TABLE VI

COMPARISON OF DECOMPOSITION RATES OF DINUCLEAR METAL ION COMPLEXES

Mode of formation	Dinuclear ion	Specific decompn. rate (25.0°), sec.$^{-1}$	Ref.	log *k* for form. of SCN$^-$ complex[a]
Cr(IV) + Cr(II) and Cr(III) + OH$^-$	CrOHCr^{5+} [b]	1.5×10^{-6} [c]	5	Cr(III), −5.7
Np(VI) + Cr(III) and Np(V) + Cr(II)	NpO$_2$Cr^{4+}	2.3×10^{-6}	*e*	Cr(III),[d] −5.7
V(IV) + V(II) and V(III) + OH$^-$	VOV^{4+}	$0.03 + 1.54[H^+]$	7	V(III), +1.8
V(IV) + Cr(II)	VO(OH)$_n$Cr^{4-n}	$0.018 + 0.645[H^+]$	This work	V(III), +1.8
Fe(IV) + Fe(II) and Fe(III) + OH$^-$	FeOFe^{4+}	$0.35 + 3.5[H^+]$	9	Fe(III), +2.1

[a] These entries represent rates of the second-order reaction of M^{3+} and SCN$^-$; they are values of log *k* (M^{-1} sec.$^{-1}$). Values from ref. 15. [b] The ion CrOHCr^{5+} is not the species formed directly in either reaction, but it is the immediate precursor of Cr^{3+} (ref. 5). [c] In 2.1 *F* HClO$_4$. [d] Cr(III) is more labile than Np(VI) as judged by the rates of H$_2$O exchange [Cr(III), J. P. Hunt and R. A. Plane, *J. Am. Chem. Soc.*, **76**, 5960 (1954); **79**, 3343 (1957); Np(VI), S. W. Rabideau and B. J. Masters, *J. Phys. Chem.*, **67**, 2655 (1963)]. [e] J. C. Sullivan, *Inorg. Chem.*, **3**, 315 (1964).

reduction reactions of aquo ions. These systems appear unique not so much for the reason that dinuclear intermediates exist, but rather that the intermediates in these cases have lifetimes sufficiently long (except FeOFe^{4+}) to be detected by conventional techniques.

To a first approximation the rates of dimer decomposition correlate with the substitution lability of the more labile metal ion component. Table VI compares the rates of decomposition of the intermediates with lability, where the rate[15] of entry of SCN$^-$ in the first coordination sphere of the more labile metal ion component is taken as a measure of the relative substitution lability of the hydrated metal ions.

Acknowledgment.—The author is grateful to Dr. T. W. Newton for helpful discussions of this work and to Drs. R. H. Moore and T. W. Newton for the computer programs used in this study, based on the report from Los Alamos Scientific Laboratory, LA 2367 + addenda.

(15) M. Eigen and R. G. Wilkins in preprints of "Mechanisms of Inorganic Reactions," a symposium sponsored by the American Chemical Society, Lawrence, Kans., June 1964, p. 75.

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Phenylphosphonitriles. II. Friedel–Crafts Reactions of 2,4,6-Trichloro-2,4,6-triphenyltriphosphonitrile with Benzene

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Reaction of *trans*-2,4,6-trichloro-2,4,6-triphenyltriphosphonitrile with benzene in the presence of AlCl$_3$ can be adjusted to give good yields of 2,4-dichloro-2,4,6,6-tetraphenyltriphosphonitrile or 2-chloro-2,4,4,6,6-pentaphenyltriphosphonitrile. Both *cis* and *trans* isomers can exist for the dichloro compound. These have been isolated and structural assignments have been made. No phenylation of the trichloro compound occurred when FeCl$_3$ or SnCl$_4$ was substituted for AlCl$_3$. Both the *cis* and *trans* isomers of 2,4,6-trichloro-2,4,6-triphenyltriphosphonitrile can be readily isomerized to mixtures of the two by refluxing with FeCl$_3$ in benzene or with AlCl$_3$ in CS$_2$. Mixtures of all reported phenylphosphonitriles can be analyzed readily by proton n.m.r. spectroscopy applied to their dimethylamido derivatives.

Introduction

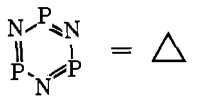
Reaction of phosphonitrilic chloride trimer with benzene in the presence of anhydrous AlCl$_3$ was first carried out by Bode and Bach.[1] They obtained good yields of 2,2-diphenyl-4,4,6,6-tetrachlorotriphosphonitrile, but were unable to substitute the phosphonitrilic ring further. More recently, Shaw and Wells[2] found that under the same experimental conditions as employed by Bode and Bach but with longer reflux

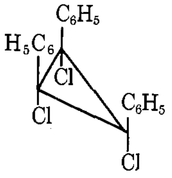
(1) H. Bode and H. Bach, *Ber.*, **75B**, 215 (1942).

(2) (a) R. A. Shaw and F. B. G. Wells, *Chem. Ind.* (London), 1189 (1960); (b) K. G. Acock, R. A. Shaw, and F. B. G. Wells, *J. Chem. Soc.*, 121 (1964).

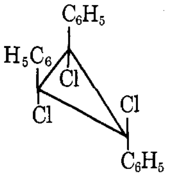
times of up to 6 weeks, further substitution of the ring could be effected. Low yields (16%) of 2,2-dichloro-4,4,6,6-tetraphenyltriphosphonitrile were obtained. More drastic conditions, in a bomb under pressure and heating for 48 hr. at 150°, gave, finally, hexaphenyltriphosphonitrile in 20% yield.

Recently the synthesis and identification of the *cis* and *trans* isomers of 2,4,6-trichloro-2,4,6-triphenyltriphosphonitrile (I) was reported.[3] The present work reports results obtained upon Friedel–Crafts phenylation of both isomers of I.





cis–I



trans–I

Experimental

Materials.—$(C_6H_5PNCl)_3$ was prepared as described previously.[3] Benzene and other solvents were dried over CaH_2 prior to use. Metal halides were anhydrous and of reagent grade.

Analyses.—Microanalyses were performed by Chemco, Inc., Washington, D. C.

Instrumental Studies.—Phosphorus-31 and proton nuclear magnetic resonance spectra were obtained on a Varian DP60 high resolution instrument. Chloroform was the solvent for obtaining P^{31} spectra, at 15.1 Mc., and referred to 85% H_3PO_4 (external). Carbon tetrachloride was the solvent for obtaining proton spectra at 60 Mc., and referred to tetramethylsilane (internal).

X-Ray diffraction data for *cis*-$(C_6H_5)_4P_3N_3Cl_2$ were obtained from a crystal about 0.2 mm. in diameter using a Buerger precession camera. Powder diffraction patterns were obtained by mixing the powders in a slurry of ethyl cellulose and toluene, rolling the mixture into a fiber, allowing this to dry, then centering the fiber in a 114-mm. Debye–Scherrer camera. Diffraction angles were measured to the nearest 0.05° 2θ and intensities were estimated visually.

Phenylation of *trans*-$(C_6H_5PNCl)_3$ with $AlCl_3$: Synthesis of $(C_6H_5)_4P_3N_3Cl_2$.—A mixture of 10 g. (0.0210 mole) of *trans*-$(C_6H_5PNCl)_3$, m.p. 155–157°, 300 ml. of dry benzene, and 60.02 g. (0.4500 mole) of anhydrous $AlCl_3$ was stirred and refluxed. Evolved HCl was swept into a watertrap with a stream of dry nitrogen, then titrated at intervals with standard NaOH. Initial HCl evolution at reflux was very rapid. After 75 min., however, the rate of HCl evolution had slowed considerably; the $AlCl_3$ and associated complexes had formed an insoluble oil after 35 min. An additional 15.0 g. (0.1124 mole) of $AlCl_3$ was added. After another 30 min. of refluxing the $AlCl_3$ again had been transformed into an oil, and the rate of HCl evolution slowed. At this time, almost 2 hr. of reflux, 0.012 mole of HCl had been evolved. A third aliquot of 15.0 g. (0.1124 mole) of $AlCl_3$ was added and the mixture stirred and refluxed another 50 min. (total HCl evolved, 0.01994 mole). Finally 10.0 g. (0.0750 mole) of $AlCl_3$ was added and the mixture heated an additional 20 min. After a total 3.0 hr. of reflux, 0.0239 mole of HCl had been evolved, and 0.75 mole of $AlCl_3$ had been added.

The oil–benzene mixture was poured into a mixture of ice, water, and 1 *N* HCl. The mixture was shaken well, the layers were separated, and the aqueous layer was extracted several times with benzene. The combined benzene portions were dried over $MgSO_4$. The mixture was then filtered and the filtrate evaporated under reduced pressure. There was obtained 10.66 g. of a very light cream-colored solid. This was recrystallized from 200 ml. of cyclohexane using Norite-A decolorizing charcoal. This gave 3.82 g. of solid (A), m.p. 180–190°. Recrystallization from $CHCl_3$–pentane gave large hexagonal crystals, m.p. 195–196°, of *cis*-$(C_6H_5)_4P_3N_3Cl_2$.

Concentration of cyclohexane filtrate A to about 75 ml., followed by cooling, gave 3.65 g. of solid (B), m.p. 164–166°. Recrystallization from cyclohexane, then $CHCl_3$–pentane, gave tiny crystals, m.p. 169–170°, of *trans*-$(C_6H_5)_4P_3N_3Cl_2$.

Dilution of filtrate B with pentane to about 250 ml. and chilling gave 2.04 g. of solid (C), m.p. 150–175°. Slow recrystallization of solid C from cyclohexane at room temperature gave 0.38 g. of crude *cis*-dichloro material, m.p. 185–189°. Dilution of this filtrate with pentane followed by chilling gave 1.02 g. of solid solution no. 1, m.p. 151–158°. Further recrystallizations from a variety of solvents failed to change the broad melting point range. The infrared spectrum of this material was identical with those of the *cis*- and *trans*-dichloro isomers.

In a similar synthesis beginning with 50 g. (0.106 mole) of *trans*-$(C_6H_5PNCl)_3$, during which 3.42 moles of $AlCl_3$ was added in four portions, there was obtained a 60% yield of $(C_6H_5)_4P_3N_3Cl_2$, less than 10% yield of $(C_6H_5)_5P_3N_3Cl$, and 3.77 g. of solid solution no. 2, m.p. 170–175°, consisting of *cis* and *trans*-dichloro material.

Synthesis of $(C_6H_5)_5P_3N_3Cl$.—To a solution of 50 g. (0.106 mole) of *trans*-$(C_6H_5PNCl)_3$ in 1 l. of anhydrous benzene was added 280 g. (2.10 moles) of anhydrous $AlCl_3$ with an additional 0.5 l. of benzene. The mixture was stirred and refluxed 5 days, during which time 0.105 mole of HCl was evolved. Destruction of the metal halide and complexes followed by the procedures as described before gave 57.6 g. of crude product which, when recrystallized from $CHCl_3$–pentane, gave an 89% yield of $(C_6H_5)_5P_3N_3Cl$, m.p. 150–152°. An analytical sample melted at 152–154°.

Other syntheses reported in Table I were carried out similarly. Analytical data for these new phenylphosphonitriles are given in Table II.

Attempted Syntheses Using $FeCl_3$ or $SnCl_4$.—A mixture of 5.00 g. (0.0105 mole) of *trans*-$(C_6H_5PNCl)_3$, 200 ml. of benzene, and 5.11 g. (0.0315 mole) of anhydrous $FeCl_3$ was stirred and refluxed as before. HCl evolution did not begin until after 2.75 hr. of reflux, and then it was very slow. After 5 hr., only 0.0020 mole of HCl had evolved. During the next 16 hr., two 0.0105-mole portions of $FeCl_3$ were added. After 0.016 mole of HCl had been collected, the complexes were destroyed and the crude product processed as before. There was recovered 4.51 g. of *trans*-$(C_6H_5PNCl)_3$, plus 0.22 g. of material, m.p. 180–185°. This was dimethylaminated and identified by proton n.m.r. spectroscopy as *cis*-$(C_6H_5PNCl)_3$.

In another experiment 28.0 g. (0.1724 mole) of anhydrous $FeCl_3$ was added to 150 ml. of benzene and the mixture stirred and refluxed 3 hr. and 10 min. HCl was evolved after 20 min., and a total of 59.05 mmoles of HCl was evolved. The mixture was quenched in water–ice–HCl and processed as before. After distillation of the benzene solvent, continued distillation of the residue yielded 5.16 g. (45.8 mmoles) of chlorobenzene, b.p. 131°, identified by infrared spectroscopy.

The use of anhydrous $SnCl_4$ produced similar results.

Synthesis of Dimethylamido Derivatives.—A solution of 1.50 g. of *cis*-$(C_6H_5)_4P_3N_3Cl_2$ in 25 ml. of anhydrous benzene was added dropwise to a well-agitated solution of excess dimethylamine in benzene. The mixture was stirred 2 hr. at room temperature and filtered. The $(CH_3)_2NH\cdot HCl$ weighed 0.44 g. (92% of that expected for disubstitution). The filtrate was evaporated to dryness at reduced pressure and the residual solid taken up in cyclohexane. The solution then was decolorized with charcoal, the mixture filtered, and the filtrate diluted to the cloud point with pentane. There crystallized 0.05 g. of *cis*-$(C_6H_5)_4P_3N_3[N(CH_3)_2]_2$, m.p. 145–146°. Evaporation of the filtrate gave a solid which on recrystallization from heptane gave 1.14 g. (77% total yield) of the bisdimethylamide, m.p.

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[3] B. Grushkin, M. G. Sanchez, and R. G. Rice, *Inorg. Chem.*, **3**, 623 (1964).

TABLE I
PHENYLATION OF *trans*-$(C_6H_5PNCl)_3$ IN BENZENE

G. of $(C_6H_5PNCl)_3$	Mole ratio $AlCl_3$/$(C_6H_5PNCl)_3$	Mole equiv. of HCl evolved	Time to evolve HCl	% yield $(C_6H_5)_4P_3N_3Cl_2$	% yield $(C_6H_5)_5P_3N_3Cl$
5	15	0.98	52 hr.	0	68.5
50	15	1.0	9 days	0	72
50	20	0.88	5 days	0	89
10	35[a]	1+	3 hr.	87.5	0
50	32[a]	1+	5.5 hr.	60	<10

[a] $AlCl_3$ was added in four approximately equal portions as HCl evolution became slow.

145–145.5°. Other dimethylamides described in Table III were prepared similarly.

When the same procedure was applied to 1.50 g. of *cis*-$(C_6H_5PNCl)_3$, 64% of the $(CH_3)_2NH \cdot HCl$ expected for trisubstitution was obtained. Two crops of needles were isolated, the first weighing 0.20 g., m.p. 125–126°, the second weighing 0.10 g. The bulk of this second crop consisted of small needles, m.p. 124.5–125.5°. However, two very large needles were separated mechanically and found to melt at 110–115°. Elemental analysis showed that the higher melting material is $(C_6H_5)_3P_3N_3Cl[N(CH_3)_2]_2$, whereas the lower melting material is $(C_6H_5)_3P_3N_3Cl_2N(CH_3)_2$.

Repeating this same synthesis, except that the reaction mixture was heated 2 hr. at 50–60°, produced 96.5% of the $(CH_3)_2NH \cdot HCl$ expected for trisubstitution; however, only a 38% yield of product, m.p. 113.5–115°, was recovered. This analyzed well for *cis*-$[C_6H_5PNN(CH_3)_2]_3$.

Dimethylamination of mixtures of *cis*- and *trans*-$(C_6H_5)_4P_3N_3Cl_2$ for proton n.m.r. analysis followed essentially the same procedure. Quantitative yields of $(CH_3)_2NH \cdot HCl$ were obtained. The mixture was filtered, and the filtrate was decolorized with charcoal and evaporated to dryness. The residue was taken up in spectrographic grade CCl_4 and adjusted to a solid content of about 20%, then examined by proton n.m.r. spectroscopy.

Isomerizations Catalyzed by Metal Halides.—To a solution of 2.0 g. of *trans*-$(C_6H_5PNCl)_3$, m.p. 155–157°, in 100 ml. of anhydrous benzene was added 2.07 g. of anhydrous $FeCl_3$. The mixture was stirred and refluxed 24 hr. under a nitrogen atmosphere. During this time 3.05 mequiv. of HCl was evolved. The complexes were destroyed as before and the crude product dimethylaminated as described above. Examination of a CCl_4 solution of this material by proton n.m.r. spectroscopy showed the complete absence of any tetraphenylbisdimethylamide. On the other hand, both *cis*- and *trans*-triphenyltrisdimethylamides were present, and in the relative proportions 35 and 65%, respectively. These data are reported as expt. no. 6 of Table VIII.

A mixture of 2.0 g. of *cis*-$(C_6H_5PNCl)_3$, 100 ml. of anhydrous CS_2, and 7.90 g. of $AlCl_3$ was stirred and refluxed 4 hr. No HCl was evolved during this period. Destruction of the mixture as usual, followed by dimethylamination of the product and examination by proton n.m.r., produced the data of expt. no. 7 of Table VIII. Data of expt. no. 8 of Table VIII were obtained in a similar manner.

Discussion

Aluminum Chloride.—When large excesses of $AlCl_3$, added batchwise, were used (30–35 moles of $AlCl_3$/mole of $(C_6H_5PNCl)_3$), 1 mole of HCl was evolved rather rapidly (3–6 hr.). Good yields of $(C_6H_5)_4P_3N_3Cl_2$ were obtained. Fractional crystallization gave a first fraction of large hexagonal crystals of an isomer believed to be *cis*-2,4-dichloro-2,4,6,6-tetraphenyltriphosphonitrile (II), m.p. 195–196°, then tiny crystals of an isomer believed to be *trans*-2,4-dichloro-2,4,6,6-tetraphenyltriphosphonitrile (III), m.p. 169–170°. Later crops of crystalline solids appeared as two solid solutions, *i.e.*, mixtures of both isomers II and III. Repeated attempts to separate these solid solutions by recrystallization employing different solvent systems failed. Melting ranges of these solid solutions were 151–158 and 170–175°.

On the other hand, when smaller excesses of anhydrous $AlCl_3$ (15–20 moles of $AlCl_3$/mole of $(C_6H_5PNCl)_3$) were added in one portion, reflux periods on the order of 2–5 days were required for the evolution of 1 mole of HCl. In striking contrast to the reactions involving large excesses of $AlCl_3$, excellent yields (70–90%) of 2-chloro-2,4,4,6,6-pentaphenyltriphosphonitrile (IV), m.p. 151–152°, were obtained.

Pertinent data relating to several syntheses of dichloro and monochloro triphosphonitriles are given in Table I. It is noteworthy that regardless of whether one or two phenyl groups are substituted on the triphenyltriphosphonitrilic ring, only one equivalent of HCl is titrated. We believe that in the case of diphenylation, in which two equivalents of phenyl group are substituted yet only one equivalent of HCl apparently is evolved, the second equivalent of HCl must be bound as a complex of some type. Similar complexes of aluminum halides with aromatic hydrocarbon solvents have been reported several times in the literature.[4] These adducts are believed to involve an equivalent of HCl in ionic types of complexes.

$FeCl_3$ or $SnCl_4$.—In experiments employing either anhydrous $FeCl_3$ or $SnCl_4$, no HCl evolution was observed until refluxing had been conducted for about 20 min. Thereafter HCl was evolved rapidly and at a steady rate. This behavior was quite different from that observed when $AlCl_3$ was used, in which case HCl evolution was rapid at first, then became very slow.

However, when the ferric or stannic chloride complexes were destroyed the only solid isolated was unreacted trichloro material, I. In one reaction employing anhydrous $FeCl_3$ and *trans*-I, about a 5% yield of *cis*-trichloro isomer was isolated, indicating that an isomerization had occurred. This topic will be discussed further below.

From a blank reaction mixture employing only $FeCl_3$ and benzene, chlorobenzene was obtained. The yield was nearly equivalent to that expected from the amount

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(4) (a) B. Menshutkin, *Chem. Zentr.*, **II**, 378 (1910); (b) J. F. Norris and J. N. Ingraham, *J. Am. Chem. Soc.*, **62**, 1298 (1940); (c) H. C. Brown and H. W. Pearsall, *ibid.*, **73**, 4681 (1951); (d) K. H. Lieser and C. E. Pfluger, *Chem. Ber.*, **93**, 176 (1960).

TABLE II

ANALYSIS OF PHENYLCHLOROTRIPHOSPHONITRILES

Compound	M.p., °C.	% C	% H	% Cl	% N	% P	Mol. wt.[a]
cis-$(C_6H_5)_4P_3N_3Cl_2$	195–196	55.78	3.25	14.33	8.66	17.04	510
trans-$(C_6H_5)_4P_3N_3Cl_2$	169–170	55.92	3.93	13.88	8.02	17.49	529
cis- + *trans*-$(C_6H_5)_4P_3N_3Cl_2$							
Solid soln. no. 1	151–158	56.21	3.98	14.27	...	...	...
Solid soln. no. 2	170–175	56.09	3.69	14.32	...	...	...
Calcd. for $C_{24}H_{20}Cl_2N_3P_3$	...	56.05	3.92	13.79	8.17	18.07	514.3
$(C_6H_5)_5P_3N_3Cl$	151–152	64.60	4.56	6.73	7.84	16.40	524
Calcd. for $C_{30}H_{20}ClN_3P_3$	...	64.81	4.52	6.38	7.57	16.72	555.9

[a] Determined by vapor phase osmometry in benzene. Concentrations ranged from 2 to 4 wt. %.

TABLE III

PHYSICAL DATA FOR DIMETHYLAMINO DERIVATIVES

Compound	M.p., °C.	% C		% H		% N		% P		% Cl		Mol. wt.[a]	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
cis-$(C_6H_5)_4P_3N_3[N(CH_3)_2]_2$	145–145.5	63.27	63.35	6.07	6.33	13.18	12.98	17.49	17.31	...	...	531.5	488
trans-$(C_6H_5)_4P_3N_3[N(CH_3)_2]_2$	123–124	63.27	63.63	6.07	6.28	13.18	13.10	17.49	16.08	...	...	531.5	532
$(C_6H_5)_5P_3N_3N(CH_3)_2$	142–144	68.08	68.13	5.54	6.00	9.92	9.70	16.46	15.87	...	...	564.5	578
cis-$(C_6H_5)_3P_3N_3[N(CH_3)_2]_3$	113.5–115	57.82	57.52	6.67	6.53	16.86	17.11	18.64	16.24	...	...	...	...
$(C_6H_5)_3P_3N_3Cl[N(CH_3)_2]_2$	124.5–125.5	53.94	54.13	5.56	5.96	14.30	14.43	18.97	18.66	7.24	7.25	490	467
$(C_6H_5)_3P_3N_3Cl_2N(CH_3)_2$	110–115	49.91	50.46	4.40	4.82	11.64	11.44	19.31	18.99	14.23	13.19	...	...
trans-$(C_6H_5)_3P_3N_3[N(CH_3)_2]_3$	93.5–94.5	57.82	58.01	6.67	7.31	16.86	16.42	18.64	19.01	...	...	498.5	507

[a] Determined by vapor phase osmometry. Concentrations ranged from 2 to 4 wt. %.

TABLE IV

P^{31} N.M.R. DATA OF PHENYLPHOSPHONITRILIC CHLORIDES

Sample no.	Molecular formula	Chemical shifts (area ratio)			
		δ_1	δ_2	δ_3	δ_4
1	$(C_6H_5)_6P_3N_3$	15.2			
2	$(C_6H_5)_5P_3N_3Cl$	17.6 (2)		28.7 (1)	
3	*cis*-$(C_6H_5)_4P_3N_3Cl_2$	19.0 (1)		30.2 (2)	
4	*trans*-$(C_6H_5)_4P_3N_3Cl_2$	19.0 (1)		28.5 (2)	
5	*gem*-$(C_6H_5)_4P_3N_3Cl_2$[a]	19.1 (2)	16.6 (1)		
6	*cis*-$(C_6H_5)_3P_3N_3Cl_3$			29.4	
7	*trans*-$(C_6H_5)_3P_3N_3Cl_3$			30.3 (2)	32.7 (1)
8	*gem*-$(C_6H_5)_2P_3N_3Cl_4$[a]	20.6 (1)	18.3 (2)		
9	$P_3N_3Cl_6$[b]	19			
10	H_3PO_4	0 (ref.)			

[a] We are grateful to Dr. Charles P. Haber for generously supplying samples of these materials. [b] M. Becke-Goehring and G. Koch *Chem. Ber.*, **92**, 1188 (1959).

of HCl isolated, one equivalent of chlorobenzene being obtained for each equivalent of HCl evolved.

Reaction of benzene with $FeCl_3$ to produce chlorobenzene was first reported by Thomas.[5] We conclude, therefore, that neither $FeCl_3$ nor $SnCl_4$ is a suitable catalyst for Friedel–Crafts phenylation of I. One experiment was carried out in which 3 mole equivalents of anhydrous $FeCl_3$ was added to a benzene solution containing 1 mole equivalent of *trans*-$(C_6H_5PNCl)_3$. Only a trace of HCl was evolved after 2.75 hr. of refluxing. In fact, after refluxing the reaction mixture 5 hr., only about 19% of one mole equivalent of HCl had been evolved. This indicates that a complex or triply ionized quasi-phosphonium salt is formed between the triphosphonitrile and metal halide in a 1:3 molar ratio. This observation is contrary to the singly-ionized quasi-phosphonium salt proposed by Shaw and co-workers[2b] for the Friedel-Crafts phenylation of $[PNCl_2]_3$.

Analytical data for the phenyl-substituted products of the Friedel–Crafts reactions are given in Table II.

Dimethylamino Derivatives.—Reaction of the phenylphosphonitrilic chlorides with an excess of dimethylamine in benzene or chloroform readily gave good yields of the expected dimethylamides. In Table III are listed pertinent physical data for these derivatives. In the case of the *cis*-trichloro starting material, a trisdimethylamide, a chlorobisdimethylamide, and a dichlorodimethylamide all were obtained by adjustment of the reaction conditions.

Nuclear Magnetic Resonance.—Phosphorus-31 n.m.r. spectra of the *cis*- and *trans*-trichloro and tribromotriphenyltriphosphonitriles have been reported.[3,6] Other chlorophosphonitriles have been examined by phosphorus-31 n.m.r. spectroscopy during the present investigation. Table IV lists the data obtained and, for completeness, the data for *cis*- and *trans*-$(C_6H_5PNCl)_3$ are included. (Absorption peaks were quite broad due to unresolved P–P and P–H coupling.)

These data are interpreted as follows: (1) The structures of compounds **1** and **2** are obvious since no isomers are possible. (2) Phosphorus atoms with two

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[5] V. Thomas, *Compt. rend.*, **126**, 1211 (1898).

[6] (a) T. Moeller and P. Nannelli, *Inorg. Chem.*, **1**, 72 (1962); (b) *ibid.*, **2**, 659 (1963); (c) *ibid.*, **2**, 896 (1963).

TABLE V

PROTON N.M.R. DATA FOR DIMETHYLAMIDES

Sample no.	Compound	M.p., °C.	No. of doublets	Chemical shifts (area ratios) τ_1	τ_2	J^1_{P-H}	J^2_{P-H}
11	$(C_6H_5)_5P_3N_3N(CH_3)_2$	142–144	1	7.58			
12	*trans*-$(C_6H_5)_4P_3N_3[N(CH_3)_2]_2$	123–124	1	7.41		12.06	
13	*cis*-$(C_6H_5)_4P_3N_3[N(CH_3)_2]_2$	145–145.5	1	7.62		12.45	
14	*cis*-$(C_6H_5)_3P_3N_3[N(CH_3)_2]_3$	113.5–115	1	7.45			
15	*trans*-$(C_6H_5)_3P_3N_3[N(CH_3)_2]_3$	93.5–94.5	2	7.53 (2)	7.74 (1)	12.23	12.23

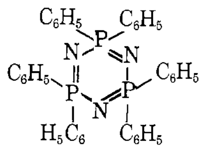
phenyl groups attached absorb at -17 ± 2. (3) Phosphorus atoms with two chlorines attached absorb at -16 to -19. (4) Phosphorus atoms with one phenyl group and one chlorine attached absorb at -30 ± 2. (5) Sample **5** is readily seen to be the *gem*-dichloro isomer since observation (4) precludes the possibility of the presence of a phosphorus atom with one phenyl group and one chlorine attached. (6) Sample **8** must be the *gem*-diphenyl isomer for the same reason. (7) Sample **6** is the *cis*-trichloro isomer since only one resonance peak was observed (all P atoms in the same environment). (8) Sample **7** is the *trans*-trichloro isomer since two resonance peaks were observed in an area ratio of 2:1 (two P atoms in one environment and the third P atom in a second environment. (9) Unfortunately, the n.m.r. data do not establish the structures of samples **3** and **4**.

Proton N.m.r. Spectra.—Dimethylamides of the two trichloro, the two dichloro, and the monochloro compounds were examined by proton n.m.r. Absorption of the N-methyl protons consisted of a doublet with additional structure between the two peaks. This multiplicity of lines in the spectra is attributed primarily to neighboring and long-range phosphorus–proton coupling. The separation between the doublet lines (J_{P-H}) is related to the actual P–H coupling constant, but is not equal to it. Additional splitting and broadening are the result of long-range P–H coupling and quadrupole broadening by the adjacent nitrogen atom. Each doublet in the spectrum of a compound represents a $N(CH_3)_2$ group in a specific electronic environment. Also, only one doublet will be observed for two or more $N(CH_3)_2$ groups which are in equivalent environments. The chemical shift values (τ), values of the apparent coupling constants (J_{P-H}), and the number of doublets observed for each compound are reported in Table V.

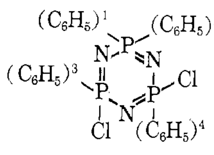
Absorption of the aromatic protons produced a multiplet extending from τ 1.7 to 3.0. The multiplicity of lines in the spectrum is due to nonequivalence of the protons and the effects of phosphorus–proton coupling. Due to the complexity of the aromatic proton absorption, no attempt was made to determine the chemical shifts of the different type protons or of the proton–proton or proton–phosphorus coupling constants. However, there are qualitative differences in the aromatic absorptions of the different compounds which are quite obvious.

As confirmation of structural assignments to the *cis* and *trans* isomers of I by P^{31} n.m.r.,[3] the proton n.m.r. spectra of compounds **14** and **15** clearly establish **14** as the *cis* isomer and **15** as the *trans* isomer. The reasoning is as follows: (a) The spectrum of **14** consisted of a doublet, as described above, with a chemical shift of τ 7.45 (all $N(CH_3)_2$ groups in an equivalent environment) plus a low-field absorption due to the presence of aromatic protons. The ratio of aromatic to nonaromatic protons was 15:18. (b) The spectrum of **15** consisted of two overlapping doublets with chemical shifts of τ 7.53 and 7.74 plus a low-field absorption due to the presence of aromatic protons. The low-field doublet–high-field doublet proton ratio was 2:1 (two $N(CH_3)_2$ groups in one environment and a third $N(CH_3)_2$ group in a different environment). Again the aromatic to nonaromatic proton ratio was 15:18.

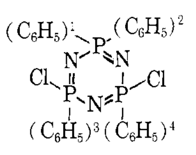
Isomers **12** and **13** can be distinguished one from the other and an analytical procedure has been developed to analyze mixtures of the isomers; however, the $N(CH_3)_2$ absorptions do not present sufficient information for conclusive assignment of the *cis* and *trans* configurations. On the other hand, by comparison of aromatic proton n.m.r. spectra of $[(C_6H_5)_2PN]_3$, **12** and **13** seem to give qualitative proof that **13** is the *cis* and **12** is the *trans* isomer.



A



B (*trans*)



C (*cis*)

In structure A all of the phenyl groups are in an equivalent environment. The phenyl groups in B are in two different environments, $(C_6H_5)^1$ and $(C_6H_5)^2$ are in one environment and $(C_6H_5)^3$ and $(C_6H_5)^4$ are in another environment. There are three different types of phenyl group in C. $(C_6H_5)^1$ is in one type of environment. $(C_6H_5)^2$ is in a different type of environment. $(C_6H_5)^3$ and $(C_6H_5)^4$ are in the same environment, which is different from $(C_6H_5)^1$ and $(C_6H_5)^2$. Thus qualitatively one would predict the aromatic proton n.m.r. spectra to show varying complexity as follows: (1) A should have the simplest spectrum. (2) C should have the most complex spectrum. (3) B should have a spectrum intermediate between A and C.

The proton n.m.r. spectra, based on the assumption that **13** is the *cis* and **12** is the *trans* isomer, follow the predicted pattern (see Figure 1).

Proton N.m.r. Analysis of Dimethylamides.—Differences in chemical shift values for the dimethylamides reported in Table V make possible qualitative identi-

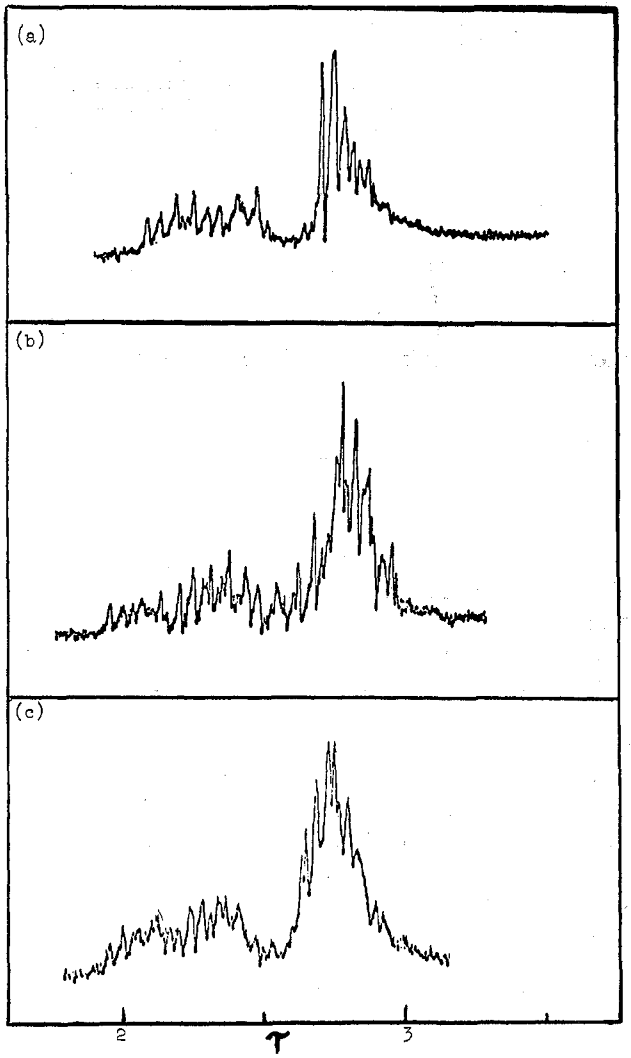


Figure 1.—Proton n.m.r. spectra of: (a), $[(C_6H_5)_2PN]_3$, structure A; (b), $(C_6H_5)_4P_3N_3Cl_2$, structure B; (c), $(C_6H_5)_4P_3N_3Cl_2$, structure C.

fication and quantitative determination of mixtures of the compounds. Synthetic mixtures of 67.8% *cis*–32.2% *trans* and 49.85% *cis*–50.15% *trans* bisdimethylamides were prepared and analyzed. The results, based on an average of six integrals, were 67.3% *cis*–32.7% *trans* and 49.8% *cis*–50.2% *trans*, respectively. Solid solution no. 1 also was dimethylaminated, then analyzed by this procedure. The solid solution, based on this type of analysis, consisted of 32% *cis* and 68% *trans* isomers.

X-Ray Diffraction Studies.—A number of well-developed crystals of *cis*-$(C_6H_5)_4P_3N_3Cl_2$ were examined by X-ray diffraction. Unit cell dimensions were recorded from a crystal about 0.2 mm. in diameter using a Buerger precession camera. The $h0l$, $0kl$, $h1l$, and $1kl$ nets were recorded. These showed a monoclinic cell with a = 16.99 ± 0.04 Å., b = 14.99 ± 0.01 Å., c = 10.46 Å. and β = 105° 25 ± 5′. Reflections of the hkl type were absent unless $h + k = 2n$. The structure was assigned, therefore, to either Cm or C2/m space groups.

TABLE VI
POWDER DIFFRACTION PATTERNS OF $(C_6H_5)_4P_3N_3Cl_2$
[d (Å.), I/I_0]

cis-$(C_6H_5)_4P_3N_3Cl_2$

10.12, s; 8.417, s; 7.928, s; 6.636, vw; 6.218, m; 5.186, s; 5.043, vw; 4.862, vw; 4.532, m; 4.055, s; 3.953, vw; 3.819, m; 3.601, m; 3.351, vw; 3.100, m; 2.724, w

trans-$(C_6H_5)_4P_3N_3Cl_2$

9.4, vs; 7.96, vs; 6.41, m; 5.94, vw; 5.63, vw; 5.40, vw; 5.00, m; 4.74, m; 4.20, s; 3.86, m; 3.64, m; 3.50, m; 3.36, m; 3.13, w; 2.91, w; 2.68, w; 2.53, vw; 2.36, vw; 2.10, vw; 1.82, vw

TABLE VII
POWDER DIFFRACTION PATTERNS OF $(C_6H_5)_3P_3N_3Cl$
[d (Å.), I/I_0]

$(C_6H_5)_5P_3N_3Cl$ (acicular)

9.81, s; 8.92, vw; 7.01, s; 6.55, vw; 5.86, vw; 5.33, vw; 4.84, s; 4.01, w; 3.65, mw; 3.46, w; 3.19, vw; 2.76, vw

$(C_6H_5)_5P_3N_3Cl$ (tabular)

10.51, s; 9.70, s; 8.58, vw; 7.89, ms; 7.49, ms; 6.60, m; 5.94, w; 5.56, w; 5.43, s; 5.00, m; 4.59, vw; 4.34, ms; 4.24, ms; 4.11, vw; 3.96, vw; 3.86, vw; 3.70, m; 3.49, m; 3.26, vw; 3.04, vw; 2.90, vw; 2.76, vw; 2.67, w; 2.58, w; 2.46, w; 2.35, w

The density of a single crystal about 1 × 1 × 3 mm. was determined using a flotation method. A value of 1.378 g./cm.^{3} was found at 24.5°. This value compared favorably to a density of 1.331 g./cm.^{3} calculated from the unit cell dimensions, assuming that two molecules are present in each cell.

We attempted to apply the Patterson method to further reveal the structure within the unit cell in the hope that the *cis* configuration could be established from X-ray data. The large cell, however, made interpretation of the data especially difficult and the structure study was not completed.

All preparations of the *trans* form of $(C_6H_5)_4P_3N_3Cl_2$ were isolated as fine powders. No crystals suitable for single crystal studies could be isolated. For identification purposes, however, powder diffraction patterns were recorded for both the *trans* and *cis* forms. Data are given in Table VI.

Relatively little X-ray work was attempted on $(C_6H_5)_5P_3N_3Cl$. Preparations of this material revealed crystals of both acicular and tabular habits. Powder diffraction patterns were recorded from crystals of each of the two habits (Table VII). The patterns differ, indicating that a least two crystal polymorphs are possible.

Isomerization of *cis*- and *trans*-$(C_6H_5PNCl)_3$.—All of the phenylations discussed thus far were carried out using the much more readily available *trans*-$(C_6H_5PNCl)_3$[3] rather than the *cis* isomer. A Friedel–Crafts reaction of *cis*-$(C_6H_5PNCl)_3$ with benzene in the presence of $AlCl_3$ was carried out; however, a considerable amount of *trans*-$(C_6H_5)_4P_3N_3Cl_2$ was obtained, along with the expected *cis*-dichloro isomer. Therefore an isomerization has occurred in which the spatial arrangement of at least one C_6H_5–P–Cl group has changed with respect to the rest of the molecule. Since infrared data have been interpreted to show that the trimeric phosphonitrilic ring is planar in solution,[7] the change

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[7] L. W. Daasch, *J. Am. Chem. Soc.*, **76**, 3403 (1954).

TABLE VIII

FRIEDEL–CRAFTS ISOMERIZATION OF *cis*- AND *trans*-$(C_6H_5PNCl)_3$

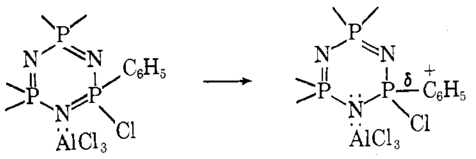
Expt. no.	Starting compd.	Equiv. of MX_3/equiv. of PN compd.	Solvent	Reflux time, hr.	Proton n.m.r. anal. of completely dimethylaminated product	
					% *cis*	% *trans*
6	*trans*-$(C_6H_5PNCl)_3$	$FeCl_3$ (3)	C_6H_6	24	35	65
7	*cis*-$(C_6H_5PNCl)_3$	$AlCl_3$ (14)	CS_2	4	60	40
8	*trans*-$(C_6H_5PNCl)_3$	$AlCl_3$ (14)	CS_2	4	25	75

probably involves movement of the phenyl or chloro groups or both.

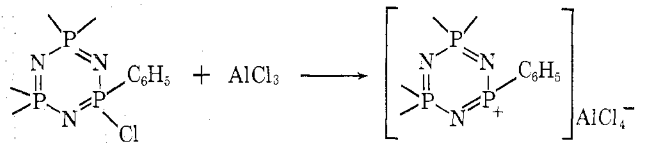
It was mentioned previously that in an attempted reaction of *trans*-$(C_6H_5PNCl)_3$ with benzene employing anhydrous $FeCl_3$ as the catalyst, no phenylation occurred. However, upon processing the reaction mixture, a small yield (5%) of *cis*-$(C_6H_5PNCl)_3$ was isolated, prior to recovery of *trans*-$(C_6H_5PNCl)_3$. Again a rearrangement has occurred. This same isomerization was repeated except that a sample of the crude material was dimethylaminated and the product analyzed by proton n.m.r. The phosphonitrilic composition was found to be 35% *cis*, 65% *trans* isomers.

Finally, mixtures of either *cis*- or *trans*-$(C_6H_5PNCl)_3$ with $AlCl_3$ in CS_2 were refluxed 4 hr., then decomposed and the solid products dimethylaminated and analyzed by proton n.m.r. Results are given in Table VIII. The product from the *trans* isomer contained 75% *trans*- and 25% *cis*-$[C_6H_5PNN(CH_3)_2]_3$. The product from the *cis* isomer contained 40% *trans*- and 60% *cis*-$[C_6H_5PNN(CH_3)_2]_3$.

As a reasonable explanation of this isomerization, it is probable that the metal halide, serving as a Lewis acid, forms a 3:1 complex with the phosphonitrilic compound. Evidence supporting the formation of such a complex was given earlier. If the Lewis acid complexes with a ring nitrogen, the electron density around the neighboring phosphorus atom will be lowered and a partial ionic charge will be formed at the phosphorus atom. When this occurs, the phenyl group, normally attached at an angle to the plane of the P–N ring, now can adjust its position so as to become planar with the PN ring.



A similar planar intermediate can be formed if the metal halide complexes with the chlorine atom.



In either case, at least three sites on the ring of $(C_6H_5PNCl)_3$ are complexed. However, during monophenylation a phenyl group is added to only one phosphorus atom. Upon destruction of the metal halide complexes in water–HCl, the substituents on the other phosphorus atoms now either can return to their former spatial positions or else will move to exactly the opposite positions, which they occupied prior to complexing. If the substituents on each of the phosphorus atoms return to the same positions then the original configurations will be retained. On the other hand, if inversion occurs at the phosphorus atom which holds the chlorine substituent, then isomerism will have occurred.

In an earlier communication[3] we reported an apparent tendency for *cis*-$(C_6H_5PNCl)_3$ to rearrange to the *trans* isomer in the solid state on standing at room temperature. This was indicated by the lowering of the melting point of 191–192° to 160–180° after several weeks. During our present studies we observed a similar lowering of the melting point of *cis*-$(C_6H_5)_4P_3N_3Cl_2$ from 195–196° to 179–186° on standing several months at room temperature.

However, when samples of the two *cis* isomers, now having lowered melting points, were dimethylaminated and these derivatives analyzed by proton n.m.r. spectroscopy, only the *cis* forms were found to be present. We conclude, therefore, that the lowering of the melting points is not a result of a solid-state isomerization.