) in water (5 mL) was purged with argon for 2 h. A solution of the triphosphine **7** (50 mg, 0.33 mmol) in Et_2O (1 mL) was then added. After 1 h, $^{31}P\{^1H\}$ NMR data reveal quantitative production of **10**, and in vacuo removal of the water and ether afforded the crude material. The white, pure solid (56 mg, 34%) was obtained by recrystallization from MeOH/H_2O (2 mL of a 5:1 volume mixture). Anal. Calcd for $C_{12}H_{32}Cl_3O_8P_3$: C, 28.62; H, 6.40. Found: C, 28.9; H, 6.2. $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 34.1 (t, 1P, *P*(CH_2OH)$_2$, $^3J_{PP}$ = 42), 30.7 (d, 2P, *P*(CH_2OH)$_3$, $^3J_{PP}$ = 42). ^1H NMR (DMSO-d_6): δ 6.61 (br s, 2H, P(CH_2OH)$_2$), 6.46 (br s, 6H, P(CH_2OH)$_3$), 4.63 (d, 4H, P(CH_2OH)$_2$, $^2J_{PH}$ = 6), 4.56 (d, 12H, P(CH_2OH)$_3$, $^2J_{PH}$ = 6), 3.01−2.77 (m, 8H, PC*H*$_2$C*H*$_2$P). Low-resolution ESI MS (H_2O): *m*/*z* 335.0 [M − 2CH_2O − 2H]$^+$; M$^{3+}_{calc}$ 397.3.

[(HOCH$_2$)$_3$P(CH$_2$)$_2$P(CH$_2$OH)$_2$CH$_2$]$_2$Cl$_4$ (11). Similar to the procedure used for **10**, **11** was obtained by reacting the tetraphosphine **8** (0.10 g, 0.47 mmol) with CH_2O (0.45 g of a 37% solution, 5.6 mmol) in the presence of HCl (0.35 g of a 20% solution, 1.9 mmol). Recrystallization from MeOH/H_2O yielded a white solid (130 mg, 42%). Anal. Calcd for $C_{16}H_{42}Cl_4O_{10}P_4$: C, 29.11; H, 6.41. Found: C, 29.3; H, 6.8. $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ 34.2 (m, 2P, *P*(CH_2OH)$_2$), 30.7 (m, 2P, *P*(CH_2OH)$_3$); see text. ^1H NMR (DMSO-d_6): δ 6.62 (br s, 4H, P(CH_2OH)$_2$), 6.45 (br s, 6H, P(CH_2OH)$_3$), 4.66 (d, 8H, P(CH_2OH)$_2$, $^2J_{PH}$ = 5), 4.56 (br s, 12H, P(CH_2OH)$_3$), 3.06−2.78 (m, 12H, PC*H*$_2$C*H*$_2$P). Low-resolution ESI MS (MeOH): *m*/*z* 425.4 (100%) [M − 3CH_2O − 3H]$^+$, 335.3 (30%) [M − 6CH_2O − 3H]$^+$; trace peaks at *m*/*z* 395.4 [M − 4CH_2O − 3H]$^+$; M$^{4+}_{calc}$ 518.4.

{[(HOCH$_2$)$_3$P(CH$_2$)$_2$]$_2$P(CH$_2$OH)CH$_2$}$_2$Cl$_6$ (12). As for **10**, **12** was obtained by reacting the hexaphosphine **9** (0.10 g, 0.3 mmol) with CH_2O (0.36 g of a 37% solution, 4.5 mmol) and HCl (0.38 g of a 20% solution, 2.1 mmol). Removal of the solvent in vacuo gave **12**, which was washed with MeOH and dried overnight under vacuum (275 mg, 94%). Anal. Calcd for $C_{24}H_{62}Cl_6O_{14}P_6$: C, 29.62; H, 6.42. Found: C, 30.0; H, 6.5. $^{31}P\{^1H\}$ NMR (H_2O, in situ): δ 38.7 (m, 2P, *P*(CH_2OH)), 29.9 (m, 4P, *P*(CH_2OH)$_3$); see text. ^1H NMR (DMSO-d_6): δ 6.62 (br s, 2H, P(CH_2OH)), 6.44 (br s, 12H, P(CH_2OH)$_3$), 4.78 (br s, 4H, P(CH_2OH)), 4.65 (br s, 24H, P(CH_2-OH)$_3$), 3.34−2.91 (br m, 20H, PC*H*$_2$C*H*$_2$P). Low-resolution ESI MS (MeOH): *m*/*z* 621.3 (68%) [M − 5CH_2O − 5H + O]$^+$, 605.3 (100%) [M − 5CH_2O − 5H]$^+$, 591.3 (25%) [M − 6CH_2O − 6H + OH]$^+$, 575.3 (30%) [M − 6CH_2O − 5H]$^+$, 561.3 (15%) [M − 7CH_2O − 7H + OH]$^+$, 545.3 (13%) [M − 7CH_2O − 5H]$^+$, 531.3 (12%) [M − 8CH_2O − 6H + OH]$^+$, 515.3 (12%) [M − 8CH_2O − 5H]$^+$; M$^{6+}_{calc}$ *m*/*z* 760.6.

{[(HOCH$_2$)$_3$P(CH$_2$)$_2$]$_2$P(CH$_2$OH)$_2$CH$_2$}$_2$(SO$_4$)$_2$ (13). Compound **13**, the sulfate analogue of **11**, was obtained (similar to the method used for **11**) by the reaction of the tetraphosphine **8** (50 mg, 0.23 mmol) with CH_2O (0.23 g of a 37% solution, 2.8 mmol) in the presence of H_2SO_4 (48 mg of a 98% aqueous solution, 0.48 mmol); according to $^{31}P\{^1H\}$ NMR data, **13** is formed quantitatively. Removal of water in vacuo afforded the crude, syrupy product that was washed with MeOH and dried under vacuum, but a satisfactory elemental analysis could not be obtained. $^{31}P\{^1H\}$ NMR (D_2O): δ 34.8 (m, 2P, *P*(CH_2OH)$_2$), 30.9 (m, 2P, *P*(CH_2-OH)$_3$). ^1H NMR (D_2O): δ 4.71 (d, 12H, P(CH_2OH)$_3$, $^2J_{PH}$ = 6), 4.56 (br s overlapping with *H*DO signal, 8H, P(CH_2OH)$_2$), 3.01−2.73 (br m, 12H, PC*H*$_2$C*H*$_2$P).

Table 1. Crystallographic Data for **14**

empirical formula	$C_8H_{22}O_6Cl_2P_2$
fw	347.10
cryst color, habit	colorless, chip
cryst size, mm^3	0.10 × 0.05 × 0.05
cryst syst	orthorhombic
space group	*Pbca* (No. 61)
a, Å	11.611(1)
b, Å	8.814(1)
c, Å	15.073(2)
V, Å^3	1542.6(3)
Z	4
ρ_{calcd}, g/cm^3	1.495
F(000)	728
μ, cm^{-1}	6.42
total reflns	11982
unique reflns	1841
R_{int}	0.070
no. of variables	94
R1 [$I > 2\sigma(I)$]	0.038 (1308 obsd reflns)
wR2[a]	0.093 (all data)
GOF	1.06 (all data)

[a] $w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 0.2315P]$, where $P = (F_o^2 + 2F_c^2)/3$.

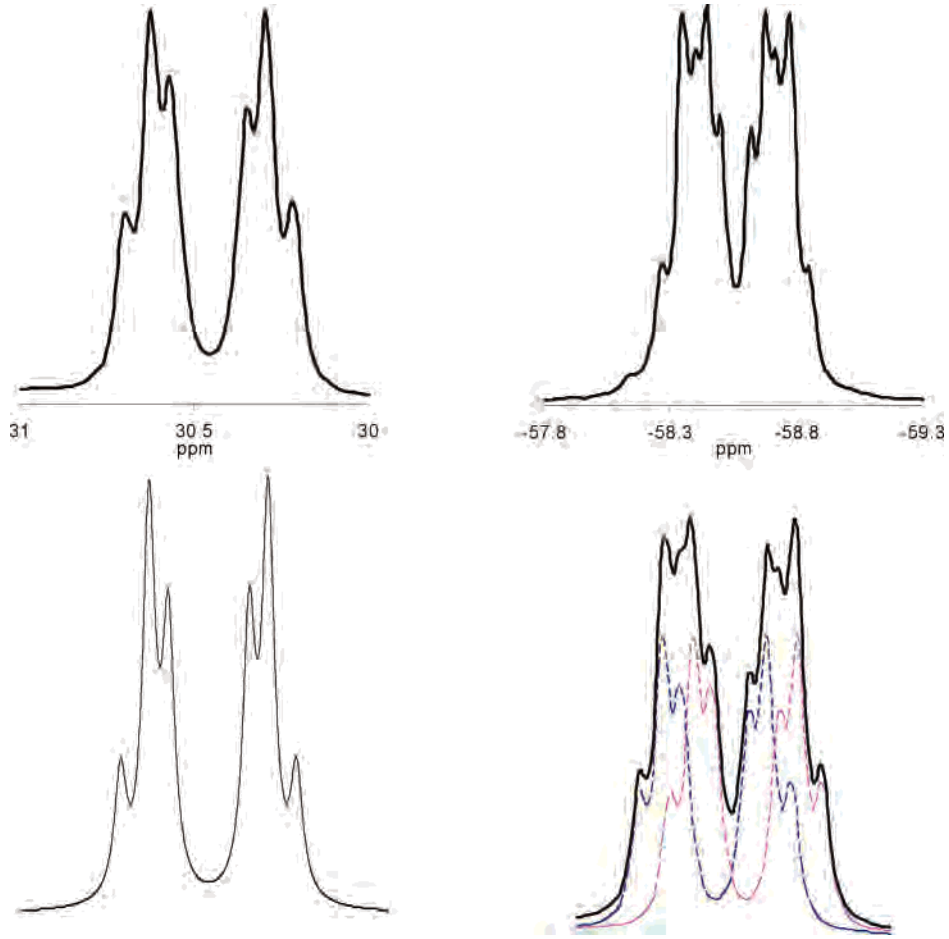


Figure 1. Experimental (top two multiplets) and simulated (bottom two multiplets; see text) $^{31}P\{^{1}H\}$ NMR spectra of compound **4** in Et_2O.

Tetrakis(hydroxymethyl)phosphonium chloride (THPC, [(HOCH$_2$)$_4$P]Cl). THPC was isolated from 100 mL of an 80% aqueous solution of the compound (kindly donated by Rhodia Consumer Specialities) by evaporation of water under reduced pressure and recrystallization of the residue from ^{i}PrOH; the resulting white solid was dried for 1 day in vacuo. Anal. Calcd for $C_4H_{12}ClO_4P$: C, 25.21; H, 6.35. Found: C, 25.6; H, 6.6. $^{31}P\{^{1}H\}$ NMR (DMSO-d_6): δ 27.7 s. ^{1}H NMR (DMSO-d_6): δ 6.25 (br s, 4H, O*H*), 4.44 (br s, 8H, CH_2). The NMR data have been reported previously in a D_2O solution, where the OH proton resonance, of course, was not seen.[15] Low-resolution ESI MS (MeOH): *m*/*z* 155.0 $[M]^+$; M^+_{calc} 155.0.

1,2-Bis[tris(hydroxymethyl)phosphonium]ethane chloride ([(HOCH$_2$)$_3$PCH$_2$]$_2$Cl$_2$, 14). 1,2-Bis(phosphino)ethane (200 mg, 2.1 mmol) and formaldehyde (1.06 g of a 37% solution, 13.0 mmol) were reacted in oxygen-free water in the presence of HCl (0.78 g of a 20% solution, 4.2 mmol), according to the procedure given for **10**. After recrystallization from MeOH/H_2O, a white solid was obtained (0.44 g, 60%). Anal. Calcd for $C_8H_{22}Cl_2O_6P_2$: C, 27.68; H, 6.39. Found: C, 28.0; H, 6.8. $^{31}P\{^{1}H\}$ NMR (DMSO-d_6): δ 30.5 s. ^{1}H NMR (DMSO-d_6): δ 6.44 (br s, 6H, P(CH$_2$O*H*)$_3$), 4.52 (br s, 12H, P(CH_2OH)$_3$), 2.82 (br d, 4H, PCH_2CH_2P, $^2J_{PH}$ = 7). Low-resolution ESI MS (H_2O): *m*/*z* 244.9 (100%) [M − CH$_2$O − H]$^+$, 215.0 (45%) [M − 2CH$_2$O − H]$^+$, 185.0 (17%) [M − 3CH$_2$O − H]$^+$; M^{2+}_{calc} *m*/*z* 276.2. This phosphonium chloride has been reported previously, but few details are available.[16]

X-ray Crystallographic Analysis. An X-ray-quality, colorless crystal of **14** was obtained by layering a solution of the compound in MeOH/H_2O (5:1 by volume) with CH_2Cl_2. Selected crystallographic data for the salt are shown in Table 1, and more details are provided in the Supporting Information. Measurements were made at 173 (± 0.1) K on a Bruker X8 APEX diffractometer using graphite-monochromated Mo Kα radiation (0.710 73 Å). Data were collected to a maximum 2θ value of 56.0°, in a series of ϕ and ω scans in 0.50° oscillations with 24.0-s exposures; the crystal-to-detector distance was 37.99 mm. Of the 11 982 reflections that were collected, 1841 were unique (R_{int} = 0.070); equivalent reflections were merged. Data were collected and integrated using the Bruker *SAINT* software package.[17] Data were corrected for Lorentz and polarization effects and for absorption effects using the multiscan technique (*SADABS*),[18] with minimum and maximum transmission coefficients of 0.616 and 0.968, respectively. The structure was solved by direct methods.[19] All non-hydrogen atoms were refined anisotropically, while all O−H hydrogen atoms were located in difference maps and refined anisotropically; all other hydrogen

(15) Ellzey, S. E.; Connick, W. J.; Boudreaux, G. J.; Klapper, H. *J. Org. Chem.* **1972**, *37*, 3453.

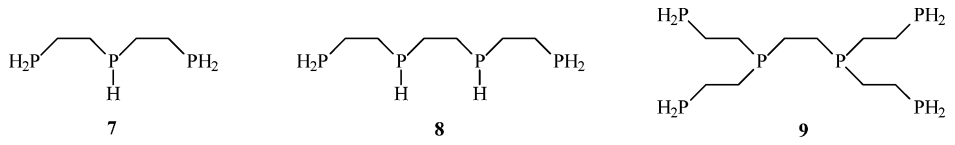
(16) (a) Mäding, P.; Klötzer, D.; Münze, R. *Isotopenpraxis* **1986**, *22*, 353 (*CAN*. *107*, 77912). (b) Mäding, P. *J. Prakt. Chem*. **1992**, *334*, 87. (c) Hoye, P. A. T. Eur. Pat. Appl. EP 380359, 1990.

(17) *SAINT*, version 7.03A; Bruker AXS Inc.: Madison, WI, 1997−2003.

(18) *SADABS, Bruker Nonius area detector scaling and absorption correction*, version 2.10; Bruker AXS Inc.: Madison, WI, 2003.

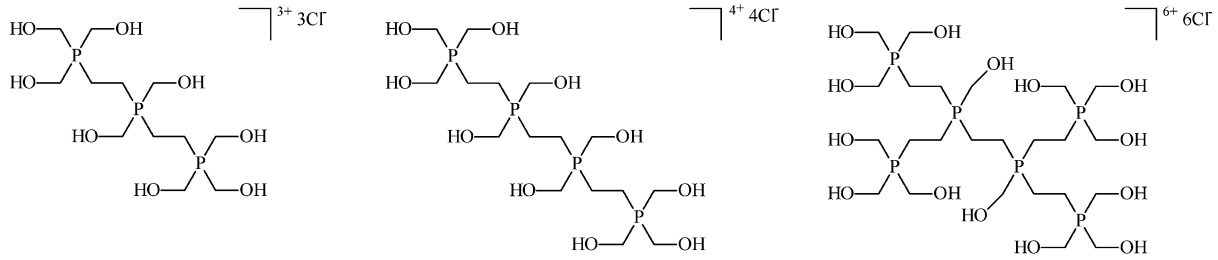
(19) (a) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr*. **1999**, *32*, 115. (b) Spek, A. L. *PLATON: A multipurpose crystallographic tool*; Utrecht University: Utrecht, The Netherlands, 2001.

Chart 1



7 **8** **9**

Chart 2



10 **11** **12**

atoms were included in calculated positions. The material crystallizes with half of the molecule in the asymmetric unit residing on an inversion center.

Results and Discussion

The general preparative methods for oligophosphines include the radical or base-catalyzed addition of a phosphorus hydride (hydrophosphination) to a phosphine containing unsaturated C═C bonds of allyl or vinyl groups;[12,20] an example of the latter is **2**. Hydrophosphination of **2** with **1** in the presence of the base KO^{t}Bu at 0 °C was found to form the four compounds **3**−**6** (Scheme 1), with the product ratio depending on the ratio of reactants used. With **2**/**1** = 1, from a mixture of **3** and **4** obtained initially with respective yields of 45 and 30% (as determined by $^{31}P\{^1H\}$ NMR spectroscopy), pure **3** was isolated (presumably as a racemate because of chirality at the central P atom) in 19% yield as a colorless oil by a distillation procedure. The $^{31}P\{^1H\}$ NMR spectrum is simple first-order and reveals a doublet at δ 31.8 ($^3J_{PP}$ = 43 Hz) for the P^V atom of the phosphonate group, a doublet of doublets at δ −59.7 for the PH group (with $^3J_{PP}$ = 43 Hz and a weaker three-bond coupling of 10 Hz to the PH_2), and a doublet at δ −128.9 for the PH_2 moiety. In the ^1H NMR spectrum, the PH signal at δ 2.84 appears as a pseudo triplet (instead of the expected doublet of quintets) with $^1J_{PH}$ = 195 Hz and a $^3J_{HH}$ coupling of 7 Hz to CH_2 protons; the PH_2 signal at δ 2.75 appears as a doublet of triplets with the same couplings as those seen for the PH proton.

When **1** and **2** were reacted in a 1:2 ratio under the same conditions, **4** was obtained in 88% yield as a mixture of diastereomers, presumably the *R*,*R*, *S*,*S*, and *meso* forms in a 1:1:2 ratio, each of which constitutes an AA′XX′ spin system in the $^{31}P\{^1H\}$ NMR spectrum, which was measured in both $CDCl_3$ and Et_2O, with the latter giving somewhat better resolution of the multiplets. That for the phosphonate P atoms centered at δ 30.4 is well simulated (Figure 1) using $J_{AX'} = J_{A'X} \leq 1$ Hz, $J_{XX'} = 0$, $J_{AX} = J_{A'X'} = 43$ Hz, and $J_{AA'} = 18$ Hz (A and A′ are the two internal P atoms, and X and X′ are the terminal ones). The δ −58.6 multiplet for the PH moieties can be simulated by superimposing (at half-intensities) the pattern of the δ 30.4 multiplet on the same pattern that is shifted by 0.1 ppm upfield (Figure 1). This implies that, at the conditions used, the *R*,*R* and *S*,*S* diastereomers have indistinguishable δ values, while the value for the *meso* species differs from this value by δ ∼0.1; i.e., the two shifts are at about δ −58.6 and −58.7; a similar difference of δ 0.1 in the shifts of enantiotopic P atoms has been noted for related bis(phosphine) species.[21] In the ^1H NMR spectrum, the PH proton is seen as a broad doublet ($^1J_{PH}$ = 198 Hz), with the smaller coupling to CH_2 protons being unresolved. The reaction of **1** with **2** in a 1:3 ratio was nonselective, giving a mixture of **4** (28%), **5** (50%), and **6** (22%). The $^{31}P\{^1H\}$ NMR spectrum of the racemic **5** shows a multiplet centered at δ 31.9 for the three $P(O)(OEt)_2$ groups, a doublet of triplets centered at δ −17.6 for the P atom of the trialkylphosphine moiety ($^3J_{PP}$ = 50 Hz for coupling to P^V; $^3J_{PP}$ = 22 Hz for coupling to PH), and a doublet of doublets centered at δ −56.6 for the PH group (with $^3J_{PP}$ = 22 and 43 Hz, the latter for coupling to P^V). The ^1H NMR signals for **5** could not be delineated from the measured spectrum for the mixture. Compound **6**, a pale yellow oil, was formed selectively from the reaction of **1** and **2** in a 1:5 ratio; its $^{31}P\{^1H\}$ NMR spectrum (an AA′X_2X_2' system) is seen as a multiplet centered at δ 32.0 for the $P(O)(OEt)_2$ groups and a multiplet centered at δ −16.5 for the two central P atoms ($J_{AX'} = J_{A'X} < 1$ Hz, $J_{XX'} = 0$, $J_{AX} = J_{A'X'} = 50$ Hz, and $J_{AA'} = 25$ Hz).

The $LiAlH_4$ reduction of the phosphonate group of **3** gave the triphosphine **7** (Chart 1) as a colorless oil in ∼50% yield; the $^{31}P\{^1H\}$ NMR spectrum showed the expected triplet at δ −62.6 for the PH group and doublet at δ −128.8 for the PH_2 group ($^3J_{PP}$ = 10 Hz). The liquid tetraphosphine **8** was similarly obtained in 45% yield from "slightly impure" **4**,

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(21) Pietrusiewicz, K. M.; Zabłocka, M. *Tetrahedron Lett.* **1988**, *29*, 1987.

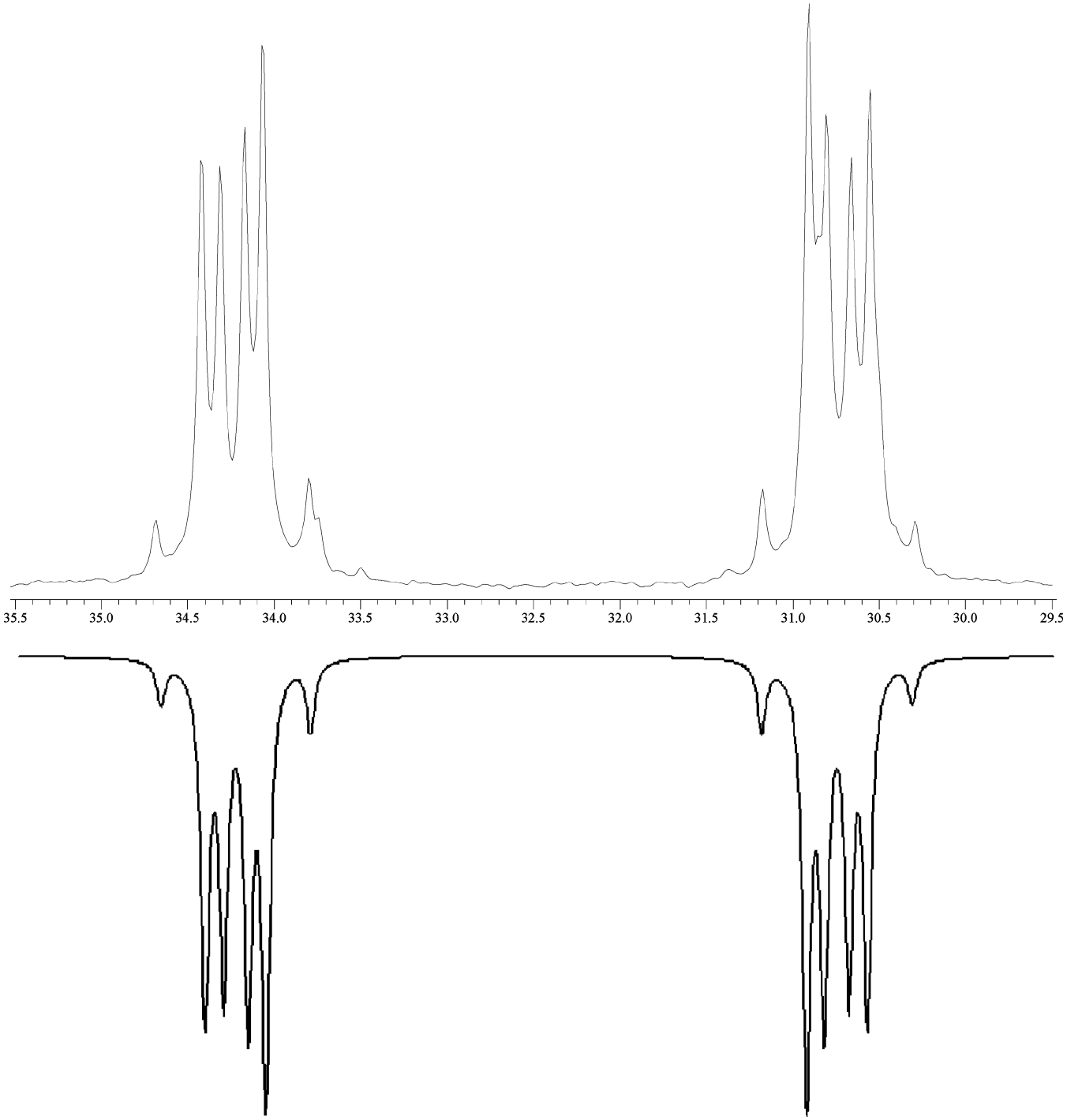

Figure 2. Experimental (top) and simulated (bottom) $^{31}P\{^1H\}$ NMR spectra of the tetraphosphonium salt **11** in DMSO-d_6; $J_{AX'} = J_{A'X} \leq 1$ Hz, $J_{XX'} = 0$, $J_{AX} = J_{A'X'} = 43$ Hz, and $J_{AA'} = 45$ Hz.

following a distillation procedure; the $^{31}P\{^1H\}$ NMR spectrum shows two broad singlets at δ −60.7 and −128.7 for the PH and PH_2 groups, respectively. The reduction of the phosphonate groups of **6** gave the solid hexaphosphine **9** in 40% yield; two broad singlets at δ −19.1 and −126.8 correspond to the two tertiary P atoms and the four PH_2 groups, respectively. The ^1H NMR data for **7**−**9** (i.e., the shifts and J values for the PH and PH_2 moieties) are analogous to those for **3**−**5**.

Yields of the oily products (phosphine products **7**−**9** and their respective phosphonate precursors **3**, **4**, and **6**) could likely be improved if the scale of the preparations were increased, thus allowing for more careful distillation.

The reaction of the extremely air-sensitive phosphines **7**−**9** with excess formaldehyde in an aqueous solution in the presence of HCl generated respectively the phosphonium salts **10**−**12** (Chart 2), which are white, hygroscopic chloride salts that are very soluble in water and in DMSO. The NMR shifts and respective integrations are entirely consistent with the proposed, anticipated structures. For **10**, the $^{31}P\{^1H\}$ NMR AX_2 pattern is seen as a triplet (δ 34.1) for the internal

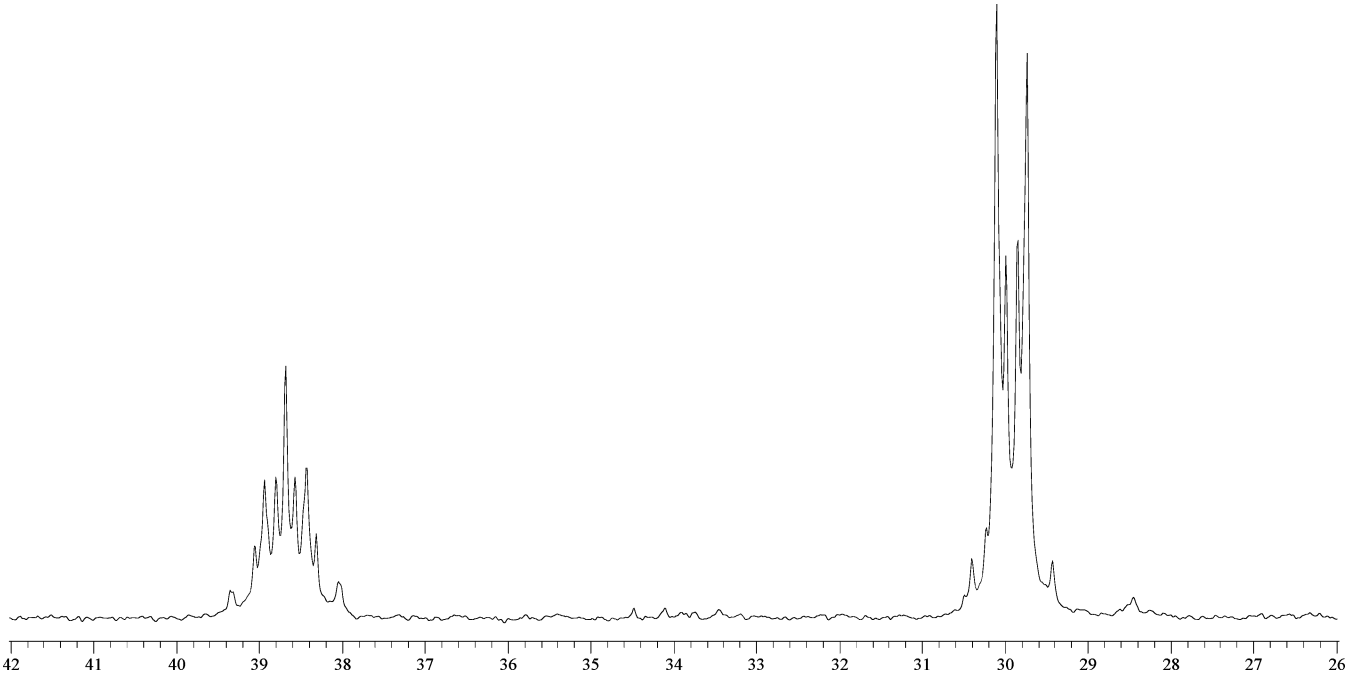

Figure 3. $^{31}P\{^1H\}$ NMR spectrum of the hexaphosphonium salt **12** in H_2O.

P atom and a doublet (δ 30.7) for the two terminal P atoms, with $^3J_{PP} = 42$ Hz; the ^1H NMR spectrum in DMSO-d_6 shows the two sets of OH protons as broad singlets at δ 6.61 and 6.46, two doublets at δ 4.63 and 4.56 ($^2J_{PH} = 6$ Hz) for the methylene protons of the two types of CH_2OH groups, and a multiplet centered at δ 2.89 for the methylene protons of the ethane linkages. For **11**, the well-simulated $^{31}P\{^1H\}$ NMR AA′XX′ spin system (Figure 2) is readily assigned upon comparison with the data for **10**, the set of signals centered at δ 34.2 corresponding to the two internal P atoms and δ 30.7 for the two terminal ones. The ^1H NMR spectrum of **11** confirms the structure: broad singlets at δ 6.62 and 6.45 for the OH groups, a doublet at δ 4.66 ($^2J_{PH} = 5$ Hz) for the methylene protons of 4 "internal" CH_2OH groups, a broad singlet at δ 4.56 for the methylene protons of 6 "terminal" CH_2OH groups, and a multiplet centered at δ 2.92 for the 12 hydrogen atoms of the ethane linkages. The $^{31}P\{^1H\}$ NMR AA′X_2X_2′ spin system for **12** (Figure 3) has multiplets at δ 38.7 for the two internal P atoms and δ 29.9 for the four terminal ones; the spectrum is well-simulated using $J_{AX'} = J_{A'X} \leq 1$ Hz, $J_{XX'} = 0$, $J_{AX} = J_{A'X'} = 45$ Hz, and $J_{AA'} = 51$ Hz. The ^1H NMR data are assigned similarly to those of **11**.

Because sulfates are typically much less corrosive than chloride salts within industrial uses, the sulfate analogue of **11**, compound **13**, was obtained by use of H_2SO_4 rather than HCl in the formaldehyde reaction with the tetraphosphine **8**. Like the chloride salts **10**−**12**, **13** is highly hygroscopic but, in contrast to the chlorides, could only be isolated as a colorless semisolid; its solubility in water and DMSO was significantly lower than that of **11**, and attempts to recrystallize the compound were unsuccessful. We were unable to obtain a satisfactory elemental analysis for **13**, but the $^{31}P\{^1H\}$ NMR spectrum in D_2O parallels that of **11** in DMSO-d_6.

It should be noted that the assignments of the ^{31}P and ^1H resonances in the NMR spectra for all of the synthesized compounds (based on shift and integration values) are internally consistent. For example, in the $^{31}P\{^1H\}$ NMR spectra, the phosphonate P^v shifts have $\delta \sim 32$, the PH shifts have $\delta \sim -60$, the PH_2 shifts have $\delta \sim -130$, and the $P(CH_2)_3$ shifts have $\delta \sim -20$, and for the phosphonium salts, δ is in the 30−40 range. Similarly, the ^1H resonances for PH and PH_2 protons have δ values in the 2.5−3.5 range with $^1J_{PH} \sim 195$ Hz. Such data are consistent with literature NMR data for these structural moieties.[22]

The low-resolution ESI MS for the cations of **10**−**12** were of some value in identifying the compounds because of the general ready loss of CH_2OH (or HCHO + H) fragments from the M^{n+} cation ($n = 3$, 4, or 6) under the experimental conditions. Thus, the single peak seen for an aqueous solution of **10** (*m*/*z* 335.0) corresponds to the monophosphonium ion $[M - 2CH_2O - 2H]^+$. Such decomposition was seen also for **14**, with the major peak being *m*/*z* 244.9 $[M - CH_2O - H]^+$, i.e., $(HOCH_2)_2PCH_2CH_2P(CH_2OH)_3^+$, although the minor ions $[M - 2CH_2O - H]^+$ (45%) and $[M - 3CH_2O - H]^+$ (17%) are seen also. The major MS peak for **11** also corresponds to that of a monophosphonium ion $[M - 3CH_2O - 3H]^+$ with a positive charge on one of the four P atoms, and again the minor ions $[M - 4CH_2O - 3H]^+$ and $[M - 6CH_2O - 3H]^+$ were seen. The MS of compound **12**, recorded in an aqueous or a methanol solution, was more complex and, as well as the major monophosphonium $[M - 5CH_2O - 5H]^+$ peak, showed a monooxide peak [M −

(22) (a) Tebby, J. C. In *Phosphorus-31 NMR spectroscopy in stereochemical analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Weinheim, Germany, 1987; Chapter 1. (b) Fluck, E.; Heckmann, G. In *Phosphorus-31 NMR spectroscopy in stereochemical analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Weinheim, Germany, 1987; Chapter 2. (c) Quin, L. D. *A guide to organophosphorus chemistry*; Wiley-Interscience: New York, 2000; Chapter 6.

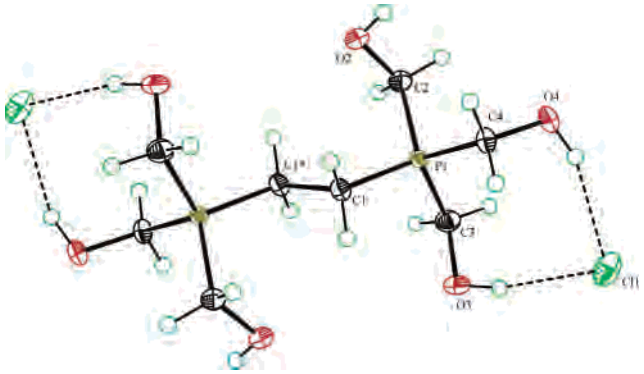

Figure 4. ORTEP diagram of **14** showing 50% probability thermal ellipsoids.

Table 2. Selected Bond Distances and Angles for **14** with Estimated Standard Deviations in Parentheses

bond	length (Å)	bond	angle (deg)
C1*−C1	1.534(4)	C1*−C1−P1	112.61(19)
C1−P1	1.796(2)	O2−C2−P1	108.81(15)
C2−P1	1.815(2)	O3−C3−P1	111.24(16)
C3−P1	1.823(2)	O4−C4−P1	109.81(15)
C4−P1	1.818(2)	C1−P1−C2	109.27(11)
C2−O2	1.411(3)	C1−P1−C4	108.61(10)
O2−H2	0.82(3)	C1−P1−C3	109.71(11)
O3−H3	0.91(3)	C4−P1−C3	111.45(11)
O4−H4	0.88(3)	O2−H2···Cl1	169(3)
H2···Cl1	2.23(3)	O3−H3···Cl1	167(3)
H3···Cl1	2.17(3)	O4−H4···Cl1	160(3)
H4···Cl1	2.23(3)		

$5CH_2O - 5H + O]^+$ and other fragmentation signals. The simplest homologue, $[(HOCH_2)_4P]Cl$, shows in MeOH just the peak for the monophosphonium ion $(HOCH_2)_4P^+$ (*m*/*z* 155.0).

Attempts to grow X-ray-quality crystals of compounds **10**−**13** were unsuccessful; however, an X-ray-quality crystal of the known[16] bis(phosphonium) chloride **14** revealed the expected structure (Figure 4). We synthesized **14** from 1,2-bis(phosphino)ethane in good yield via the same route as that used for the other chloride salts **10**−**12**; the same method has been used previously to synthesize **14**, but details were unavailable.[16] Selected structural parameters for **14** are given in Table 2. The distance between the C atoms of the ethane bridge, 1.534(4) Å, and the P−C distances are in the range seen for the reported structures of $(HOCH_2)_2PCH_2CH_2P(CH_2OH)_2$,[23] $[HO(CH_2)_3]_2PCH_2CH_2P[(CH_2)_3OH]_2$,[10c] and $R_2PCH_2CH_2PR_2$ (R = Me, Et, or ^{i}Pr).[24] The P atoms exhibit tetrahedral coordination with C−P−C angles in the range of 108.61−111.45°. Of note, the chloride anions are hydrogen-bonded to the hydrogen atoms of the hydroxymethyl groups: within the O···H···Cl bonds, the O···H distances are from 0.82 to 0.91 Å and the H···Cl distances are from 2.17 to 2.23 Å, implying relatively strong hydrogen bonding.[25]

Tests on the bleaching properties of the phosphonium salts **10**−**13** are being carried out. Of note, $P(CH_2OH)_3$ has been used for the removal of trace Ru species from polymers synthesized by Grubbs-type carbene catalysts,[26] and related polyphosphines (which, in principle, can be made from the above phosphonium salts by treatment with a base)[1,4c] should prove to be powerful metal sequestering agents; they will certainly have a rich coordination chemistry.

Conclusions

The newly synthesized tri-, tetra-, and hexaphosphines $(H_2PCH_2CH_2)_2PH$, $[H_2PCH_2CH_2P(H)CH_2]_2$, and $[(H_2PCH_2CH_2)_2PCH_2]_2$ have been converted into the corresponding water-soluble, tri-, tetra-, and hexaphosphonium chlorides by incorporation of hydroxymethyl groups at the P atoms. These chlorides are of interest for potential use in the bleaching of pulps, where the known monophosphonium chloride $[P(CH_2OH)_4]Cl$ has recently been shown to have marked activity.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for funding via an Idea to Innovation (I2I) grant and Drs. Nick Burlinson and Maria Ezhova for discussions about the NMR data.

Supporting Information Available: X-ray crystallographic data (CIF) for the structure of **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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