

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA

## Reactions of Triethylaluminum with Diphosphines, Bis(diphenylphosphino)amines, and Aminophosphines

BY DONALD F. CLEMENS, HARRY H. SISLER, AND WALLACE S. BREY, JR.

Received July 12, 1965

Triethylaluminum reacts with tetraphenyldiphosphine, bis(diphenylphosphino)methylamine, and bis(diphenylphosphino)ethylamine to produce  $(C_6H_5)_2PP(C_6H_5)_2 \cdot Al(C_2H_5)_3$ ,  $CH_3N[P(C_6H_5)_2]_2 \cdot Al(C_2H_5)_3$ , and  $C_2H_5N[P(C_6H_5)_2]_2 \cdot Al(C_2H_5)_3$ , respectively. Nuclear magnetic resonance and infrared data indicate that the two phosphorus atoms in each of these products are equivalent and that the aluminum atom in the complexes is pentacoordinate. Triethylaluminum reacts with isopropylaminodiphenylphosphine, *t*-butylaminodiphenylphosphine, and bis(diphenylphosphino)amine to produce  $\{(CH_3)_2CHN\{Al(C_2H_5)_2\}P(C_6H_5)_2\}_2$ ,  $(CH_3)_3CNHP(C_6H_5)_2 \cdot Al(C_2H_5)_3$  and  $(CH_3)_3CN[Al(C_2H_5)_2]P(C_6H_5)_2$ , and  $\{(C_6H_5)_2AlN\{P(C_6H_5)_2\}_2\}_2$ , respectively. Triethylaluminum reacts with tetramethyldiphosphine and dimethylaminodimethylphosphine to produce  $(CH_3)_2PP(CH_3)_2 \cdot 2Al(C_2H_5)_3$  and  $(CH_3)_2NP(CH_3)_2 \cdot Al(C_2H_5)_3$ , respectively. Triethylaluminum reacts with diethylaminodiphenylphosphine to produce a mixture of hydrocarbons including ethylene.

Very little information concerning the reactions of aluminum alkyls with phosphorus-containing polynuclear bases is available. Issleib and Krech<sup>1</sup> have reported the preparation of the 1:1 molecular addition compound of triethylaluminum with tetraphenylbiphosphine. These authors reported elemental analysis and melting point but did not give infrared or nuclear magnetic resonance data, nor did they refer to the possibility of the aluminum in this compound being pentacoordinate. Prior to the publication of the above paper<sup>1</sup> we had obtained this 1:1 molecular addition compound and, as data below indicate, showed that this compound does, indeed, contain pentacoordinate aluminum. Pentacoordinate aluminum has been postulated by Wiberg<sup>2</sup> and by Ruff and Hawthorne<sup>3</sup> and the existence of pentacoordinate aluminum in solid  $AlH_3 \cdot 2N(CH_3)_3$  has recently been established by Parry, *et al.*, by X-ray studies of single crystals.<sup>4</sup> Proton nuclear magnetic resonance data have recently been used by the present authors<sup>5</sup> as well as others<sup>6</sup> as a basis for postulating the existence of pentacoordinate aluminum in complexes of aluminum alkyls with tetramethylhydrazine and *N,N,N',N'*-tetramethylethylenediamine, respectively.

This study was conducted to determine how triethylaluminum reacts with polynuclear phosphorus and nitrogen bases and to examine the possibility of the existence of pentacoordinate aluminum in the reaction products.

### Experimental Section

**The Manipulation of Reagents.**—All organoaluminum compounds were handled either in a drybox (D. L. Herring Dri-Lab and Dri-Train) in an atmosphere of dry nitrogen or in an all-glass vacuum line. Oxygen and moisture were rigorously excluded from all operations. Before reaction, all materials were degassed by freezing with liquid nitrogen, evacuating the reaction

flask, closing the manifold stopcock, and allowing the material to warm to ambient temperature, this operation being carried out three times. In those reactions in which ethane was a product the liberated ethane was collected, purified, identified by its vapor pressure at  $-126.3$  and  $-111.6^\circ$  (lit.<sup>7</sup> 55 mm; 178 mm), and its volume was measured.

**Materials.**—Solvents were dried by distillation over calcium hydride and then stored over the same reagent. Triethylaluminum obtained from the Ethyl Corporation was fractionally distilled and the fraction boiling at  $56^\circ$  (0.5 mm) was used. Tetraphenylbiphosphine was prepared by the method of Frazier, *et al.*<sup>8</sup> Tetramethylbiphosphine was prepared by the method of Maier.<sup>9</sup> The aminophosphines and the bis(diphenylphosphino)amines were prepared by allowing the appropriate chlorophosphine to react with the appropriate amine.<sup>10-13</sup>

**Analyses.**—Elemental analyses were carried out by the Schwarzkopf Microanalytical Laboratory. Melting points were obtained in sealed capillary tubes in a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Molecular weights were determined cryoscopically in benzene. An attempt to use a vapor pressure osmometer was unsuccessful because the compounds decomposed in the short time they were in the instrument. A standard freezing point depression apparatus was modified to provide a nitrogen flush so that contact of the solution with the atmosphere could be minimized. The molecular weights obtained vary considerably from theory. The values are generally low, indicating that the compounds may have partially hydrolyzed despite all the precautions taken to exclude moisture from the cryoscopic system. Analytical and molecular weight data are recorded in Table I.

**Infrared Spectra.**—The infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer using sodium chloride optics. The spectra of the solids were obtained from Nujol mulls. In all cases the samples were prepared in a drybox and stored under dry nitrogen until placed in the instrument. A summary of the infrared data is found in Table II.

**Nuclear Magnetic Resonance Spectra.**—Nuclear magnetic resonance spectra were obtained using a Varian DP-60 spectrometer. The proton shift values were obtained by sweeping through the field slowly and interchanging a reference sample of acetaldehyde and the sample being studied. The method pro-

- (1) K. Issleib and F. Krech, *Z. Anorg. Allgem. Chem.*, **328**, 21 (1964).
- (2) E. Wiberg, H. Graf, and R. Uson, *ibid.*, **272**, 221 (1958).
- (3) J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **83**, 535 (1961).
- (4) C. W. Heitsch, C. E. Nordman, and R. W. Parry, *Inorg. Chem.*, **2**, 508 (1963).
- (5) D. F. Clemens, W. S. Brey, Jr., and H. H. Sisler, *ibid.*, **2**, 1251 (1963).
- (6) N. R. Fetter, B. Bartocha, F. E. Brinckman, Jr., and D. W. Moore, *Can. J. Chem.*, **41**, 1359 (1963).

- (7) "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Table 1K.
- (8) S. E. Frazier, R. P. Nielsen, and H. H. Sisler, *Inorg. Chem.*, **3**, 292 (1964).
- (9) L. Maier, *J. Inorg. Nucl. Chem.*, **24**, 275 (1962).
- (10) A. B. Burg and P. J. Slota, Jr., *J. Am. Chem. Soc.*, **82**, 2145 (1960).
- (11) H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 611 (1961).
- (12) G. Ewart, A. P. Lane, J. McKechnie, and D. S. Payne, *J. Chem. Soc.*, 1543 (1964).
- (13) D. F. Clemens and H. H. Sisler, *Inorg. Chem.*, **4**, 1222 (1965).

TABLE I  
ANALYTICAL DATA

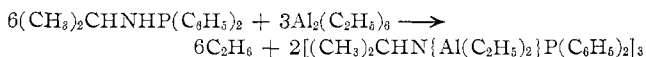
Compound	% C		% H		% N		% P		% Al		Mol wt.	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$(C_6H_5)_2PP(C_6H_5)_2 \cdot Al(C_2H_5)_3$	74.36	71.02	7.28	6.87			12.79	12.40	5.57	5.58	485	464
$C_2H_5N[P(C_6H_5)_2]_2 \cdot Al(C_2H_5)_3$	72.84	73.07	7.64	7.56	2.66	2.87	11.74	11.50	5.11	5.19	528	303
$CH_3N[P(C_6H_5)_2]_2 \cdot Al(C_2H_5)_3$	72.49	72.50	7.46	7.43	2.73	2.94	12.06	11.83	5.25	5.60	514	422
$[(C_2H_5)_2AlN\{P(C_6H_5)_2\}]_2$	71.63	71.93	6.44	6.67	2.98	3.04	13.20	12.91	5.78	5.88	939	870
$\{(CH_3)_2CHN\{Al(C_2H_5)_2\}P(C_6H_5)_2\}_3$	69.71	69.50	8.31	8.07	4.28	4.49	9.46	9.18			982	983
$(CH_3)_3CNHP(C_6H_5)_2 \cdot Al(C_2H_5)_3$	71.13	71.16	9.50	9.60	3.77	3.79	8.34	8.29	7.76	7.21	371	412
$(CH_3)_3CN[Al(C_2H_5)_2]P(C_6H_5)_2$	70.35	70.25	8.56	8.58	4.10	4.24	9.07	8.89	7.90	7.86	341	320
$(CH_3)_2PP(CH_3)_2 \cdot 2Al(C_2H_5)_3$	54.84	54.79	12.08	12.26			17.68	17.72	15.40	15.13	350	292 <sup>a</sup>
$(CH_3)_2NP(CH_3)_2 \cdot Al(C_2H_5)_3$	54.77	54.53	12.41	12.07	6.39	6.29	14.13	14.11	12.30	12.59	219	213
$(C_2H_5)_2NP(C_6H_5)_2Al(C_2H_5)_2H$	69.94	70.15	9.10	8.95	4.08	4.11	9.02	9.07	7.86	7.61	343	283

<sup>a</sup> Rast method 392.

duces the sample peaks and the acetaldehyde peaks on the same spectrum and from this the chemical shifts may be calculated in approximate  $\tau$  values. For the phenyl protons, only the position of the most intense peak is reported. Phosphoric acid (85%) was used in a similar manner for measuring the <sup>31</sup>P chemical shifts. The <sup>1</sup>H spectra were determined at 56.4 or 60.0 Mc; the <sup>31</sup>P spectra, at 19.3 Mc. A summary of the nuclear magnetic resonance data is found in Table III.

**Procedure.**—As an example of the procedure used in the reactions of triethylaluminum with polynuclear bases, the following description of the reaction of triethylaluminum with isopropylaminodiphenylphosphine is presented.

A 1.66-g (0.0146 mole) sample of triethylaluminum was placed in a 100-ml, two-neck reaction flask containing a Teflon-coated magnetic stirring bar. Isopropylaminodiphenylphosphine (3.54 g, 0.146 mole) was placed in a tipping tube and attached to the reaction flask. A vacuum stopcock was fitted into the other neck of the reaction flask and the entire apparatus was attached to the vacuum line. After degassing the reactants the isopropylaminodiphenylphosphine was added to the reaction flask, which was cooled with liquid nitrogen. The reaction flask was allowed to warm slowly to room temperature during which time a gas was slowly evolved. The reaction flask was then heated for 40 hr at 50–55° to ensure completion of the reaction. Fractional condensation yielded 0.0127 mole of ethane. The apparatus was then transferred to the drybox and the white crystalline solid was recrystallized from hot hexane. This material melted at 189° with decomposition. The yield was 87% based on the equation



Data concerning the various reactions are recorded in Table IV.

### Discussion

The reactions of triethylaluminum with tetraphenyldiphosphine, bis(diphenylphosphino)ethylamine, and bis(diphenylphosphino)methylamine produce 1:1 addition compounds. In Figures 1 and 2 are reproduced the proton nmr spectra of two of these adducts. The resonance patterns of the phenyl groups in the adducts are no broader than those observed in the parent base and thus give no indication that the phenyls have been made nonequivalent by unsymmetrical addition of triethylaluminum. Both spectra include the typical A<sub>2</sub>B<sub>3</sub> pattern for the ethyl group attached to aluminum; in the spectrum of the tetraphenyldiphosphine adduct, there is an extra peak in the methylene pattern, which may result from coupling to the phosphorus atom or from nonequivalence of methylene hydrogens. The N-methyl resonance in the spectrum of the bis(diphenylphosphino)methylamine adduct is a triplet because of coupling with the two phosphorus atoms.

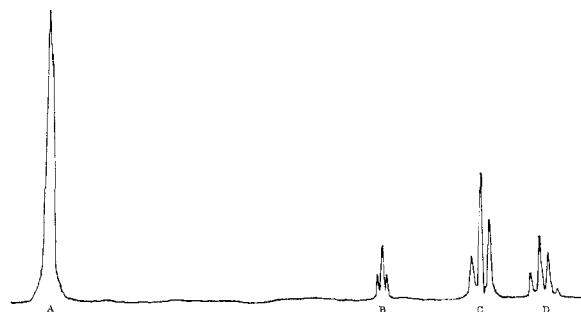


Figure 1.—<sup>1</sup>H nuclear magnetic resonance spectrum of  $CH_3N-[P(C_6H_5)_2]_2 \cdot Al(C_2H_5)_3$ . Peak A arises from the phenyl protons, peak B from the nitrogen-methyl protons, peak C from the methyl protons of the ethyl groups, and peak D from the methylene protons of the ethyl groups.

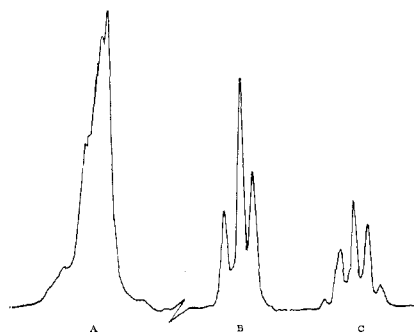
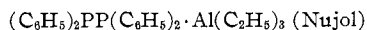


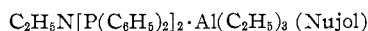
Figure 2.—<sup>1</sup>H nuclear resonance spectrum of  $(C_6H_5)_2PP(C_6H_5)_2 \cdot Al(C_2H_5)_3$ . Peak A arises from the phenyl protons, peak B from the methyl protons of the ethyl groups, and peak C from the methylene protons of the ethyl groups.

In the <sup>31</sup>P nuclear magnetic resonance spectrum of each of the three addition compounds, there is a single peak, confirming the fact that the two phosphorus atoms are equivalent. If the aluminum were bonded to only one of the phosphorus atoms, the <sup>31</sup>P nmr spectrum would be expected to show two peaks. It has been noted previously<sup>5</sup> that an alternative explanation of the nmr results involves the postulation of very rapid transfer of alkylaluminum groups from one phosphorus atom to the other phosphorus atom in the addition compound. If the rate at which such exchange occurs were greater than the frequency separation of the resonance peaks corresponding to the two environments, the two peaks would merge into a single peak of intermediate chemical shift. Therefore, since the

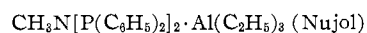
TABLE II

INFRARED ABSORPTION (CM<sup>-1</sup>)<sup>a</sup>

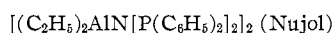
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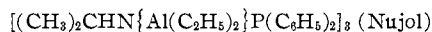
3110 (sh, s), 2960 (vs), 2840 (sh, s), 1970 (vw), 1900 (vw), 1820 (vw), 1660 (vw), 1590 (vw), 1470 (sh, s), 1460 (vs), 1430 (vs), 1400 (m), 1380 (s), 1310 (m), 1230 (w), 1180 (m), 1150 (s), 1100 (s), 1090 (s), 1060 (s), 1030 (m), 980 (m, b), 948 (m), 921 (d, m), 884 (s, b), 974 (s), 972 (sh, s), 743 (vs), 700 (vs, b)



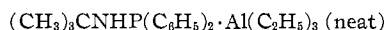
3120 (sh, s), 2960 (vs), 1970 (w), 1890 (w), 1820 (w), 1590 (w), 1480 (s), 1460 (s), 1430 (vs), 1400 (m), 1370 (m), 1300 (w), 1220 (w), 1180 (m), 1160 (sh, w), 1100 (vs), 1080 (vs), 1070 (s), 1030 (w), 995 (sh, m), 987 (m), 969 (m), 948 (m), 916 (w, b), 866 (vs), 747 (vs), 698 (vs)



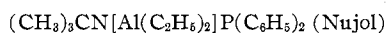
3110 (sh, m), 2990 (vs), 2900 (sh, vs), 1970 (vw), 1900 (vw), 1820 (vw), 1590 (w), 1470 (sh, m), 1460 (vs), 1440 (s), 1380 (s), 1310 (vw), 1230 (w), 1180 (w, b), 1160 (w), 1100 (s), 1070 (w), 1030 (w), 1000 (m), 988 (sh, w), 964 (w), 924 (m), 901 (vs), 810 (s), 792 (vs), 752 (sh, m), 741 (vs), 704 (sh, s), 694 (vs)



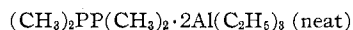
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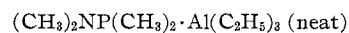
3460 (m), 3130 (s), 2970 (vs), 2840 (sh, s), 1970 (vw), 1900 (vw), 1820 (vw), 1660 (vw), 1590 (w), 1570 (sh, vw), 1490 (s), 1470 (s), 1440 (vs), 1410 (s), 1370 (vs), 1310 (w), 1220 (vs), 1200 (vs), 1190 (sh, s), 1160 (sh, w), 1120 (sh, w), 1100 (vs), 1070 (m), 1040 (sh, m), 1030 (s), 1010 (vs), 998 (vs), 990 (sh, vs, b), 951 (vs), 922 (m), 855 (sh, w, b), 840 (m, b), 778 (w), 746 (vs), 732 (vs), 694 (vs)



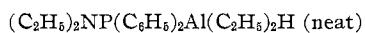
3110 (sh, s), 2950 (vs), 1970 (vw), 1900 (vw), 1820 (vw), 1580 (vw), 1460 (vs), 1440 (vs), 1410 (m), 1390 (sh, s), 1370 (vs), 1360 (s), 1310 (w), 1220 (m), 1210 (sh, m), 1180 (s), 1160 (sh, m), 1090 (s), 1080 (sh, w), 1040 (s), 1030 (m), 982 (vs), 959 (s), 924 (m), 855 (vs), 847 (sh, vs), 975 (s), 739 (vs), 708 (m), 696 (vs)



2910 (vs), 1450 (vs), 1410 (vs), 1360 (m), 1280 (m), 1220 (m), 1170 (m), 980 (vs, b), 943 (vs), 909 (sh, s, b), 889 (sh, vs), 881 (vs), 821 (w, b), 734 (m, b), 699 (sh, w, b), 676 (s, b)



2940 (vs), 2840 (s), 1470 (sh, m), 1460 (s), 1420 (s), 1410 (s), 1370 (m), 1330 (s), 1280 (s), 1270 (m), 1230 (s), 1180 (vs), 1170 (sh, m), 1140 (vw), 1120 (s), 1060 (s), 1040 (s), 1020 (m), 980 (vs), 945 (vs), 902 (vs), 851 (s), 826 (w), 745 (w), 708 (s, b)



3130 (s), 2870 (vs), 1970 (w), 1890 (w), 1820 (w), 1770 (vw), 1660 (w), 1590 (m), 1490 (s), 1470 (vs), 1410 (s), 1380 (vs), 1350 (m), 1310 (sh, m), 1290 (s), 1230 (m), 1200 (vs), 1180 (vs), 1100 (vs), 1070 (s), 1060 (s), 1030 (vs), 1000 (s), 980 (sh, s), 950 (sh, s), 939 (s), 926 (s), 849 (w), 794 (s), 746 (vs, b), 696 (vs, b)

<sup>a</sup> s, strong; m, medium; w, weak; sh, shoulder; d, doublet; b, broad.

chemical shift difference of the phosphorus atoms would be expected to be greater than for the phenyl protons, the <sup>31</sup>P nmr data provide better evidence for pentacoordinate aluminum in the compound (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>·Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> than do the <sup>1</sup>H nmr data.

Additional evidence for the pentacoordinate nature of aluminum is to be found in the infrared spectrum of the molecular adduct. Sheldon and Tyree<sup>14</sup> have noted the presence of a strong sharp band at about 1120 cm<sup>-1</sup> in the infrared spectra of compounds containing tetracoordinate phosphorus. Hart and Sisler<sup>15</sup> showed that the appearance of this band requires that one of the four bonds attached to the phosphorus atom be a P-phenyl bond. Paciorek and Kratzer<sup>16</sup> attributed this peak to pentavalent phosphorus, but this conclusion does not fit the data obtained by Hart and Sisler. The infrared spectrum of the adduct (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>PP(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>·Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> does not contain this band. Hence, we may presume that the normal tetracoordinate phosphorus which is postulated if we assume rapid exchange of the aluminum between the two phosphorus atoms is not present, and the postulate of rapid exchange is untenable.

The question might be raised as to whether a tetra-coordinate phosphorus atom having a P-phenyl bond would be expected to show the peak in the 1120 cm<sup>-1</sup> region of the infrared spectrum if an aluminum atom were bonded to it. Since the aluminum-phosphorus bond would reduce the electron density on the phosphorus atom one might argue that the normal peak for tetracoordinate phosphorus would be shifted by the presence of the aluminum atom. This question is answered by the fact that the compound [C<sub>3</sub>H<sub>7</sub>N{Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}<sub>2</sub>P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub>, which almost certainly contains Al-P bonds, does show the characteristic peak at 1120 cm<sup>-1</sup>. On the other hand, if a tricoordinate phosphorus atom became tetracoordinate through the formation of a highly strained small ring, as in the case of triethylaluminum reacting with tetraphenylbiphosphine to give pentacoordinate aluminum, the resulting tetra-coordinate phosphorus atom would not be expected to absorb infrared energy at the same frequency as a normal tetracoordinate phosphorus atom.

In the case of the bis(diphenylphosphino)methylamine and the bis(diphenylphosphino)ethylamine adducts one might argue that the aluminum atom may be attached to the nitrogen atom. However, we must note that 2:1 molecular addition compounds could not be obtained. If the aluminum atom were attached to the nitrogen atom we would predict that a second and possibly a third molecule of triethylaluminum could react with the phosphorus atoms. Hence, the failure to obtain a 2:1 adduct minimizes the possibility of the aluminum atom being attached to the nitrogen atom. This conclusion is made more attractive by results obtained<sup>13, 15</sup> from the chloramination and alkylation of many phosphorus-nitrogen compounds which show

(14) J. C. Sheldon and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **80**, 2117 (1958).

(15) W. A. Hart and H. H. Sisler, *Inorg. Chem.*, **3**, 617 (1964).

(16) K. L. Paciorek and R. Kratzer, *ibid.*, **3**, 594 (1964).

TABLE III  
 NUCLEAR MAGNETIC RESONANCE DATA

Compound	<sup>1</sup> H shifts in approximate τ values <sup>a</sup>								<sup>31</sup> P shifts in ppm from H <sub>3</sub> PO <sub>4</sub>
	C <sub>6</sub> H <sub>5</sub> <sup>c</sup>	NCH <sub>2</sub>	NCH <sub>3</sub>	PCH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub> on AlCH <sub>2</sub>	AlCH <sub>2</sub>	Δτ in AlCH <sub>2</sub> CH <sub>3</sub>	
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PP(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	2.82					9.07 (t 7.8)	10.31 (p 7.8) <sup>b</sup>	1.24	+13
C <sub>2</sub> H <sub>5</sub> N[P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> ·Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	2.73	6.46 (q)			9.13 (t)	8.64 (t 7.8)	9.53 (q 7.8)	0.89	-59
CH <sub>3</sub> N[P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> ·Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	2.70		7.62 (t 3.7)			9.08 (t 7.7)	9.95 (q 7.7)	0.87	-64
[(CH <sub>3</sub> ) <sub>2</sub> CHN{Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> }P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> <sup>d</sup>					9.48 (d 2.3)	9.50	10.21 (q)	0.71	-32
(CH <sub>3</sub> ) <sub>3</sub> CNHP(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> <sup>e</sup>	2.84 3.11				9.24	9.26	10.32	1.06	-24
(CH <sub>3</sub> ) <sub>3</sub> CN[Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ]P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	2.55 3.52					9.44	10.45 (q)	0.84	-38
(CH <sub>3</sub> ) <sub>2</sub> PP(CH <sub>3</sub> ) <sub>2</sub> ·2Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>				8.07 (t 3.3)		9.05 (t 7.7)	10.15 (q 7.7)	1.10	+50
(CH <sub>3</sub> ) <sub>2</sub> NP(CH <sub>3</sub> ) <sub>2</sub>			7.81 (d 10.1)	9.37 <sup>f</sup> (d 5.7)					-39
(CH <sub>3</sub> ) <sub>2</sub> NP(CH <sub>3</sub> ) <sub>2</sub> ·Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>			7.59 (d 10.7)	8.91 (d 3.4)		9.10 (t 8.4)	10.41 (q 8.4)	1.31	+41
Same as above but heated to 50° for 70 hr			7.78	9.31 (d 7.1)		9.15 (t 7.9)	10.28 (q 8.0)	1.13	-36
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NP(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> H	3.02	7.16 (p)			9.39 (t)	9.16 (t)	10.15 (q 7.8)	0.99	-54

<sup>a</sup> The chemical shift values were obtained by sweeping through the field slowly and interchanging a reference sample, acetaldehyde, and the sample being studied. Parenthetical values are coupling constants in cps; d, doublet; t, triplet; q, quartet; p, pentet. <sup>b</sup> It is not known whether the pentet is caused by nonequivalence in the methylene groups or whether the methylene protons are coupled with the phosphorus atom. <sup>c</sup> The chemical shift values of the phenyl peaks were obtained by measuring to the highest part of the peak; the spectra of the compounds containing *t*-butyl groups contained two well-separated regions of absorption for aromatic protons. <sup>d</sup> Benzene was used as a solvent in this case; CH resonance appears at τ 7.29. <sup>e</sup> Resonance of NH appears at τ 8.19. <sup>f</sup> These data represent corrected values replacing those previously erroneously reported (*Inorg. Chem.*, **4**, 1222 (1965)).

 TABLE IV  
 REACTIONS OF POLYNUCLEAR BASES WITH TRIETHYLALUMINUM

Reactant	Mole ratio triethylaluminum: base	Vol of toluene, ml	Recrystallization medium	Principal product	Mp, °C	
					or bp, °C (mm)	Yield, %
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PP(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	0.0123:0.00610	8	Hexane	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> PP(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	99-101	61
C <sub>2</sub> H <sub>5</sub> N[P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub>	0.00977:0.00977	5	Hexane	C <sub>2</sub> H <sub>5</sub> N[P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> ·Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	78-82	45
CH <sub>3</sub> N[P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub>	0.0113:0.00566	5	Hexane	CH <sub>3</sub> N[P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> ·Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	130-132	80
HN[P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub>	0.0246:0.0123	5	...	[(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> AlN{P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> }] <sub>2</sub>	189 dec	94
(CH <sub>3</sub> ) <sub>2</sub> CHNHP(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	0.0146:0.0146	...	Hexane	[(CH <sub>3</sub> ) <sub>2</sub> CHN{Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> }P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub>	189 dec	87
(CH <sub>3</sub> ) <sub>3</sub> CNHP(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	0.0197:0.0197	10	...	(CH <sub>3</sub> ) <sub>3</sub> CNHP(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	<i>a</i>	100
(CH <sub>3</sub> ) <sub>3</sub> CNHP(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ·Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	...	...	Benzene	(CH <sub>3</sub> ) <sub>3</sub> CN[Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ]P(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	166-167	96
(CH <sub>3</sub> ) <sub>2</sub> PP(CH <sub>3</sub> ) <sub>2</sub>	0.0143:0.0143	...	...	(CH <sub>3</sub> ) <sub>2</sub> PP(CH <sub>3</sub> ) <sub>2</sub> ·2Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	102 (0.15)	66
(CH <sub>3</sub> ) <sub>2</sub> NP(CH <sub>3</sub> ) <sub>2</sub>	0.0386:0.0386	5	...	(CH <sub>3</sub> ) <sub>2</sub> NP(CH <sub>3</sub> ) <sub>2</sub> ·Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	80.5 (0.06)	68
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NP(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	0.364:0.364	...	...	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NP(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> H	163 (2.4)	82

<sup>a</sup> Liquid thermally unstable.

that the point of attack is invariably the phosphorus rather than the nitrogen atom. It has been postulated that the free pair of electrons on the nitrogen atom is at least partially donated into the phosphorus d orbitals, giving the phosphorus atoms greater electron density and making them stronger electron donors than the nitrogen atoms.

The combination of infrared and nmr spectral data and chemical evidence thus strongly supports the postulation of a structure in which the phosphorus atoms are symmetrically located with respect to the aluminum atom and in which the aluminum atom is, therefore, pentacoordinate.

Studies have shown that hydrocarbon elimination occurs when electron donors, such as aminophosphines, containing a hydrogen atom bonded to the nitrogen atom are allowed to react with aluminum alkyls. The reaction of triethylaluminum with isopropylamino-diphenylphosphine yields a trimeric material, with the formula [(CH<sub>3</sub>)<sub>2</sub>CHN{Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>]<sub>2</sub>, after undergoing ethane elimination.

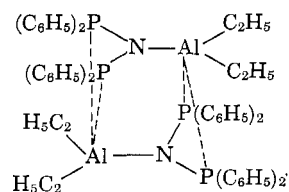
The reaction of *t*-butylaminodiphenylphosphine with triethylaluminum yields the molecular addition compound at room temperature. It is interesting to note that this adduct does not show the peak at 1120 cm<sup>-1</sup> in the infrared spectrum. This suggests that a normal

tetracoordinate phosphorus atom is not present in the molecule. If we examine the  $\Delta\tau$  values in Table III we note that, with the exception of the adducts of the bis(diphenylphosphino)amines, bonding of the aluminum atom to a phosphorus atom but not to a nitrogen atom leads to a value greater than unity; if the aluminum atom is bonded only to a nitrogen atom, the value of  $\Delta\tau$  is less than unity. This difference is in accord with the results of Cavanaugh and Dailey,<sup>17</sup> who showed that  $\Delta\tau$  may be correlated with the effective electronegativity of the group to which an ethyl group is bonded. For the *t*-butylaminodiphenylphosphine adduct, the  $\Delta\tau$  value of 1.06 combined with the absence of the 1120  $\text{cm}^{-1}$  bond in the infrared spectrum suggests that the aluminum atom may be bonded to both the nitrogen and the phosphorus atoms.

For the bis(diphenylphosphino)amine adducts, the bonding of the aluminum atom to both phosphorus atoms requires the ethyl groups attached to aluminum to be wedged between the phenyl groups attached to the phosphorus atoms. Consequently, the magnetic anisotropy of the phenyl groups would be expected to modify greatly the  $\Delta\tau$  value for the ethyl groups in these compounds.

When the *t*-butylaminodiphenylphosphine triethylaluminum adduct is warmed above room temperature a slow evolution of ethane begins. After the gas evolution has ceased the resulting compound has the formula  $(\text{CH}_3)_3\text{CN}[\text{Al}(\text{C}_2\text{H}_5)_2]\text{P}(\text{C}_6\text{H}_5)_2$ . This monomeric compound is in contrast to the trimeric compound formed in the reaction of isopropylaminodiphenylphosphine with triethylaluminum.

Ethane elimination also occurs in the reaction of bis(diphenylphosphino)amine with triethylaluminum. Molecular weight measurements on the resulting compound indicate that it exists as a dimeric species. An interesting conjecture concerning the structure of this dimer is to consider again the aluminum atom to be pentacoordinate, bonding to two phosphorus atoms from another monomeric species to form the dimer.



A model of this compound shows that the large size of the phosphorus atoms tends to cover or hide the nitrogen atoms. The infrared spectrum of this compound does not show the normal tetracoordinate phosphorus peak, so there is a good possibility that the aluminum atom is pentacoordinate in this compound.

Tetramethyldiphosphine combined with two molecules of aluminum triethyl yielding a product presumably containing two normal tetracoordinate aluminum atoms per molecule. Burg<sup>18</sup> has shown that tetramethyldiphosphine reacts with diborane to form both

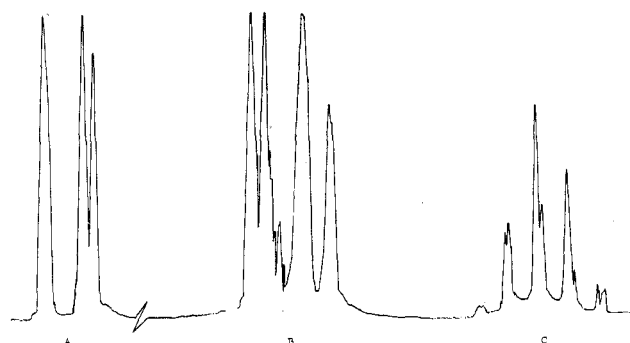


Figure 3.— $^1\text{H}$  nuclear magnetic resonance spectrum of  $(\text{CH}_3)_2\text{NP}(\text{CH}_3)_2 \cdot \text{Al}(\text{C}_2\text{H}_5)_3$  before heating. Peak A arises from the nitrogen-methyl protons, peak B from the phosphorus-methyl protons and the methyl protons of the ethyl groups, and peak C from the methylene protons of the ethyl groups.

the mono- and the diadducts,  $(\text{CH}_3)_2\text{PP}(\text{CH}_3)_2 \cdot \text{BH}_3$  and  $(\text{CH}_3)_2\text{PP}(\text{CH}_3)_2 \cdot 2\text{BH}_3$ . It is interesting to note that, in the reaction of tetramethyldiphosphine with triethylaluminum, the 1:1 molecular addition compound could not be isolated, under the conditions of our experiments. The fact that tetraphenyldiphosphine forms a 1:1 adduct with triethylaluminum and tetramethyldiphosphine forms a 1:2 adduct with triethylaluminum might be explained in terms of the greater basicity of tetramethyldiphosphine than of tetraphenyldiphosphine, resulting presumably from the electron-withdrawing effect of the phenyl groups and the opposite effect of the methyl groups. Models of the two bases, tetramethyldiphosphine and tetraphenyldiphosphine, indicate that steric factors are probably not critical.

The reactions of dimethylaminodimethylphosphine would be expected to be similar to the reactions of tetramethyldiphosphine because of structural similarities. Holmes and Wagner have shown that dimethylaminodimethylphosphine reacts with trimethyl- and triethylboron to form 1:1 adducts.<sup>19</sup> It has also been shown that dimethylaminodimethylphosphine reacts with diborane to form both the 1:1 and the 1:2 adducts,  $(\text{CH}_3)_2\text{NP}(\text{CH}_3)_2 \cdot \text{BH}_3$  and  $(\text{CH}_3)_2\text{NP}(\text{CH}_3)_2 \cdot 2\text{BH}_3$ .<sup>10</sup> In the work of Holmes and Wagner the reaction of trimethylboron with dimethylaminodimethylphosphine also produced products resulting from cleavage of the P-N bond, *viz.*,  $(\text{CH}_3)_2\text{NB}(\text{CH}_3)_2$  and  $(\text{CH}_3)_3\text{P} \cdot \text{B}(\text{CH}_3)_3$ .

The proton nuclear magnetic resonance spectrum for the 1:1 adduct, Figure 3, shows one extraneous peak in the region of the doublet peak assigned to the methyl groups attached to nitrogen. This spectrum should be compared with Figure 4, which is the spectrum of a product synthesized by the same method except that material was heated to about 50° for 24 hr prior to distillation. The boiling point and infrared spectrum of this material are virtually the same as those of the material shown to be the 1:1 adduct. The nmr spectrum shows a considerable difference, however. The intensity of the doublet peak which arises from the

(17) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1964).

(18) A. B. Burg, *J. Am. Chem. Soc.*, **83**, 2226 (1961).

(19) R. R. Holmes and R. P. Wagner, *ibid.*, **84**, 357 (1962).

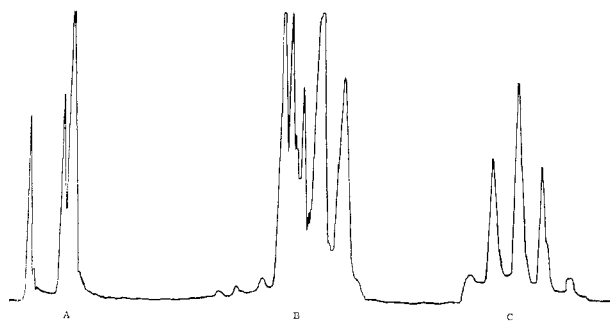


Figure 4.— $^1\text{H}$  nuclear magnetic resonance spectrum of  $(\text{CH}_3)_2\text{NP}(\text{CH}_3)_2 \cdot \text{Al}(\text{C}_2\text{H}_5)_3$  heated during synthesis. Peak A arises from the nitrogen-methyl protons, peak B from the phosphorus-methyl protons and the methyl protons of the ethyl groups, and peak C from the methylene protons of the ethyl groups.

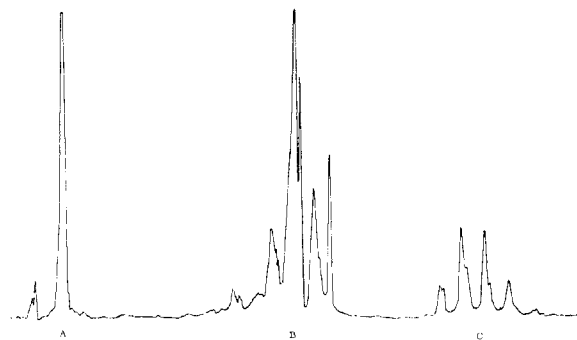


Figure 5.— $^1\text{H}$  nuclear magnetic resonance spectrum of  $(\text{CH}_3)_2\text{NP}(\text{CH}_3)_2 \cdot \text{Al}(\text{C}_2\text{H}_5)_3$  heated to  $50^\circ$  for 70 hr. Peak A arises from the nitrogen-methyl protons, peak B from the phosphorus-methyl protons and the methyl protons of the ethyl groups, and peak C from the methylene protons of the ethyl groups.

protons of the methyl group on nitrogen has decreased considerably in the heated sample and the extraneous singlet peak has increased markedly. Careful examination of the heated sample reveals a second doublet that in the original sample is hidden under the doublet caused by the methyl groups on phosphorus and under the triplet caused by the methyl portion of the ethyl groups. The  $^{31}\text{P}$  nmr spectrum shows the phosphorus peak of the heated material to have about the same chemical shift as the free base. This information leads one to postulate that the material produced in heating is an isomer in which the aluminum atom is bonded only to the nitrogen atom rather than to the phosphorus atom or to both the nitrogen and the phosphorus atoms. Whereas the  $\Delta\tau$  value of the heated sample is larger than the values found in other compounds having the aluminum atom bonded to the phosphorus atom, it is appreciably smaller than the value in the unheated sample. This difference is consistent with the postulated change from phosphorus to nitrogen bonding. If the aluminum atom is bonded to the nitrogen atom the availability of electrons at the nitrogen atom is reduced and we might predict that this would reduce the coupling of the nitrogen methyl protons with the phosphorus. This would account for the fact that the  $\text{N}-\text{CH}_3$  proton peak is a singlet.

On the basis of the above discussion the 1:1 adduct may be postulated to be a mixture which contains approximately 80% of the aluminum atoms bonded to phosphorus and 20% bonded to nitrogen. In order to determine the full extent of the effect of heat on this mixture a sealed tube containing a sample of the unheated 1:1 adduct was heated to  $70^\circ$ . The nmr spectrum of the sample was obtained at room temperature periodically during a 50-hr period. After 50 hr of heating, the singlet peak, Figure 5, had increased in size compared to the doublet peak to indicate a 95% concentration of the material postulated to contain an aluminum-nitrogen bond. The methylene group on aluminum is noted to be a pentet in Figures 3 and 4 but Figure 5 contains a quartet which is shifted downfield, indicating that the pentet is caused by the superposition of the two quartets.

It is possible that the kinetics of the initial reaction favors formation of the phosphorus-aluminum bond but that the nitrogen-aluminum bond is thermodynamically more stable. In any case, it is apparent that two products are being formed and that the product responsible for the anomalous peak is being generated as the mixture is heated.

The interaction of diethylaminodiphenylphosphine with triethylaluminum is very interesting inasmuch as a simple molecular addition compound is not obtained. The reaction proceeds with the elimination of a mixture of hydrocarbon compounds, ethylene being the only one positively identified. The proton nmr spectrum of the distilled product gives a great deal of information concerning this material. This spectrum indicates that there are two ethyl groups on the nitrogen atom, two ethyl groups on the aluminum atom, and two phenyl groups on the phosphorus atom. Heating the original reaction mixture for distillation might allow ethylene to be evolved by a known thermal reaction. The ethylene could then react with the aluminum-carbon bond in a growth reaction to form a variety of long-chain substituents on the aluminum atom. This product could then break down to yield olefins and the compound with two ethyl groups on the aluminum atom.

The fact that the aluminum atom contains only two ethyl groups coupled with the molecular weight determination which show the compound to be monomeric indicates that the product might be an odd-electron molecule. The magnetic moment of a sample of this compound was measured on the Gouy balance and it was found to be diamagnetic. The electron spin resonance spectrum confirmed the fact that there are no unpaired electrons. This leads us to postulate the presence of an unseen hydrogen atom. A careful check of the nmr data and the infrared spectrum does not reveal a single hydrogen atom such as in an  $\text{AlH}$ ,  $\text{NH}$ , or a  $\text{PH}$  group. A peak for H attached directly to an aluminum or nitrogen atom might, however, not be seen in the nmr spectrum. The spin of the aluminum nucleus is  $5/2$  and thus an  $\text{AlH}$  peak would be a multi-

plet resulting from coupling with the aluminum nucleus and this multiplet would be broadened by the quadrupole moment. An NH peak is often too broad to be seen for reasons similar to those given for the AlH peak. A PH proton resonance would probably be observed in the nmr spectrum because it is split by about 200–300 cps giving two peaks, and it is improbable that both peaks would be hidden. The solvolysis of a sample of this material does not produce hydrogen gas, indicating that there is no hydrogen bonded to aluminum. This

leads us to postulate the presence of a hydrogen atom attached to nitrogen. If the hydrogen atom were attached to the nitrogen atom, the molecule would be a zwitterion because the nitrogen and the phosphorus would each be charged.

**Acknowledgment.**—The authors gratefully acknowledge the receipt of a grant from the donors of the Petroleum Research Fund administered by the American Chemical Society.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA

## Reactions of Phenyl Azide or Hydrogen Azide and Chlorophosphines<sup>1</sup>

By R. K. BUNTING AND C. D. SCHMULBACH<sup>2</sup>

Received October 18, 1965

The phosphine imines  $C_6H_5NPCl_3$ ,  $C_6H_5NPCl_2C_6H_5$ , and  $C_6H_5NP(ClC_6H_5)_2$  have been prepared by the reaction of phenyl azide and the appropriate phosphine or phosphorus trichloride. Photolysis with ultraviolet light of hydrogen azide in phosphorus trichloride gives a viscous liquid with the stoichiometry  $P_3N_3Cl_9$  instead of the anticipated trichlorophosphine imine. Evidence in support of a linear structure for the compound  $P_3N_3Cl_9$  is given. Indirect evidence for the existence of a reactive trichlorophosphine imine intermediate in the photolysis reaction is discussed. Pyrolysis of the  $P_3N_3Cl_9$  polymer gives a new, highly polymeric compound with the stoichiometry  $P_3N_3Cl_9$  as well as trimeric and tetrameric cyclic chlorophosphonitriles and uncharacterized solids. Chlorodiphenylphosphine imine has been prepared from the photolytic reaction of hydrogen azide and chlorodiphenylphosphine in benzene. The strong tendency of this compound to dehydrochlorinate with the formation of phenyl-substituted phosphonitriles is described. A stable adduct,  $HN_3 \cdot PCl(C_6H_5)_2$ , has been isolated from the reaction that produced the chlorodiphenylphosphine imine.

### Introduction

Trichlorophosphine imine,  $HNPCl_3$ , has been proposed as a reactive intermediate in the formation of chlorophosphonitrile polymers from the reaction of ammonium chloride and phosphorus pentachloride.<sup>3,4</sup> There is a considerable body of indirect evidence to support the existence of trichlorophosphine imine and the related phosphine imines,  $HNPCl_2(C_6H_5)$  and  $HNPCl(C_6H_5)_2$ .<sup>5</sup> Whereas the reactions of primary amines (or their hydrochloride salts) with  $PCl_5$  in an inert solvent results in the formation of N-substituted trichlorophosphine imines with the elimination of hydrogen chloride,<sup>6</sup> the reaction of ammonia and ammonium chloride with phosphorus pentachloride results always in chlorophosphonitrile polymers.<sup>3,7</sup> All evidence suggests that for those phosphine imines which contain an imino functional group and a chloride func-

tional group, the stability of the compound is reduced or the chemical activity increased to such an extent that a rather facile dehydrochlorination occurs with the formation of polymeric linear or cyclic phosphonitriles.

The principal objective of this research was to prepare phosphine imines that contain the imino and chloro functional groups. A demonstration of the ease with which these phosphine imines would dehydrochlorinate and the conditions for this dehydrochlorination were sought.

The failure to isolate trichlorophosphine imine was thought to stem from the rather severe reaction conditions to which others had subjected the ammonium chloride–phosphorus pentachloride system. Reaction temperatures in excess of 150° were always employed. Since a reduction in reaction temperatures greatly enhances the probability of isolating a highly reactive species or one of low thermal stability, the reaction of phosphines and azides, which are known to give phosphine imines under mild conditions,<sup>8–10</sup> was considered a promising route for the synthesis of HN-containing chlorophosphine imines. (No phosphine imines containing both the imino and chloro functional groups have been reported.) Furthermore, photolysis of covalent azides produces a short-lived nitrene radical,

(1) Abstracted in part from the Ph.D. thesis of Roger K. Bunting, The Pennsylvania State University, Sept. 1965.

(2) Department of Chemistry, Southern Illinois University, Carbondale, Ill.

(3) N. L. Paddock and H. T. Searle, *Advan. Inorg. Chem. Radiochem.*, **1**, 347 (1959).

(4) M. Becke-Goehring and W. Lehr, *Z. Anorg. Allgem. Chem.*, **327**, 128 (1964).

(5) For a detailed summary see N. L. Paddock, *Quart. Rev.* (London), **18**, 168 (1964).

(6) I. N. Zhmurova and A. V. Kirsanov, *Zh. Obshch. Khim.*, **30**, 3044 (1960); *Chem. Abstr.*, **55**, 17551 (1961).

(7) C. P. Haber, "Inorganic Polymers," Special Publication No. 15, The Chemical Society, London, 1961, pp 115–146.

(8) H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 861 (1921).

(9) H. Staudinger and J. Meyer, *ibid.*, **2**, 635 (1919).

(10) L. Horner and A. Gross, *Ann.*, **591**, 117 (1955).