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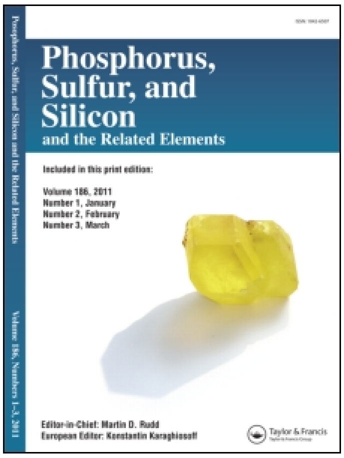

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THE SYNTHESIS AND CHARACTERIZATION OF TETRAKIS(ALKYLAMINO)PHOSPHONIUM COMPOUNDS[1]

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The synthesis of tetrakis(alkyl/arylamino)phosphonium compounds of type $(RNH)_4PX$, where R = n-C_3H_7 (**1**), i-C_3H_7 (**2**), n-C_4H_9 (**3**), s-C_4H_9 (**4**), n-C_5H_{11} (**5**), n-C_6H_{13} (**6**), c-C_6H_{11} (**7**), n-C_7H_{15} (**8**), $C_6H_5CH_2$ (**9**) and C_6H_5 (**10**), and where X = Cl, Br, I and ClO_4, is described. These compounds have been characterized by elemental analysis, melting point and ^1H and ^{31}P NMR spectroscopy. Solubility characteristics in water and organic solvents are given for the chlorides, which have been found in general less soluble than the corresponding perchlorates. Metathesis reactions of the $(RNH)_4PCl$ compounds are shown to proceed with relative ease and have provided an adequate method for the conversion of the chlorides to bromides, iodides and perchlorates. Hydrolysis reactions for compounds **3**, **9** and **10** have been studied and compared. Their relative stability toward base hydrolysis is demonstrated by the conditions used and the isolated intermediates identified, consistent with the postulated base hydrolysis scheme. NMR results are consistent with a structure for these compounds similar to the regular phosphonium salts, and represented as $[(RNH)_4P]^+X^-$, where the amino groups are arranged around the phosphorus atom in a tetrahedral fashion. Finally, N—H stretching frequencies are presented for the series $(n\text{-}C_4H_9NH)_4PX$, where X = Cl, Br, I, ClO_4, and it is suggested on this basis that hydrogen bonding for the cases where X = Cl, Br, I plays an important role in the chemistry and structure of these compounds.

Key words: Synthesis; aminophosphonium compounds; solubility; hydrolysis.

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INTRODUCTION

Early attempts to characterize the products of the reaction of phosphorus trihalides and pentahalides were largely unsuccessful due to difficulties resulting from instability of the products and problems in separating them from the ammonium halide byproduct.[4] A product of empirical formula $(NH)_2PNH_2$ was isolated by Moureu and Rocquet[5] from the reaction of phosphorus pentachloride and ammonia. Audrieth and Sowerby[6] have shown that this reaction leads to a mixture containing polyphosphazenes, $[NP(NH_2)_2]_x$, among other components. Only the reaction of phosphorus oxychloride with ammonia has been well characterized, yielding phosphorotriamide and ammonium chloride.[7]

Gilpin[8] and Lemoult[9] isolated compounds of the formula $(ArNH)_4PCl$ from the reaction of phosphorus pentachloride with aniline or substituted anilines:

$$8\ ArNH_2 + PCl_5 \rightarrow (ArNH)_4PCl + 4\ ArNH_3Cl \qquad (1)$$

The reactions were carried out either by direct combination of the reactants or using excess amine as the solvent. The compounds were difficult to purify, being insoluble in water and most organic solvents.

The first aliphatic compound of this type was prepared by allowing n-butylamine to react with phosphorus pentachloride in anhydrous benzene,[10] and other alkylamino derivatives soon followed.[1a] A patent[11] has also been awarded for their use as effective broad-spectrum fungicides. The present study was undertaken to characterize the chemical and physical properties of these compounds.

RESULTS AND DISCUSSION

Synthesis and Characterization of Aminophosphonium Compounds

Several important aspects must be considered when synthesizing aminophosphonium compounds by the method represented in (1). First, the reagents must be kept in an anhydrous environment until the reaction has reached completion, due to their hygroscopic character[12]:

$$PCl_5 + H_2O \rightarrow (Cl)_4P(OH)(aq) + HCl(g) \quad (2)$$

$$(Cl)_4P(OH)(aq) + H_2O \rightarrow (Cl)_3P(O)(aq) + HCl(g) \quad (3)$$

$$(Cl)_3P(O)(aq) + H_2O \rightarrow (Cl)_2(OH)P(O)(aq) + HCl(g) \quad (4)$$

$$(Cl)_2(OH)P(O)(aq) + H_2O \rightarrow (Cl)(OH)_2P(O)(aq) + HCl(g) \quad (5)$$

$$(Cl)(OH)_2P(O)(aq) + H_2O \rightarrow (OH)_3P(O)(aq) + HCl(g) \quad (6)$$

All the syntheses were performed in dry hydrocarbon solvents, such as n-hexane, toluene and benzene, and under a dry N_2 gas stream, to ensure a moisture-free environment and a higher phosphonium compound yield. When n-hexane was used as the reaction solvent, a larger volume was needed to incorporate the PCl_5 solid into a fine-particulate suspension and to carry it into the amine solution while keeping reagent losses to a minimum.

The order of addition of reagents[13] was also found to be important, since keeping the amine in excess at all times during the reaction strongly favors a higher yield of completely substituted phosphonium product, as opposed to the formation of stable, partially substituted intermediates which would yield partially hydrolyzed products in contact with moisture upon completion of the reaction:

$$RNH_2 + PCl_5 \rightarrow (RNH)Cl_3PCl(s) + HCl(g) \quad (7)$$

$$RNH_2 + 2\ PCl_5 \rightarrow Cl_4P\text{-}N(R)\text{-}PCl_4 + 2\ HCl(g) \quad (8)$$

Furthermore, since formation of a precipitate was observed to take place upon addition of each drop of reactant it was decided to perform the addition step very slowly. Fast precipitation rates can cause the formation of agglomerates which are insoluble in the reaction solvent, or contain a fully reacted surface layer which prevents complete reaction of the PCl_5 enclosed within it. Upon separation of the products in moisture-containing or aqueous solvents, the unreacted or partially reacted PCl_5 solid forms undesirable hydrolysis products. Very slow, dropwise addition, combined with efficient stirring of the solution provide the necessary conditions to avoid the latter problem and substantially increase the reaction yields. This problem deserves special attention when R is a long alkyl chain, branched

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alkyl chain, or aromatic, due to the much lower solubility of the intermediates formed.

The product yields were found to vary depending on the nature and boiling point of the amine reagent, the reaction solvent used and the solubility characteristics of the desired product. However, no specific trends were observed.

Physical Properties

The solubility properties for compounds **1–10** are given in Table I. In general, aromatic amine derivatives are the most insoluble in all the solvents studied, and the solubility trends seem to follow rather strongly the nature and type of the amino substituents. Most aminophosphonium products are insoluble in water, making their isolation from the water-soluble ammonium salt byproducts relatively easy to accomplish. In several instances, however, due to low solubility or lack of solubility in adequate solvents, spectroscopic measurements were difficult to perform for some of the products.

Surprisingly, while the starting materials and any partially substituted intermediates are very prone to hydrolysis in the presence of moisture, the completely substituted aminophosphonium compounds are not. They are, in fact, quite stable in water under neutral or acidic conditions, and their insolubility in water may be thought to be responsible for such behavior. However, even in those cases where partial solubility in water is observed, hydrolysis does not take place and the compounds can be completely recovered, suggesting an alternate reason for their stability.

The melting points determined for the aminophosphonium chlorides (compounds **1–10**) do not follow any simple trend with respect to the nature of the organic substituent. Nevertheless, it is usually observed that if two $(RNH)_4PX$ compounds with substituents (R) having the same number of carbons are compared, the one with higher branching on the carbon chain displays the higher melting point. The

TABLE I
Solubility of $(RNH)_4PCl$ compounds

R	CCl_4	C_6H_6	Et_2O	$CHCl_3$	CH_2Cl_2	$Me_2C{=}O$	EtOH	MeOH	DMF	CH_3CN	H_2O
n-C_3H_7	PS	PS	I	PS	S	PS	S	I	PS	PS	I
i-C_3H_7	I	PS	I	S	PS	I	S	S	S	PS	PS
n-C_4H_9	PS	PS	I	PS	S	PS	S	I	PS	PS	I
s-C_4H_9	S	PS	I	S	S	S	S	S	S	S	PS
n-C_6H_{13}	S	S	PS	S	S	PS	S	S	PS	PS	I
c-C_6H_{11}	S	PS	I	S	S	I	S	S	S	PS	I
$C_6H_5CH_2$	I	I	I	I	PS	I	PS	S	S	I	I
C_6H_5	I	I	I	I	PS	I	S	PS	S	PS	I

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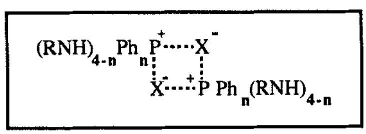
aminophosphonium perchlorates are also found to melt, in general, at lower temperatures than their chloride analogs. Since the perchlorates also display much greater solubility in most solvents investigated, both of the latter observations indicate a larger crystal lattice energy and electrostatic interaction between the chloride anions and the phosphonium cations, $[(RNH)_4P^+ \cdots Cl^-]$, when compared to their perchlorate counterparts, and suggest this to play an important role in determining their properties. Furthermore, a clear trend can be observed in the melting points of $(C_6H_5CH_2NH)_4PX$, when X is Cl (mp 206–210°C, **9**), I (mp 136–139°C, **12**), and ClO_4 (mp 106–107°C, **19**), which correlate well with the change in the size of the anion and are consistent with an inverse relation between anion size and crystal lattice energy.

In addition, the tendency to form ion pairs of the type



should increase in the order X = ClO_4, I, Cl, and is expected to contribute considerably to the much lower solubility of the chlorides in nonpolar (or less polar) organic solvents, as observed in our experiments.

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Reactions of Tetrakis(amino)phosphonium Compounds

Metathesis Reactions. Since it was usually difficult to dissolve the phosphonium chloride compounds **1–10** in appropriate solvents for spectroscopic characterization, metathetical replacement of chloride was attempted as represented in (9):

$$(RNH)_4P^+Cl^- + M^+Z^- \rightarrow (RNH)_4P^+Z^- + M^+Cl^- \qquad (9)$$

Where M = Na; Z = ClO_4, Br, I. The reactions were performed using ethanol as solvent and under mild conditions. Replacement of chloride was found to take place with ease, and the products obtained were easy to purify. The fact that anion replacement takes place easily indicates the presence of ionic character in the structures of these compounds, as well as its importance in determining their properties.

Hydrolysis Reactions. The complete hydrolysis of the tetrakis(amino)phosphonium compounds should lead to the formation of orthophosphoric acid. However, the possibility of isolating intermediate hydrolysis products seems realizable by controlling the reaction conditions appropriately.

The hydrolysis of dialkylamino-substituted arylphosphonium compounds, $[(C_6H_5)_3PNR_2]^+X^-$, has been shown[14] to yield $(C_6H_5)_3P(O)$ and R_2NH. Since Becke-Goehring and Niedenzu[15] claim to have isolated $(NH_2)_3P(O)$ from the reaction of PCl_5 and NH_3 in the presence of water, based on their postulated hydrolysis scheme the following base hydrolysis sequence can be proposed for tetrakis(amino)phosphonium compounds:

$$(RNH)_4P^+ \xrightarrow[H_2O]{} (RNH)_3P{=}NR \xrightarrow[H_2O]{} (RNH)_3P(O) \xrightarrow[H_2O]{} (OH)_3P(O) \qquad (10)$$

In order to attempt the isolation of the intermediates proposed in (10), hydrolysis experiments were carried out for compounds **3**, **9** and **10**, under the mildest possible conditions.

Compound **3** was recovered unchanged after boiling for several hours in an ethanol-water mixture. However, when it was dissolved in ethanol and treated with dilute KOH/EtOH solution, K_3PO_4 inmediately precipitated indicating the instability of the intermediate $(n\text{-}C_4H_9NH)_3P(O)$ toward base hydrolysis. Furthermore, the small number of aliphatic compounds of type $(RNH)_3P(O)$ known may be explained by their susceptibility to hydrolysis under mildly basic conditions, and is consistent with the typical synthetic route employed[16] which requires an excess amount of amine.

More drastic conditions were required to hydrolyze compound **9**. A 1N KOH-EtOH solution was added to a solution of $(C_6H_5CH_2NH)_4PCl$ in ethanol until a white precipitate appeared. This precipitate was recrystallized from 70% aqueous ethanol and identified as $(C_6H_5CH_2NH)_3P(O)$, as previously reported by Audrieth and Toy,[16] mp 98–99°C.

Hydrolysis of compound **10** was accomplished by treating a DMF solution of the phosphonium chloride with 50% aqueous NaOH and heating for several minutes. A white solid precipitated upon addition of water and was identified as the imide derivative of formula $(C_6H_5NH)_3P{=}NC_6H_5$, mp 250–255°C, on the basis of elemental analysis and IR spectroscopy. This imide derivative was found to be easily converted to the corresponding phosphonium chloride compound by treatment with an equimolar amount of HCl:

$$(C_6H_5NH)_3P{=}NC_6H_5 + HCl \rightarrow (C_6H_5NH)_4PCl \qquad (11)$$

All the intermediates proposed in (10) have been isolated by carrying out the base hydrolysis of the appropriate phosphonium chlorides under specific experimental conditions which are determined by the stability of the intermediates. As such, it has been shown that the relative stability toward base hydrolysis of $(RNH)_4PCl$ compounds increases in the order R = n-butyl, benzyl, phenyl.

Structural Chemistry

NMR Spectroscopy. ^1H NMR results are summarized for several representative aminophosphonium compounds in Table II. These results are consistent with a bonding situation where four amino substituents are tetrahedrally arranged around a cationic phosphorus center, indicating an ionic structure, $[(RNH)_4P]^+Cl^-$, for all these compounds. The alternative covalent structure, $[(RNH)_4PCl]$, would not result in four equivalent amino substituents and is not consistent with the ^{31}P NMR results obtained. The ^{31}P NMR chemical shifts obtained for all the compounds presented here lie in the range expected[17] for tetracoordinate phosphonium compounds (+5 to +40 ppm with respect to 85% H_3PO_4, used as the reference), deshielded with respect to the reference. However, the range for pentacoordinate phosphorus compounds is quite large, between 0 and −100 ppm, shielded with respect to the reference, and in most cases distinctly different from values found for tetracoordinate phosphorus. Thus, both ^1H and ^{31}P NMR results suggest the compounds reported here display very similar structure to the well known phosphonium salts, $R_4P^+X^-$.[13]

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TABLE II
^1H NMR Spectral data for $(RNH)_4PX$ compounds

Peak	$(n\text{-}C_3H_7NH)_4PCl$	$(i\text{-}C_3H_7NH)_4PCl$	$(C_6H_5CH_2NH)_4PCl$
$C_6H_5(C)$	-	-	7.4 (S)
N-H	5.0 (M)	4.8 (M)	5.0 (M)
			5.2 (B)[a]
CH(N)	-	3.3 (M)	-
$CH_2(N)$	2.9 (M)	-	4.0 (DD)
			3.8 (DD)[a]
$CH_2(C)$	1.4 (M)	-	-
$CH_3(C)$	0.9 (T)	1.2 (D)	-

a Phosphonium Iodide in CCl_4.

B : Broad; D : Doublet; M : Multiplet; DD : Doublet of doublets; S : Singlet; T : Triplet.

In order to positively identify the chemical shift of the N—H group in each of the compounds shown on Table II, it was necessary to perform two NMR experiments. The first one was in $CDCl_3$, to obtain the regular spectrum of the phosphonium compound in solution. The second experiment was performed by adding a small amount of D_2O to the original NMR tube used to obtain the first spectrum. The D_2O addition causes a hydrogen-deuterium exchange which suppresses the original N—H peak dramatically. In addition, Figure 1(a) gives the spectrum obtained for compound **9**, where a doublet of doublets arising from the splitting of the benzyl protons by =N—H and =N—P is identified. Upon addition of D_2O (Figure 1b) the original N—H peak disappears, while the doublet of doublets turns into one single doublet due to H—D exchange at the amino proton site. The remaining doublet arises due to coupling between the methylene protons and the phosphorus center.

IR Spectroscopy. IR data is summarized in Table III for several derivatives of compound **3**. The purpose of the data is to illustrate a correlation between the counteranion size and the N—H stretching frequency observed. Since the effect of hydrogen bonding on the N—H stretching mode is to shift the absorption to lower frequencies and to increase the width and intensity of this mode,[20] the results shown in Table III indicate that hydrogen bonding increases in the series $ClO_4 < I < Br < Cl$. The order was found to be the same in the solid state (Nujol mull) as in 0.01 M CCl_4 solution. The total shift in this series is approximately 200 cm^{-1}. Since it is generally agreed that a free N—H stretch does not occur below ca. 3000 cm^{-1},[19,20] it is reasonable to conclude that a significant amount of hydrogen bonding is occurring in the chloride, bromide, and iodide compounds of this series. From this data, the presence of N—H···X type hydrogen bonding, (where X = Cl, Br,

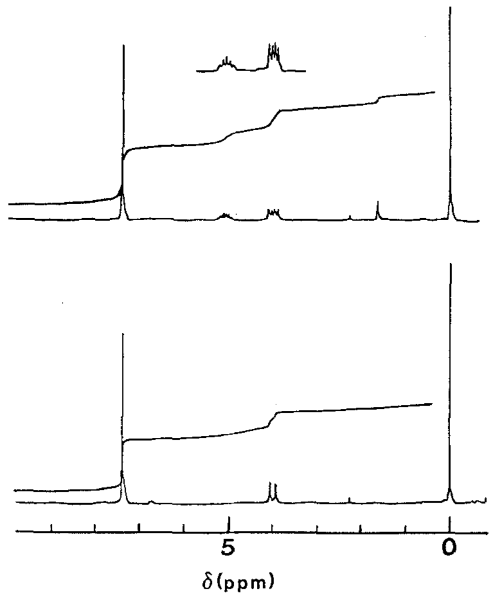

FIGURE 1 ^{1}H NMR spectrum obtained for $(C_6H_5CH_2NH)_4PCl$ in $CDCl_3$ (top), and $CDCl_3$ + D_2O (bottom).

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TABLE III
IR Spectral data for $(C_4H_9NH)_4PX$ compounds

X	Nujol	0.01 M CCl_4
Cl	3158	3160
Br	3190	3171
I	3197	3209
ClO_4	3352	3322

Numbers are given in cm^{-1}.

I), can be postulated. IR spectra determined in Nujol mulls[21] and in solution[22] for hexaammine cobalt(III) complexes confirm the order found in Table III, and give more evidence to support the postulated presence of hydrogen bonding involving the proton on the substituent amino group with the I^-, Br^- and Cl^- anions.

Other Methods. Conductance studies[23] have shown that alkylaminophosphonium chloride and perchlorate behave as strong electrolytes in dimethylformamide solution, supporting the phosphonium ion formulation. In addition, the crystal structures of tetrakis(n-propylamino)phosphonium chloride and tetrakis-(anilino)phosphonium chloride have confirmed the presence of tetrahedral cations in the solid.[24]

Conclusion

A number of tetrakis(amino)phosphonium compounds of formula $(RNH)_4PX$, where R = aliphatic, aromatic, and X = Cl, Br, I, ClO_4 have been synthesized. Their physical properties have been characterized and their metathesis and hydrolysis reactions have been studied. These compounds have been found to be similar in structure to the typical phosphonium salts, R_4PX, by ^{31}P and ^{1}H NMR spectroscopy. IR spectra of a series of these compounds suggest the presence of hydrogen bonding involving the anion, when X = Cl, Br and I.

EXPERIMENTAL

Starting Materials. Benzene, barium oxide, sodium perchlorate, n-propylamine, isopropylamine and n-butylamine were obtained from Fisher Scientific. Deuterochloroform was obtained from Norell, Inc. Acetone, acetonitrile, aniline, benzaldehyde, bromine, chloroform and sodium hydroxide were obtained from J. T. Baker Chemical Co. d,l-sec-Butylamine and triphenylphosphine were obtained from Matheson, Coleman and Bell. d,l-Alphamethylbenzylamine, isoamylamine, cyclohexylamine, n-heptylamine and n-hexylamine were obtained from the Eastman Kodak Co. Benzylamine, anhydrous calcium chloride and phosphorus pentoxide were obtained from Mallinckrodt, Inc. All starting materials used were of reagent grade quality, unless otherwise specified.

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General Procedures. Solvents were dried over anhydrous calcium chloride for several days prior to their use. Amines were stored over sodium hydroxide for several days, and were subsequently distilled from fresh sodium hydroxide and collected over barium oxide. All other reagents were used as received. Reactions were carried out under a stream of nitrogen gas passed through a $CaCl_2$ drying tube, an H_2SO_4 gas-washing bottle and a P_2O_5 drying tube.

Measurements. Phosphorus (^{31}P) NMR spectra were recorded on a Varian XL-100 FT spectrometer coupled to a Nicolet Multi-Observe Nuclei Accessory (MONA) unit (23.5 KG, 40.5 MHz). Several measurements were performed on an IBM 200 spectrometer. H_3PO_4 (85%) was used as an external reference (in a concentric tube) for all ^{31}P NMR measurements. The chemical shifts are listed as positive downfield and negative upfield with respect to the phosphoric acid reference peak (0.0 ppm). Proton (^{1}H) NMR spectra were recorded on a Varian EM 360 spectrometer, operating at 60 MHz, and also on a Varian XL-100 FT spectrometer, operating at 100 MHz. Tetramethylsilane was used as an internal reference while deuterochloroform was used as solvent and internal lock. Mixtures of $CDCl_3$ and other solvents such as CH_3CH_2OH, CH_3OCH_3, C_6H_6, and CH_2Cl_2, were used for those compounds which were insoluble in pure $CDCl_3$.

IR spectra were recorded on a Perkin-Elmer Model 281 spectrophotometer using both CCl_4 and Nujol mulls to obtain solution and solid state spectra, respectively.

Melting points were obtained using an Electrothermal melting point apparatus, and are not corrected. Elemental analyses were performed by Dr. F. Kasler, Department of Chemistry, University of Maryland.

Reaction of amines with PCl_5. Synthesis of tetrakis(alkyl/arylamino)phosphonium chlorides $(RNH)_4PCl$ (R = n-C_3H_7 (**1**), i-C_3H_7 (**2**), n-C_4H_9 (**3**), sec-C_4H_9 (**4**), C_5H_{11} (**5**), n-C_6H_{13} (**6**), cyclo-C_6H_{11} (**7**), n-C_7H_{15} (**8**), $C_6H_5CH_2$ (**9**), C_6H_5 (**10**)). These substituted aminophosphonium compounds were prepared similarly. The typical procedure described below is for **3**. The yields quoted are for the isolated compounds and are not adjusted for recovered unreacted PCl_5 (due to its insolubility in hexane). A suspension of PCl_5 (20 g, 0.1 mol) in dry hexane (350 ml) was added dropwise (from a side-arm addition funnel with a dry N_2 (g) inlet) into a solution of n-butylamine (160 ml, 1.6 mol) in dry hexane (350 ml) inside a 3-neck round-bottom flask under constant stirring (with a magnetic bar). The drop-wise addition rate was controlled so that the temperature of the product solution would not rise above 65°C. Upon completion of the addition step, the resulting solution was refluxed for one-half hour. The reaction set-up included a side-arm addition funnel, a thermometer, and a condenser fitted with a $CaCl_2$ (anhydrous) drying tube outlet. After the refluxing period, and upon cooling to room temperature, a large amount of white precipitate settled at the bottom of the reaction flask. A clear solution remained above it. The precipitate (53.9 g) was washed with hot, acidified water in order to dissolve the amine hydrochloride salt. The remaining water-insoluble solid (18.8 g) was recrystallized from acetone (12.8 g). Shiny, translucent platelets were obtained. For most reactions the approximate reflux periods were in the order of 30 to 80 min, with the exception of **4** and **5**, where they were 4 h and 13 h, respectively.

Addition steps were performed at ca. 5°C for **1** and **2**, and at room temperature for all others. Hexane was used as reaction solvent for **1**, **2**, **3**, and **7**; toluene for **6**, **9**, and **10**; benzene for **5**; a mixture of CCl_4, n-C_6H_{14} and C_6H_6 for **4**. Products **1**, **2**, **3**, **6**, and **8** were recrystallized from acetone. Ethanol and ethanol-water were used to recrystallize **10** and **7**, respectively. **1**: yield 53%; m.p. 112–114°C; ^{31}P NMR 28.5 ppm. Anal. Calcd for $C_{12}H_{32}N_4PCl$: C, 48.23; H, 10.79; N, 18.75. Found: C, 48.32; H, 10.90; N, 18.77. **2**: yield 60%; m.p. 230–235°C dec; ^{31}P NMR 20.4 ppm. Anal. Calcd for $C_{12}H_{32}N_4PCl$: C, 48.23; H, 10.79; N, 18.75. Found: C, 48.32; H, 11.00; N, 19.00. **3**: yield 53%; m.p. 97–99°C; ^{31}P NMR 28.5 ppm. Anal. Calcd for $C_{16}H_{40}N_4PCl$: C, 54.15; H, 11.36; N, 15.79. Found: C, 54.37; H, 11.60; N, 15.90. **4**: oil; ^{31}P NMR 20.9 ppm. No anal. obtained. **6**: yield 69%; m.p. 75–77°C; ^{31}P NMR 28.5 ppm. Anal. Calcd for $C_{24}H_{56}N_4PCl$: C, 61.71; H, 12.08; N, 11.99. Found: C, 61.85; H, 12.25; N, 11.90. **7**: yield 80%; m.p. 227–230°C dec; ^{31}P NMR 20.3 ppm. Anal. Calcd for $C_{24}H_{48}N_4PCl$: C, 62.79; H, 10.54; N, 12.20. Found: C, 62.31; H, 10.58; N, 12.51. **8**: yield 81%; m.p. 67–68°C; ^{31}P NMR 28.5 ppm. No satisfactory anal. obtained. **9**: yield 96%; m.p. 210–211°C; ^{31}P NMR 28.6 ppm. Anal. Calcd for $C_{28}H_{32}N_4PCl$: C, 68.49; H, 6.57; N, 11.41. Found: C, 68.29; H, 6.68; N, 11.25. **10**: yield 48%; m.p. 338–350°C dec; ^{31}P NMR 6.2 ppm. Anal. Calcd for $C_{24}H_{24}N_4PCl$: C, 66.28; H, 5.56; N, 12.88. Found: C, 66.06; H, 5.47; N, 12.69.

Metathesis Reactions of Aminophosphonium Chlorides. Synthesis of aminophosphonium bromides, iodides and perchlorates. $(RNH)_4PBr$ (R = n-C_4H_9) (**11**); $(RNH)_4PI$ (R = $C_6H_5CH_2$) (**12**); $(RNH)_4PClO_4$ (R = n-C_3H_7 (**13**), i-C_3H_7 (**14**), n-C_4H_9 (**15**), n-C_6H_{13} (**16**), n-C_6H_{11} (**17**), n-C_7H_{15} (**18**), $C_6H_5CH_2$ (**19**), C_6H_5 (**20**)).

These aminophosphonium salts were prepared similarly. The typical procedure described below is for **15**. The yields were quantitative in all cases. To a vigorously stirred solution of (n-$C_4H_9)_4PCl$ in ethanol (95% aqueous) was added an equimolar amount of sodium perchlorate. The resulting solution was then heated for one hour. Distilled water was then added until the solution became slightly cloudy. Upon cooling to room temperature, the expected (n-$C_4H_9)_4PClO_4$ product crystallized. This product was filtered, washed with distilled water, and recrystallized from acetone. For **11** and **12** an equimolar mixture of NaBr and NaI were used, respectively. Acetone was also used to recrystallize compounds **11**, **12**, **13**, **14**, **16**, **17** and **18**. Ethanol was used to recrystallize compounds **19** and **20**. **11**: m.p. 115–116°C; ^{31}P NMR 28.4 ppm. Anal. Calcd for $C_{16}H_{40}N_4PBr$: C, 48.12; H, 10.10; N, 14.03. Found: C, 48.28; H, 10.60; N, 14.22. **12**: m.p. 136–139°C; ^{31}P NMR 28.6 ppm. Anal. Calcd for $C_{28}H_{32}N_4PI$: C, 57.74; H, 5.54; N, 9.62. Found: C, 57.73; H, 5.59; N, 9.78. **13**: m.p. 72.5–73.5°C; ^{31}P NMR 28.3 ppm. Anal. Calcd for $C_{12}H_{32}N_4PClO_4$: C, 39.70; H, 8.89; N, 15.44. Found: C, 39.54; H, 8.96; N, 15.40. **14**: m.p. 227–229°C; ^{31}P NMR 20.2 ppm. Anal. Calcd for $C_{12}H_{32}N_4PClO_4$: C, 39.70; H, 8.89; N, 15.44. Found: C, 39.65; H, 9.10; N, 15.29. **15**: m.p. 81–83°C; ^{31}P NMR 28.2 ppm. Anal. Calcd for $C_{16}H_{40}N_4PClO_4$: C, 45.87; H, 9.62; N, 13.37. Found: C, 45.83; H, 9.80; N, 13.37. **16**: m.p. 74°C; ^{31}P NMR 28.4 ppm. Anal. Calcd for $C_{24}H_{56}N_4PClO_4$: C, 54.27; H, 10.63; N, 10.55. Found: C, 52.99; H, 10.51; N, 10.25. **17**: m.p. 190°C dec; ^{31}P NMR 20.3 ppm. Anal. Calcd for $C_{24}H_{48}N_4PClO_4$: C, 55.54; H, 9.32; N, 10.79. Found: C, 55.22; H, 9.48; N, 10.83. **18**: m.p. 89–90°C; ^{31}P NMR 28.3 ppm. Anal. Calcd for $C_{28}H_{64}N_4PClO_4$: C, 57.27; H, 10.98; N, 9.54. Found: C, 57.54; H, 11.03; N, 9.29. **19**: m.p. 106–107°C; ^{31}P NMR 28.5 ppm. Anal. Calcd for $C_{28}H_{32}N_4PClO_4$: C, 60.60; H, 5.81; N, 10.10. Found: C, 60.32; H, 5.64; N, 10.23. **20**: m.p. 230–231°C dec; ^{31}P NMR 6.8 ppm. Anal. Calcd for $C_{24}H_{24}N_4PClO_4$: C, 57.78; H, 4.85; N, 11.23. Found: C, 58.52; H, 4.56; N, 11.12.

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