TABLE V
COMPARISON OF LOG K_1 VALUES FOR FORMATION OF THE FIRST PICOLINATO COMPLEX OF DIVALENT METAL IONS AT 25°

	log K_1	Medium	Author
Copper(II)	8.6	0.1 M NO_3^-	Suzuki, *et al.*[25]
Zinc(II)	5.12	0.1 M NO_3^-	Suzuki, *et al.*[25]
Cadmium(II)	4.36	0.1 M NO_3^-	Suzuki, *et al.*[25]
Lead(II)	4.82	0.1 M NO_3^-	Suzuki, *et al.*[25]
$(CH_3)_2Sn$(IV)	5.1	0.1 M NO_3^-	This work

picolinato complex is more stable than the phenanthroline complex because of the affinity of the dimethyltin(IV) ion for oxygen donors. The stability of the picolinato complex is not appreciably different from that of the lead(II) complex and probably is similar to that of the tin(II) complex. This is in accord with earlier observations that the dimethyltin(IV) and tin(II) ions exhibit similar chemical behavior.[12,26]

(25) K. Suzuki, M. Yasuda, and K. Yamasaki, *J. Phys. Chem.*, **61**, 229 (1957).
(26) E. G. Rochow, D. Seyferth, and A. C. Smith, Jr., *J. Am. Chem. Soc.*, **75**, 3099 (1953).

The properties of the $(CH_3)_2Sn^{+2}$ ion appear to be quite different from those of the $(CH_3)Hg^+$ ion, for the latter forms very stable complexes with nitrogen donors.[10] It is perhaps not surprising that there is no indication of back bonding in the phenanthroline complex of $(CH_3)_2Sn^{+2}$, since the dimethyltin(IV) ion has a net charge of +2. The d orbital contraction caused by this charge also is abetted by the rather high effective nuclear charge acting on the 4d orbitals. On the other hand, these are just the characteristics which confer a large polarizing power on an ion, and it seems likely that it is this property which leads to stable complexes with sulfur donors. This subject has been reviewed by Parry and Keller,[27] and recently Williams[28] has discussed the stability of complexes of the alkyltin(IV) ions and sulfur donors in terms of these concepts.

(27) R. W. Parry and R. N. Keller, "Chemistry of the Coördination Compounds," J. C. Bailar, Jr., Ed., Reinhold Publishing Co., New York, N. Y., 1956, Chapter 3.
(28) R. J. P. Williams, *Proc. Chem. Soc.*, 20 (1960).

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Chemistry of Ethylenimines. X. Reactions with Phosphorus Nitrilochloride Trimer[1]

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Received June 14, 1962

The stereochemistry of two aziridine derivatives of $(PNCl_2)_3$ has been determined by n.m.r. Geminal chlorines in the trimer are replaced by two and four ethylenimino groups, respectively, following the behavior of a weak nucleophile like *p*-toluidine. This behavior is in contrast to that of the more closely related dimethylamine, which replaces chlorine on successive phosphorus atoms. The stereochemistry of other derivatives is correlated with the two established by n.m.r.

The stereochemistry of derivatives of the trimer of phosphonitrilic chloride, $(PNCl_2)_3$, was suggested for phenyl derivatives obtained by Friedel-Crafts reactions in 1942[2] and for aryl amino derivatives in 1948.[3] These substitutions were established as being for geminal chlorines in the phenylation experiments and Bode suggested the same structure for the aryl amino compounds. Non-geminal substitution has been confirmed for reactions of the trimer with ammonia, methylamine, and dimethylamine by phosphorus nuclear magnetic resonance spectra[4] and by proton n.m.r. in the case of the latter reagent.[5]

The present work establishes the structure of the di- and tetraaziridinyl derivatives, II and IV, by n.m.r. spectra on the P^{31} nucleus by the argument that follows.

It would be expected that the trimer, $(PNCl_2)_3$, and the hexaaziridinyl derivative, VI, would exhibit single peaks in the n.m.r. spectra since they contain a single type of phosphorus atom. The chemical shift of the $(PNCl_2)_3$ peak, relative to orthophosphoric acid, the standard, was measured as 19 ± 1 p.p.m., exactly the figure given by Becke-Goehring[4] for this compound.

Since phosphorus bonded to nitrogen exhibits a greater chemical shift than phosphorus bonded to chlorine,[4] one would predict that the relative positions of peaks in the n.m.r. spectra would be about the same for geminal substitution of two aziridine groups as for non-geminal substitution (Fig. 2). However, the relative intensities of the peaks would be reversed due to the difference in environment of the P atom in the two cases. In geminal substitution, there are one $\equiv PN_2$ and two $\equiv PCl_2$ groups (ratio 0.5); but two $\equiv PNCl$ and one $\equiv PCl_2$ groups (ratio 2.0) for non-geminal substitution. Experimentally the ratios of areas under the peaks was about 0.6–0.9 for the diaziridinyl derivative, suggesting geminal substitution.

(1) The work was supported by Public Health Service Grant CY-3092.
(2) H. Bode and H. Bach, *Chem. Ber.*, **75B**, 215 (1942); R. A. Shaw and F. B. G. Wells, *Chem. Ind.* (London), 1189 (1960).
(3) H. Bode, *Angew. Chem.*, **60**, 67 (1948); H. Bode, K. Bütow, and G. Lienau, *Chem. Ber.*, **81**, 547 (1948).
(4) M. Becke-Goehring, K. John, and E. Fluck, *Z. anorg. allgem. Chem.*, **302**, 103 (1959); M. Becke-Goehring and K. John, *Angew Chem.*, **70**, 657 (1958).
(5) S. K. Ray and R. A. Shaw, *J. Chem. Soc.*, 872 (1961), reporting the work of R. F. M. White.

In the tetraaziridinyl derivative, the same shifts would be expected for geminal substitution but the intensities as reflected by areas under the peaks should be in reverse ratio (2.0 for geminal substitution and 0.5 for non-geminal substitution). Experimentally the area ratio was about 1.7. Furthermore, addition of $(PNCl_2)_3$ to the tetraaziridinyl sample enhanced the relative size of the nearer peak ($\equiv PCl_2$). The n.m.r. spectra therefore give very strong evidence that ethylenimine substitutes for geminal chlorines in both cases and the structures are IIa and IV.

In view of the close structural relationship of ethylenimine and dimethylamine, the difference in their behavior in the reaction with $(PNCl_2)_3$ may be noted. Ethylenimine is known[6] to be a weaker base than ammonia, methylamine, and dimethylamine, but no quantitative measure of its nucleophilic strength is available. If strong nucleophiles replace chlorines on successive phosphorus atoms as is argued,[4,5,7] then ethylenimine must be called a weak nucleophile.

Five of the six possible compounds of formula $P_3N_3Cl_{6-n}(N\langle CH_2 \rangle)_n$, where $n = 1$, 2, 4, 5, and, 6 were prepared in the course of this work (numbered I, II, IV, V, and, VI for subsequent discussion). Previously no one had prepared a penta-substituted derivative of $(PNCl_2)_3$.

TABLE I

N.M.R. SPECTRA

Compound	$\equiv PCl_2$ shift[a]	$\equiv PN_2$ shift[a]
$(PNCl_2)_3$	-19 ± 1	
$P_3N_3Cl_4(N\langle CH_2 \rangle)_2$	-22 ± 1	-34 ± 1
$P_3N_3Cl_2(N\langle CH_2 \rangle)_4$	-24 ± 1	-35 ± 1

[a] Shift given in parts per million, reference H_3PO_4; solvent, CS_2.

Recently Russian workers have reported melting points for all members of the series with aziridine,[8a] morpholine,[8b] pyrrolidine,[8c] and piperidine.[9] They report three isomers of IV, which is incompatible with the present results only if geminal substitution is exclusive. The yields of pure products in the aminolysis reactions are not high enough to exclude non-geminal substitution. The Russian workers did not identify the three isomers and we were unable to reproduce their work without experimental details; they gave no analysis.

(6) C. E. O'Rourke, L. B. Clapp, and J. O. Edwards, *J. Am. Chem. Soc.*, **78**, 2159 (1956); W. G. Barb, *J. Chem. Soc.*, 2564 (1955).

(7) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962).

(8) (a) A. A. Kropacheva and L. E. Mukhina, *Zh. Obshch. Khim.*, **31**, 2437 (1961); (b) **32**, 521 (1962); (c) **32**, 652 (1962).

(9) A. A. Kropacheva, L. E. Mukhina, N. M. Kashnikova, and B. A. Parshina, *ibid.*, **31**, 1036 (1961).

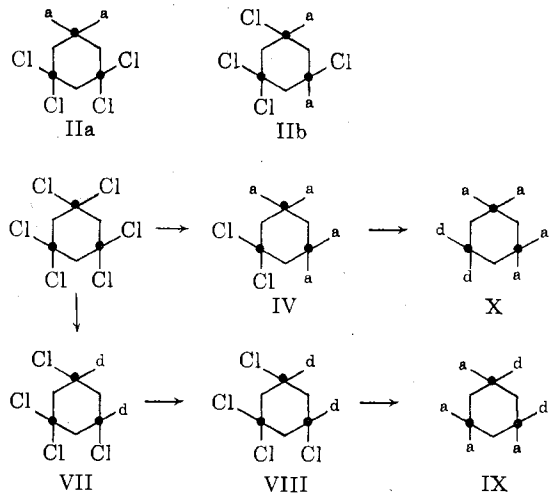

Fig. 1.—$(PNCl_2)_3$ derivatives are pictured with a dot for P, other vertices of the hexagon for N, a represents ethylenimine (aziridine), d represents dimethylamine, and Cl chlorine.

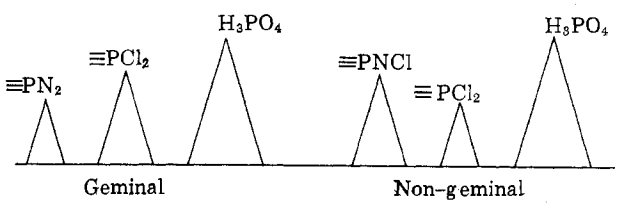

Fig. 2.—Schematic diagram of expected chemical shifts on P^{31} in $(PNCl_2)_3$ derivatives with respect to H_3PO_4 as standard.

The assigned structures of II and IV are compatible with interrelated assignments of Becke-Goehring[4] and Shaw.[5] When $(PNCl_2)_3$ was treated with dimethylamine to give the non-geminal bis-derivative, VII, and this in turn with ethylenimine, the final product, IX, was an isomer of X, obtained by the reverse order of addition.

In another series of reactions mixed *p*-toluidinyl–aziridinyl derivatives XI to XIV were obtained but unfortunately compound IV could not be converted to tetraethylenimido-bis-*p*-toluidotriphosphonitrile, XIV, directly as a further cross-check on the assigned structure of IV. Neither the unreactivity of the remaining two halogens in IV nor the low reactivity of *p*-toluidine can be offered as an explanation for this failure since the hexa-substituted *p*-toluidine derivative has long been known.[10]

Difficulty in substituting the last two halogens in tris-dimethylamidotrichlorotriphosphonitrile, XV, also was encountered in reaction with ethylenimine since only a monoaziridinyl derivative, XVI, could be obtained.

Experimental[11]

Monoethylenimidopentachlorotriphosphonitrile (I).—To an ice-cold solution of 41 mmoles of $(PNCl_2)_3$ and 14 mmoles of

(10) A. W. Hofmann, *Ber.*, **17**, 1909 (1884).

(11) Melting points are corrected. Analyses were carried out by the Microchemical Laboratory, MIT, Cambridge, Mass. Generous supplies of triphosphonitrilochloride were made available to us by the Hooker Electrochemical Company, Niagara Falls, N. Y. A Varian nuclear magnetic resonance spectrometer operating at a fixed frequency of 24.3 Mc. was used to measure the phosphorus-31 spectra.

triethylamine in 100 ml. of benzene, a solution of 14 mmoles of ethylenimine in 50 ml. of benzene was added dropwise with stirring. The reaction mixture was kept at 10° overnight and then allowed to stand at room temperature for 48 hr. After removing the triethylamine hydrochloride by filtration, the solvent was removed *in vacuo* at room temperature. The residue was washed with water, taken up in benzene, and dried with Na_2SO_4. Heptane precipitated 4.15 g. (81%) of colorless prisms (I), m.p. 69–70°, from the benzene solution; reported[8a] m.p. 68–70°. An analytical sample was recrystallized from the benzene-heptane solvent pair.

Anal. Calcd. for $C_2H_4N_4P_3Cl_5$: C, 6.77; H, 1.12; N, 15.82. Found: C, 6.70; H, 1.08; N, 15.58.

To show that compound I was not a molecular compound of $(PNCl_2)_3$ and II (below) which would result in the same analysis, the molecular compound was prepared by allowing equimolar quantities of the two to crystallize from benzene. This substance had a sharp melting point of its own, 86°.

Although the procedures for compounds II, IV, and V appear to be closely analogous to that just given for I, the volumes of solvent, solvent mixtures, temperature, and other details of procedure are critical for these compounds. Compounds I and V are especially sensitive to conditions and easily changed to polymeric materials.

Bis-ethylenimidotetrachlorotriphosphonitrile (II).—A solution of 41 mmoles of ethylenimine in 20 ml. of anhydrous ether was added dropwise to a solution of 10 mmoles of $(PNCl_2)_3$ in 30 ml. of anhydrous ether while the stirred solution was kept below 10°. After standing overnight at room temperature, the imine hydrochloride (possibly a polymer) was removed by filtration and the product obtained in a similar manner to I (above). Colorless prisms (1.41 g., 38%), m.p. 105°, were obtained from ether and a small amount of heptane; reported[8a] m.p. 104–105.5°.

Anal. Calcd. for $C_4H_8N_5P_3Cl_4$: C, 13.30; H, 2.21; N, 19.39. Found: C, 13.72; H, 2.21; N, 19.29.

All attempts to convert compound II into a triethylenimido compound (III) with 1 mole of ethylenimine and 1 mole of triethylamine resulted only in sirups that could not be induced to crystallize or in intractable polymers. Larger amounts of ethylenimine converted II into crystalline IV (below).

Tetraethylenimidodichlorotriphosphonitrile (IV).—A solution of 10 mmoles of $(PNCl_2)_3$ in 40 ml. of anhydrous ether was treated with 82 mmoles of ethylenimine in 40 ml. of anhydrous ether in the same way as described for II. Colorless prisms (1.32 g., 35%), m.p. 131°, were obtained from benzene and heptane.

Anal. Calcd. for $C_8H_{16}N_7P_3Cl$: C, 25.66; H, 4.27; N, 26.20. Found: C, 25.33; H, 4.10; N, 26.72.

Kropacheva and Mukhina[8a] reported three isomers without details of isolation of m.p. 99–101°, 114–115°, and 129–130°.

Pentaethylenimidomonochlorotriphosphonitrile (V).—A solution of 10 mmoles of $(PNCl_2)_3$ and 50 mmoles of triethylamine in 70 ml. of dry benzene was allowed to stand for 10 days at room temperature. The mixture was warmed for 2 hr. at 55° and then cooled. The same work-up previously given to compound I gave 1.7 g. (40%) of colorless prisms, m.p. 122°; reported[8a] m.p. 108–109°. The compound was recrystallized from benzene and heptane for the analytical sample.

Anal. Calcd. for $C_{10}H_{20}N_8P_3Cl$: C, 31.51; H, 5.25; N, 29.43. Found: C, 31.04; H, 5.05; N, 29.14.

Bis-ethylenimido-bis-dimethylamidodichlorotriphosphonitrile (VIII).—A dry benzene (20 ml.) solution of 1.5 mmoles of bis-dimethylamidotetrachlorotriphosphonitrile,[4] m.p. 102–103°, was cooled to 10° and a solution of 1.5 mmoles of ethylenimine in 20 ml. of benzene was added in 20 min. After stirring continuously for 6 hr. at room temperature, the imine salt was removed and the solution was concentrated by removing benzene *in vacuo*. The residue was recrystallized from ligroin to give 0.22 g. (41%) of colorless needles, m.p. 121°.

Anal. Calcd. for $C_8H_{20}N_7P_3Cl_2$: C, 25.39; H, 5.29; N, 25.92. Found: C, 25.68; H, 5.12; N, 26.22.

Tetraethylenimido-bis-dimethylamidotriphosphonitrile (IX).—By using a twofold excess of ethylenimine on the bis-dimethylamidotetrachlorotriphosphonitrile[4] and allowing it to stand at room temperature for 1 week, the fully substituted derivative was obtained by a procedure similar to the one described for VIII. An analytical sample of colorless needles, m.p. 99–101°, was obtained from ligroin.

Anal. Calcd. for $C_{12}H_{28}N_9P_3$: C, 36.83; H, 7.15; N, 32.22. Found: C, 37.19; H, 7.33; N, 31.38.

X.—Tetraethylenimidodichlorotriphosphonitrile (IV) (2 mmoles) was allowed to stand 1 week at room temperature with 2 mmoles of triethylamine and 4 mmoles of dimethylamine in dry benzene. The solution was kept at 60° for 3 hr. and then worked up as described for compound VIII above. The product, an isomer of IX, was recrystallized from benzene and heptane to give 0.42 g. (57%) of colorless prisms, m.p. 129–130°.

Anal. Calcd. for $C_{12}H_{28}N_9P_3$: C, 36.83; H, 7.15; N, 32.22. Found: C, 36.33; H, 7.44; N, 31.75.

Tetrachloro-bis-*p*-toluididotriphosphonitrile (XI).—A solution of 10 mmoles of *p*-toluidine in 250 ml. of anhydrous ether was added dropwise to a solution of 5 mmoles of $(PNCl_2)_3$ and 10 mmoles of triethylamine in 100 ml. of anhydrous ether. After standing 3 days at room temperature the ether was removed *in vacuo* and the sirupy residue was washed with dilute acetic acid and water in turn. The residue was dissolved in ether and dried over Na_2SO_4. Removal of the ether and recrystallization from ligroin gave 0.081 g. (33%) of colorless needles, m.p. 138°.

Anal. Calcd. for $C_{14}H_{16}N_5P_3Cl_4$: C, 34.35; H, 3.29; N, 14.31. Found: C, 34.56; H, 3.37; N, 14.03.

Diethylenimidotetra-*p*-toluidotriphosphonitrile (XIII).—The hexa-substituted compound (XIII) was obtained from dichlorotetra-*p*-toluidotriphosphonitrile[3b] (XII) in benzene overnight at room temperature by the procedure described for VIII above. Colorless needles, m.p. 222°, were obtained from benzene in 95% yield.

Anal. Calcd. for $C_{32}H_{40}N_9P_3$: C, 59.72; H, 6.22; N, 19.59. Found: C, 59.72; H, 6.28; N, 19.56.

Tetraethylenimido-bis-*p*-toluidotriphosphonitrile (XIV).—By the method used for XIII but with a 3-day reaction time after initial mixing of reactants below 10°, an 84% yield of compound XIV was obtained from XI; m.p. 154°, fine needles from hot benzene.

Anal. Calcd. for $C_{22}H_{32}N_9P_3$: C, 51.26; H, 6.21; N, 24.46. Found: C, 51.11; H, 6.26; N, 24.20.

Ethylenimido-tris-dimethylamidomonochlorotriphosphonitrile (XIV).—Treatment of tris-dimethylamidotrichlorotriphosphonitrile[4] with an eightfold excess of ethylenimine in dry benzene overnight gave 37% of the monoethylenimido derivative but extended treatment for as long as 1 week gave no triethylenimido derivative. The product was recrystallized from benzene and heptane giving colorless plates, m.p. 90–91°.

Anal. Calcd. for $C_8H_{22}N_7P_3Cl_2$: C, 25.26; H, 5.79; N, 25.79 Found: C, 25.58; H, 5.70; N, 25.69.

Acknowledgment.—The authors are grateful to Dr. J. F. Neumer for valuable conversations and interpretation of the n.m.r. spectra and to Mr. Henry Klos for technical assistance in taking the spectra.